Lancaster Environment Centre, Lancaster University

Biomonitoring of Wild Fish to Assess Chemical Pollution in English Rivers – An Application of a Fish Tissue Archive

Monika Dorothee Jürgens

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Degree of Doctor of Philosophy

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Abstract

Since 2007 CEH and the Environment Agency are building a Fish Tissue Archive by annually collecting roach (and in 2007/08 also some eels and bleak) from a number of English river sites and storing them long-term at -80°C. This provides a resource for retrospective monitoring of bioaccumulative pollutants in the fish tissue - allowing future scientists to answer questions that cannot yet be answered or are not yet asked. By the end of 2014, 1684 fish had been collected of which 179 have so far been analysed for one or more groups of chemicals: metals, organochlorine pesticides, PCBs and PBDEs. The results from the individual fish were compared to each other as well as to regulatory standards and previously published UK and European data. Some of the results are:

With the exception of lead in 3% of analysed individuals, no food standards were exceeded, but the environmental quality standard (EQS) for mercury was exceeded in the majority of samples (111/144) and the very low EQS for PBDEs was greatly exceeded in all samples.

Some patterns found were:

- Mercury and selenium increased with size of the fish and to some extent with the distance of the sampling site from the river source.
- PBDE concentration correlated well with the modelled concentration of treated sewage at the sampling site
- A hotspot was found for DDTs (banned in 1981) and to a lesser extent lindane, chlordane and copper. Further investigations revealed that a pesticide factory had been located close to the sampling site for much of the 20th century. This shows how unexpected results can point to previously unknown issues, which warrant further investigation.
- Compared to previous European data, eels were generally less contaminated with organic pollutants and roach were low in mercury and cadmium, but relatively high in lead.

Declaration

I hereby declare that this work has been originally produced by myself for the present thesis and it has not previously been submitted for the award of a higher degree at any other institution. Inputs from co-authors and collaborators are acknowledged throughout.

Monika Jürgens

Wallingford, UK, June 2015

Acknowledgements

I wish to thank my supervisors Kevin Jones and Andrew Johnson for always being encouraging and helpful and sometimes giving constructive criticism.

CEH is funding the Fish Tissue Archive as part of activities classed as National Capability (formerly Science Budget) and Andrew Johnson is credited with convincing the decision makers of its value, so that it could move from a discussion topic at coffee breaks to an actual project. Additional funding came from the Environment Agency for the nalysis of the eel samples and DEFRA for the collection and analysis of 39 roach, which were part of the project "Effects of complex chemical 'cocktails' on the genetic diversity of fish populations".

This project would not have got off the ground without the collaboration of the Environment Agency in England and Wales. I am especially grateful to the Fisheries teams in the Thames South East, Thames West, Anglian and Midlands Central regions for providing more than 1500 fish over the years.

Dave Hughes, John Crosse, Chakra Chaemfa, Montserrat Auladell-Mestre and Aşkın Birgül from Lancaster University and Qiong (Janet) Lu from Oxford University extracted and analysed batches of fish for persistent organic pollutants at Lancaster University. Having - under Dave and John's excellent instructions - done a few batches myself and double checked the peaks on many more, I really appreciate the large amount of effort involved. Athanasios Katsogiannis also from Lancaster University greatly helped me to understand what had happened when those results didn't make sense. Qiong also did some cryogrinding for me and numerous work experience students have helped to vacuum pack frozen fish. At CEH Lancaster Alan Lawlor taught me how to acid-digest my samples and he and Hayley Guyatt, Sarah Beith and Sarah Thacker ran all my digested fish samples through the AAS for metals analysis as well as doing the cold extraction lipid content determination, running the first batch of samples through the GALAHAD mercury analyser and instructing me how to do the second, and helping to organise the samples so that the required fish can be found in the freezer without too much difficulty.

I am also grateful to lots of present and former staff and students at CEH Wallingford and Lancaster, who offered help and advice with various aspects of the work, among them, but not at all limited to: Cynthia Davies who introduced me to the wonders of Microsoft Access, Ilaria Prosdocimi, who is always happy to talk about questions of statistics, and Richard Williams and Virginie Keller for providing information about the rivers and sewage works.

Thanks go also to Liz Nicol from Brunel University and our various collaborators from other institutions both in Britain and abroad and last but not least, to my friends and family for trying to keep me sane and putting up with my moaning about the discrepancy of the amount of work to be done and the amount of time left in which to do it.

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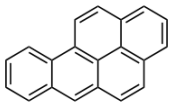
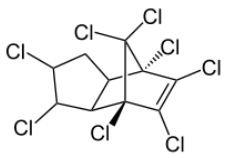
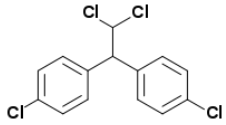
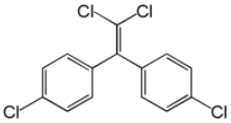
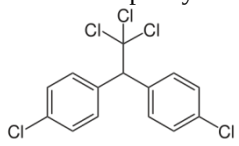
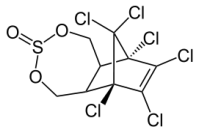
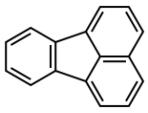
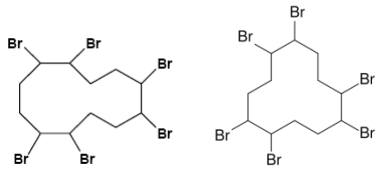
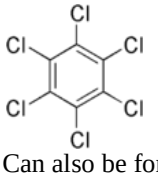
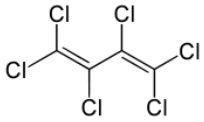
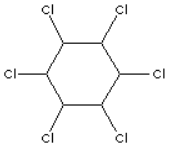
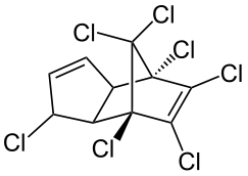
Terms and acronyms

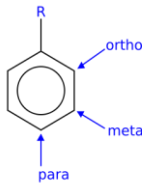
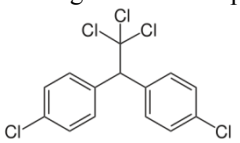
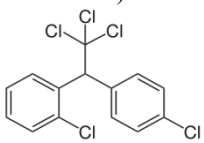
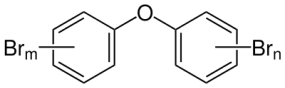
Acronym or term	Explanation
ABM	active biological monitoring: eg. putting fish from a clean site in a cage at a contaminated site and then measuring their contamination after few weeks → PBM
ADI	Acceptable daily intake In the HCBD dossier (European Commission 2006b) they use TDI and ADI in this way: "no more than 10% of the TDI should come from food from an aquatic source then they use average fish consumption (115 g/d) to decide the acceptable daily intake [from this source], leaving space for the other 90% from other sources. Therefore the ADI is lower than the TDI since ADI only considers one food source (in this case fish) whereas TDI is for intake from all sources
AES	atomic emission spectrum, used as a detector with →ICP
ANOVA	Analysis of Variance
B(a)P	Benzo(a)pyrene  product of incomplete combustion and therefore a component of soot. carcinogenic. First documented environmental carcinogen – correlation of soot and chimney sweeps carcinoma (or "soot warts") a scrotal cancer described in 1775 (Percivall Pott), but only in the early 20th century it was shown that a component of the soot was a carcinogen, rather than physical irritation from soot causing the cancer and in 1932, B(a)P was identified as highly carcinogenic component of pitch. (Waldron 1983) Has biota standard (5 µg/kg) in updated priority substances legislation as marker for PAH contamination (European Union 2013)
BDE	brominated diphenyl ether (see → PBDE)
benthos, benthic	organisms living on the floor of a water body ↔ pelagic
BFR	brominated flame retardants They can be used as additive or reactive compounds. Reactive means that they become part of the molecular structure of a polymer and are hard to release, but additive ones get into the environment much more easily
BHC	benzene hexachloride, another name for Hexachlorocyclohexane → HCH
BCF	bioconcentration factor
BMF	biomagnifications factor → similar to TMF: trophic magnification factor
bioaccumulation	general term for all mechanisms by which the concentration of a pollutant in an organism is magnified compared to the environment
bioconcentration	only the uptake from the water leading to higher concentration in the organism than in the water
biomagnification	bioaccumulation through food
chlordane	 Contact insecticide consisting of a mixture of related compounds. Banned for agricultural use in the EU since 1981 (EEC 1978), some non-agricultural use as a lumbricide (agent that kills instestinal worms) continued in the UK (http://www.provet.co.uk/lorgue/5a6d247.htm accessed 29.4.09)

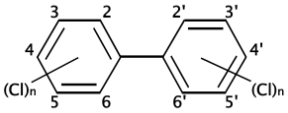
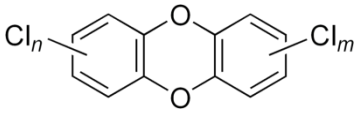
Acronym or term	Explanation
(Fulton's) condition factor	K= weight/length^3 x 100 [g/cm^3] (Fulton 1904)
condition index	Ricker's Condition index = weight/length^a x 1000 (quoted from Maes *et al.* 2013) a is determined by fitting all the data to a curve, therefore it shows best whether the fish is different from "normal" and takes into account that the general shape might change with size and therefore the exponent may not be exactly 3 as in Fulton's condition factor
CBR	Critical Body Residue
DDD	dichloro-diphenyl-dichloroethane, also called TDE (CAS: 72-54-8)  formed from DDT, was also sometimes used as an insecticide itself mainly on tobacco http://ntp.niehs.nih.gov/ntp/htdocs/lt_rpts/tr131.pdf
DDE	Dichloro-diphenyldichloro-ethylene formed from DDT by loss of one chlorine atom. Main DDT degradation product found in the environment  pp'DDE is an anti-androgen. This also applies to fish (Bayley *et al.* 2002) the op' forms (op'DDT, op'DDE, op'DDD) are more estrogenic than their respective pp' forms, see also → Nomenclature of some of the POPs used
DDT	Dichloro-Diphenyl-Trichloroethane  this is pp'DDT pesticide, first synthesized in 1874 but the insecticidal properties were only discovered in 1939 (http://npic.orst.edu/factsheets/ddttech.pdf, accessed 16.7.2013), severely restricted in EU since 1981
dioxin	see PCDD
DOM	dissolved organic matter
dw	dry weight
EFSA	European Food Safety Authority
endosulfan	Insecticide. Developed in the 50s now severely restricted or banned in many countries including the USA and EU, but still widely produced and used in India. Technical mixture is 70% α and 30% β  In 2006, a consortium of endosulfan manufactures including Bayer CropScience and Makhteshim-Agan sued the Commission, alleging that endosulfan had been unfairly excluded. In September 2008 the European court of justice dismissed the case, leaving the de facto ban on endosulfan in place. http://www.panna.org/node/1686

Acronym or term	Explanation
European Regulation	A „European Law“ directly applicable in all Member States without prior integration in national legal systems. Member States may not apply a regulation incompletely or choose among the stipulations. The stipulations contained in a regulation are binding on Member States and financial penalties may be assigned if the regulation is not observed in full (ONEMA 2008)
European Directive	A legal act taken by the Union, but that is not directly applicable in the Member States. It must be taken up in national law. A directive allows Member States to select the ways and means of achieving Union objectives in the framework of their own, internal legal system. Member States must adapt their legal system to the stipulations contained in the directive. (ONEMA 2008)
EQS	Environmental Quality standard Standards have been set for different types of water for the EU. In the original Priority Substances Directive (European Union 2008a), there was an option for member states to set biota or sediment standards which offer “at least the same level of protection”. Only for 3 substances have values been given should the biota option be chosen: mercury (Hg) 20 µg/Kg wet weight Hexachlorobenzene (HCB) 10 µg/Kg wet weight Hexachlorobutadiene (HCBD) 55 µg/Kg wet weight (European Union 2008a, Article 3(2a)) “The Commission shall, by 2018, verify that emissions, discharges and losses as reflected in the inventory are making progress towards compliance with the reduction or cessation objectives laid down in Article 4(1)(a)(iv) of Directive 2000/60/EC, subject to Article 4(4) and (5) of that Directive.” Art. 5(5) An EQS is defined as ‘the concentration of a particular pollutant or group of pollutants in water,sediment or biota which should not be exceeded in order to protect human health and the environment’ (WFD Article 2(35)) The updated Priority Substances directive has biota standards for an additional 8 substances (or groups) and is more specific on their use: not really optional any more and normally “fish” as opposed to the more generic “prey” to be used (European Union 2013).
FEP	Fluoro-Ethylene-Propylene, a material similar to Teflon
fluoranthene	 contains **no fluorine** , but is **fluorescent**, hence the name Combustion product –indicator of other more dangerous PAH, biota standard (30 µg/kg) in the new Priority Substances Directive (European Union 2013), but not measured in this study.
Fulton’s condition factor	see condition factor
fw	fresh weight (also ww: wet weight)
GALAHAD mercury analyser	A carrier gas (N_2?) is bubbled through the sample (acid digested -same as for ICPMS, diluted if necessary, then treated to convert all forms of mercury to metallic Hg), driving out the Hg, this is then trapped by condensation and amalgamation with gold and released all at once to analyse

Acronym or term	Explanation
HBCD or HBCDD	Hexabromocyclododecane. Flame retardant. CAS No.: 3194-55-6 On 28 October 2008 the European Chemicals Agency decided to include HBCD in the list of Substances of Very High Concern (SVHC), within the REACH framework.  both these structure images are correct, and are just different 2-dimensional representations of the 3-dimensional structure with rotations around single bonds.
HCB	Hexachlorobenzene, was used as a fungicide for seed treatment, banned in the EU since 1981 EEC (1978) now banned under the United Nations' Stockholm Convention on Persistent Organic Pollutants, which was adopted in May 2001 and came into force May 2004  Can also be formed unintentionally during combustion processes involving chlorine and organic matter, eg in waste incineration a biota →EQS was set for HCB
HCBD	Hexachlorobutadiene  Historically HCBD was used as a solvent in the production of rubber and other polymers and also as a fungicide and seed dressing. Today the use has virtually ceased in Europe but it is still generated as a by-product of tetrachloroethylene and tetrachloromethane production. (http://www.eurochlor.org/hexachlorobutadiene, 25/7/2011) a biota →EQS was set for HCBD

Acronym or term	Explanation
HCH	Hexachloro-Cyclo-Hexane, formerly also called BHC (benzene hexachloride)  technical HCH: (CAS RN: 608-73-1) is an isomeric mixture that contains mainly five forms of HCH. The five principal isomers are present in the mixture in the following proportions: α-HCH (55%–80%), β-HCH (5%–14%), γ-HCH (8%–15%), δ-HCH (2%–16%) and ε-HCH (1%–5%) (Breivik *et al.* 1999). The γ-isomer is the only isomer showing strong insecticidal properties. After almost forty years of extensive use worldwide, there has been a gradual replacement of technical HCH by lindane (γ-HCH, CAS 58-89-9). No significant uses of technical HCH have been reported after 2000 at worldwide level. (http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=COM:2009:0027:FIN:EN:DOC 1.3. accessed 22.12.09). In the EU technical HCH was banned 1981 (EEC 1978) alpha HCH alpha-Lindane **gamma HCH** **Insecticide Lindane**. Was used in agriculture since the 40s, banned 2002 (European Commission 2000), also used to kill head lice and mosquitoes. It is no longer used in the UK as an agricultural and domestic insecticide and in 2003 the EU agreed to ban all its agricultural uses. (WWF accessed 25/6/2009), the last exception for Lindane to be used for treating timber etc. expired September 2006 and remaining allowed use of technical HCH in the EU expired December 2007. Today both technical HCH and Lindane are banned in the EU, though it is still allowed [I think] for public health purposes i.e. treating head lice or scabies in some countries. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=COM:2009:0027:FIN:EN:DOC
Heptachlor	 the chemical structure is similar to chlordane (which has an additional Cl instead of the double-bond in the pentagonal structure) "New" EU EQS (European Union 2013) is 6.7 ng/kg for heptachlor+heptachlor epoxide
ICES	International Council for the Exploration of the Sea
ICES7 PCBs	7 Commonly determined PCBs (28, 52, 101, 118, 138, 153, and 180), which give an indication of general PCB contamination. (Breivik *et al.* 2007) estimates that these 7 accounted for 17.8% (14.7-22.8%) of total global PCB production
ICES6 PCBs	common non-dioxin-like PCBs – leaving out the mono-ortho-substituted PCB118 from ICES6
ICP	Inductively coupled plasma. Usually used with a second process as a detector: ICP-OES, ICP-AES, → ICP-MS
ICP-MS	inductively coupled plasma mass spectrometry Argon gas with a few free electrons is passed through an induction coil with extremely fast alternating current (radio frequency), the induction from the fast changing field causes the electrons to accelerate and collide with argon atoms stripping off a further electron. This way an argon plasma "fireball" containing free electrons and Ar+ ions as well as uncharged Ar at a temperature of several thousand Kelvin is formed. A nebuliser produces sample droplets which are passed into this fireball where they immediately vaporise and ionise. The positive ions are then detected by Mass Spectrometry according to their mass to charge ratio.

Acronym or term	Explanation
K_{ow}	octanol-water partinioning coeffient, the higher the K_{ow} (usually expressed as Log_{10} K_{ow}, the more hydrophobic a chemical is
Lindane	see gamma-HCH
NCI	negative chemical ionisation (in gas chromatography)
nomenclature of some of the POPs used	ortho (o), meta (m), para (p) position of eg. chlorine with respect to another substituent on the molecule  for example pp'DDT (both Chlorine atoms on the rings are in the p-positions) and op'DDT (one ring has the Cl in p position the other in o): pp'DDT:  op'DDT: 
NOEC	no observed effect concentration
OES	Optical emissions spectrometry
PAH	polyaromatic hydrocarbon
PBDE	Polybrominated diphenyl Ether (eg. used in flame retardants). 209 congeners are possible, equivalent to the ones for PCBs  less brominated penta- and octa- formulations have been banned but there are few restrictions on the use of Deca-BDE (number 209), but voluntary restrictions are in place In a fire PBDEs release Br atoms (low energy free radicals) which react with the very reactive OH· and H· radicals that are formed during combustion and keep the fire going. By "catching" the radicals it makes them harmless and thus slows or stops the fire spreading
PBDE Octa mix	La Guardia *et al.* (2006) analysed the components of two commercial octa-mixes. Despite the name, the congeners contributing almost half to the total were hepta-BDEs 183/175 (not well separated in the chromatogram) in one of them and deca BDE 209 in the other with actual octa-BDEs only contributing 38 and 22% respectively.
PBDE Penta-mix	consists of mainly of Penta BDEs 99 and Tetra-BDE 47, with some Penta BDEs 100 and 85 and Hexa BDEs 153 and 154. Penta and Octa BDE mixes were banned in the EU from 2004 (European Union 2003b)
PBM	passive biological monitoring: using animals that are there already → ABM

Acronym or term	Explanation
PCB	Polychlorinated Biphenyls. With 1-10 Cl attached, there are 209 possible congeners which are referred to by their number.  For the full list see for example: http://en.wikipedia.org/wiki/PCB_Congener_List Worldwide production ceased in 1984 except for two plants in the USSR which continued until 1990 and 1993 respectively. In the UK PCB production ceased in 1977 open uses restriced 1972 in W.Germany (self imposed restriction of Bayer company) "In the UK, closed uses of PCBs in new equipment were banned in 1981, when nearly all UK PCB synthesis ceased, but closed uses in existing equipment containing in excess of 5 litres of PCBs were only stopped in 2000 with very limited exceptions for some transformers still in place today Log Kow between about 4.4 and 8, depending on the chlorination with higher chlorinated ones generally having higher Kow Old equipment that contains more than 5 L PCBs must be registered with the Environment Agency
PCDD	Polychlorinated dibenzodioxins 
pelagic	living in the water column ↔ benthic
PNEC	predicted no effect concentration
ppm	parts per million eg. mg/kg, mg/L
TDE	tetrachlorodiphenylethane see → DDD
TDI	tolerable daily intake. see → ADI for an explanation
TEQ TEF	TEQ: Toxic equivalent concentration (quantity?). A toxic equivalency factor (TEF) is assigned to each related chemical (usually relative to the most toxic in the group). The TEQ is the weighted sum of the concentrations. Eg. for dioxins and dioxin like PCBs see (DEFRA 2002, page 45-46) 2,3,7,8-TCDD is the standard: TEF=1, others have a TEF<1, TEQ=conc1 x TEF1 + conc2 x TEF2 etc
TMF	Trophic Magnification Factor
WFD	Water Framework Directive : Directive 2000/60/EC (European Union 2000). This is just the framework - doesn't have EQS values except pointing to very few already established ones. Priority substances directive is a "daughter directive"
ww	wet weight (also fw: fresh weight)

1 Introduction

1.1 Background of the project

Our interpretation of recent results in environmental monitoring is often hampered by a lack of knowledge of what happened in the past. If well preserved samples from previous years are available, this knowledge gap can be addressed by analysing those alongside modern samples. This allows using methods that were not yet available at the time of sampling or measuring parameters that were not yet thought of importance or interest. While in some other countries environmental specimen banks with various sample types from various environmental compartments have been well established (see Table 1.3-2), there was no systematic sample collection and storage for the UK freshwater environment. The only UK sample collections suitable for monitoring environmental chemical residues, that we were aware of, were the Predatory Bird Monitoring Scheme based at CEH Lancaster (Walker *et al.* 2008) and the Cardiff University Otter Project (COUP, Chadwick 2007). Both of those rely on opportunistic sample collection, by asking members of the public to submit animals that have been found dead. A systematic sample collection for the UK freshwater environment was lacking. By 2007 CEH could be convinced that starting a sample archive of freshwater fish would be a worthwhile activity and that CEH would be well placed to run it in connection with the regular fish population monitoring by the Environment Agency. That autumn the first trial was run to collect bleak and roach from the lower River Thames, Lancaster University was sub-contracted to analyse a sub-set of them for organic pollutants, and the Environment Agency asked for pesticide and PCB analysis of eels that had been caught to investigate their parasite burdens. The next financial year, 2008/09, running the new Fish Archive became a large proportion of my work at CEH and I enquired whether I could do a PHD thesis in connection with it.

1.2 Aims and objectives

While the primary purpose of the Fish Archive lies in building up a sample base for future retrospective monitoring and the benefits and practical considerations

of setting it up are discussed, the main focus of this thesis is on the results of the approximately 10% of collected samples, that have already been analysed for one or more of the following groups of chemicals: organochlorine pesticides, PCBs, PBDEs, metals.

Measuring chemicals in fish is driven both by an interest in chemicals — fish can be used as an integrating sampler to monitor the chemical pollution in a water body — and by an interest in fish and the health of their populations — this is for example very pertinent in the case of eels, whose numbers have reduced dramatically over recent decades. Monitoring pollution in their bodies helps to ascertain whether chemicals caused their decline.

Comparing the results from individual fish to each other and to literature data and regulatory limits allows to address a number of questions:

- Are food standards exceeded in any of the samples?
- Are environmental standards exceeded in any of the samples?
- Are the contamination levels likely to have negative effects on the fish themselves or their predators (including human consumers)?
- Are the differences in chemical contamination between individual fish samples related to other fish parameters, such as size/age, lipid content, species, etc. and can normalisation to account for those differences make values more comparable?
- Are different or similar patterns observed with different compounds?
- Are there spatial patterns in the results from this study and what may have caused them?
- Are there regional trends when compared to other European data?
- Are there temporal trends when compared to previous UK data?

1.3 Monitoring chemicals in rivers using fish

1.3.1 Approaches to monitoring environmental water quality

1.3.1.1 Water samples

When monitoring pollution of a water body, several approaches can be taken. The first and most common one is to take **water samples** at regular intervals, but the instantaneous concentrations of any chemical can fluctuate wildly principally due to flow rates, and therefore dilution, varying by several orders of magnitude throughout the year (Johnson 2010). Sometimes extremely variable concentrations are observed even within a single day, for example, because of fast changes in flow rate during a storm or because of diurnal patterns in sewage effluent quantity and quality. This variability should be accounted for by repeat sampling and/or composite samples, all of which increase the cost and effort involved. Water concentrations of many chemicals of interest are furthermore often present only at very low concentrations which can be a problem with precision and repeatability within and between laboratories (Hanke *et al.* 2012). For mercury for example, in monthly water surveys of the Thames at Caversham (an area covered by this survey), about 70% of values were below the detection limit of 0.01 µg/L since 1994 when the method became sensitive enough to measure at that level (data provided by Environment Agency from the WIMS database, Figure 1.3-1). Over the same period, there was no exceedance of the maximum water EQS of 0.07 µg/L (European Union 2013) or the former annual average limit of 0.05 µg/L (European Union 2008a) which has been replaced by compulsory biota monitoring (European Union 2013) and yet mercury was detectable above the biota EQS in all fish samples from the same stretch of the river (see Figure 3.2-18). The example for mercury shows that largely non-detectable water concentrations may still give rise to tissue concentrations that could be of concern for top predators (see also chapter 4.2). Trends of a chemical in biota may also be substantially different than those in water, for example, Mathews *et al.* (2013) found little or no change in fish tissue concentrations of mercury in a highly contaminated stream over a 20-year period despite a five-fold decrease in the concentration in the

water during the same time. While such discrepancies may make it difficult to relate results from biota and water monitoring to each other, they can be seen as complimentary. Additionally biota concentrations are in most cases more relevant to the health of the species monitored and their predators than water- or sediment concentrations (see below).

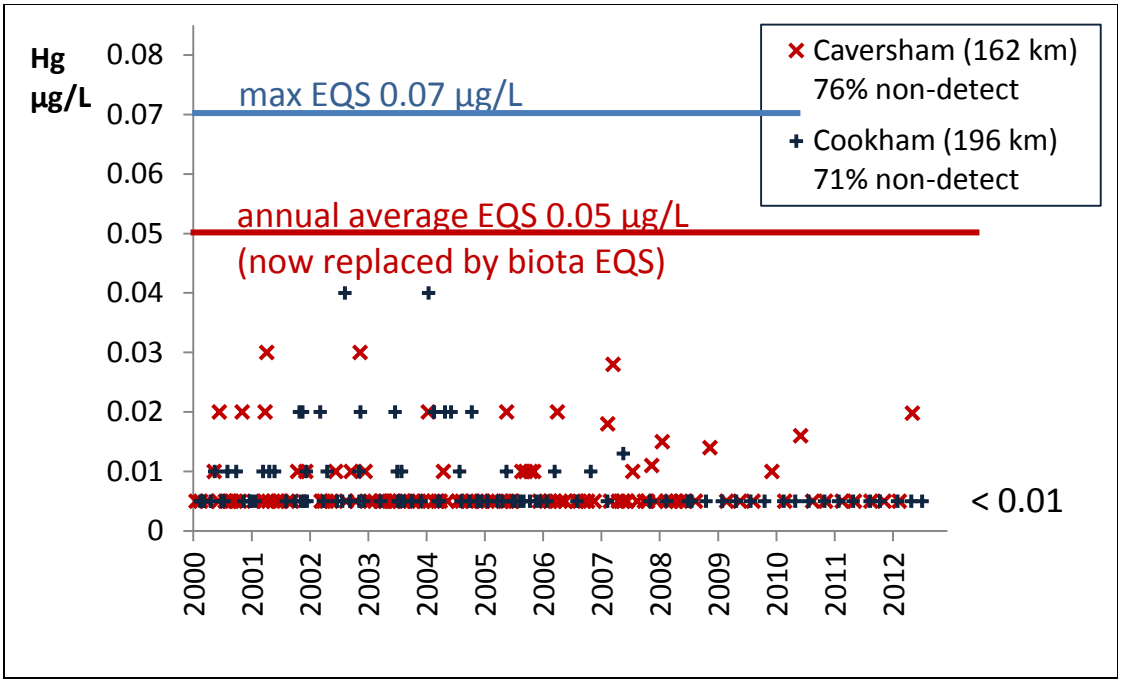


Figure 1.3-1 Mercury water concentrations at two sites on the river Thames (162 and 196 km from source), 2000 – 2012 compared to the water EQS (European Union 2008a, 2013). Data provided by the Environment Agency WIMS database.

1.3.1.2 Passive samplers

To avoid the problems with short term fluctuation and low concentrations in water samples, **passive samplers** have been developed. Different types are optimized for different groups of chemicals and new ones are constantly developed. These are typically left in the water for a few weeks during which time they accumulate chemicals from the water. From the point of view of protecting wildlife, this approach, while being better than water grab samples, still suffers from the drawbacks that the exposure period is relatively short and uptake from food or sediment — either directly or via the food web — is not taken into account. When trying to back calculate the water concentration of HCB or PCBs from passive samplers or caged fish, quite different values were arrived at for the same stretch of river (Verweij *et al.* 2004). Whilst it could be argued over which values were 'right' there can be no argument

over which were more relevant for wildlife. From the point of view of long term monitoring of trends, there is the additional worry as to whether the chosen type of passive sampler will still be available many years into the future.

1.3.1.3 Active biomonitoring

Another approach is **active biomonitoring** for example with caged fish (e.g. Verweij *et al.* 2004, Besse *et al.* 2012), allowing them to accumulate chemicals both from the water (bioconcentration) and to some extent the food web (biomagnification). Fish, whether wild or caged, can also be monitored for relatively polar contaminants, such as endocrine disrupting compounds, for example through examining the contents of their gall bladders (Fenlon *et al.* 2010, Mehinto *et al.* 2010, Brozinski *et al.* 2012) or blood (plasma) (Brown *et al.* 2007, Fick *et al.* 2010). Blood and bile both represent relatively recent or ongoing exposure as these fluids are renewed much faster than tissues.

Active biomonitoring is more realistic with regards to protecting wildlife than the other approaches described above, because it takes into account the availability of a chemical. Caged fish have some advantage over wild ones, in that factors, such as size, species, sex etc. can be tightly controlled making it easier to compare different sites or times. A disadvantage is however, that in general the fish cannot be left for more than a few weeks because of problems with mortalities. This means that the resulting chemical concentrations may still be a long way from equilibrium with the (average) water concentrations. Also, the cage severely restricts their opportunities to hunt for prey and often the stress associated with being in a cage prevents fish from feeding normally. If the fish are fed, then their food source must also be tested for all the chemicals of concern to check for contamination.

1.3.1.4 Wild fish or other biota

Wild fish and other biota accumulate chemicals from food and water over their whole lifetime. That way an indication is obtained of average concentration over several years and levels of pollutants are often much higher in fish or other organisms than in the surrounding water, making them easier to measure, despite the more complex matrix. Both uptake from polluted water or food and depuration, when the

water or food is cleaner again, is possible, but neither process is instantaneous. Due to these kinetics, which are often slower for depuration than for uptake (De Boer and Brinkman 1994), the chemical concentrations found in fish are neither exactly an equilibrium reflection of current water concentrations, nor an exact measure of average concentrations over the lifetime of the fish, but rather somewhere in between those two values if there is no significant influence of the uptake with food, while for many chemicals the food chain also plays an important role. Measuring the concentration in fish in order to get an accurate measure of the water concentration is therefore not a practical proposition, but if the reason for monitoring a pollutant is to protect wildlife from its effects, then it is neither the aqueous, nor the sediment concentration that is most relevant, but their own tissue concentration or that of their prey.

A practical issue is the occasional absence of wild fish of the selected species from the reach on the day of study and the possibility of movements due to migration or stocking confounding the results. In England and Wales the Environment Agency monitor fish every year in most of the major river basins, thus, a good database on fish abundance at different river reaches exists. This can help select locations where fish are likely to be found and also where removing a small sub-set of fish is sustainable. On the basis of this information, a fish monitoring exercise can be sustained. Stocking can be a problem but, unless the fish have been stocked very shortly before they are collected or they originated from a much more polluted site (which in the case of fish farms is unlikely), their chemical pollution would still be mainly influenced by the water in which they were captured.

1.3.1.5 Overview of the advantages and disadvantages of monitoring different matrices

There are advantages and disadvantages to all the sampling strategies for monitoring freshwater quality discussed in this chapter (summarised in Table 1.3-1) and therefore all are valid approaches in at least some circumstances. The focus of this thesis is on monitoring chemicals in wild fish, so the other approaches will not be further discussed.

Table 1.3-1 Pros and cons of different sampling types

Parameter	Water	Passive samplers	Sediments	Caged fish	Wild fish	Invertebrates or algae
Time scales	Concentrations are very variable over time	Integrate over a few weeks. Longer timescales would create problems of fouling and saturation	Integrate over long periods Sometimes stratification allows to take dated samples. High spatial variability over short distances	Integrate over a few weeks	Integrate over a few years	Integrate over a few weeks or months
Uptake kinetics	Not applicable	Defined by the diffusion through the outer membrane. Approaching saturation is to be avoided	Both uptake and release is possible, but often release is slower than uptake, preserving past contamination	Relatively short deployment means that measured body burdens may be far from equilibrium	Both uptake and release is possible, but often release is slower than uptake, preserving past contamination	Small size and rapid metabolism means that concentrations are likely to be relatively close to equilibrium w. regards to water and food
Concentration	Often too low to measure	Higher conc. of chemical of interest	High conc. of some chemicals	Higher conc. than water of many chemicals of interest	Higher conc. than water of many chemicals of interest	Difficult to get large enough sample
Medium	Water only	Water only	Sediment (+pore water) only	Mostly water, though some exposure via food is possible	Water and food, via the food also some exposure to sediments	Water and sometimes sediment depending on species
Relevance for toxic effects	Dissolved chemicals are likely to be bioavailable, but how much is taken up varies between chemicals and species	Mimics uptake via gills or skin to some extent, but not uptake with food	Often not clear whether the chemical is bioavailable	Finding a chemical inside the fish suggests it was bioavailable	Finding a chemical inside the fish suggests it was bioavailable	Finding a chemical inside biota suggests it was bioavailable
Level of standard-isation	Very standardised	Very standardised → very reproducible, but long term the type of sampler used may not always be available	Not very standardised	Can be standardised in terms of species, weight, length of exposure etc.	Less standardised: Not always possible to get sufficient numbers of particular species, age, size, weight, condition factor etc.	Less standardised: Not always possible to get sufficient numbers of particular species, age, size, weight, etc.

1.3.1.6 Which species or which part to monitor

The EU legislation to define good chemical quality of freshwater bodies with regards to priority substances, colloquially known as the Priority Substances Directive had originally optional biota standards for just three chemicals (mercury, hexachlorobenzene, and hexachlorobutadiene) and required to monitor "prey" chosen as "the most appropriate indicator from among fish, molluscs, crustaceans and other biota" (European Union 2008a), but in the updated version (European Union 2013) additional chemicals have been added to the biota standards and fish specified as the default biota to monitor in most cases. The priority substances directive aims to protect both wildlife and human consumers, but does not make clear which of the standards are based on risk to humans and which on risk to wildlife.

Most non-human predators would eat the whole of their prey, whereas human fish consumption in mostly restricted to the fillet (i.e. muscle tissue). Therefore the most appropriate sample depends on the protection goal. The focus of the Fish Tissue Archive is mainly on wildlife protection although where appropriate monitoring results will also be compared to food standards. Therefore, using whole body homogenates of the fish collected seems a sensible approach. There is, however, an argument for removing the gut content on the basis that it may contain a large proportion of non-digestible matter, which would remain non-digestible in a predator. Therefore, including the gut content could lead to an overestimate for some chemicals if the concentration is high compared to the rest of the body. In this case the whole-body homogenate could be seen as a worst-case scenario and exceedances of EQS's could trigger a follow up investigation, which could look at gut contents separately from the actual body of the animals. On the other hand, chemicals may be found at lower concentration in the essentially non-digestible gut contents which would lead to an underestimate of the amount available to a predator. At least in the case of fish this does not seem to be a large problem as the gut content is only a small proportion of the total weight of a fish.

In many cases a decision is made to monitor the organs that accumulate a chemical most or where the toxic effects are expected to be strongest. Which organ is the most contaminated and/or the most susceptible depends, however, on the chemical; for example, methylmercury tends to accumulate in muscle tissue more than in the liver (eg. Wiener *et al.* 2003) while the opposite is true for many hydrophobic

organic chemicals (eg. Teil *et al.* 2012). Lastly, the use of whole body homogenates allows for large enough sample sizes to enable multiple analyses, even from relatively small individuals, without having to resort to composite samples. For the Fish Archive it was decided to focus mainly on roach but clearly other species could and should be considered too. In particular eels have a lot of advantages in terms of monitoring (Belpaire and Goemans 2007), because they spend a long time in the same river during which time they don't spawn which might otherwise periodically reduce the body burden of some chemicals, they have a high lipid content increasing the capacity to accumulate hydrophobic substances, and they are closely associated with the sediments, where much of the pollution is located. For these and other reasons, there is a larger body of knowledge on eel pollution than on any other freshwater species. However, given that European eels are now classified as a critically endangered species (Freyhof and Kottelat 2010), and that numbers in the UK in general tend to be lower the further away from the south and east coast they are (Ibbotson *et al.* 2002), the regular removal of significant numbers in order to monitor chemical pollutants would not be recommended. However, in terms of establishing the cause(s) of the decline in eel numbers and hopefully reversing it, more needs to be known about all aspects of eels and their life cycle and that includes their contaminant burden, especially with chemicals that may interfere with aspects of reproduction (Jürgens *et al.* 2015). Monitoring the chemical contamination of eels for that purpose will then also give information about the water bodies from which they were taken.

Ideally, a range of species from different trophic levels and/or a range of other samples such as water and sediment would be monitored to allow for temporal and spatial trends to be observed even when they differ between species (Bhavsar *et al.* 2010) or media and to test for the impact of factors such as sex differences, age, home range etc., but this has to be balanced with the expense of time and money involved and the need to limit the impact on the studied ecosystems from removing too many individuals. For the current study roach were chosen as a relatively common species where sufficient numbers are present at most sites to allow for removal of usually 10 individuals without negative impact on the populations. In the initial trial period bleak were also collected, but proved to be fairly impractical due to their very small size.

1.3.2 Why and how to archive fish samples

Our understanding of environmental pollution is often hampered by insufficient knowledge of the past. Collecting samples and storing them for future use can address that issue, allowing spatial and temporal trends to be determined even for chemicals which were not measured at the time of sampling, for example, because they were not considered a concern or because the methods were not available. Provided the storage conditions are suitable, measuring both old and recent samples at the same time and with the same methods reveals trends more reliably than looking at published data to which to compare more recent measurements. Such retrospective monitoring can for example help to establish whether voluntary or regulatory restrictions were sufficient to reduce the occurrence of a harmful chemical in the environment or whether the concentrations of a replacement are increasing to potentially harmful amounts. Archiving thus allows today's samples to be used to answer tomorrow's questions.

As discussed above, fish samples are particularly suitable for monitoring chemicals.. In terms of storage, when the Fish Tissue Archive was started in 2007, it was decided to freeze fish in a liquid nitrogen cooled container on site and then store whole or homogenized fish at -80°C, which should ensure very little change for most parameters that could be analysed. In the case of whole fish it still allows to analysis of individual organs if desired. Most samples in environmental specimen banks are stored frozen, although the temperatures vary between -20°C and liquid nitrogen storage and for some purposes (freeze) dried samples stored at room temperature or samples stored in a refrigerator may be suitable. Essentially, the colder the temperature and the faster the freezing the less change that might influence the sample is to be expected over time. Table 1.3-2 gives an overview of environmental specimen banks currently in use along with the time since when they have been operational. Some, such as the Swedish and (originally West) German specimen banks and the UK predatory bird monitoring scheme started as long ago as the 1960s or 70s, therefore having already built up about four decades worth of samples and data, while others were only opened recently or still in the planning phase at the time of writing.

The set-up depends among other things on the purpose of the collections. For example: should specific (known) polluted sites be monitored to demonstrate

improvements or is the purpose to watch "background" pollution at relatively clean sites? Collecting samples before and after a major planned modification of a local environment allows monitoring its impact and learning for any similar future plans. An example of this is happening in France at the moment, where an effort is underway to collect a large number of samples from the area of a planned large nuclear storage site (Bure, see Table 1.3-2) before it is built to provide a baseline and then continue the sampling into the future to monitor what changes occur as a result of construction and use of the site.

Although the intended purpose of the samples determines how, when, and where they are collected, processed, and stored, future uses may well be different or more wide-ranging than those originally envisaged. Victorian egg collectors would have never guessed that their samples, together with more recent ones, would one day help to prove the harmful effect of an insecticide (DDT) to birds. It is therefore advisable to collect and store samples with the widest possible range of future uses in mind, while at the same time ensuring that the conditions are suitable for the purpose initially in mind. Practically, it is not possible to optimise sample collection and storage for every imaginable purpose simultaneously. For example for trace chemical analysis one would avoid contact with the relevant chemical groups or materials that interfere with them as much as possible, which may mean avoiding the use of plastics when trace organics are to be analysed or avoiding the use of metals and glass when the sample is for trace metal analysis. However when the same sample is (or may be) analysed for both trace organics and trace metals and maybe genetic material too, reasonable compromises need to be made.

In addition to monitoring chemical pollution over time, some environmental specimen banks are designed to store genetic materials for research into genomics, proteomics, gene regulation processes, biodiversity, etc. While not designed for this purpose, the samples in the fish tissue archive, especially those that have not yet been homogenized, are probably suitable for most or all of those purposes.

Other biobanks store viable gametes, embryos or seeds and sometimes just any material that can be used to extract DNA or produce cell lines. Often the targets are endangered or otherwise important species, such as rare varieties of food crops, and the material is collected for conservation and breeding purposes and in-vitro studies. Examples are the Frozen Ark Consortium (http://www.frozenark.org/), which links organisations which hold such cell or tissue collections, for example of the Cryo-

Brehm[1] (http://cryo-brehm.de) German cell archive for wild animals or the Japanese National Bioresource Project http://www.nbrp.jp, whose aim is "to collect, preserve, and provide bioresources (such as experimental animals and plants) that are essential experimental materials for life sciences research".

[1] Named after Alfred Brehm, who in the 19th century documented details about a vast number of animal species in Brehm's Thierleben (various editions from 1864 onwards, some running to more than 4000 pages). The Cryo-Brehm aims to continue his work of documentation of living species by collecting information stored in the cells.

Table 1.3-2 Currently operating or planned environmental specimen banks (Asmund *et al.* 2010, Day *et al.* 2014) with additional information from the banks' websites and (Claisse 1989, Vázquez *et al.* 2007, Becker and Wise 2010, Braune *et al.* 2010)

Country	Name	City	Start year	Spatial coverage	Type (reference/ polluted)	Frequency[a]	Storage Temperature	Ecosystems	Samples
Sweden	Environmental Specimen Bank	Swedish Museum of Natural History, Stockholm	1964	Whole country	Mainly reference	systematic	-25°C -80°C Liquid N2	Marine Limnetic Terrestrial	marine: seals, fish, mussels, seabird eggs limnetic: fish, sediment terrestrial: reindeer, moose, birds, voles, earthworms, mosses, sludge
Denmark	Tissue and Data Bank for Greenland	National Environmental Research Institute, Århus	2000	Greenland	Reference	systematic	-21°C	Marine Terrestrial	seals, polar bears, fish, birds birds
Faroe Islands (DK)	Faroe Islands Environmental Specimen Bank	Torshavn Environment Agency, Traðagøta, Faroe Islands	1998	Whole country	Reference	systematic	-25°C	Marine Limnetic Terrestrial	whales, seal, dolphin, fish fish sheep, hare, grass, soil
Finland	Paljakka Environmental Specimen Bank	Finnish Forest Research Institute, Paljakka/Helsinki	1994	Whole country	Both	systematic	Liquid N2 Room T	Marine Limnetic Terrestrial	Marine+limnetic:fish Terrestrial: mosses, lichen, pine bark, seeds, needles
Norway	Norwegian Environmental Specimen Bank	Oslo Centre for Interdisciplinary Environmental and Social Research	2005	Whole country	Both	systematic	-25°C -80°C	Marine Limnetic Terrestrial	seals, polar bears, fish, mussels, crab, seabird eggs, sediment fish reindeer, birds, mosses, sludge
Germany	Umweltprobenbank	Schmallenberg/ Münster	1976	Whole country	Both	systematic	-80°C, Liquid N2	Marine Limnetic Terrestrial	several types (plants, animals, sediments) from each ecosystem, also human hair and body fluids
France	Mythilotheque	IFREMER, Nantes	1979	French coastlines		systematic	freeze dried	Marine	mussels (mytilus edilus, mytilus galloprovincialis), oysters

Country	Name	City	Start year	Spatial coverage	Type (reference/ polluted)	Frequency[a]	Storage Temperature	Ecosystems	Samples
France	L'Observatoire de Recherche sur la Qualité de l'Environnement du grand Sud-Ouest Européen (ORQUE SUDOE)	Pau	2004	Gironda, Landes, Pyrenees		systematic	-80°C	Marine Terrestrial	oysters, bivalves, eels, sediment pine needles, leaves, lichens, soils, SPM
France	Observatoire Perenne de l ' Environnement (OPE)	Bure	2009	Bure (future nuclear storage site)	Reference	systematic	-80°C	Terrestrial	leaves, tree bark, soils, birds, earth worms, food products
UK	National Fish Tissue Archive	CEH Wallingford/ Lancaster	2007	several rivers in England (Thames, Nene, Glen, Welland, Anker)	Both	systematic	-80°C	Limnetic	fish (mainly roach)
UK	Cardiff University Otter Project	Cardiff	1992	England and Wales (Scotland?)	Both	Occasional	-80 °C	Terrestrial	otter
UK	Predatory Bird Monitoring Scheme	CEH, Lancaster	1960s	Whole country		Occasional	-18°C		
Poland		Warsaw	planned	Whole country		-	-80 °C	Marine Limnetic Terrestrial	Several specimens from each ecosystem, very similar to the German ESB specimen collection
Portugal		Braga / Aveiro	2000	Mediterranean coastlines	Both	occasional	?	Marine	animal tissues
Spain		Pontevedra	1990		Both	occasional	?	Marine	animal tissues
Spain	Environmental Specimen Bank of Galicia (BEAG)	University of Santiago De Compostela	1996	Galicia					
Spain	Biscay Bay Environmental Biospecimen Bank	University of the Basque Country, Plentzia	2007	Biscay Bay	Both	systematic	-80°C	Marine Terrestrial	fish, bivalves, eels earths worms
Italy	Mediterranean Marine Mammal Tissue Bank	Padua	2002	Mediterranean coastlines	Both	occasional	-80°C	Marine	marine mammal animal tissues

Country	Name	City	Start year	Spatial coverage	Type (reference/ polluted)	Frequency[a]	Storage Temperature	Ecosystems	Samples
Italy	Antarctic Environmental Specimen Bank (BCAA)	Genoa	1994	Antarctic sites	Reference	systematic	-25°C -80°C -135°C	Marine Limnetic Terrestrial	seawater, sea-ice, SPM, sediment, fish, molluscs, sponges water, macro-algae, sediment snow, firn, soil, mosses, atmospheric particulate matter
Canada	National Wildlife Specimen Bank	Carleton University, Ottawa, ON	1974	Canada + 5% from other countries			-40°C -80°C LN2		ca 820 species, but mainly birds
Canada	National Aquatic Biological Specimen Bank and Database	Canada Centre for Inland Waters, Burlington, ON	1977	Canada, mainly Great Lakes		systematic and occasional		only limnetic?	53 fish species, also invertebrats
USA	Marine Environmental Specimen Bank	National Institute of Standards and Technology Charleston, SC						marine	fish, molluscs, marine mammals, eggs of marine birds
USA	CDC and ASTDR Specimen Packaging, Inventory, and Repository	Centers for Disease Control and Prevention							
USA	Alaska Frozen Tissue Collection	Museum of the North, University of Alaska, Fairbanks							
South Africa	Biological Resource Bank	National Zoological Gardens							
South Korea	National Environmental Specimen Bank	National Institute of Environmental Sciences, Seoul	in develo pment						
South Korea	South Sea Research Institute (SSRI)	Geoje							
China	Yangtze Environmental Specimen Bank	Tongji University, Jiaxing							

Country	Name	City	Start year	Spatial coverage	Type (reference/ polluted)	Frequency[a]	Storage Temperature	Ecosystems	Samples
Japan	Environmental Specimen Bank for Global Monitoring (es-BANK)	Center for Marine Environmental Studies, Ehime University	1960s (?)	worldwide	both			various	various: more than 100,000 samples from more than 1300 species
Japan	Time Capsule for Environment and Endangered Wildlife	National Institute of Environmental Studies, Tsukuba	1979 (pilot)	Tokyo Bay (fish) around Japanese coast (molluscs)	both	annual or "non-scheduled"	-20°C LN_2 since 2004	mainly marine	mainly marine molluscs and fish, some human breastmilk, atmospheric samples, and marine reptiles

[a] systematic: collected from specific sites at specific intervals (e.g. annually); occasional/opportunistic: often animals that have been found dead, e.g. roadkill, beached marine mammals

1.3.3 Introduction to the species monitored in this study

1.3.3.1 Roach (Rutilus rutilus)

Roach are cyprinid fish, feeding on benthic invertebrates, zooplankton, plant material and detritus. They may shift from littoral to pelagic habitats and between benthic food and zooplankton when abundance of a specific food item is high or for avoidance of predation and/or competition. They are very adaptable and can tolerate a wide range of conditions with regards to temperature, turbidity, salinity, organic pollution etc. and are found in most British rivers. They have a limited home range, although sometimes related to their spawning between April and early June short migrations to suitable spawning grounds in weedy areas occur (http://fishbase.org/summary/272). Roach are the species used routinely for the Fish Tissue Archive, because they are very commonly found in most rivers in the UK, are not much sought after by anglers and tend to remain in one area. Since they often feed on benthos there is a link with the sediment allowing for sediment-borne contamination to be detected in the fish. They are larger than bleak (see below), allowing for multiple analysis from the same specimen and/or larger sample sizes to give lower quantification limits.

1.3.3.2 Bleak (Alburnus alburnus)

Common bleak were included in the Fish Archive originally for practical reasons: They are a fairly common species that is not sought after by anglers and they often die during capture by electrofishing in the annual Environment Agency fish surveys. However, after the initial trials in 2007 and 2008, bleak were no longer included routinely as their small size limits the practical use (very few of the sampled individuals weighed more than 25 g and some weighed as little as 5 g, which is the sample size normally used for the analysis of persistent organics, leaving no sample for analysing another parameter or repeating a measurement). Like roach, bleak are pelagic cyprinids, but they are significantly smaller than roach and their occurance in the UK is mostly limited to the Southeast. They feed mainly on invertebrates (http://www.fishbase.org/summary/SpeciesSummary.php?ID=4730).

1.3.3.3 Eel (Anguilla anguilla)

The eel species found in UK freshwaters is the European eel (*Anguilla anguilla*), which is not completely accurately named because it also occurs in large parts of northern Africa. Eels have attracted a lot of attention in the scientific community recently, because since the 1980's a strong decline in recruitment across its range has been observed for the European eel as well as for the related Japanese and American eels. Total reported landings in 2010 were just 13% of the average of the 1960s (ICES 2011) and recruitment of glass eels (the juvenile stage that arrives at the shores of Europe) may have declined by as much as 95-99% compared to the average of 1960-1979 (ICES and EIFAC 2012). A specific review for England concluded that both catches and recruitment have declined by more than 70% (Aprahamian and Walker 2009). The European eel is now on the IUCN Red List classified as a "critically endangered species" (Freyhof and Kottelat 2010) and in appendix II of the convention on international trade in endangered species of wild fauna and flora (CITES). This means that international trade needs export permits and these will only be granted if the authorities are satisfied that trade will not be detrimental to the survival of the species in the wild. In the European Union a temporary total ban on all imports and exports of glass eels (juvenile eels, also known as live eel fry) is in place since December 2010 and at least 60% of eels <12 cm caught are to be used for re-stocking within the EU, with the rest mostly used for farming eel in commercial aquaculture.

The cause(s) for the eel decline are however still uncertain. Climate change, overfishing (either by humans or for example by fish eating birds), obstacles such as locks, diseases or parasites as well as chemical pollution may all be contributing factors. Despite not being clear about the main causes, some of these factors have been tackled in recent years, for example, by building eel passes into locks and restricting fishing and international trade (see above). The most recent data shows a modest increase in eel recruitment (Dekker and Casselman 2014), but it is too early to know whether that means that the eels are finally "turning a corner" or whether this is just a short pause in the decline. Hopefully, it means that measures put in place are successful in preventing the status changing from "critically endangered" to "extinct".

Eels have an unusual and complicated life cycle, which makes them at once very suitable for studying chemical contamination and vulnerable to these chemicals. Born in the Sargasso Sea, they travel thousands of kilometres to Europe where they disperse over coastal regions, rivers, streams and even ponds. During this time they develop from the transparent leaf shaped larvae *(leptocephalus)* found in the sea to transparent glass eels which enter the estuaries and rivers, pigmented elvers and then yellow eels. A random dispersion comparable to the dispersion of molecules due to Brownian motion fits quite well with the observed numbers and ages of eels, at least for the non-tidal regions (Ibbotson *et al.* 2002). In the UK the eels arriving from the Sargasso Sea have a shorter migration to the Eastern and Southern estuaries than to those on the West coast. The males spend typically 6-12 and the females 9-18 years (FAO 2004-2013) and sometimes much longer in the same freshwater system, while they build up the fat reserves needed for the spawning migration. Consequently the numbers found in the East and South are higher, but consist mainly of smaller predominantly male individuals, whereas in the West and higher up the river network smaller numbers consisting mostly of larger and longer lived female eels are found.

In most fish species the females and to a lesser extent males offload part of their contaminant burden annually during spawning, but because eels only spawn at the end of their lives they do not have that opportunity. The long life span and high fat content mean that eels accumulate higher amounts of persistent chemicals than other species (Belpaire and Goemans 2007). These characteristics and the fact that they remain in the same freshwater system for many years make them ideal for monitoring chemical pollution in the water systems where they reside, but may also quite literally store up problems for their own future or present a problem to their predators including humans. Once they reach maturity the eels change into a blueish silver colour and set off in the autumn to migrate some 6000 km back to the Sargasso Sea, where they spawn and die. In this stage they are known as silver eels and they no longer feed, relying instead entirely on their fat reserves for the migration and the spawning itself and thus either remobilizing chemicals that were incorporated into the fat, or leading to higher contaminant concentrations in the remaining fat, much of which is incorporated into the eggs. Estimates for the proportion of fat reserves used during the spawning migration vary between 39% (Palstra *et al.* 2007) and 60% (van den Thillart *et al.* 2004).

In 2007, the Environment Agency initiated a study of eels from the Thames with regards to their parasite infections. They then passed some of the remaining tissues from 35 eels (11 from a non-tidal reach and 24 from the estuary) to us to analyse for persistent organic pollutants.

1.4 Introduction to some of the chemicals currently studied

The methods used (ICP-MS after acid digestion for metals and GC-MS after Soxhlet extraction and cleanup for persistent organic pollutants, see chapter 2) have the advantage of being able to analyse a large number of similar compounds at the same time and all the measured data is reported in this thesis, but the discussion will mainly focus on those compounds for which environmental or food quality standards exist or which are otherwise interesting or likely to be of concern. Therefore only four metals with high toxicity are introduced in this chapter rather than all 17 that were measured.

The Priority Substances Directive of the EU, which defines good chemical quality for water bodies has biota standards for a small number of substances: In the original version of the legislation, which entered into force in January 2009 (European Union 2008a) environmental quality standards (EQS) for biota were only set for three chemicals: mercury at 20 µg/kg wet weight, hexachlorobenzene at 10 µg/kg ww and hexachlorobutadiene at 55 µg/kg ww. The current version (European Union 2013) added a further eight biota standards to the existing three: polybrominated di-phenyl-ethers (PBDEs, flame retardants), fluoranthene (as a marker for (incomplete) combustion products), B(a)P (to represent PAHs), the pesticide dicofol, the stainguard and firefighting foam ingredient perfluorooctane sulfonate (PFOS) and its derivatives, dioxin-like chemicals (summed up as 2,3,7,8-TCDD-equivalent toxicity), the flame retardant hexabromocyclododecane (HCBDD), and the insecticide heptachlor (incl. heptachlor epoxide). Of these only the PBDEs and some of the dioxin-like PCBs were included in the analytical suite used. Adding one or more of the other chemicals for which a biota EQS was introduced in 2013 would have been a significant effort in terms of method development, which was not possible this late in the project, but looking for some or all of those could be a good future use of the stored samples.

1.4.1 Metals

With metals it is in the element itself that is of concern and monitored. Although the toxicity and bioavailability depends on the speciation, the total concentration of a metal is much easier to analyse than the separate forms and often gives a good enough measure for what an organism is exposed to. This makes metals very different from harmful *organic* pollutants which can be destroyed by microbial degradation or other processes. With a metal on the other hand, the only known process to destroy it is nuclear fission and that is not really relevant in this context. This persistence means that there may be a large potential for bioaccumulation.

Improving environmental quality with regards to metals is not about reducing the total global amount of a metal (which is essentially fixed), but about trying to keep the bioavailability and/or toxicity (depending on the molecule the metal is in) to a minimum. For example mercury in a piece of coal has essentially no bioavailability, but when that coal is burned it is released as mercury vapour into the atmosphere from where it can enter soil and water making it far more available. Conversely both natural processes such as sedimentation and eventual ore and rock formation and deliberate human action such as storage of liquid mercury and other toxic chemicals in saltmines or binding them into insoluble compounds with low volatility can remove them from the bioavailable pool.

The “heavy metals” tend to be more toxic and therefore important to monitor, while most of the light metals (atomic number less than about 20) are essential for life as trace elements, but can nevertheless be toxic in higher concentrations. In the environment the dissolved metal ion is often more relevant for toxicology than the total concentration, because that is the easily bioavailable fraction. However, poorly soluble forms can become available for example when exposed to stomach acids and there may be different soluble forms which have different toxicities.

1.4.1.1 Example: Mercury

1.4.1.1.1 Environmental and food quality standards

A metal of particular interest is **mercury** due to the high toxicity in particular in the common form of methylmercury and similar organo-mercury compounds. It is currently the only metal for which there is a biota environmental quality standard in the EU (European Union 2013). Many countries have set standards to protect human consumers from mercury in food (Commission Regulation (EC) No 1881/2006a), but only the EU and Canada have a standard designed to protect fish eating animals. The EU standard is 20 µg/kg and the Canadian guideline is slightly higher at 33 µg/kg wet weight (Canadian Council of Ministers of the Environment 2000). The food standard for fish is much higher than the EQS at 500 µg/kg for "normal" fish and 1000 µg/kg for eel (European Commission 2005b).

1.4.1.1.2 Sources and uses

Mercury is a very rare element, comprising only 0.08 ppm in the earth's crust on average, although local concentrations can be much higher (Jonasson and Boyle 1971). It is only one of two elements that are liquid at room temperature (the other one being bromine) and evaporates easily even at relatively low temperatures, so it can spread via the atmosphere and enter surface waters through wet and dry deposition.

Mercury has been used in relatively large quantities in the chemical industry as well as in consumer products in the past. Good electrical conductivity together with the fact that it is a liquid gives it useful properties for electronics etc., while the precise reaction to temperature and pressure is used in thermometers and barometers and related applications. Mercury has also been used in pesticides or as fungicide additive for example in outdoor paints. Due to its known toxicity mercury has now been replaced or at least reduced in most applications and where it is still used, tighter safety measures are in place. Nevertheless significant amounts are still used and released into the environment. Current uses in the UK include certain types of batteries, amalgam ("silver") dental fillings (which contain about 50% mercury with the other half being silver and small amounts of other metals), fluorescent tubes or

energy-saving light bulbs where mercury vapour is an essential ingredient for which, as yet, no good alternative has been found. In addition to anthropogenic emissions to water air or soil, the natural circulation of this metal can be important. While the bioavailability of the mercury stored in natural ores is extremely low, significant amounts are released into the atmosphere when such ores are heated, for example during a volcanic eruption, and weathering of mercury containing rocks can release the metal into the aquatic environment. Burning of wood or fossil fuels, which contain traces of mercury also releases quite large amounts and accounts for the majority of mercury emissions to the atmosphere in much of the world. Deposition from the atmosphere is an important route whereby mercury enters water systems, but mercury release from the water, especially oceans, is also an important source of atmospheric mercury. It has been estimated in a number of models that about 2/3 of the current release of mercury from oceans to the atmosphere is due to previously deposited anthropogenic mercury (Selin 2009).

While most of the studies concern mercury release to the atmosphere and are therefore only indirectly relevant to freshwater systems, Water UK estimated that about half of mercury entering sewage works stems from industrial processes with the other half almost completely from "services", mainly dental surgeries (Water UK 2001). Across the world the main deliberate uses of mercury are in small scale gold (and silver) mining, as a catalyst in the production of PVC from coal and in the chloralkali industry. Of these only the chloralkali industry remains important in the EU, where the Castner-Kellner process (invented in the 1890s, also called mercury cell) for electrical hydrolysis of a NaCl solution to produce NaOH, H_2 and Cl_2 involves a bed of liquid mercury. Although the concerns about the toxicity of mercury have led the replacement of this process with mercury-free technologies in many plants, EURO CHLOR, the trade organisation of the European Chlorine industry, estimates that its members still had a total of over 6000 t of metallic mercury at their production sites at the end of 2013 (Euro Chlor 2013), while a complete voluntary phase out of the technology by its members is planned by 2020 (Euro Chlor 2011). The only UK plant on the EURO CHLOR list is in Runcorn, at the outskirts of Liverpool, which at the end of 2013 had about 418 t metallic mercury, 357 t of which was used in cells and the remainder stored, which makes it second only to BASF in Ludwigshafen (Germany) both by total amount on site or amount in use in the cells. Apart from the intended end products, the highly toxic calomel (mercurous chloride)

is formed as a by-product in the Castner-Kellner process (EU 2008), which needs to be carefully managed.

Relatively large amounts of mercury are used as a catalyst in the production of polyvinylchloride (PVC) from coal. This is very important in China, a major producer of PVC products, while most other countries, including those in the EU use oil or gas as raw material to produce the vinylchloride monomer, which does not require a catalyst. China's consumption of mercury for this process is thought to have amounted to about 800 t/year in 2012 (UNEP 2013). How much of this is released into the environment is unknown (UNEP 2013), but one estimate puts it at 24 t/year or about 1% of the total global anthropogenic emissions (Pirrone *et al.* 2010), which are estimated to be around 2000 t/year for the sum of all current anthropogenic emissions to the atmosphere (not including the re-emission of previously deposited anthropogenic mercury from land and sea) (Pirrone *et al.* 2010, UNEP 2013).

The application of metallic mercury in small scale ("artisan") gold mining is important mainly in developing countries where it poses a serious health risk to the workers involved as well as contaminating the wider environment and food sources: mercury is used to extract the gold (or silver) from crushed rocks and the gold is then recovered from the amalgam by boiling off the mercury, exposing the workers to intensive mercury fumes, often without any protection. The United Nations Environment Programme (UNEP) estimated that in 2010 (the latest figures available) small scale gold mining was the largest (>35%) contribution to global anthropogenic mercury emissions (UNEP 2013). In order to reduce the supply of mercury to dangerous practices such as the small scale gold-mining described above, an export ban for mercury and mercury compounds such as the ore cinnabar from the EU was introduced in 2008 and entered into force on 15.3.2011 (European Union 2008b). At about the same time the US also passed the mercury export ban act of 2008 banning the export of elemental mercury from 1.1.2013 (United States of America 2008), so companies in both the EU and the US, that no longer need the mercury they possess, are not able to export it to areas where there is still a demand for mercury, but instead have to store it securely e.g. in salt mines within the EU or the US respectively. Some people worry however, that a reduction in mercury supply to countries in Africa and Asia where most of the (often illegal) mercury use for extracting gold takes place may lead to an increased mercury price encouraging the re-opening of closed mercury mines with insufficient safety measures. This would be counterproductive as it would

essentially remove the metal from the relatively safe form of the ores into much less safe metallic mercury.

1.4.1.1.3 Toxicity

All forms of mercury are toxic to humans and animals, but the toxicity of the organic mercury compounds, particularly methylmercury and di-methylmercury is much higher than the inorganic forms: metallic mercury (Hg^0) and the Hg^+ and Hg^{2+} ions in inorganic mercury salts (Gochfeld 2003). In the environment microbial action readily transforms inorganic mercury into more toxic organo-mercury compounds, in particular methyl-mercury. For that reason methylmercury is the form most widely found in the environment (Gochfeld 2003). Methylmercury is associated with many neurological disorders such as memory loss and other negative effects, especially on the developing nervous system. Several outbreaks of mercury poisoning due to people eating mercury treated grain meant for planting were reported. The worst of these happened in Iraq in 1972, where more than six thousand people were admitted to hospital with mercury-related neurological symptoms and more than 400 died (Bakir *et al.* 1973). Even in the UK where very little mercury is used today, a recent study (Bellanger *et al.* 2013) estimated that mercury exposure is still high enough to reduce the intelligence quotient (IQ) of about 1/3 of babies born, and that the loss of earnings due to mercury related reduced intelligence amounts to 8-9 billion Euro per year for the European Union. Mercury contamination of fish is of particular interest because for most people fish and seafood is considered to be the main source of mercury intake. Top predators such as tuna are a main concern because of the bioaccumulation. This became very well known when in the 50s and 60s many people in Minamata and Niigata in Japan suffered from methylmercury poisoning after eating highly contaminated fish. The symptoms became known as Minamata disease (Takeuchi *et al.* 1962, Bakir *et al.* 1973).

Most literature data (including the values we measured) is for total mercury regardless of the speciation and assumes that in biota samples the majority of the mercury is in the form of methylmercury. It is much easier to measure total mercury than to specify the different forms. Assuming that ALL the measured mercury is the toxic methyl-mercury can be seen as a precautionary worst-case scenario. In many

cases this is not far off the truth because methylmercury accumulates much better than other forms. For fish the proportion of methylmercury in the total mercury is typically 75-95% (Gochfeld 2003). Care needs to be taken when comparing toxicities from laboratory experiments however, because where the form of the mercury is not clear, one might not compare like with like and potentially infer lower toxicity because some or all of the mercury was in a less toxic or less bio-available form. Since mercury toxicity has been so extensively studied especially over the last half-century, there is plenty of evidence of the short- and long-term effects on humans and wildlife, even at quite low concentrations. As the present thesis is concerned with tissue burdens in fish, a review by Sandheinrich and Wiener (2011) of observed effects on fish experimentally exposed to methylmercury via food or water and expressed as the observed body burdens, is particularly relevant. At body burdens in the hundreds of µg/kg various negative effects, including effects on survival and growth, and suppression of fertility, were observed. For example, when grayling eggs were exposed to methylmercury via the water for 10 days, those groups that had body burdens of 270 µg/kg, or over, as newly hatched fry still showed reduced feeding efficiency and competitive abilities as 3 year old adults (Fjeld *et al.* 1998). Field studies also found correlations between mercury concentrations and sex hormones, enzyme activities, histological changes, condition factor, gonadosomatic index, and hepatosomatic index at concentrations well below 1000 µg/kg (reviewed in Wiener *et al.* 2003). Sandheinrich and Wiener (2011) concluded that the threshold for negative effects on fish is between 300 and 700 µg/kg for whole body homogenates. Safe levels for mercury in fish in the diet of otters have been proposed between 100 µg/kg and 500 µg/kg (Boscher *et al.* 2010). The EU environmental quality standard is 20 µg/kg fresh weight (European Union 2013) and therefore lower than the levels at which the negative effects described above were observed, but the safety factor is only in the region of one order of magnitude. Considering that the levels in higher predators may be higher than in the prey species monitored, this does not seem to be an overly cautious value. Many countries have set standards to protect human consumers from mercury in food, but apart from the EU only Canada (Canadian Council of Ministers of the Environment 2000) has a standard designed to protect fish eating animals, which is 33 µg/kg fresh weight compared to the EU's 20 µg/kg.

1.4.1.1.4 Bioaccumulation

Methylmercury accumulates in fish to a much greater degree than its octanol-water partition coefficient (K_{ow}) would predict and higher concentrations are usually found in the muscle tissue than in the liver (Barak and Mason 1990a, c) unlike other hydrophobic chemicals where higher concentrations are normally found in the liver due to the higher lipid content of the liver (e.g. this study for POPs, Barak and Mason 1990a). In Barak and Mason (1990c), only in one case, where the mercury contamination was exceptionally high, were higher concentrations found in the liver than in the muscle tissue. Barak and Mason (1990c) say that this is acute contamination with metallic mercury and doesn't stay in the body long, whereas the methylmercury in the muscle typically reflects long term contamination. From the data given in Sandheinrich and Wiener (2011), it can be estimated that the biomagnification factor of methylmercury between the contaminated food and the experimental fish is usually around 4, although none of the reviewed studies exposed fish for a full life cycle, so this may be an underestimate.

A lot of the mercury in the environment is in an inorganic form, which does not bio-accumulate, but when it is converted by micro-organisms to organic mercury, mainly methylmercury it bio-accumulates very strongly. Therefore the concentration of mercury higher up the food web is very strongly influenced by processes such as the microbial methylation of Hg(II) to methylmercury which happens mainly in anaerobic sediments and algal films (Gochfeld 2003) and microbial demethylation and photo-demethylation. Bio-dilution during an algal bloom (leading to lower concentration in the algae and therefore lower contamination of their consumers) can also influence the methylmercury concentration (Wenning *et al.* 2011, p171).

1.4.1.1.5 Reported concentrations

Environment Agency water monitoring at Caversham on the river Thames returned 78% non-detects for mercury between 2006 and 2012 with the highest recorded value being 28 ng/L (Figure 1.3-1). This is below both the maximum and former annual average EQS for water. In a study of the R. Lee catchment, a highly impacted river of the Thames catchment, mean Hg values of 40 ng/L were recorded for the period of 1991-2000 (Snook and Whitehead 2004). The Europe-wide

geochemistry survey (FOREGS project, Salminen *et al.* 2013) reported a median river bed-sediment concentration for mercury as 38 µg/kg. Mercury concentrations in freshwater fish have been monitored in many countries and species. The best datasets exist for eels, which often have higher contamination than other freshwater species from the same site (eg. Downs *et al.* 1999, Edwards *et al.* 1999, Yamaguchi *et al.* 2003, Noël *et al.* 2013). Noël *et al.* (2013) provided an overview for recent European monitoring data in several species of fish including roach and eel: For eel the overall range in concentrations was almost two orders of magnitude from about 10 to 800 µg/kg but most studies had average concentrations around 100-200 µg/kg, whereas in roach the concentrations were mostly between 50 and 100 µg/kg with the exception of some higher values in Slovakia and the Czech Republic. There are indications of a reduction in mercury contamination of freshwater fish in the UK (eg. Downs *et al.* 1999) or elsewhere (eg. Lepom *et al.* 2012), but most measured concentrations remain clearly above the EQS of 20 µg/kg fresh weight.

1.4.1.2 Example: Selenium

1.4.1.2.1 Environmental and food quality standards

In the EU there is currently no EQS for selenium either in water or biota, but the United States Environmental Protection Agency (US EPA) has published a 637-page draft document for external peer review on selenium standards for water (US EPA 2014). Although acute toxicity is possible, the main risk to aquatic wildlife is from accumulation from the diet and and the main risk to aquatic wildlife from selenium is due to its transfer to eggs and the toxicity to developing embryos (deForest and Adams 2011, US EPA 2014). Fish appear to be more sensitive than other aquatic species, so it is enough to focus the attention just on fish. Both water and fish tissue standards are suggested, with the fish standards taking precedence (US EPA 2014). As the developing embryo is the most sensitive, the concentration in the eggs is the most relevant parameter and therefore the best site to monitor. A threshold of 15.2 mg/kg dry weight in the eggs or ovaries has been set in the EPA draft. The second best option is to monitor fish whole body or fillet concentrations, so the EPA authors made an extrapolation from the egg/ovary threshold to what would be the corresponding whole body or fillet concentration, which yields about half to three

quarters of the egg/ovary concentration with 8.1 mg/kg dry weight for whole body and 11.8 mg/kg for the fillet. Water standards then involve a further extrapolation into what concentration in water would produce that concentration in the fish, which is different in standing or flowing waters and is divided into 30-day-average and maximum values. The EQS for the monthly average are 1.3 µg/L for lentic systems (= still waters, such as lakes and ponds) and 4.8 µg/L for lotic (flowing) systems. The maximum values are based on the same monthly averages, assuming that any spot samples are valid for that day, so if only 1 day in a month had a high value and all others were zero then it would be allowed to be 30 times as high as the average EQS, and if the elevated concentrations occurred for more than one day or the background was not 0, then the EQS_{max} would be proportionally lower so that it would still comply with the 30-d average value. The water standards are only to be used if fish concentrations have not been measured.

1.4.1.2.2 Sources

Selenium is a natural component of rocks and soils and there are about 40 selenium-containing minerals, which can contain up to 30% Se, but all are rare and generally occur together with sulphides of other metals, such as copper, zinc and lead (US EPA 2014). Therefore mining and processing of these other metal ores can release Se to air and water and it can also be released into the atmosphere from the burning of fossil fuels in which small amounts of Se are present. Another important source of Se to water is runoff from soils naturally high in Se, especially with (excessive) irrigation. Selenium enters the environment mainly as inorganic selenate or selenite, but it is transformed to organic forms and incorporated into enzymes etc. by primary producers. At low levels this is beneficial as it is the way primary or secondary consumers get the essential selenium they need, but at higher levels it can become a problem (see toxicity).

1.4.1.2.3 Toxicity

Selenium is an essential metal needed in a number of enzymes and selenium deficiency has been extensively studied in laboratory species mainly to ensure that a lack of selenium doesn't influence the studies. However, the difference between

selenium deficiency and toxic effects is only around one or two orders of magnitude for fish, with reported required amounts as body burdens ranging between 0.05 and 1 mg/kg dw and toxic levels of 8 mg/kg (at least for some species) (US EPA 2014). The most severe effects are on larval development, but effects on growth have also been observed at body burdens about 8 mg/kg dry weight (US EPA 2014).

Several incidents of fish population collapses have been (sometimes tentatively) linked to Selenium poisoning and where they have been measured, Se concentrations in fish from the affected lakes were between 8-38, 6-36 and 15-50 mg/kg dw in three separate incidents in the US and Sweden (reviewed in: deForest and Adams 2011)

1.4.1.2.4 Bioaccumulation

As with mercury, it is mainly the organic forms of selenium that bio-accumulate and are responsible for toxic effects (US EPA 2014) and biological action is necessary to convert inorganic selenium into an organic form that is bioavailable. The difference to mercury and other heavy metals is however that selenium is an essential element, so at the lower end of the concentration range uptake is desirable and necessary, while higher concentrations are harmful.

1.4.1.2.5 Reported concentrations

Selenium is part of the monitoring suite of the Environment Agency. Data for the sites chosen for the Harmonised Monitoring Scheme (usually the lowest site sampled in a river, i.e. near the confluence or tidal limit) is publicly available from http://www.geostore.com/environment-agency/WebStore?xml=environment-agency/xml/ogcDataDownload.xml, while CEH has received data for other sites directly from the Environment Agency (WIMS data). Most reported concentrations were below the quantification limit. Some examples for rivers from which fish were collected are: In the river Lee (near the confluence with the river Thames) only 43 of the 299 sampling occasions between 9/83 and 11/14 (14%) had measurable levels at a LOQ of 1 µg/l (dissolved + suspended). For a site on the river Welland (Tinwell pumping station) all 79 sampling occasions between 2006 and 2012 (Environment Agency WIMS data) were below the detection limit of 1 µg/L, and the same was the case for all 274 samples from the Thames at Teddington between 1988 and 2013.

1.4.1.3 Example: Lead

1.4.1.3.1 Environmental and food quality standards

There is currently no environmental quality standard for lead in biota, but there is a food standard, which is 300 µg/kg (European Commission 2005b). There is also an EQS for inland surface water, which is 1.2 µg/l annual average and 14 µg/l maximum for the bioavailable fraction.

1.4.1.3.2 Sources and use

As a soft metal that is easily shaped, lead had many uses since antiquity. The malleability means that it is relatively straightforward to form a watertight seal and therefore lead was not only used for drinking vessels in ancient times but also well into the 20th century for drinking water pipes, some of which are still in use today. However, apart from local hotspots involved with industries such as lead mining and smeltering, the main source of available lead in the environment was until recently lead added to petrol to improve the smoothness and efficiency of cars. Worries about long term health issues for humans led to restrictions starting in the early 70s and from 1.1.2000 a total ban of lead in petrol sold in the EU.

The main source of bioavailable lead in a river is from wet and dry atmospheric deposition of the lead which entered the atmosphere mainly from the internal combustion engine. In addition solid lead can enter a river as lead shot, lead weights from fishing and as lead containing dust for example from paints and the abrasion of machinery parts. Depending on pH the lead in these particles will slowly be converted into a soluble, i.e. bioavailable form. Sometimes animals accidentally ingest a piece of lead, which can lead to serious effects as the strong acids in the stomach dissolve much of the solid metal. This is a known problem for ducks and other water fowl who frequently ingest lead shot, presumably mistaking it for grit which they need for their digestion.

1.4.1.3.3 Toxicity

There is more information on toxicity to humans than on wildlife. Lead mainly affects the developing nervous system leading to impairments of cognitive function to various degrees. For humans, lead exposure in early life has been associated with mental retardation and even increased tendencies towards crime and anti-social behaviour in adulthood (Nevin 2007, 2009, Mielke and Zahran 2012). The current opinion is that as with carcinogenic substances there is no threshold level, below which no adverse effects will ever occur. Nevertheless, levels can be defined that represent an acceptable risk. The European Food Safety Authority (EFSA) suggested that a one-point drop in IQ in 1% of the population would be acceptable and estimated that this would correspond to a blood lead concentration of 12 µg/l (EFSA 2010). However the current (since 1991) action level set by the Centre for Disease Control (CDC) in the USA and the World Health Organisation (WHO) is at 100 µg/l, reduced several times since it was set at 600 µg/l in 1970 (CDC: 1970: 600 µg/l, 1971: 400 µg/l, 1978: 30 µg/l, 1985: 25 µg/l). Data from Umweltbundesamt (UBA, http://www.umweltprobenbank.de/en/documents, checked 27.5.2015) in Germany show that Students in Münster had average blood lead levels of 90 µg/l (median 85, min 13, max 255 µg/l) in 1981, which reduced steadily to an average of 13.8 (5.3-37.5, median 12.9) in 2008. So despite the dramatic decrease over those 27 years, more than half the students measured still exhibited lead levels deemed above the acceptable risk of harm in 2008, although it has to be said that the levels EFSA suggested are for young children whose developing brains are more susceptible than those of the students in their 20s monitored by the UBA (Figure 4.3.1).

1.4.1.3.4 Reported concentrations

The Environment Agency has monitoring data lead in surface waters in the WIMS database, but most values are below the LOQ of 2 µg/l. Since the annual average EQS is 1.2 µg/kg, i.e. lower than the LOQ it is not possible to say from this data whether the English rivers monitored are compliant with the EQS. Of 354 freshwater samples taken between 2006 and 2012 only 14 unfiltered and none of the filtered (=dissolved) samples were above the LOQ.

1.4.1.4 Example: Cadmium

1.4.1.4.1 Environmental and food quality standards

The environmental quality standard for cadmium currently covers only water, not biota. For inland surface waters it is between ≤ 0.08 and 0.25 µg/L annual average and between ≤ 0.45 and 1.5 µg/L maximum, depending on the hardness of the water. There is a food standard for fish of 50 µg/kg fresh weight for most fish and 100 µg/kg for eel (European Commission 2005b).

1.4.1.4.2 Toxicity

A famous example of humans being poisoned with cadmium became known as the Itai Itai disease from the Japanese word for "ouch". It took many decades to conclude that the cause for the prevalence of the disease in a particular region of Japan was cadmium-contaminated river water, which was used for irrigation leading to accumulation in the rice crop (Tsuchiya 1969a, b). Chronic cadmium exposure causes bone damage which caused the intense pain felt by the Japanese Itai Itai sufferers. Even concentrations found among people not occupationally exposed, can negatively affect kidney function and lead to low bone mineral density (osteoporosis) as well as increase the risk of cancer (reviewed by Järup 2003 and Järup and Åkesson 2009).

1.4.1.4.3 Reported water concentrations

Of 344 measurements between 2006 and 2012 provided by the Environment Agency for the rivers, where fish were collected for this project (WIMS database), only 12 had detectable concentrations: dissolved Cd exceeded the LOQ 0.1 µg/L in 1/90 samples and Cd (not specified, so perhaps unfiltered) was above the LOQ of 0.1 µg/l in 3 of 254. For a few samples from one site the detection limit was lower at 0.01 µg/l and 8 of 15 of those were detectable. The environmental quality standard is between <0.45 for very soft water and 1.5 µg/l for very hard water for maximum dissolved water concentrations (European Union 2013). Even 0.45 µg/l was only exceeded once - in a sample from the Thames, which had 0.61 µg/l. Although hardness is not available for this sample, it is not likely to be very soft, because the Thames catchment is strongly influenced by chalk and therefore the water tends to be

hard for surface water. The annual average EQS's for soft to medium waters (<0.08-0.09 µg/l) are lower than the LOQ in the WIMS data, so it is not clear whether these would be exceeded, but the annual average EQS for hard or very hard water (0.15 or 0.25 µg/l) was definitely not exceeded in the WIMS data available.

1.4.2 Pesticides

Organochlorine pesticides were hailed as part of the agricultural revolution after the war but concerns about their bio-accumulating properties led to a ban or severe restriction for many of the originally developed compounds since about the 1980s (EEC 1978).The individual pesticides measured in this study are discussed in more detail below.

1.4.2.1 Hexachlorobenzene (HCB)

1.4.2.1.1 Environmental quality standard

Hexachlorobenzene is one of the three substances for which the priority substances directive had a biota standard from the first version (European Union 2008a), It gave an annual average water EQS 10 ng/L (which should be stricter if biota standard is not used) and max 50 ng/L. The biota standard is 10 µg/kg. The current version (European Union 2013) no longer has the annual average standard and instead makes the biota standard compulsory, specifying "fish" rather than the more generic "prey".

1.4.2.1.2 Sources and use

Hexachlorobenzene was used as a fungicide for seed treatment, especially on wheat to control a fungal infection called bunt and is now banned under the United Nations' Stockholm Convention on Persistent Organic Pollutants, which was adopted in May 2001 and came into force in May 2004.

In the UK it has not been used as a fungicide since 1975 but still occurred as an impurity in other pesticides after that. Another important source were aluminium smelters, where a degassing agent, hexachloroethane (HCE), was used until 2000. HCE can be transformed into HCB (Conolly *et al.* 2010). HCB can also be formed

unintentionally during combustion processes involving chlorine and organic matter, e.g. in waste incineration and the production of other chlorinated products.

1.4.2.1.3 Toxicity

Euro Chlor (2002a) states that a PNEC of 0.37 µg/l was derived from toxicological studies using organisms from three trophic levels (aquatic plants, invertebrates, and fish) and that the lowest long term NOEC is 3.7µg/l. Using the lowest NOEC and the almost lowest BCF of 2040 l/kg (the range quoted is 300-35000), Euro Chlor calculate the (more or less) lowest NOEC expressed as body burden as 7.5 µg/g wet weight. The same document reports a PNEC for mink of 0.4 µg/kg bodyweight/d and a maximum feeding rate of 0.15 kg/kg bodyweight/ day. The acceptable contamination of the mink's prey can therefore be calculated as 0.4/0.15 µg/kg = 2.7 µg/kg, which is about a factor 3 lower than the EU EQS of 10 µg/kg.

The Niagara River Biota Project (Newell *et al.* 1987) also tried to estimate what HCB contamination in fish would be safe for mink to feed on. Using a number of estimates to convert data from laboratory studies of food borne exposure of other mammals and birds to the estimated intake by a 1 kg mink eating 150 g fish/day, Newell *et al.* (1987) concluded that the lowest NOEL for non-carcinogenic effects based on the results from a study on pigs would be 330 µg/kg in the prey fish. HCB also has carcinogenic effects, for which there is no threshold level. Newell *et al.* (1987) estimated that a contamination of 20 µg/kg in the fish would give mink a lifetime cancer risk of 1/1000, whereas 200 µg/kg would lead to a 1/100 risk of cancer for the mink.

The US EPA fact sheet on HCB (US EPA year unknown) states:" animal studies suggest that humans who eat food containing 0.17 parts per million (ppm, mg/kg) of HCB for over 15 weeks or 0.029 ppm for 130 weeks may experience health effects" and "the level of exposure resulting in harmful health effects is unknown."

In Turkey in the late 1950s approximately 4000 people developed *porphyria cutanea tarda,* a liver condition which results in skin lesions after eating HCB treated wheat meant as seeds and many babies died due to the high levels of HCB in the milk of their mothers. In a follow up study in the 80s elevated HCB levels were still found

in the milk of mothers who had been exposed as children and many of the other symptoms still persisted (Gocmen *et al.* 1989).

In fish HCB has been shown to have endocrine effects, for example it increased estradiol in females and reduced 11-keto-testosterone in males of crucian carp (Zhan *et al.* 2000).

1.4.2.1.4 Reported concentrations

The Environment Agency provided data from the WIMS dataset for some sites from the rivers sampled for fish:

- River Welland, Tinwell Pumping station: quarterly samples 2006-2012, always non –detects (< 1 ng/L)
- Spotsamples Thames at Sunbury 21.12.2011: water <1 ng/L, sediment <1 µg/kg dw, fish: 0.4 and 0.9 µg/kg ww (not clear what species of fish they are)
- River Thames at Shepperton: < 1 ng/L (Dec 2011)
- River Thames at Caversham: sediment samples were taken in 2006, 2007, 2008 and 2011, but all were below the LOQs of 6 µg/kg dw in 2006, 3 µg/kg dw in 2007/08 and 1 µg/kg dw in 2011. Water: 30 samples: monthly in 2006 then quarterly for 2007-2012, one detection at 2 ng/L all others <1 ng/L
- Tidal river Thames at Woolwich: 77 samples 2006-2012, all <1 ng/L
- Total for provided water measurements since 2006: 1/136 measurements above the LOQ of 1 µg/l (Caversham 2 µg/l – see above)
- Sediment concentrations were always < LOQ (LOQ between 1 and 6 µg/kg), but only 6 samples were analysed
- Fish were 0.4 and 0.5 µg/kg at Shepperton and 0.4 and 0.9 µg/kg at Sunbury in four samples from 2011

1.4.2.2 Hexachlorobutadiene (HCBD)

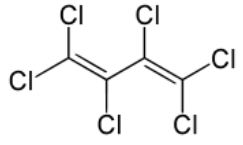


Figure 1.4-1 Structure of HCBD

1.4.2.2.1 Environmental quality standards

Hexachlorobenzene (HCBD) is a priority substance in the Water Framework Directive for which a

biota EQS of 55 µg/kg has been set (European Union 2008a, 2013).

1.4.2.2.2 Sources

Although hexachlorobutadiene (HCBD) is a pesticide that was used in agriculture as a seed dressing and fungicide, its main use was as a solvent in the production of rubber and other polymers. It was also used in hydraulic fluids and a number of other industrial processes. Now intentional production has practically ceased in the EU but it is formed as an unintended by-product during the production of tetrachloroethylene and tetrachloromethane. Improved manufacturing processes, however, mean that today very little is released (Euro Chlor 2002b). HCBD does not occur naturally. Due to the widespread use in the past, relatively high HCBD concentrations may be found in the environment of former industrial plants. In the UK 37 houses were demolished in 2002 after HCBD was found to seep into them from a landfill site associated with the ICI chemical plant in Runcorn near Liverpool, UK (Scott 2002). At the time that the HCBD contamination was discovered there were no recommended standards for indoor air pollution, so a new standard was established by the U.K. Government's committee on toxicity which recommended an acceptable level of exposure to HCBD in air of 0.6 parts per billion — a level matched or exceeded in most of the contaminated homes.

1.4.2.2.3 Toxicity

Studies in rats and humans show that HCBD undergoes several metabolisation steps in the body forming the highly toxic trichlorovinyl-chlorothioketene (TCCT) in the kidney, where it binds to adjacent tissue. Most of the toxic and carcinogenic effects of HCBD are therefore restricted to the kidney (Staples *et al.* 2003). Mild kidney problems were observed in about half of the tested residents from contaminated homes in the village mentioned above and their kidney function improved after they had moved to uncontaminated sites (Scott 2001, 2002, Staples *et al.* 2003).

Newell et al (1987) used the same approach as described above for HCB and concluded that 1300 µg/kg HCBD in the diet would not have negative non-carcinogenic effects on mink, while the dose associated with a 1/1000 and 1/100 cancer risk would be 450 and 4500 µg/kg in the diet respectively.

1.4.2.2.4 Reported concentrations

The Environment Agency monitored HCBD at the same sites as HCB since 2006 (WIMS database), but all 136 samples were below the LOQ limit (usually 3 ng/L). It was not detected in sediments (LOQ 1 µg/kg dw) or fish (LOQ 0.05µg/kg ww) either, but there were only six sediment samples (three of those were older and had higher LOQs) and four fish samples.

In a study of fish from a contaminated wetland in Louisiana in the USA back in the 1990s HCB and HCBD concentrations were well above the current EU EQS with mean HCB concentrations 23.52 ±53.54 µg/kg and HCBD 226.33 ±778.40 µg/kg at the contaminated site, compared to 2.00 ±5.62 µg/kg (HCB) and 6.84 +/- 10.41 µg/kg (HCBD) at a control site (Tchounwou *et al.* 1998). In a recent survey of eels in Scotland (Macgregor *et al.* 2010), HCBD was only detected in one of 150 samples at detection limits of either 1 or 3 µg/kg and the authors of a recent French study also failed to detect any HCBD in fish from the river Rhone in France at a detection limit of 2-3 µg/kg ww and consequently questioned the need for a European EQS for this substance (Miege *et al.* 2012). Roose *et al.* (2003) found a maximum of 12 µg/kg in eel from an industrial area of Belgium. The river Rhine with its associated chemical industry appears more contaminated — at least in the past — where concentrations over 100 µg/kg were measured in some eels in 1993 (Heinisch *et al.* 2004).

1.4.2.3 DDT (dichloro-diphenyl-trichloroethane)

1.4.2.3.1 Environmental and food quality standards

The EU doesn't currently have an EQS for DDT in biota, but there is one in Canada, which is 14 µg/kg for "total DDT" = sum of op' and pp' DDT, op' and pp'DDE, op' and pp'DDD and there is a food standard in the EU for meat for total DDT of 1000 µg/kg

1.4.2.3.2 Sources

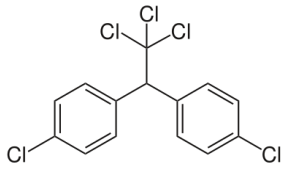


Figure 1.4-2 Structure of DDT

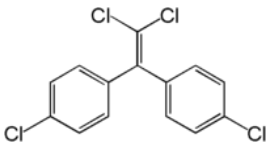


Figure 1.4-3 Structure of DDE

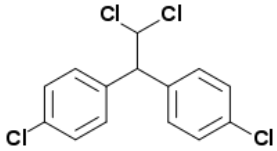


Figure 1.4-4 Structure of DDD

DDT was first synthesized in 1874 but its insecticidal properties were not discovered until 1939 (National Pesticide Information Center 2000). During World War II it was used to control diseases and after the war production and use both for disease control and as a pesticide increased dramatically. Due to its high efficiency, speed of action, relatively low toxicity to humans, low cost and persistence in the environment, it was seen as almost a miracle pesticide, said to save millions of people from insect borne disease and starvation due to crop losses (Mellanby 1992). The enthusiasm for DDT waned when the negative effects on non-target species became known and particularly when these effects were widely made public in Rachel Carson's bestselling book "Silent Spring" in 1962 (Carson *et al.* 1962). Most agricultural uses were banned in the EU from 1981 (EEC 1978).

Technical DDT consists of about 85% pp'DDT and about 15 % op'DDT and trace amounts of oo'DDT, DDE and DDD may also be present (ATSDR 2002). DDT degrades to DDE and DDD. DDE is relatively stable, therefore pp'DDE (as the degradation product of pp'DDT) is the compound typically found in the highest concentrations in the environment.

1.4.2.3.3 Toxicity

In technical DDT pp'DDT is the active ingredient, killing insects by interfering with their nervous system (ATSDR 2002). The smaller constituent of the original formulation, op'DDT, has been found to be estrogenic in vitro and in vivo (reviewed in Rogan and Chen 2005). In the environment, DDT degrades to DDE and DDD and the main DDT degradation product is pp'DDE, which is anti-androgenic (reviewed in Rogan and Chen 2005). Due to these properties exposure to DDT has been linked to early onset of puberty and various other effects on fertility and development in humans and other mammals (reviewed in Rogan and Chen 2005).

The estrogenic properties of op'DDT and technical DDT were already known or at least suspected within the first decade of its insecticidal use when reduced sperm count was observed in aviation crop dusters handling DDT (Singer 1949) and these have been confirmed by lab experiments showing for example the ability of DDT to stimulate uterus growth (a marker for estrogen exposure) in rats (Welch *et al.* 1969).

For fish there is a quite high acute toxicity which was also noted early on, e.g. Surber (1946) observed large and immediate fish kills when areas were sprayed with DDT from the air (the spraying from planes meant that streams and ponds in the area were directly hit) at concentrations commonly used in the early days. Sublethal effects were not studied in fish in the early years of use of DDT but by the 70s effects on osmoregulation became apparent (Janicki and Kinter 1971, Kinter *et al.* 1972, Riou *et al.* 2012) and later the estrogenic effects or reproductive effects particularly of op'DDT and the anti-androgenic effects of pp'DDE (Baatrup and Junge 2001) were also demonstrated in various fish species. Already in the 1950s it was observed that high DDT concentrations in eggs from contaminated lake trout appeared to be the cause of reproductive failure, whereby the fry died at a young age, even when eggs from contaminated females were fertilized with sperm from uncontaminated males and reared in clean water, whereas the contaminated males were able to reproduce normally when paired with uncontaminated females (Burdick *et al.* 1964).

Table 1.4-1 Effects of DDT and its degradation and by-products on fish

species	effect	LOEC in water	LOEC in tissue	reference
Lake trout	lethality		0.29 mg/kg	(Berlin et al. 1981, quoted from Lydy *et al.* 2011)
Pinfish	lethality		0.55 mg/kg	(Butler 1969, quoted from Lydy *et al.* 2011)
Cutthroat salmon	lethality		1 mg/kg	(Allison et al. 1963,1964, quoted from Lydy *et al.* 2011)
Goldfish	behaviour		1.65 mg/kg	(Davy et al. 1972, quoted from Lydy *et al.* 2011)
Chinook salmon	lethality		3.65 mg/kg	(Buhler 1969, quoted from Lydy *et al.* 2011)
Brook trout	Reproduction		7.5 mg/kg	(Macek 1968b, quoted from Lydy *et al.* 2011)
Brook trout	growth		11 mg/kg	(Macek 1968a, quoted from Lydy *et al.* 2011)
Coho Salmon	lethality		34 mg/kg	(Buhler 1969, quoted from Lydy *et al.* 2011)

species	effect	LOEC in water	LOEC in tissue	reference
juvenile rainbow trout	vitellogenin ↑ Hepatic estrogen binding sites ↑		45 mg/kg op' DDT 90 mg/kg op'DDE (total dose injected)	(Donohoe and Curtis 1996)
Fathead minnow	lethality		112 mg/kg	(Jarvin et al. 1976, 1977, quoted from Lydy *et al.* 2011)
adult Japanese medaka	gene expression for choriogenins	1 µg/L op' DDT, 48h		(Uchida *et al.* 2010)
Killifish	acute toxicity	LC50 (2 days) 75 µg/L		(Kinter *et al.* 1972)
adult Japanese medaka	gene expression for vitellogenins and estrogen receptor α	100 µg/L op' DDT, 48h		(Uchida *et al.* 2010)
American eel	osmoregulation	serum osmolarity increased after 6 hrs at 250 µg/L various parameters measured after 6 hrs, but concentrations used are lethal		(Kinter *et al.* 1972)
American eel (in vitro study)	inhibits the (Na(+) and K(+)) activated, Mg(2+)-dependent adenosine triphosphatase in homogenates of the intestinal mucosa	5 mg/L, 50 % inhibition at ca. 15 mg/L		(Janicki and Kinter 1971)
American eel (in vitro study)	impaired osmoregulation in eels adapted to sea water	50 mg/L, single concentration pumped through isolated intestines → water absorption reduced by 47%		(Janicki and Kinter 1971)
male summer flounder	endocrine disruption	op'DDT had similar effects to E2		(Mills *et al.* 2001)
Tilapia	osmoregulation	environmental DDT concentrations		(Riou *et al.* 2012)
Japanese medaka	comparison in vivo-in vitro	op'DDT		(Chakraborty *et al.* 2011)
African sharptooth catfish	monitored easy to measure markers, but failed to find an effect of pp'DDT (lab) or technical DDT (field) at environmental concentrations	pp'DDT, techn DDT		(Brink *et al.* 2012a, Brink *et al.* 2012b)
adult male guppy	ejaculated sperm↓ sexual colouration ↓ courtship behaviour ↓	pp'DDE		(Baatrup and Junge 2001)
juvenile guppy	same as for adults + skewed sex ratio	pp'DDE		(Bayley *et al.* 2002)

1.4.2.3.4 Reported water concentrations

The Environment Agency has been monitoring DDTs in river water since the 1970s. Data for the lower end of many medium to large rivers is publicly available in the Harmonised Monitoring Scheme (HMS). At the time of writing the available time period was from 1974 to 2013 (available from http://www.geostore.com/environment-agency/) but most of the samples were recorded as non-detects for all the DDTs measured (pp'DDT, pp'DDE, pp'DDD). For example for the most commonly found degradation product pp'DDE only 7 of the over 800 samples analysed between 1974 and 2013 were measurable in the River Thames at Teddington (LOQ reduced from 20 ng/L in the 1970s to 1 ng/L by 2000) and even in the Lee, where this study found high concentrations of DDTs in fish higher up in the river (see Chapters 3 and 4), pp'DDE was only detected 11 out of 360 times and 6 of those positive detections were in the first two years (1974/75).

1.4.2.4 Lindane (γ-HCH), chlordane and endosulfan

The other pesticides in this study, while less intensely studied than DDT, are also all known or suspected endocrine disruptors in fish. For example, the insecticide lindane (γ-HCH) caused reduction in sex steroid hormones along with other effects on the reproductive axis of both sexes of catfish (Singh and Canario 2004), the contact insecticide chlordane was linked to thyroid problems in wild fish (Brar *et al.* 2010), and endosulfan was shown in vitro to stimulate medaka estrogen receptor α (Chakraborty *et al.* 2011).

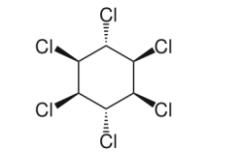


Figure 1.4-5 Lindane (γ-HCH)

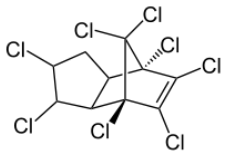


Figure 1.4-6 Chlordane

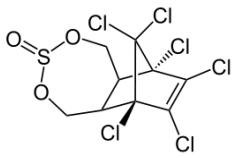


Figure 1.4-7 Endosulfan

Chlordane and technical HCH (which is typically dominated by the α-congener) were banned in the EU in 1981 (EEC 1978) and the sale of technical HCH was banned in the UK in 1979 (Breivik *et al.* 1999) while (almost) pure γ-HCH (lindane) and endosulfan could be used until 2002 European Commission (2000) and 2007 European Commission (2005a) respectively. It was estimated that, between 1970 and 1996, 382 000 t of technical HCH and 81 000 t of

lindane were used in Europe (Breivik *et al.* 1999). In the 1970s most of that was technical HCH, but after 1981 only γ-HCH was allowed. The result of this was that the major component of technical HCH, α-HCH, was almost totally eliminated, reducing from an estimated 25,000 t across Europe in 1970 to an estimated 366 t in 1996 - from remaining uses in non-EU countries. The estimates for the active ingredient γ-HCH by contrast only reduced from nearly 7900t to 2300 t in the same time span (Breivik *et al.* 1999).

Table 1.4-2 Relative contribution of the different isomers to technical HCH (%) from Breivik *et al.* (1999)

α	β	γ	δ	ε	Reference
55–80	–	–	–	1–2	UNEP (1995)
55–80	5–14	8–15	2–16	1–5	Hayes (1982)
65–70	7–10	14–15	6–10		Von Eichler (1983)
60–70	5–12	10–15	6–10	3–4	Kutz et al. (1991)
55–80	5–14	8–15	2–16	3–5	Metcalf (1955)
65–70	5–6	13–15	6	–	ECDIN (1998)

1.4.3 Polychlorinated biphenyls (PCBs)

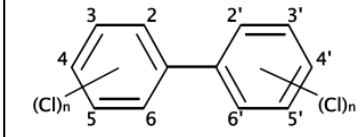


Figure 1.4-8 Structure of PCBs

Polychlorinated biphenyls are a group of a possible 209 congeners, of which about 130 were used in commercial products. They are usually referred to by an ID number between 1 and 209, which depends on the number and position of the Cl atoms. Biphenyl itself is sometimes included in the list as number 0 (the full list is given in the appendix). Six or seven commonly detected PCBs (ICES6= PCBs 28, 52, 101, 118, 153 and 180, or ICES7 = ICES6 + dioxin-like PCB138) are used as indicators for PCB contamination.

1.4.3.1.1 Environmental and food quality standards

There are currently two food standards concerning PCBs in wild fish. The limit for non dioxin-like PCBs is 300 µg/kg ww for eel and 125 µg/kg for other freshwater fish for the sum of ICES6 PCBs. There is also a standard for dioxin-like toxicity for the sum of dioxins, furans and dioxin-like PCBs expressed as TCDD-toxicity equivalents. This is 6.5 ng/kg, except for eel where 10 ng/kg are allowed

(European Commission 2005b). For dioxin-like toxicity, there is an environmental quality standard which is set in line with the food standard at 6.5 ng/kg (European Union 2013).

1.4.3.1.2 Sources

PCBs were widely used in the 1950s and 1960s as their chemical stability, good thermal conductivity, and electrical insulating properties seemed to make them ideal for use as cooling fluids in transformers and many other uses. Their input into the environment peaked in the 1960s before concerns over human and environmental health effects led to severe restrictions from the 1970s onwards and eventually a ban on all use in new products in the UK in 1986. Now existing PCBs are being systematically destroyed (DEFRA 1997, 2002). In the only UK plant (Monsanto) production of PCBs ceased in 1977 and worldwide most plants ceased production by 1984 except for two USSR plants which continued until 1990 and 1993 respectively (Breivik *et al.* 2007). Closed uses in existing equipment containing in excess of 5 L PCB were allowed to continue until the end of 2000 and some equipment containing smaller amounts may still be in use today. The total worldwide production of PCBs since their invention has been estimated as 1.3 million tons and they are now globally distributed, but compared to many other POPs atmospheric PCB concentrations have a distinctly "urban" distribution, because they were used in industry and power generation. Because of this usage pattern, which correlates with population density, population density can be used as a surrogate to model PCB releases to air (Breivik *et al.* 2007).

1.4.3.1.3 Toxicity

Several PCBs are chiral (existing in two different forms which cannot be superimposed on each other). This is caused by restricted rotation around the single bond due to the large substitutes (in this case the Cl atoms) and is called atropisomery (Smith 2009). 19 of the PCBs have atropisomers that are stable at room temperature (defined as taking >1000 s to convert from one form to the other; at higher temperatures the conversion is faster). Both versions of the molecule are produced in equal amounts and have the same chemical and physical properties except when they interact with other chiral structures. Enzymes and receptors are often chiral, therefore

the enantiomers are selectively transformed and/or can exhibit differential toxicity. Finding an enatiomer fraction that is significantly different from 0.5 therefore suggests that biotransformation has taken place. Different organisms may be able to metabolise one or the other of the enantiomers, so the enantiomer fraction may be less than 0.5 in one and more than 0.5 in another. For example for PCB 91 Dang *et al.* (2010) found more than 60% of one enantiomer in fine benthic organic matter (fine fraction of sediments) and in semipermeble membrane extracts, which may have received desorbed chemical originating from the sediments, while in fish (yellowfin shiner) there was more than 60% of the other enantiomer and in coarse particulate organics (rotting leaves) and mayflies the enantiomer fractions were close to 0.5.

A number of PCBs have structural features that are similar to 2,3,7,8-tetra-chloro-dibenzo-dioxin (TCDD). These "dioxin-like" PCBs are the non-ortho and mono-ortho substituted PCBs and have been assigned toxicity equivalency factors (TEF) by the World Health Organization (Van den Berg *et al.* 1998, Van den Berg *et al.* 2006). There are indications that contamination with dioxin-like PCBs has adverse effects on fish: For example Sures and Knopf (2004) found that the most potent dioxin-like PCB126 (not analysed here) completely suppressed the immune response of eels experimentally infected with the nematode *A. crassus*, making them much more susceptible to this disease. PCBs have also been linked to thyroid hormone disruption (Brar *et al.* 2010) and reduced reproductive success (Daouk *et al.* 2011) in fish

Fish can accumulate PCBs either directly from their water environment or from their diet, but as with other persistent and hydrophobic chemicals the dietary exposure is the major contributor.

1.4.4 Flame retardants: Polybrominated diphenyl-ethers (PBDEs)

1.4.4.1.1 Environmental quality standards

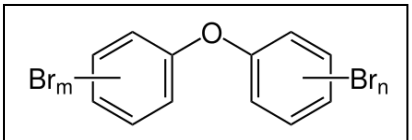


Figure 1.4-9 Structure of PBDEs

The previous version of the Priority Substances Directive (European Union 2008a) had an annual average water EQS of 0.0005 µg/L for the sum of six commonly found PBDEs (congener numbers: 28, 47, 99, 100, 153, 154),

but this has now been replaced with the biota EQS of 0.0085 µg/kg ww and a maximum water concentration of 0.14 µg/L for inland surface waters was added (European Union 2013).

1.4.4.1.2 Sources

Polybrominated diphenyl ethers (PBDEs) were until relatively recently, extensively used as flame retardants mainly in electronic equipment and polyurethane foams used in upholstery. In 2000, brominated flame retardants accounted for 38% of the global demand share of bromine, a stark increase compared with 8% in 1975 (Birnbaum and Staskal 2004). 209 congeners are theoretically possible, equivalent to the ones for PCBs (the full list for PCBs is reproduced in the appendix).

Usually PBDEs are used as additive flame retardants meaning that they are not chemically bound to the product they are protecting. The so-called penta-mixes, consisting mainly of congeners 99 (2,2',4,4',5-penta-BDE) and 47 (2,2',4,4'-Tetra-BDE) with smaller amounts of penta-BDE 100, hexa-BDEs 153 and 154 and Penta-BDE 85, were the most commonly used until they were banned in the EU under the recast Restriction of Hazardous Substances Directive (European Union 2002). Due to their high Log K_{ow}s (6.57 for penta-BDE, 8.35-8.9 for octa, and 9.97 for deca), very little is found dissolved in water with the majority being bound to the organic fraction of suspended particles and bed-sediments, or the lipid in aquatic organisms (Wenning *et al.* 2011, Tlili *et al.* 2012). Airborne particle transport is believed to be responsible for PBDEs being found in ice cores as far away as the arctic circle from the 1970's onward (Hermanson *et al.* 2010) but compared to HCB there is a much greater geographical variation of atmospheric concentrations with the UK being a European hotspot in samples from 2002, which was believed to be related to their high production and use there (Jaward *et al.* 2004). In a survey of eels across Europe the UK sample also had the highest PBDE concentrations (Santillo *et al.* 2005).

Industry in the EU signed up to a voluntary ban of penta-BDE which was formalised in July 2003, but reductions in use occurred already before that, which was followed by a European Union directive restricting the use of penta-BDE and octa-BDE in electrical and electronic equipment by 1 July 2006 (European Union 2002, Birnbaum and Staskal 2004). Deca-BDE was initially exempted and its use increased briefly following the ban on the others, but for electrical and electronic components

the exemption was reversed and it too can no longer be used in electrical appliances since July 2008. This ban does not apply to other applications such as soft furnishings. Because different analytical methods would be needed for deca-BDE it was not measured along with the other BDEs.

1.4.4.1.3 Toxicity

Few studies on the toxicity of PBDEs to aquatic wildlife exist, but Muirhead *et al.* (2005) found a clear reduction in fertility and condition factor in male fathead minnows exposed to BDE 47 contaminated food. Extrapolating from studies on the neurodevelopment in mice the EFSA (2011) derived body burdens at which an effect might be expected in humans by calculating the $BMDL_{10}$ (bench mark dose, lower 95% confidence level for a 10% response) as 309 µg/kg for BDE-47; 12 µg/kg for BDE-99, 83 µg/kg for BDE-153 and 1,700 µg/kg for BDE-209. Fish take up PBDEs mainly through their food and since the chemical tends to be associated with sediments, bottom dwelling fish are often more contaminated than pelagic fish (Wenning *et al.* 2011). Tomy et al. (2004) reported biomagnification factors between 35 and 45 for the 6 PBDEs, which are in the EQS, when juvenile lake trout were fed PBDE spiked food at high concentrations.

1.4.4.1.4 Reported concentrations

Lower brominated BDESs are more volatile than higher brominated ones, so are more likely to be found in air samples. There is an indication that some photo de-bromination occurs (Söderström *et al.* 2003).

Law *et al.* (2008) reviewed PBDE concentrations in a variety of matrices including fish: Typical concentrations for European freshwater fish are from the hundreds of ng/kg to the low tens of µg/kg for the sum of 6 BDEs. Roosens *et al.* (2008) reported similar values when reviewing BDE 47 (which is typically about 3/4 of the sum of 6 BDEs) in eels, although samples taken from an industrialized region of Belgium were higher with an average of 77 µg/kg ww. From the data given in a further Belgian study (Roosens *et al.* 2010) wet weight concentrations for the sum of 6 BDEs in eels can be estimated as having a median of 5 µg/kg in 2006 with a wide

variation of concentrations (ca. 0.2-750 µg/kg ww). Recent European river water concentrations for the sum of 6 PBDE were reported well below the water (maximum) EQS of 0.14 µg/L at 0.37 ng/L in the river Po (Italy), 0.3 ng/L in the river Danube in Hungary and 0.23 ng/L in the river Meuse (Netherlands) rivers (Hanke *et al.* 2012) and 0.02-0.27 ng/L for the sum of 11 tri-hepta BDEs (including the 6 in the EQS) in the river Seine (France) (Tlili *et al.* 2012). In an inter-laboratory comparison exercise only 20% of participating laboratories were able to detect all 6 EQS PBDEs at the requisite limit of quantification (LOQ) of 30% of the **old** EQS (European Union 2008a) of 0.5 ng/l annual average for the sum of 6 BDEs, therefore for each individual one the LOQ should be 5% of EQS (Hanke *et al.* 2012). The current directive no longer has an annual average value for PBDEs in water and the maximum value is more generous at 0.14 µg/l for inland surface waters, but the very low biota standard which replaced the annual average value (European Union 2013) is no less challenging to measure.

Although BDE 209 is the most commonly used congener it is not found very much in biota. Viganó *et al.* (2008) found it in sediments but not in fish. This may be because the molecule is so big that it is hard to move at all (Birnbaum and Staskal 2004). BDE 209 is, however, found as the congener with the highest level for most human food stuffs other than fish (EFSA 2011). In sediments collected in the Clyde estuary in 2002/03 PBDEs were found to increase towards the surface for most sites and most congeners measured and BDE 209 was found at the highest concentrations (Vane *et al.* 2010).

2 Methods

For the Fish Tissue Archive samples of roach (and in 2007 and 2008 also bleak) were collected annually (if possible) from a number of river locations in England. All fish samples are stored for future use, but a subset has also been analysed already. Details of the collection, storage and analytical methods are given in this chapter.

2.1 Sampling sites

2.1.1 Locations

Fish were caught at several sites along the Rivers Glen, Nene and Thames as well as the Thames tributaries Kennet, Lee (also spelled Lea) and Stort (Figures 2.1-1 to 2.1-3). The sites were chosen from Environment Agency fish population monitoring sites, as having sufficient roach populations to support a regular sample collection. All sites, sampled so far, were thought to represent fairly typical pollution levels for their area, rather than choosing known pollution hotspots. They represent a mix of agricultural and urban land uses as detailed below, but are not in or near major industrial areas.

Using data from the National River Flow Archive (NRFA), Landcover map 2000, and standard-period average annual rainfall (SAAR) for 1961-90 (summarized in Marsh and Hannaford (2008) and detailed in the IRN/RACQUEL program developed by CEH: http://wlwater.ceh.ac.uk/racquel/), the catchments (non-tidal area only) can be characterized as follows.

The **Glen** is a 71 km long river in the eastern UK with a catchment area of 213 km^2 mainly through agricultural land (70%) which is low lying and therefore known locally as "Holland". Only 5% is occupied by urban or rural settlements and 15% is grassland.

The River **Nene,** in the same area, is 169 km long to the tidal limit and has a catchment area of 1,666 km^2 upstream of the lowest gauging station (36 km from the tidal limit). 53% of the catchment is taken up by agriculture with about 10% urban or rural settlements.

The **Kennet** is a 92 km long tributary of the Thames with a catchment area of 1144 km^2, which is dominated by chalk geology. The annual rainfall in this catchment is about 750 mm. The sampling point was about 58 km from the source. At that point the catchment size is 543 km^2, which is dominated by rural areas: 3/4 of the area is taken up by cereals, other arable land (horticulture) and improved grassland in roughly equal proportions. Another 14% is occupied by forests and only just over 3 % is classed as urban or suburban/rural developed.

The **Lee (or Lea)** is a 93 km long tributary of the River Thames originating in Luton north of London and joining the tidal Thames in London. The sampling point was about 24 km from the source and the catchment upstream of that point is 89 km^2. It is dominated by settlements (34% classed as suburban/rural developed and 12 % as continuous urban). As with the other Thames tributaries the geology is dominated by chalk.

The **Stort** is a 45 km long tributary to the Lee sharing many of its characteristics. The sampling site at Tednambury Mill (Little Hallingbury) is 29 km downstream of the source. The catchment area above the sampling site is 135 km^2 with horticulture (38%) and cereals (20%) being the dominant land uses. About 10 % is urban or suburban/rural developed.

Both the Lee and the Stort site were chosen for having a relatively high percentage of treated sewage effluent (estimated average 28% and 43% of the flow on average) and therefore high predicted estrogenic activity in the river water.

The **Thames** in southern England has a catchment area of 9,948 km^2, a length of 255 km to the tidal limit, 14% of the catchment is taken up by settlements (classes: urban or suburban/rural developed), agriculture covers 36%, grassland 32%, and woodland 16%. The catchment receives 700 mm annual rainfall. The Thames is the only river were samples were also taken in the tidal area (eels in 2007). The Thames, especially in the densely populated area around London, has a long and well documented history of man-made pollution and recovery from pollution. In the past organic carbon from untreated sewage consumed most of the oxygen in the water culminating in "the great stink" of 1858. Matters were improved in the latter part of the 19th century by building an extensive sewer network (the first modern sewer system in the world) to transport the waste away from London to a discharge point lower in the estuary, but even in 1957s parts of the river were declared "biologically dead" by the Natural History Museum. Major improvements to sewage treatment as

well as other measures have since greatly improved the water and quality and availability of different habitats in and around the Thames, winning it the Thiess International River Prize in 2010. Further projects are still underway, for example, to improve the capacity of the London sewer system, which was designed 150 years ago for a then almost unimaginably large population of 4 million but is by now serving double that, leading to frequent (about 50-60 times a year in some places) discharges of untreated stormwater overflow (about 5% sewage and 95% urban runoff). (http://www.thameswater.co.uk/about-us/10092.htm, Figure 2.2-2).

Further fish were collected for the Archive from the rivers **Welland**, which joins with the Glen near their tidal limits, and the river **Anker** between Birmingham and Leicester. Those have not yet been analysed for any chemical compounds, but are stored for future use.

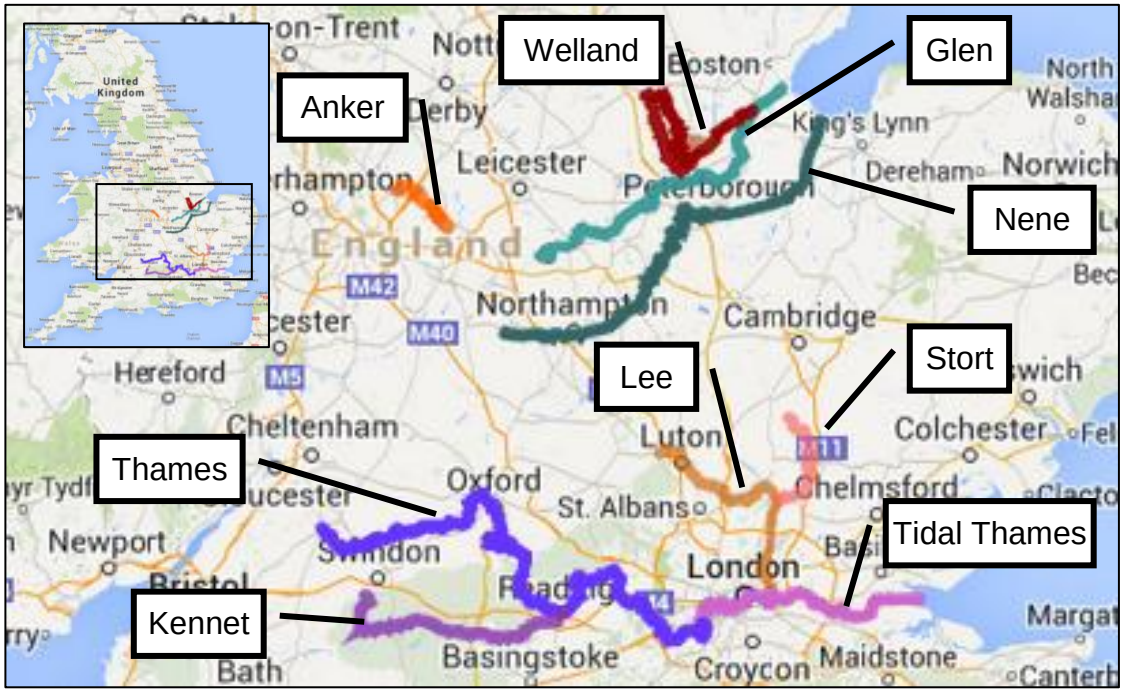


Figure 2.1-1 Map of the UK showing the names of all the rivers from which fish were collected for the Fish Tissue Archive.

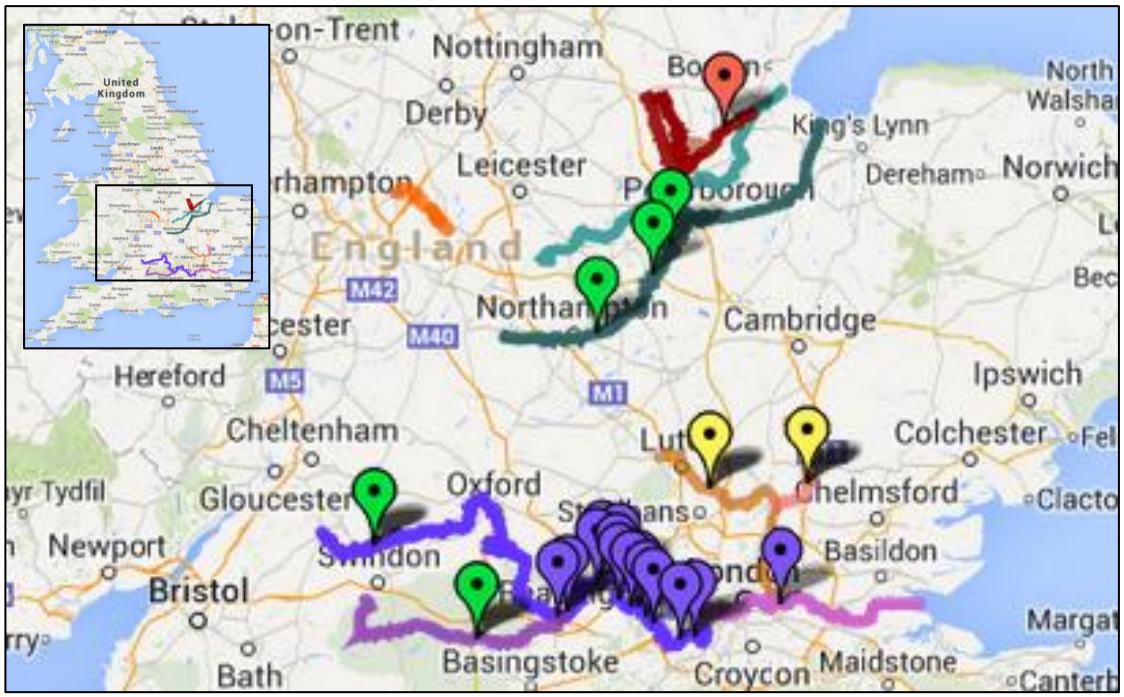


Figure 2.1-2 Sites marked from where fish were analysed for any parameter. Generally, the markers denote the middle of a short (usually 200 m) sampling stretch, but on the lower non-tidal Thames (purple, see Figure 2.1-1 for river names) they mark upstream and downstream limits of sampling stretches of several km length.

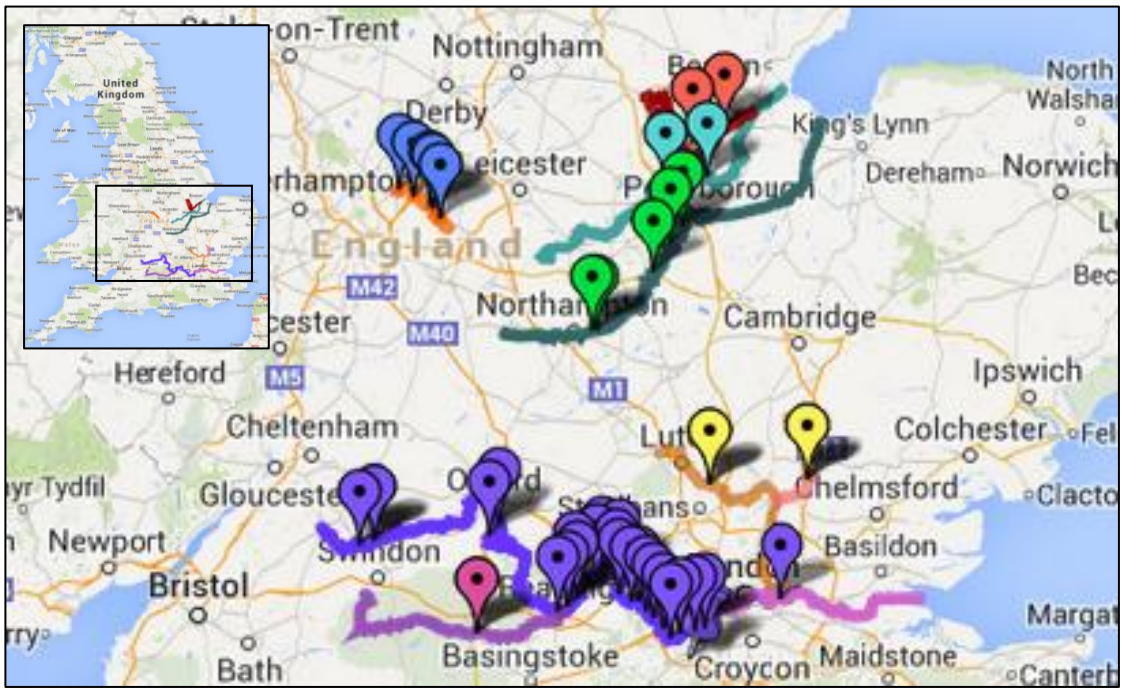


Figure 2.1-3 All sampling sites. Generally, the markers denote the middle of a short (usually 200 m) sampling stretch, but in the middle and lower non-tidal Thames (purple markers, except the two most eastern ones and the most western one in the estuary) they mark upstream and downstream limits of longer river stretches. See appendix (Section 8.1) for full details of all sampling sites and dates.

2.1.2 Estimated sewage content at the sampling sites

The estimated sewage effluent content (Figure 2.2-2) at the sampling sites was provided by Richard Williams (personal communication) using the Low Flows 2000 Water Quality eXtension model (LF2000 WQX, Wallingford HydroSolutions, Wallingford, UK). The mean percentage effluent calculated by the model is the mean concentration seen by fish that live at that point for several years calculated from the long term flow statistics. The model calculates the concentrations in a Monte Carlo framework to account for the variability in river flows, and per capita influent load. Essentially, the model does 2000 mass balance calculations using a different river flow and effluent flow for each calculation, randomly selecting the river and effluent flows from a defined distribution. The river flows used to estimate dilution were taken from flow distributions in databases within the LF2000-WQX model and are log-normally distributed and the effluent flows are normally distributed. The model outputs provide mean and 90th percentile concentrations (concentration exceeded 10% of the time). The mean percentage effluent is the average of the 2000 mass balance calculations (effluent flow/river flow). Because the river flow distribution is log-normal there are more flows less than the mean flow value than above, hence the percentage effluent is higher than if one divided the mean effluent flow by the mean river flow. For example, for the Cricklade site on the upper Thames (36 km from the source, not yet used for chemistry) the mean effluent flow divided by the mean river flow is 5.1% while the mean calculated from 2000 (random) combinations of effluent flow with river flow is 13.3% sewage effluent and is what fish would experience on average. By comparison the mean effluent flow divided by the mean river flow is the concentration when the river and sewage are both at mean flow.

The model divides the river network into stretches between “nodes” with nodes defining the start of a new stretch wherever there is a junction with a tributary or a sewage discharge. The modelled % sewage applies to the whole stretch using long term data sets for flow from 1961-1990. Thus occasionally two sampling stretches can fall within the same modelled stretch. This is the case for the adjacent stretches of Sunbury to Molesey and Molesey to Kingston on the River Thames.

2.2 Overview of the site properties

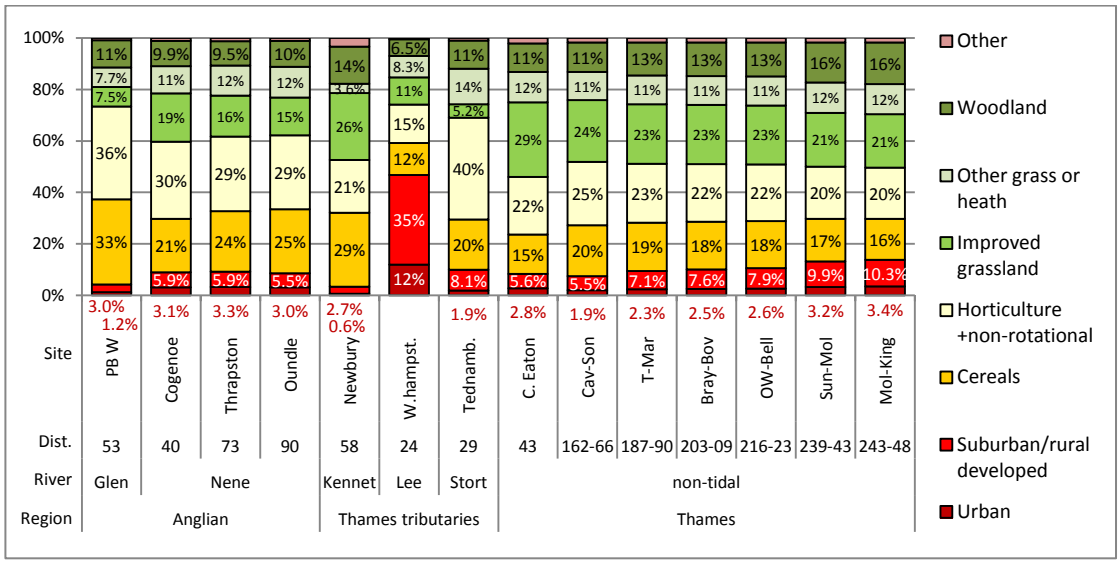


Figure 2.2-1 Landcover in the catchment above the sampling sites (data retrieved from http://wlwater.ceh.ac.uk/racquel/; see also Table 2.2-1; no data is available for the tidal area).

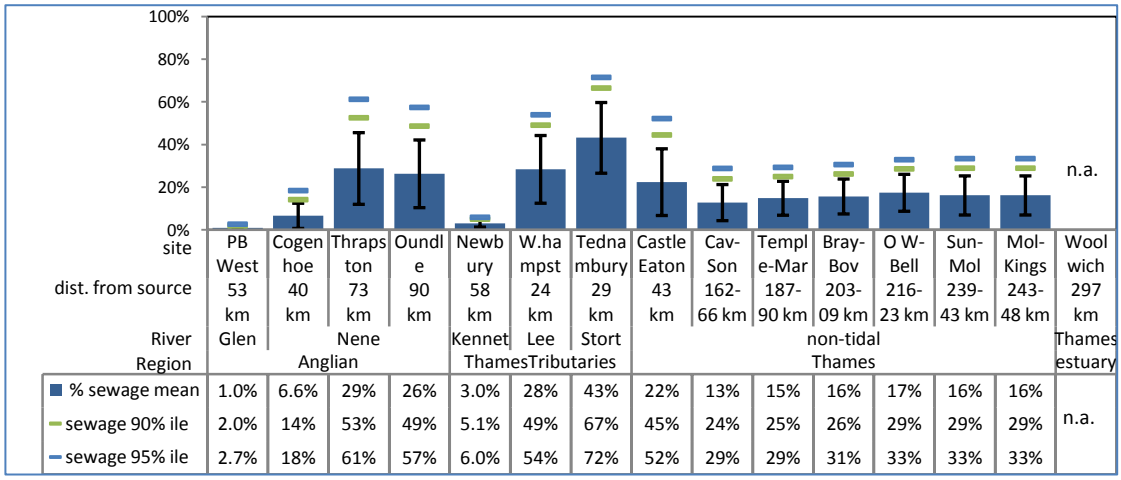


Figure 2.2-2 Modelled average and extreme (90%ile or 95%ile) sewage content at the fish sampling sites, for which chemical analyses are available (see also maps above). The two lowest sites on the non-tidal Thames Sunbury to Molesey (Sun-Mol) and Molesey to Kingston (Mol-Kings) were in the same stretch for the model, so were assigned the same values. No modelled sewage data is available for the tidal river at Woolwich.

Table 2.2-1 Landcover, rainfall and elevation in the catchments above the sampling sites. Data from Racquel website http://wlwater.ceh.ac.uk/racquel/. Some categories have been summarized, for example "woodland" consists of class 11: broadleaved/mixed woodland and class 21: coniferous woodland.

Area	Anglian				Thames tributaries			non-tidal Thames							tidal Th.
River	Glen	Nene	Nene	Nene	Kennet	Lee	Stort								
Site	Pinchbeck West	Cogenhoe	Thrapston	Oundle	Newbury	Wheathampstead	Tednambury	Castle Eaton	Caversham-Sonning	Temple-Marlow	Bray-Boveney	OW-Bell	Sunbury-Molesey	Molesey-Kingston	Woolwich
Dist. from source[a] [km]	53	40	73	90	58	24	29	43	162-66	187-90	203-09	216-23	239-43	243-48	297
Dist. to tidal limit[a] [km]	18	129	96	79	127	69	53	213	94-90	68-65	52-47	39-32	17-12	12-4	-42
Catchment area[b] [km^2]	187	612	1129	1314	543	88	135	547	5786	6700	7041	7169	9337	9852	n.a.
Urban	1.2%	3.1%	3.3%	3.0%	0.6%	11.9%	1.9%	2.8%	1.9%	2.3%	2.5%	2.6%	3.2%	3.4%	
Suburban/rural developed	3.0%	5.9%	5.9%	5.5%	2.7%	34.9%	8.1%	5.6%	5.5%	7.1%	7.6%	7.9%	9.9%	10.3%	
Cereals	33.2%	20.8%	23.5%	24.9%	28.7%	12.4%	19.6%	15.2%	19.8%	18.8%	18.5%	18.3%	16.6%	16.0%	
Horticulture +non-rotational	36.1%	29.9%	29.0%	28.7%	20.6%	15.0%	39.6%	22.5%	24.6%	22.9%	22.4%	22.1%	20.3%	19.9%	
Improved grassland	7.5%	18.9%	15.9%	14.7%	26.0%	10.6%	5.2%	29.0%	24.0%	23.2%	23.0%	22.9%	20.8%	20.8%	
Other grass or heathland	7.7%	10.5%	11.7%	12.0%	3.6%	8.3%	13.8%	11.8%	10.9%	11.2%	11.3%	11.3%	11.8%	11.8%	
Woodland	10.6%	9.9%	9.5%	10.0%	14.4%	6.5%	10.9%	11.1%	11.5%	12.8%	13.1%	13.2%	15.6%	16.1%	
Other	0.8%	1.1%	1.2%	1.1%	3.4%	0.5%	1.0%	2.1%	1.7%	1.7%	1.7%	1.7%	1.8%	1.7%	
estimated sewage content	1.0%	6.6%	29%	26%	3.0%	28%	43%	22%	13%	15%	16%	17%	16%	16%	
annual rainfall [mm]	597	641	629	625	772	664	613	766	694	696	696	696	704	707	
ave elevation [m]	56	114	102	97	166	133	95	131	121	117	116	115	111	109	
min elevation [m]	4.5	50	28	17	74	77	49	76	33	25	21	15	7	4	
max elevation [m]	132	224	224	224	294	226	144	295	330	330	330	330	330	330	

Table 2.2-2 Underlying geology in the catchments above the sampling sites. Data from Racquel website http://wlwater.ceh.ac.uk/racquel/.

Area	Anglian				Thames tributaries			non-tidal Thames							tidal Th.
River	Glen	Nene	Nene	Nene	Kennet	Lee	Stort								
Site	Pinchbeck West	Cogenhoe	Thrapston	Oundle	Newbury	Wheathampstead	Tednambury	Castle Eaton	Caversham-Sonning	Temple-Marlow	Bray-Boveney	OW-Bell	Sunbury-Molesey	Molesey-Kingston	Woolwich
Dist. from source[a] [km]	53	40	73	90	58	24	29	43	162-66	187-90	203-09	216-23	239-43	243-48	297
Catchment area[b] [km^2]	187	612	1,129	1,314	543	88	135	547	5,786	6,700	7,041	7,169	9,337	9,852	n.a.
Chalk including Red Chalk					88.4%	99.2%	50.5%	0.3%	21.9%	24.2%	26.5%	26.1%	29.7%	28.9%	
Great Oolite	25.8%	9.4%	19.8%	21.0%				43.5%	14.8%	12.8%	12.2%	12.0%	9.2%	8.7%	
Inferior Oolite	18.9%	29.2%	28.3%	26.4%				8.4%	5.2%	4.5%	4.3%	4.2%	3.2%	3.1%	
London Clay					1.9%		34.5%		3.1%	6.3%	6.8%	7.8%	9.7%	10.1%	
Oxford Clay and Kellaways Beds	35.5%	0.3%	3.1%	8.5%				30.2%	14.1%	12.2%	11.6%	11.4%	8.7%	8.3%	
Kimmeridge Clay and Ampthill Clay								6.4%	6.1%	5.3%	5.0%	4.9%	3.8%	3.6%	
Oldhaven, Blackheath, Woolwich, Reading and Thanet beds					5.9%	0.8%	15.1%		2.3%	2.8%	3.0%	3.5%	4.2%	4.0%	
Barton, Bracklesham and Bagshot Beds					0.8%				2.0%	5.5%	5.5%	5.4%	7.0%	6.9%	
Upper Lias		37.7%	34.0%	29.8%				0.8%	4.0%	3.4%	3.3%	3.2%	2.5%	2.3%	
Middle Lias		13.3%	7.4%	6.4%					4.2%	3.7%	3.5%	3.4%	2.6%	2.5%	
Lower Lias		8.9%	4.8%	4.1%					4.0%	3.5%	3.3%	3.3%	2.5%	2.4%	
Upper Greensand and Gault					3.1%			0.9%	8.0%	6.9%	6.6%	6.5%	5.8%	5.8%	
Lower Greensand								0.0%	1.1%	1.0%	0.9%	0.9%	4.4%	4.6%	
Cornbrash	19.7%	0.1%	2.0%	3.3%				5.4%	2.9%	2.5%	2.4%	2.4%	1.8%	1.7%	
Corallia								3.9%	4.7%	4.0%	3.9%	3.8%	2.9%	2.8%	
Other		1.2%	0.6%	0.5%				0.1%	1.6%	1.4%	1.3%	1.3%	1.9%	4.4%	

[a] distance along the channel

[b] catchment area above a point approximately in the centre of the sampling reach

2.3 Overview tables of how many fish have been caught on each occasion and what has been measured

Table 2.3-1 Total number of fish collected per year for the Fish Tissue Archive as of December 2014. A small subset of those has been analysed (see Table 2.3-3)

year	roach	bleak	eel	other	total	number of sampling sites
2007	44	127	35[a]		206	13
2008	125	61			186	17
2009	269				269	18
2010	200				200	16
2011	192			1[b]	193	19
2012	222				222	20
2013	251				251	22
2014	156				166	13
sum	1459	188	35	1	1683	138[c]

[a] one additional eel was recorded for weight and length, but no sample was provided
[b] one dace collected by accident
[c] total sampling occasions

Additionally, a number of samples are stored that were not originally collected for the Fish Tissue archive but donated after they had fulfilled their original purpose. These are wild roach samples which were used by Patrick Hamilton from Exeter University in breeding experiments and fish intended for human consumption from the Food and Environmental Research Agency (FERA).

Table 2.3-2 Overview how many fish were analysed for each group of chemicals[a]

Parameter	Fish analysed
Metals and dry weight	112 roach, 34 bleak
Lipid content	118 roach, 34 bleak, 35 eels, 8 roach livers, 5 bleak livers
Pesticides: HCB, DDTs, chlordanes	81 roach, 17 bleak, 35 eels, 9 roach livers, 9 bleak livers
Pesticides: HCHs and endosulfanes	56 roach, 16 bleak, 35 eels, 5 roach livers, 9 bleak livers
PCBs	81 roach, 17 bleak, 35 eels, 9 roach livers, 9 bleak livers
PBDEs	81 roach, 17 bleak, 9 roach livers, 9 bleak livers
Estrogens, alkylphenols, and BPA in bile [b]	*42 roach from 2007 were analysed by Kate Fenlon from Sussex University, but most were non-detects*
Pharmaceuticals in plasma [b]	*38 roach, 1 bleak were analysed by Jerker Fick from Umeå University (Sweden), but most were non-detects*

[a] Replicate measurements are only counted once, invalid measurements are not counted. HCBD was attempted in one batch, but large problems made all the results from that batch unreliable.

[b] As these analyses were done by outside groups and yielded mostly non-detectable concentrations, they are not further discussed.

Table 2.3-3 Overview of parameters measured in fish from each site[ab] (R: roach, B: bleak, E: eel). For a complete list of fish sampled, including those for which no chemical data exists yet, please refer to Appendix 9.1.

Region	River	site	km ds of source[c]	year	fish caught	dry weight	lipid content	metals	pesticides 1: HCB, DDTs + Chlordanes	pesticides 2: HCHs + endosulfans	PCBs	PBDEs	EDCs in bile[d]	pharmaceuticals in plasma[e]
Anglian	Glen	Pinchbeck W.	53	2009	30 R	5 R	5 R	5 R	4 R	-	4 R	4 R	-	-
	Nene	Cogenhoe	40	2008	10 R	10 R	5 R	10 R	5 R	5 R	5 R	5 R	-	-
		Thrapston	72	2008	10 R	10 R	10 R	10 R	5 R	-	5 R	5 R	-	-
		Oundle	90	2008	9 R	10 R	10 R	10 R	5 R	5 R	5 R	5 R	-	-
Thames tributaries	Kennet	Newbury	58	2011	9 R	9 R	9 R	9 R	9 R	9 R	9 R	9 R	-	-
	Lee	Wheathamp-stead	24	2011	10 R	10 R	10 R	10 R	10 R	10 R	10 R	10 R	-	-
	Stort	Tednambury Mill	29	2011	10 R	10 R	10 R	10 R	10 R	10 R	10 R	10 R	-	-
Thames	non-tidal Thames	Castle Eaton	43	2011	10 R	10 R	10 R	10 R	10 R	10 R	10 R	10 R	-	-
		Caversham-Sonning	162-166	2008 2010 2012	10 R, 13 B 26 R 10 R	10 R, 13 B - -	10 R, 13 B 1 R 5 R	10 R, 13 B - -	2 R, 3 B 1 R 5 R	2 R, 3 B - -	2 R, 3 B 1 R 5 R	2 R, 3 B 1 R 5 R	- - -	- - -
		Temple-Marlow	187-190	2007	5 R, 12 B	5 R, 5 B	4 R, 4 R liver, 5 B	5 R, 5 B	4 R (only DDTs), 4 R liver (only DDTs), 5 B, 4 B liver	5 B (only HCH), 4 B liver	4 R, 4 R liver, 5 B, 4 B liver	4 R, 4 R liver, 5 B, 4 B liver	4 R	
		Marlow-Cookham	190-196	2007	4 R, 11 B	-	-	-	-	-	-	-	3 R	
		Cookham-Boulters	196-200	2007	5 R, 10 B	-	-	-	-	-	-	-	5 R	
		Boulters-Bray	200-203	2007	6 R, 12 B	-	-	-	-	-	-	-	5 R	
		Bray-Boveney	203-209	2007 2008 2009 2012	8 R, 10 B 11 R, 6 B 10 R 10 R	- 3 R, 1 B 5 R -	- 3 R, 1 B 5 R 2 R	- 3 R, 1 B 5 R -	- - - 2 R	- - - -	- - - 2 R	- - - 2 R	8 R - - -	 - - -

Region	River	site	km ds of source[c]	year	fish caught	dry weight	lipid content	metals	pesticides 1: HCB, DDTs + Chlordanes	pesticides 2: HCHs + endosulfans	PCBs	PBDEs	EDCs in bile[d]	pharmaceuticals in plasma[e]
Thames	non-tidal Thames	Boveney-Romney	209-211	2007	6 R, 12 B	-	-	-	-	-	-	-	6R	
		Romney- Old Windsor	211-216	2007	5 R, 10 B	-	-	-	-	-	-	-	5 R	
		Old Windsor - Bell	216-223	2007	5 R, 10 B	5 R, 5 B	5 R, 4 R livers, 5 B, 5 B livers	5 R, 5 B	5 R, 5 R livers, 5 B livers	5 R, 5 R livers, 5 B livers	5 R, 5 R livers, 5 B livers	5 R, 5 R livers, 5 B livers	5 R	
		Sunbury-Molesey	239-243	2007 2012	10 B, 12 E 10 R	10 B -	10 B, 11 E 4 R	10 B -	9 B, 11 E 4 R	9 B, 11 E -	9 B, 11 E 4 R	9 B 4 R	- -	- -
		Molesey-Kingston	243-251	2009	10 R	10 R	10 R	10 R	-	-	-	-	-	-
	Thames Estuary	Woolwich area	297	2007	24 E	-	24 E	-	24 E	24 E	24 E	-	-	-

[a] Invalid measurements, where something went wrong during the process, are not included.

[b] HCBD was only attempted in one batch (analysed by Lancaster University). There were problems with the analysis of that batch preventing accurate quantification, but nevertheless it was clear that HCBD concentrations were very low, mostly non-detectable.

[c] Internationally different conventions exist on how sites on large rivers are defined, e.g. km or miles upstream of the tidal limit, or downstream of the source, or downstream of the country border etc. For the Thames "Miles above the boundary stone at Teddington Lock" (= approximately the tidal limit) is traditionally used, but for the purpose of this study the SI unit km was chosen and distances were measured from the source (longest tributary). Giving distance from the source reflects roughly the type of river or stream (small upland stream vs large lowland river) regardless of how large the whole catchment is, whereas distance from the tidal limit does not distinguish between a small tributary or the main stem of the river at the same distance from the tidal limit.

[d] Bile from a small number of fish from 2007 was analysed for estrogens and some xeno-estrogens by Elizabeth Hill's team at Sussex University, but most values were < LOQ..

[e] Plasma from some of the same fish was analysed by Jerker Fick from Umeå University, Sweden, for about 100 pharmaceuticals, but most values were < LOQ.

2.4 Fish collection

Fish sampling was carried out by fish monitoring teams of the Environment Agency of England and Wales (EA) using either seine nets or electro-fishing by wading or from a boat depending on the depth of the river. The annual EA fish monitoring strategy is to catch all the fish in a stretch of river and record species, numbers, and lengths before releasing them back into the river. This takes place between April and October and subject to weather and other constraints the same sites are always surveyed at the same time of year. For the Fish Tissue Archive the aim is to collect a sub-sample of 10 roach (*Rutilus rutilus*) of approximately 15 cm length per year at each sampling site, though actual sizes and sometimes numbers varied depending on availability. In 2007 and 2008 additionally bleak (*Alburnus alburnus*) were collected and samples of eels (*Anguilla anguilla*) were also provided by the EA in 2007. Most or all of the eels were probably in the yellow eel stage with most having very limited or no gonad development, but their silvering status was not recorded.

The fish were killed using an overdose of 2-phenoxyethanol (ca. 4 ml in a 10 L bucket), weight and length recorded, packaged in suitable bags and frozen on site in the gas phase of liquid nitrogen in a dry shipper (Air Liquide, Voyageur Plus or Taylor-Wharton CX500). On return to the laboratory the frozen fish were transferred to a -80°C freezer. Originally fluoro-ethylene-propylene (FEP) bags were used for packing fish, as this material is chemically inert and remains flexible at liquid nitrogen temperatures, but improved handling procedures allowed to switch to much more economical polyacryle/polyethylene (20/70 µm) vacuum bags, which are sufficiently flexible at the long-term storage temperature of -80°C, but brittle at the much lower temperatures used during transport in the dry shippers. For long-term storage the bags containing the frozen fish were placed inside a second vacuum bag and heat-sealed after removing as much air as possible.

2.5 Sample processing

For all analysed samples from 2008 onwards the whole frozen fish were ground into a powder without defrosting them using a cryogrinder (SPEX SamplePrep

6850): Whole frozen fish were placed in a liquid nitrogen cooled stainless steel gastronorm food container and broken into pieces with a stainless steel chisel and a hammer. The pieces were then placed in a SPEX grinding vial, with an iron impactor inside it. The crygrinder operates by submerging the vial, containing the sample, in liquid nitrogen and moving the impactor inside it between the two ends of the grinding vial at great speed using strong electro-magnets, which smashes the fish pieces into a snow-like powder.

The resulting frozen fish powder was divided into pre-cooled 20 ml glass scintillation vials and stored at -80°C until use. In the initial setup phase of the fish archive in 2007 the cryogrinder was not yet operational. Therefore the eels were cut into sections before freezing and one section was used for analysis and the roach and bleak were briefly defrosted and dorsally divided in half, with one half being analyzed for persistent organic chemicals and the other half returned to the -80°C freezer and later ground for analysis of metals. A few of the fish sampled in 2007 had blood samples taken and the liver and gall bladder dissected out. Livers were analyzed for persistent organic pollutants separately from the remaining carcass and bile for endocrine disruptors (Fenlon *et al.* 2010), while pharmaceuticals were investigated in some of the plasma samples by Jerker Fick from Umeå University, Sweden.

Non-detects were more frequent in liver samples than in whole fish. Due to the small size of the livers the amount extracted had to be reduced, sometimes more than 10 fold, increasing the detection limits, so the study subsequently focused on whole body extractions.

2.6 Dry weights

Dry weight was determined after drying the samples over night at 105°C, then letting them cool down in a desiccator with silicagel.

2.7 Quantification of metals

2.7.1 Method development: Effect of grinding and difference between contamination of skin and muscle tissue for metals

To test whether the cryogrinding process introduced metal contamination of the sample, four trout fillets were purchased from a local supermarket. Half were skinned and the other half retained the skin. The fillets and skins were then cut into approximately 2 cm strips with alternating strips being used in the cryogrinder and left unground.

Thus the following 12 samples were analysed

	ground	unground
fillet 1 skinned	x	x
fillet 2 skinned	x	x
fillet 3 with skin	x	x
fillet 4 with skin	x	x
skin of fillet 1	x	x
skin of fillet 2	x	x

2.7.2 Sample digestion

To prepare samples for metal analysis, they were digested following CEH Lancaster's standard operating procedure (SOP) number 3157. The following description gives a brief overview. A subsample of 1-2.5 g wet weight (equivalent to ca. 0.25-0.6g dry weight) frozen homogenized fish (or a few small pieces in the case of the un-ground trout fillets, see above) and 10 ml ultrapure nitric acid (Baker, Ultrex II, 67-70%) was added into a PTFE microwave digestion vessel and digested in a microwave digester (MARSXpress, CEM) programmed to ramp up the temperature to 200°C over 15 min and then hold it at 200°C for 15 min. This produced a clear solution. After cooling down, this was transferred into acid washed (2% nitric acid overnight) disposable polypropylene centrifuge tubes and made up to the final volume of 25 ml with ultrapure water (>18 MΩ/cm). Blanks containing only nitric acid and

certified reference materials (0.5 g dried fish muscle, DORM-3 and additionally dried fish liver DOLT-4 for later batches, both from National Research Council, Canada) were run with each batch.

2.7.3 Metal quantification by ICPMS

For metal quantification the method, registered as CEH Lancaster Standard operating procedure (SOP) 3504 was used. The digest was further diluted 10 fold and analysed using a Perkin Elmer Elan DRC II inductively coupled plasma mass spectrometer (ICPMS) instrument. Certified reference materials (DORM-3 and additionally DOLT-4 for later batches, both from National Research Council, Canada) were analysed alongside each batch and the readings were corrected by those of the procedural blanks.

Table 2.7-1 Method LOQs given in the SOP for metals. In the first row the instrument LOQ is given as reported and in the following two rows it is converted to µg/kg ww for a digested sample size of either 1 g or 2.5 g ww of fish. In the first batch approx. 1 g ww was digested for each sample, but for the further batches this was increased to 2-2.5 g in order to reduce the LOQs. Concentrations <LOQ were reported in the results section, but need to be treated as estimates with lower confidence.

metal	Al	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Mo	Ni	Pb	Sb	Se	Sr	V	Zn
LOQ µg/L	0.6	0.008	0.012	0.006	0.04	0.029	1	0.1	0.24	0.03	0.01	0.06	0.13	0.03	0.03	0.02	1.0
LOQ µg/kg (1g)	150	2.0	3.0	1.5	10	7.25	250	25	60	7.5	2.5	15	32.5	7.5	7.5	5.0	250
LOQ µg/kg (2.5 g)	60	0.8	1.2	0.6	4.0	2.9	100	10	24	3.0	1.0	6.0	13	3.0	3.0	2.0	100

2.7.4 Mercury by GALAHAD mercury quantifier

The principle on which this method operates can be described by the following chemical reactions associated with a number of colour changes (see equations below). KBr-BrO3 solution produces brown bromine (Eq. I). Any organic mercury compounds in the aqueous sample solution are converted to inorganic mercury ions (mercury II) by oxidation with this bromine (Eq II). Leftover free bromine or other free halogens, which would interfere with the analysis, are converted to their ionic form by hydroxylamine hydrochloride (Eq. III), removing the brown colour. Then tin chloride reduces the Hg (II) to metallic Hg (0) (Eq. IV), which is then purged from the

sample by an inert carrier gas (nitrogen or argon) and is trapped on a gold impregnated silica trap, forming an amalgam with the gold. This allows all the mercury from a relatively large sample volume (18 ml in this case) to be collected on the gold before it is heated to release all the mercury at once and measure it by atomic fluorescence spectrometry.

$$(I)\quad 5Br^- + BrO_3^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

$$(II)\quad CH_3 - Hg^+ + H^+ + \frac{1}{2}Br_2 \rightarrow Hg\ (II)^{2+} + CH_4^+ + Br^-$$

$$(III)\quad 2\ Br_2 + NH_2OH + H_2O \rightarrow 4Br^- + NO_2^- + 5H^+$$

(decolourisation=removal of brown Br_2)

$$(IV)\quad Hg(II)^{2+} + Sn^{2+} \rightarrow Hg(0) + Sn^{4+}$$

In detail, 1-10 ml (depending on the expected mercury content) of the 10 fold diluted digests from section 2.7.3 were added to 50 ml plastic centrifuge tubes and topped up with ultra-pure de-ionized water and 2.5 ml ultra-pure HCl (JT Baker 36.5-38%) and 1 ml 0.1 N KBr-BrO_3 solution to produce a final volume of 50 ml. This was shaken and left for at least 1 hr to allow the organic mercury compounds to be transformed into the inorganic ion. 50µl hydroxylamine hydrochloride (NH_2-OH·HCl) solution (12% w/v) was added shortly before anyalyis to remove remaining free Br_2. In the analyser (PS Analytical 10.525 Sir Galahad analyser with a 20.400 autosampler) the tin (II) chloride solution: 2% w/v $SnCl_2$ with 150 ml/L conc. HCl is added at a ratio of 1 ml reductant to 2 ml sample to reduce the inorganic mercury ion to metallic mercury, which is then carried to the gold trap by an inert gas (cold vapour) and measured by atomic fluorescence spectrometry.

2.8 Quantification of organic compounds

2.8.1 Extraction and purification

For the organic analysis, around 5 g of the whole fish homogenate was mixed with 30 g sodium sulphate to remove the water. This was done by grinding the sample with the sodium sulphate in a pestle and mortar for the earlier non-homogenized samples, and by quickly mixing the frozen fish powder with sodium sulphate for the homogenized samples. Procedural blanks consisting only of sodium sulphate were run with each batch. Then recovery standards ($^{13}C_{12}$ PCB mix: 28, 52,

101, 138, 153, 180 and PBDE mix 51, 128, 190) were added and the mixture extracted overnight with dichloromethane (DCM) in a Soxhlet apparatus. The DCM was evaporated in a vacuum rotary evaporator and replaced with 10 ml hexane, which was reduced to about 1 ml. This was added to a glass column with 11 g acidified silica (200 ml silica baked at 450°C and acidified with 25 ml concentrated sulfuric acid) and eluted with hexane as a first clean up step, which removes the fats. Then the sample was passed through a gel permeation chromatography column with 50:50 Hexane:DCM and only the fraction from 17 to 51 ml collected as second clean up step to remove molecules outside the size range of interest. The solvent was then again replaced with hexane and the sample added to 25 µl internal standards (PCB 30, ^{13}C-PCB141, ^{13}C-PCB208, BDE69, BDE181) in dodecane, before evaporating the hexane, so that the whole sample was contained in the 25 µl dodecane.

2.8.2 Lipid content

A subsample of the soxhlet extract (before any further purification, see 2.8.1 above) was used to determine the lipid content, by weighing the oily residue after the DCM had evaporated. Alternatively, for some samples, lipid content was determined separately by cold extraction: 1 g homogenized fish powder was ground with sand and mixed with anhydrous Na_2SO_4 to remove the water and extracted 3 times 30 minutes with a 1:1 mixture of acetone and hexane. The supernatant was then transferred into a measuring cylinder and topped up to 40 ml and any remaining particles left to settle overnight. 20 ml of that extract was left to evaporate to dryness and the weight of the lipid residue determined.

2.8.3 GCMS Analysis

The extracts were analysed by gas chromatography – mass spectrometry, single ion monitoring using negative chemical ionisation (NCI) with a 30m DB-5, 0.25 µm ID, 0.1 µm film (J&W Scientific) for HCH and endosulfans and a 50m Varian CP-SIL8 CB Pesticide column (Varian-Chrompack, Middelburg, The Netherlands) with electron impact + ionisation for all other pesticides, PCBs and PBDEs. Standards and blanks were run along with the samples. The instrument blank contained only solvent and procedural blanks went through the whole extraction and

cleanup procedure without the addition of fish homogenate (i.e. extracting only sodium sulphate). The regression for the standard curve was by peak area done $1/x^2$ weighted, which means that the **relative error** is minimized, and all peaks were manually checked for correct selection of peaks and correct positioning of the base-line and outliers removed from the standard calibration. The list of organic pollutants analysed is in Table 2.8-1. The instrument limit of detection (LOD), defined as the lowest observable standard was between 1 and 6.25 pg/µl for the analysed chemicals, which is equivalent to 5-31 ng/kg for a 5 g sample. In some cases concentrations were estimated even if they were less than the lowest standard.

Table 2.8-1 Parameters analysed

Determinand (acronym)	Comments	bans in the UK
PCBs	Polychlorinated bi-phenyls: A group of 209 theoretically possible congeners of which about 130 were used in commercial products. In this study 41 congeners: numbers 18, 22, 28/31, 41/64, 44, 49, 52, 54, 56/60, 70, 74, 87, 95, 90/101, 99, 104, 105, 110, 114, 118, 123, 138, 141, 149, 151, 132/153, 155, 156, 157, 158, 167, 170, 174, 180, 183, 187, 188, 189, 194, 199, 203 were analysed (underlined: the eight mono-ortho substituted PCBs for which the WHO has set Toxic Equivalence Factors (TEF) relative to 2,3,7,8-tetra-chloro-dibenzo-dioxin (TCDD, "dioxin" (Van den Berg *et al.* 1998, 2006)) "/" indicates that the congeners were poorly separated in the GC-MS method and had to be quantified together.	"open uses" prohibited 1972 PCB production in UK ceased: 1976 ban in all new systems: 1986 existing equipment > 5L: 2000 existing transformers: end of life span[ab] destruction plans 1997[c]
Sum ICES7 PCB	7 Commonly determined PCBs (28, 52, 101, 118, 138, 153, and 180), which give an indication of general PCB contamination. Breivik *et al.* (2007) estimated that these 7 accounted for 17.8% (14.7-22.8%) of total global PCB production. There may be a small contribution of other congeners in the data in the current report, because 28/31, 90/101 and 132/155 co-eluted	
ICES6 PCB	non-dioxin like indicator PCBs - see above without the dioxin-like PCB118	
PBDEs	Polybrominated di-phenylethers Flame retardants As with PCBs 209 congeners are theoretically possible, but only some of them were actually used. numbers 17, 28, 32, 35, 37, 47, 49, 66, 71, 75, 85, 99, 100, 118, 119, 126, 138, 153, 154, 166, 183, 196, 197 were measured	
indicator PBDEs	a set of six commonly found BDEs: 28, 47, 99, 100, 153, 154	
total DDT	the insecticide DDT and its degradation products sum of: op' DDT, pp' DDT, op' DDE, pp' DDE, op' DDD, pp' DDD	1986[de]
pp' DDE	main degradation product of DDT insecticide.	
α-chlordane β-chlordane	Chlordane: contact insecticide consisting of a mixture of related compounds, mainly □-chlordane.	1981[d]
α-HCH β-HCHγ-HCH	Hexachlorocyclohexane, γ-HCH is the insecticide Lindane.	α,β 1981[d] γ 2002[f]
α-endosulfan β-endosulfan	Insecticide	2007[g]
HCB	Hexachlorobenzene, fungicide for seed-treatment, now banned under the Stockholm Convention on Persistent Organic Pollutants	1981[ed]

[a] but need to be registered and pay an annual fee

[b] DEFRA (2002)

[c] DEFRA (1997)

[d] banned or severely restricted in EU since 1981 (EEC 1978)

[e] DEFRA (2007)

[f] complete ban in EU since 2002 (European Commission 2000)

[g] European Commission (2005a)

2.9 Fish age

2.9.1 Roach

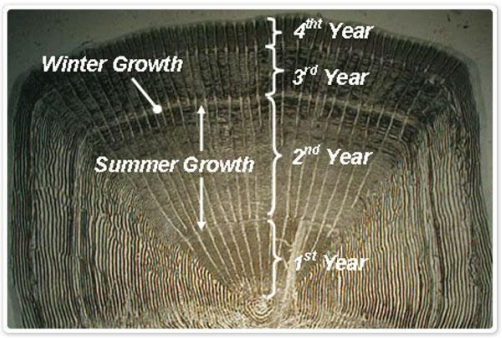
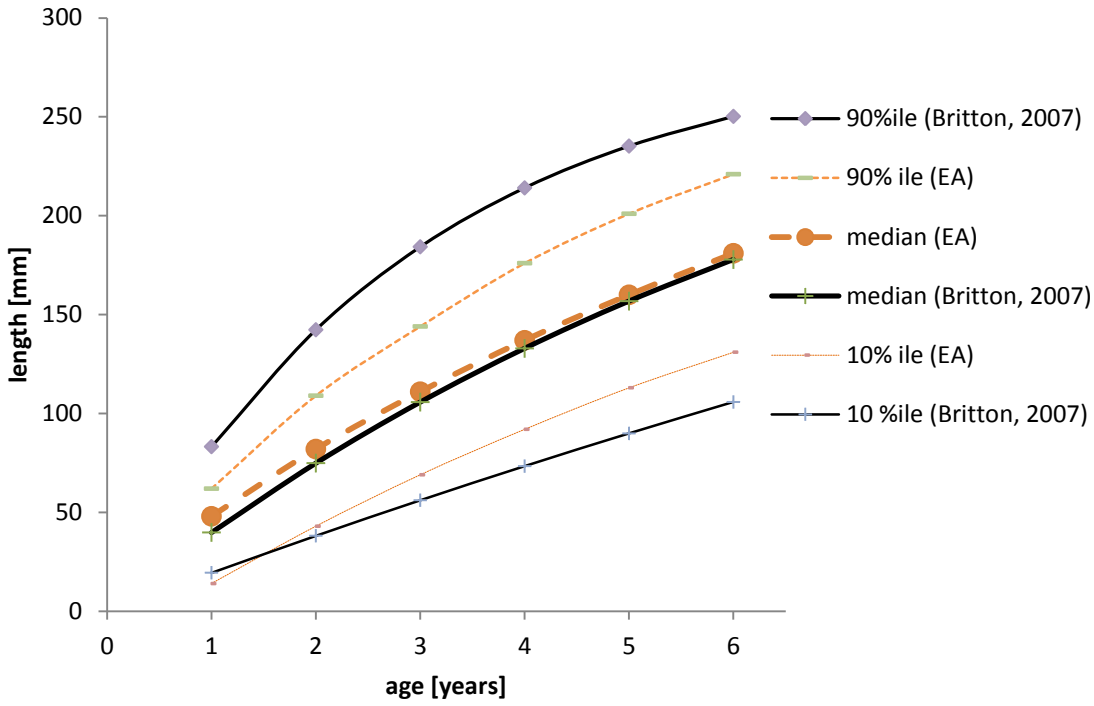


Figure 2.9-1 Illustration of growth rings on a fish scale (from http://www.bradshawsdirect.co.uk/blog/wp-content/uploads/2012/05/blogimage_fishgrowthscale.jpg)

For 29 individual roach caught in the river Anker in 2013, age and growth rate has been determined from scales by the Environment Agency Labs using the Dahl-Lea method (Dahl 1907, Lea 1910) and a further 39 roach caught in 2011 from the upper Thames and the Thames tributaries Kennet, Lee and Stort were aged by Liz Nicol from Brunel University. Slower growth during winter results in denser lines on the scales, whereas in summer the lines are more spaced out. These year rings are known as annuli. Counting the dense rings determines how many winters the individual has lived through, and hence how old it is. Using the average distance between the rings compared to the total size of the scale could be used to estimate the age to less than one year accuracy (eg. a fish caught in late autumn would have a large area outside of the last dense rings as it has spent a long summer growing fast after the last winter whereas for one caught in spring, the dense material would be right at the edge), but in practice the ages are recorded as year classes, eg. 3+ (more than 3 years old, but less than 4). The relative distance between the rings is proportional to the length of the fish, therefore together with the final length at capture it can be used to estimate the size the fish was at every year of its life.

Where this data is not yet available, ages were estimated from lengths by using the median growth curves published in Britton (2007). Those growth curves are very similar to the standard growth rates for Southern rivers which the Environment Agency uses to compare with observed growth rates (National Fisheries Services unpublished data). As the National Fisheries graphs only concern rivers in Southern England, whereas Britton (2007) gives data for all kinds of water bodies across all of

the UK, Britton's spread of growth rates is wider but the median is almost identical (Figure 2.9-2).



Britton, J. R. (2007). Reference data for evaluating the growth of common riverine fishes in the UK. *Journal of Applied Ichthyology* 23(5): 555-560.

EA: Standard growth of roach in southern rivers (National Fisheries Technical Team unpublished data)

Figure 2.9-2 Standard growth curves for roach, showing median and extremes (10%ile and 90%ile) as published by (Britton 2007) (solid black lines) and those used by the EA (orange dotted lines). The growth rates published by Britton (2007) follow the equation: $Age=\log_k(1- L_t/L_\infty)$. With L_t = current length (mm), L_∞=maximum length (mm), k=growth factor. The age is given in years. The median growth in this graph has L_∞=332 mm and k= 0.88.

2.9.2 Bleak

Although scales have been collected for the purpose of aging the fish, this has not yet been carried out in any of the samples. Instead bleak ages were estimated from their lengths using reference data for average length-age relationships in UK rivers (Britton 2007).

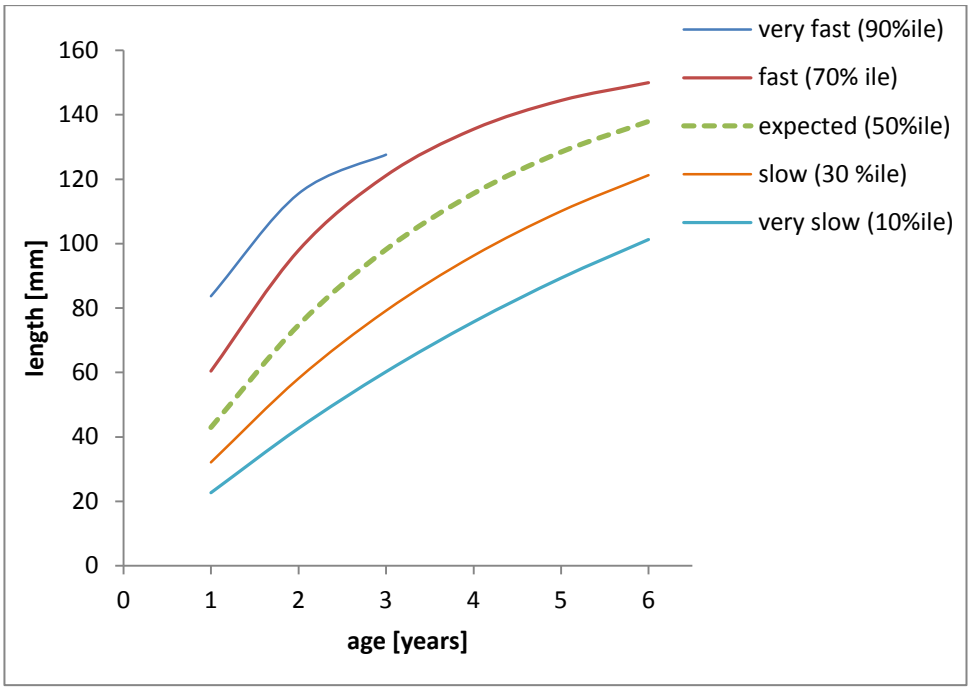


Figure 2.9-3 Standard growth curves for bleak from Britton (2007). The growth rate follows the equation: $Age=\log_k(1- L_t/L_\infty)$. With L_t = current length, L_∞=maximum length, k=growth factor. The median or expected growth in this graph has L_∞=165 mm and k= 0.74.

2.9.3 Eels

For 22 of the 36 eels in this dataset plus a further 8 from the tidal reach, continental age was available from otolith (earstone) studies done by Alan Walker's group at CEFAS (Lowestoft, Suffolk). Otoliths were stained then cut in half and polished so that the translucent rings corresponding to slower growth of the eels in winter could be counted. The more commonly used crack and burn (or burn and crack – either order has its proponents) method could not be used because the otoliths were intended for otolith microchemistry studies. For the remaining eels, for which due to unclear or duplicated lines, the age could not be determined from the otolith, age was estimated from the linear length-age relationship established for the 30 with age data.

2.10 Reliability of results/caveats

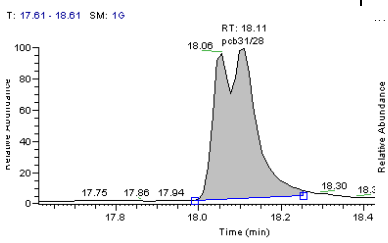
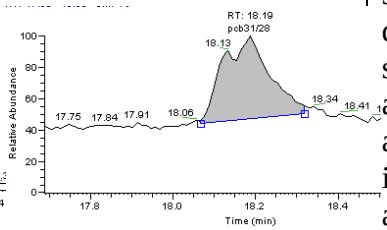
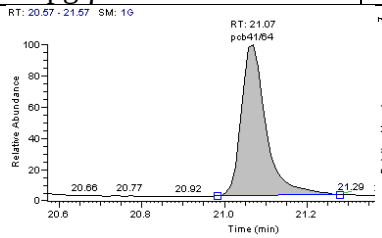
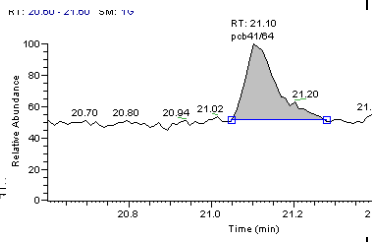
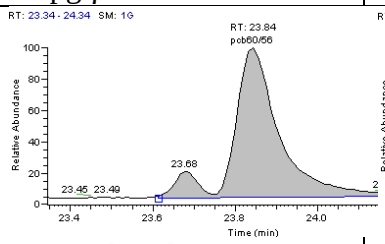
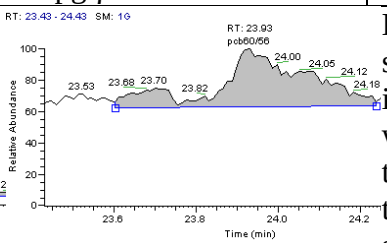
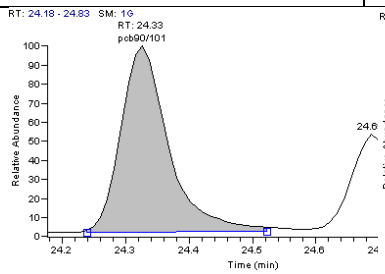
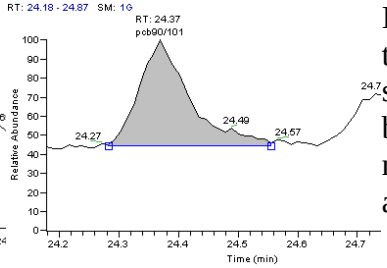
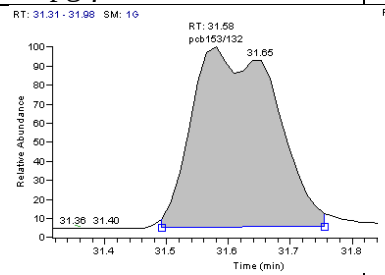
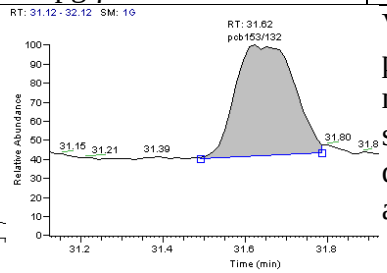
2.10.1 Double peaks for POPs

In some cases two compounds cannot be clearly separated in the chromatography (co-elution, double-peaks). They are therefore evaluated as the sum

of the two compounds, both for the standards and the samples. If the sensitivity of the detector is the same for both compounds therefore giving very similar standard curves for each of the compounds (if they were measured individually without the co-eluting one present), this works very well and gives an accurate calculation for the sum of both even though the distribution between them is not known. However, when the sensitivity of the detector is different for the two compounds, the total peak size depends not only on the sum of the two compounds but also on the distribution between them. Assuming that the calibration curve is done with equal amounts of both compounds, there is then the problem that the real sample probably does not contain equal amounts and for any actual sum of compound a and b the calculated sum depends on the proportion of each in the sample. If the compound producing the larger peak dominates, the sum will be overestimated and if the one with the smaller peak dominates, it will be underestimated. In the example below (Table 2.10-1 and Figure 2.10-1), data is used for a batch where PCBs 56 and 60 were unusually well separated making it possible to quantify them separately. The standards contained the same concentration of both compounds but the samples turned out to have mainly PCB56, which produced the second, larger peak. For the standards there is very good agreement between quantifying the two peaks separately and then adding the results or quantifying them together, but the quantification as one double peak overestimates the total concentration in all except one of the nine fish samples (Figure 2.10-1). The one sample that had good agreement between the two methods of quantification had about 40% PCB60 and 60% PCB56, i.e. a distribution that is quite close to the 50:50 in the standards, whereas for most samples the proportion of PCB60 was less than 10% of the sum.

Table 2.10-1 Compounds that co-eluted leading to double peaks. In these cases the quantification was for the sum of the two compounds, but this may be less accurate in the case of differing peak sizes for standards of the same concentration

Co-eluting peaks	High standard (usually 2.highest)	Low standard (usually 2.lowest)	Warnings
BDE 51/75 138/166	BDE51/ 75 and BDE 138/166 were only quantified together in an early batch of bleak carcasses and livers, which was eventually rejected for BDEs because the normally highest BDE47 was not found		

Co-eluting peaks	High standard (usually 2.highest)	Low standard (usually 2.lowest)	Warnings
PCB 31/28*			As the peaks are similar, the total quantification should be quite accurate, although there is a difference at low concentration
	50 pg/µl each	2.5 pg/µl each	
PCB 41/64			Impossible to tell whether the quantification of the sum is accurate.
	50 pg/µl each	2.5 pg/µl each	
PCB 60/56			Differently sized peaks introduce error when quantified together, but they can sometimes be done separately
	50 pg/µl each	2.5 pg/µl each	
PCB 90/101*			Impossible to tell what the situation is because there is no separation at all.
	50 pg/µl each	2.5 pg/µl each	
PCB 153*/132			Very similar peak sizes means that the sum can be quantified quite accurately
	50 pg/µl each	5 pg/µl each	

* among the ICES7 (or ICES6) PCBs, therefore more important to get it right than those that are not routinely monitored

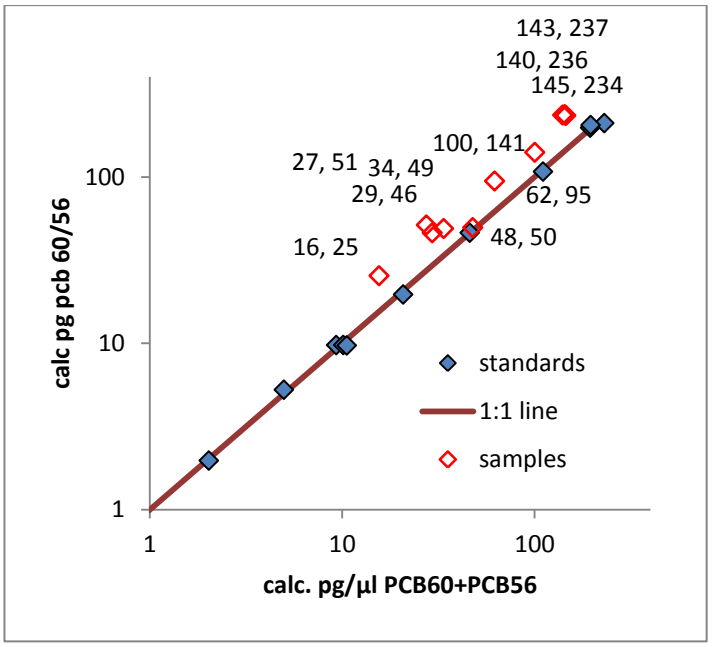


Figure 2.10-1 PCB 60 + PCB 56, quantified separately (x-axis) compared to quantified together (y-axis) for 9 samples. Data labels show the calculated values as (PCB60 +PCB56 quantified separately, PCB60/56 quantified together) for the samples. For simplicity the standards do not have data labels.

2.10.2 Metals – possible contamination in the grinding process

While the influence of the grinding itself has been tested (see chapter 3.2.1), ideally this should be repeated to test ALL the steps involved separately, both using the latest method and earlier versions, when some refinements were not yet in place. In the current method a stainless steel (surgical steel) chisel and a hammer is used to break the frozen fish into pieces inside a stainless steel food container, but for the first batches of fish ground up, the stainless steel chisel was not yet available so "ordinary" DIY chisels were used instead, or in some cases the fish were broken by hitting the FEP bag containing the fish with a hammer or for some very small or half fish breaking them by hand inside the bag. Both from the cryo-grinding itself and from breaking the fish into suitable size pieces beforehand there is therefore some potential for contamination with metals used in the production of steel, but the consistent patterns found for many metals suggests that this was not a major problem.

3 Results

The following paragraphs show the parameters that have been measured in whole body homogenates or in half fish after the liver and bile have been removed.

- The concentrations are given with regards to fresh weight
- Most results are presented as bar graphs (Figure 3.1-2 and following) where:
  - Each bar represents an individual fish
  - Fish are ordered by:
    1. region
    2. river
    3. site: upstream to downstream
    4. species
    5. sampling year
    6. fork length: small to large

3.1 Basic fish parameters

3.1.1 Dry weight

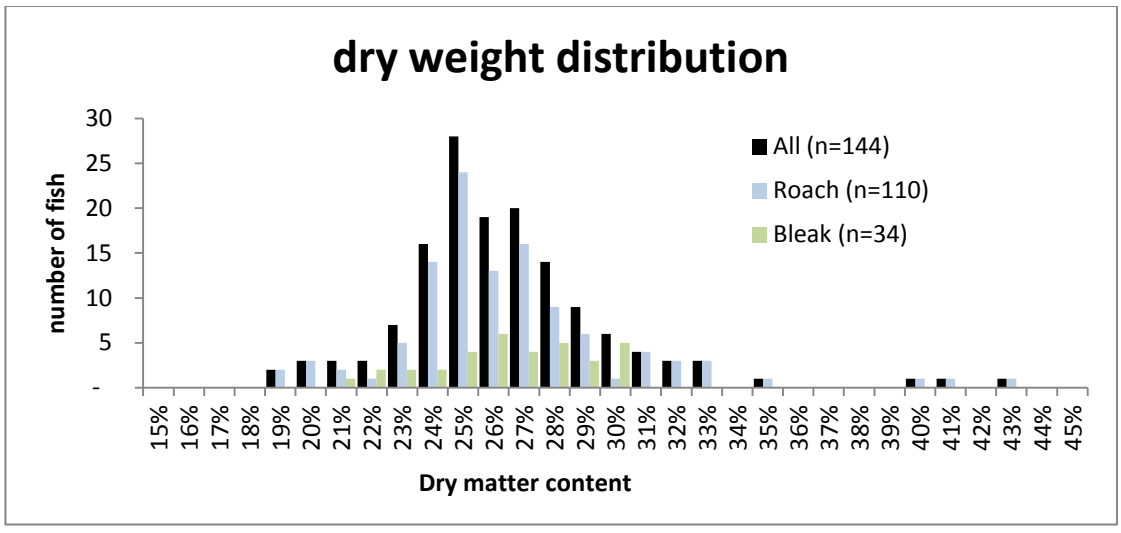


Figure 3.1-1 Distribution of dry weights for all the fish analysed for this parameter. Where individual fish were analysed several times, the average concentration was used.

The dry weight content of the bleak and roach analysed only varies on a relatively small scale (Figure 3.1-1). It is also close to normal distributed with the average very

close to the 26% specified as standard in the guidelines for biota monitoring (European Commission 2014(draft)), at least for the roach (average 26.0% if the 4 highest outliers are excluded, or 26.5% with all values). For bleak there is not enough data (34 individuals analysed) to see clearly whether they are normally distributed, but the average of 26.4% is also very close to the standard value. The four individuals with very high dry weights (35-43%) may have been errors, such as partially drying out before the measurements were taken or not being completely dry when dry weight was determined. There is little difference between the sites (Figure 3.1-2), but there is some correlation between size and dry weight overall (Figure 3.1-3) for roach.

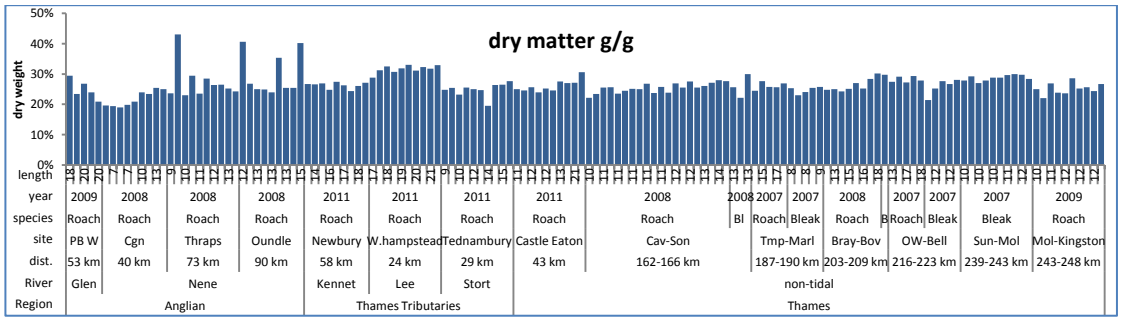


Figure 3.1-2 All dry weights determined. Sorted by region, river, site (km refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

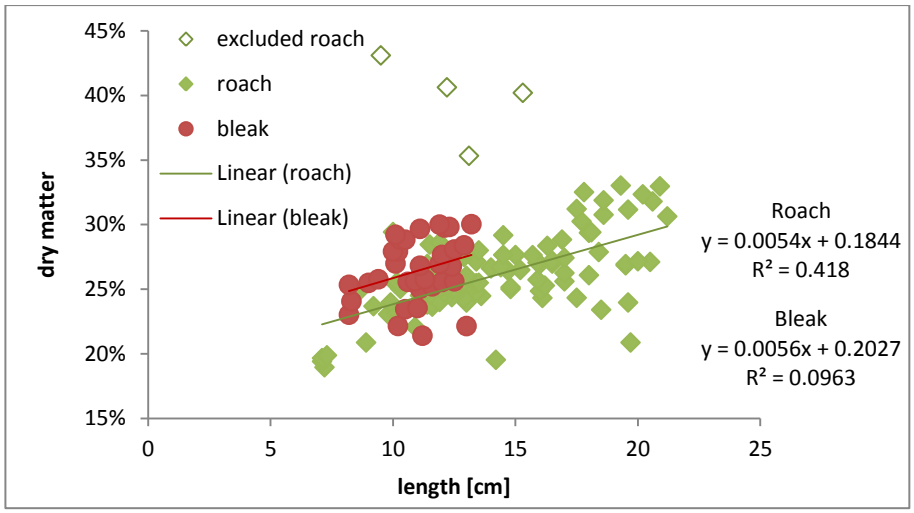


Figure 3.1-3 Correlations (linear regression) between length of individuals and dry matter.

3.1.2 Lipid content

Two different methods were used for extracting the lipid prior to gravimetric determination: Soxhlet extraction overnight with DCM and simpler cold extraction with a mix of 50:50 acetone and hexane. The cold extraction was done mainly to check a batch of analyses where it was suspected that something had gone wrong with the soxhlet extraction. Therefore all the samples in the "suspect" group (n=33) and a selection of other samples (n=20) were repeated by cold extraction. There was good correlation between the two methods for the normal samples with the cold extraction method yielding about 80% of the Soxhlet method (Figure 3.1-4) but for the "suspect" group there was no correlation, confirming that problems had occurred during the soxhlet extraction and therefore the results for the POPs analysis of this batch could not be trusted (Figure 3.1-5) and were removed from the following data analysis. In the following results the cold extracted lipid content values were corrected for the lower extraction efficiency by dividing them by 0.8.

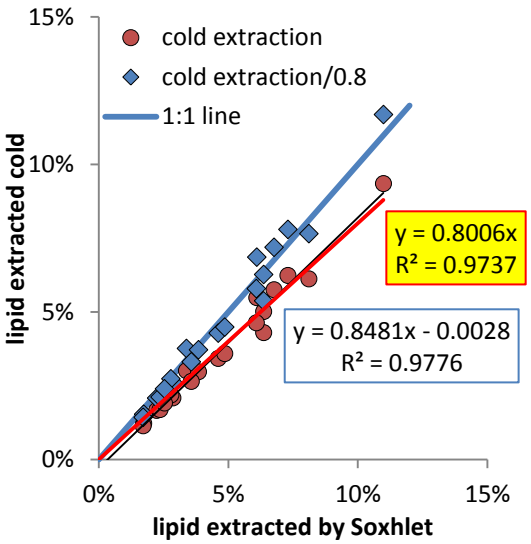


Figure 3.1-4 Correlation between cold extraction method and soxhlet extraction to determine lipid content in "normal" samples.

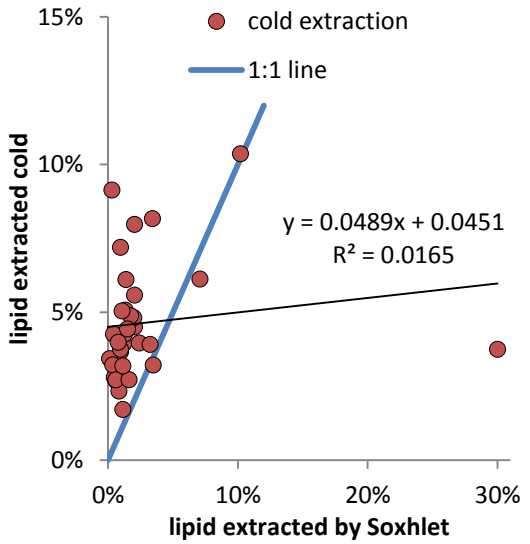


Figure 3.1-5 Comparison between cold extraction and soxhlet extraction for samples, where a problem with the soxhlet extraction had been suspected.

Figure 3.1-6 shows the lipid content for all the fish where this parameter was determined. There are clearly site and species differences with the highest values being reported in the tidal eels, although there were large variations. The Wheathampstead roach also stand out for having high lipid contents. These were also

among the largest roach analysed, but the difference is not explained by size. Within each group the individuals were ordered by length in Figure 3.1-6, showing no clear trend between size and lipid content and there are also roach in other groups which are as big as those from Wheathampstead without having the same high lipid contents.

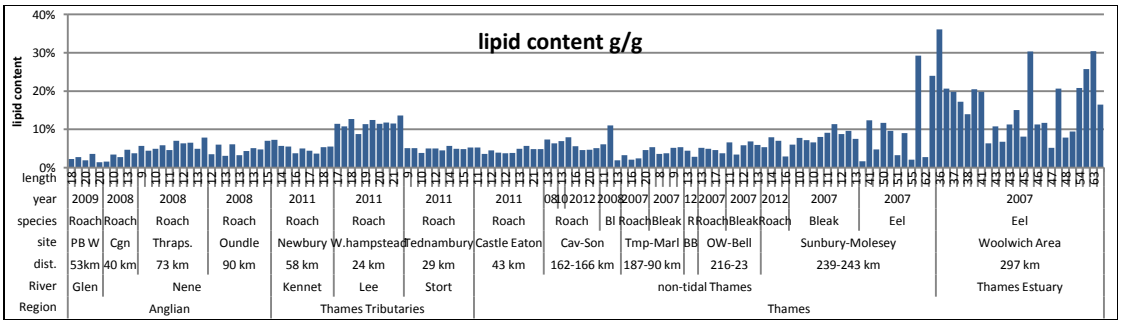


Figure 3.1-6 Lipid content of all fish analysed. Cold extracted values were corrected for the lower extraction efficiency (see Figure 3.1-4). Individuals at each site are ordered by species (roach, bleak, eel), year, and length (cm). Sites on each river are ordered by distance from the source (river-km). BB: Bray-Boveney 203-209 km.

3.2 Metals

Values recorded as <LOD (peaks not found) are plotted as 0. Values between LOD and LOQ (peak found, but less than lowest standard or less than 3*standard deviation of the blanks) were estimated from raw data, if available, otherwise also plotted as 0.

3.2.1 Method validations

3.2.1.1 Reproducibility

Figure 3.2-1 shows the repeatability of the ICP-MS analysis: Subsamples from seven homogenized fish were digested and analysed two times (in one case three times) in different years. The bars show the relative difference between the results. Short bars showing that two or three replicates are similar to their average (i.e. similar to each other), whereas long bars suggest poor agreement. In most cases the difference to the average is 20% or less, but notable exceptions are nickel and vanadium and to some extent antimony (Sb), although its concentrations were always very low (about

1-15 µg/kg, which was near or below the LOQ of 13-33 µg/kg depending on sample volume– see methods section 2.7.3).

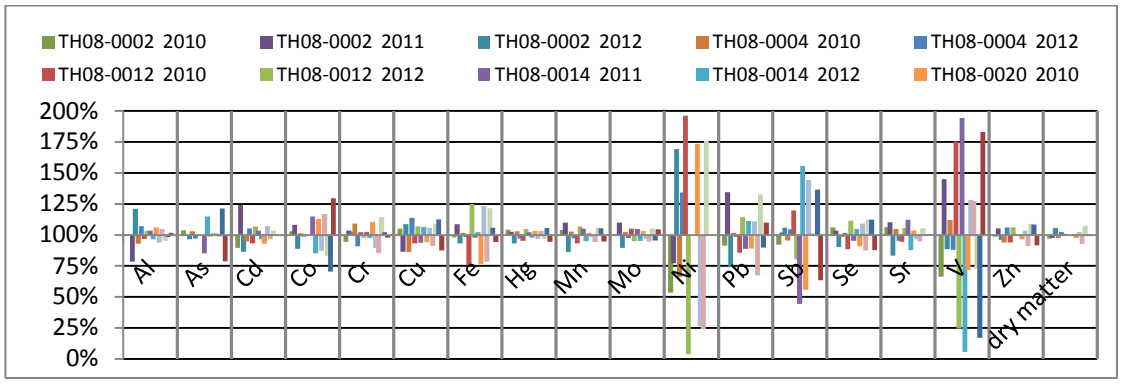


Figure 3.2-1 Repeatability: comparison of the results from fish that have been analysed 2 or 3 times. The bars show the % difference of the individual results compared to the average, i.e. replicate 1/(average of replicates 1 and 2), replicate 2/(average of replicate 1 and 2). A pair of replicates therefore gives one bar above and one below 100%, while triplicates have two bars on one side and the third on the other.

3.2.1.2 Certified reference materials

The results for the certified reference materials were in most cases within about +/- 20% of the published values. Exceptions were one of the 14 Ni values and 2 of the 14 Hg values that were out by more than 25% and lead, which was only published for DOLT was consistently underestimated (58-88%). The recoveries for the "information values" were less good, but as they are not certified, it is also possible that the published value is not accurate.

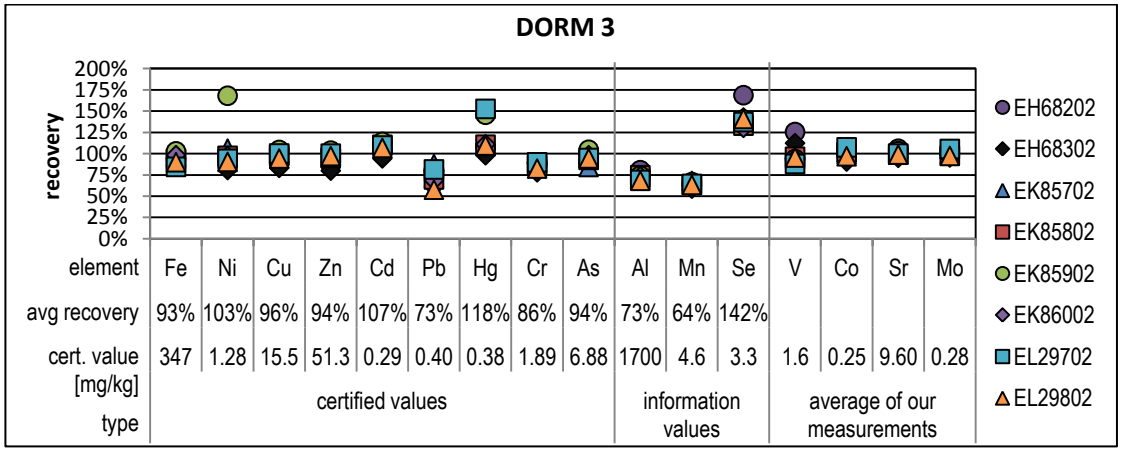


Figure 3.2-2 Recoveries for certified reference material DORM 3 (National Research Council, Canada). The markers indicate the individual results for the standards run with each batch compared to the published certified values (first block) or not (yet) certified "information values". Where no concentration was published, the repeat results are compared to each other by plotting them against the average or our measurements.

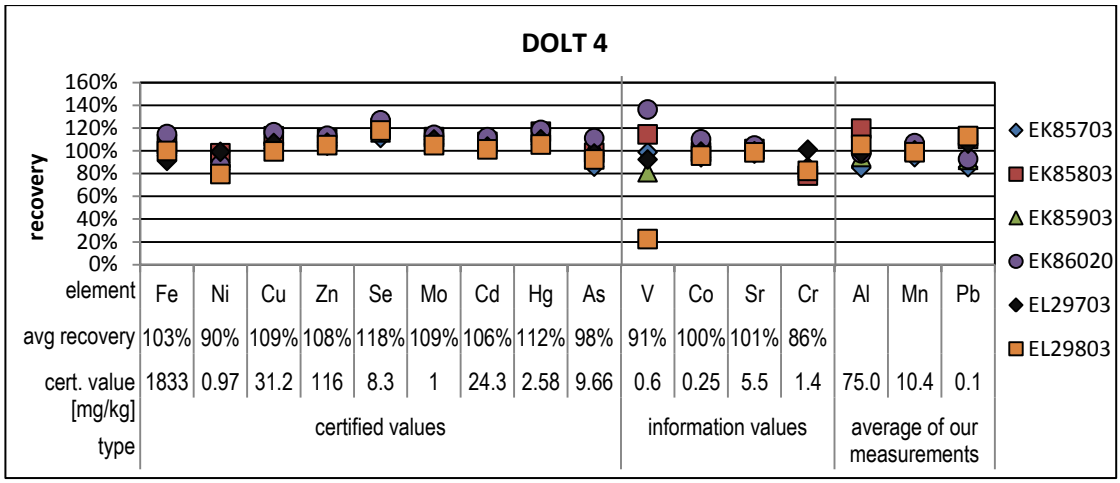


Figure 3.2-3 Recoveries for certified reference material DOLT4 (National Research Council, Canada). The markers indicate the individual results for the standards run with each batch compared to the published certified values (first block) or not (yet) certified "information values". Where no concentration was published, the repeat results are compared to each other by plotting them against the average or our measurements.

3.2.1.3 Effect of grinding and difference between skin and muscle for selected metals

The only metal for which the ground trout samples (2 with and 2 without skin + the skins from those that had it removed), were always higher than the un-ground ones was chromium (Figure 3.2-4), suggesting that small amounts of this metal may be introduced during the processing. For iron, manganese and arsenic the ground samples had higher readings in most, but not all, cases, suggesting that those may also be introduced to a small extent (nickel is not further regarded due to the poor reproducibility, see above). Selenium concentrations were always a little bit lower (1-30%) in the ground samples than the respective un-ground ones. The reason for that is not known. For all other metals the picture was inconsistent, but it is worth pointing out that this first batch only used 1 g fresh weight for the digestion, leading to relatively high LOQs, but values below the official LOQ were estimated and used in the calculations. Mercury was found in higher concentrations in the muscle than in the skin, while the opposite is the case for zinc, strontium and manganese (Figure 3.2-5).

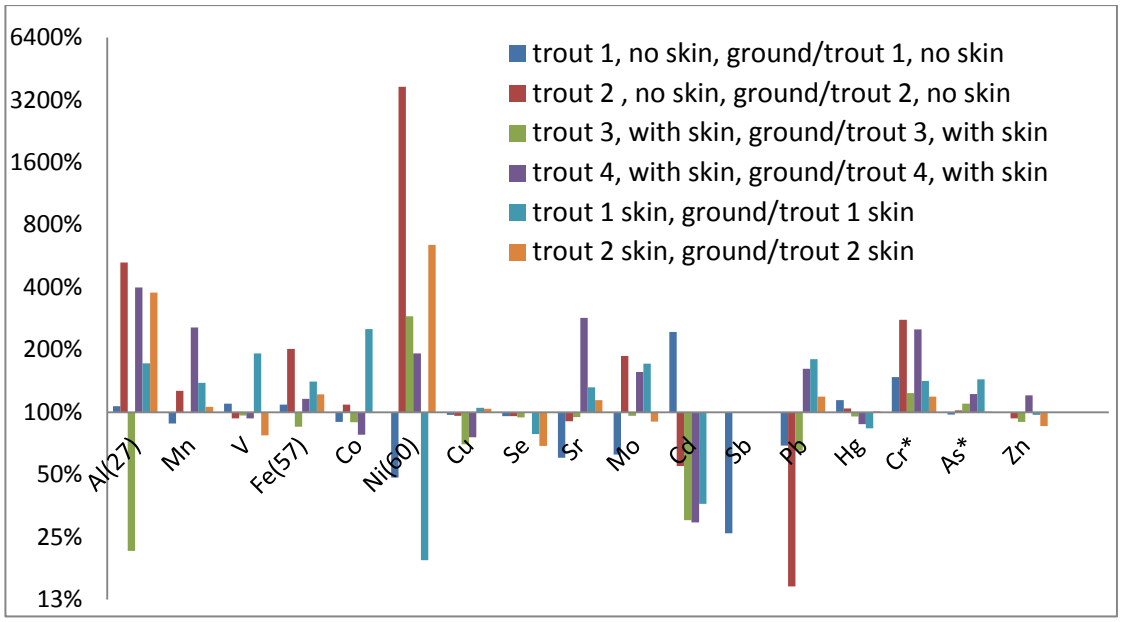


Figure 3.2-4 Relative difference, between the cryo-ground and unground samples. For each sample the bar shows the results from the ground sample divided by its unground counterpart.

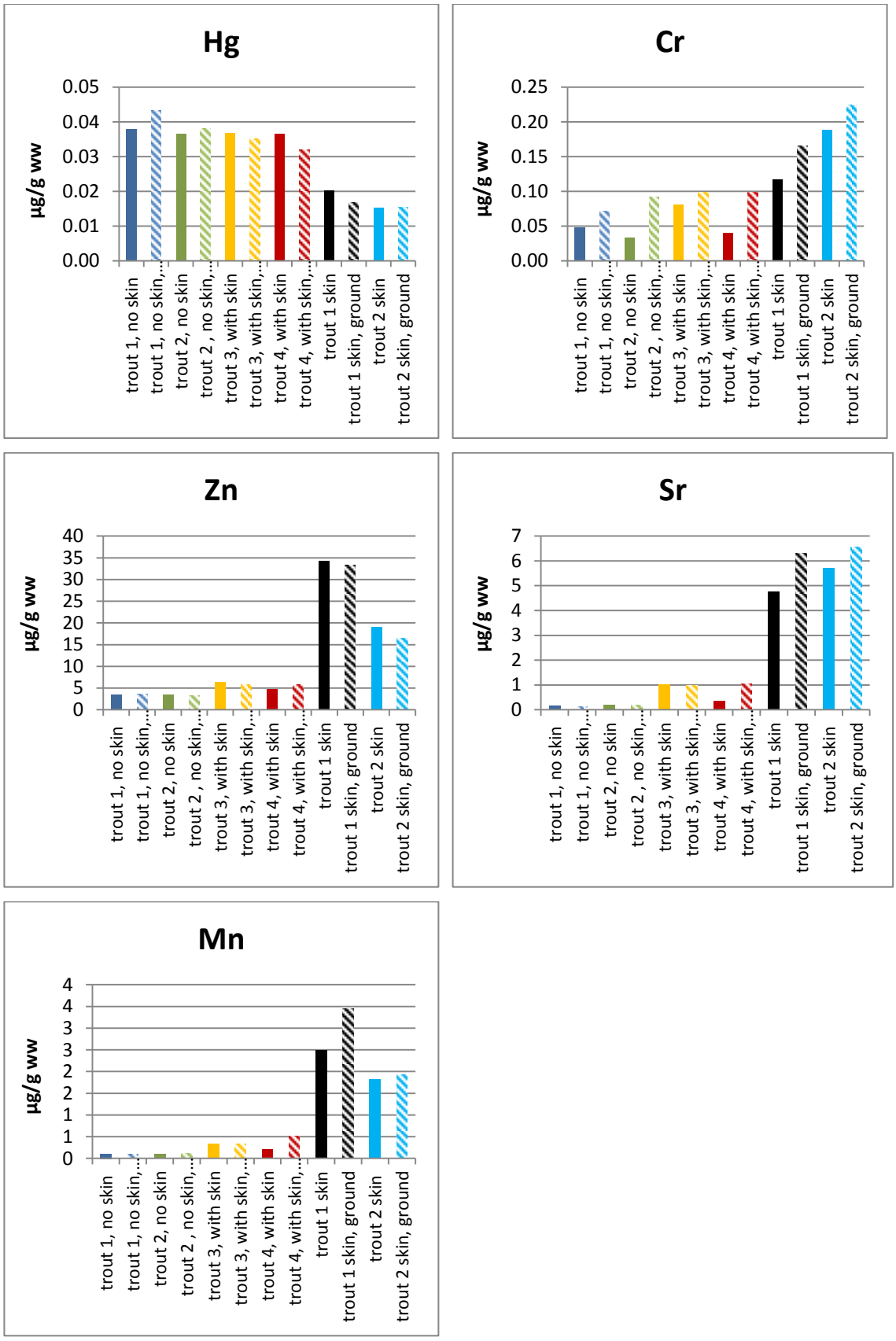


Figure 3.2-5 Distribution of selected metals in the trout fillets and skin.

3.2.2 Detailed results for all metals

In this sections graphs for all the metals measured are presented in alphabetical order for easy reference.

3.2.2.1 Aluminium (Al)

Measured aluminium concentrations varied by a more than a factor of 1000 between 0.1 and over 100 mg/kg (Figure 3.2-6). While some groups are consistently low (most bleaks) and others are consistently high (Castle Eaton roach), for many sites there is a mix of high and low values making it difficult to draw any firm conclusions.

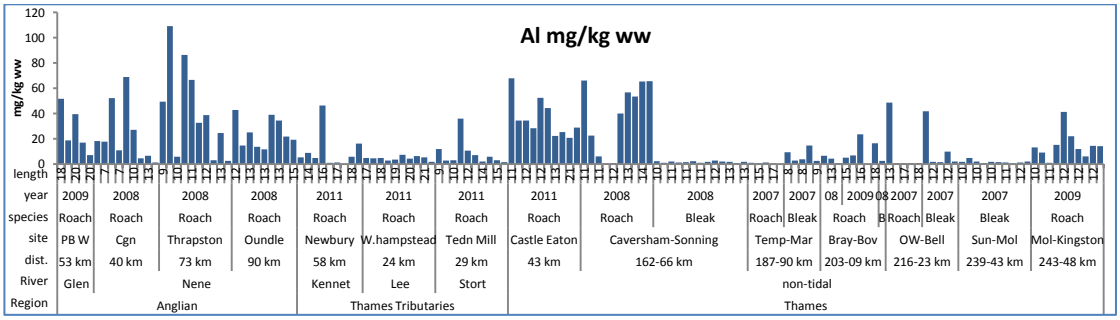


Figure 3.2-6 All aluminium contents determined. Sorted by region, river, site (dist. refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length. Note that the x-axis is in mg/kg ww, not µg/kg as in most of the other graphs.

3.2.2.2 Antimony (Sb)

Antimony had fairly poor reproducibility (see chapter 3.2.1.1) and nearly all the values are below the official LOQ of 13-33 µg/kg (depending on sample weight used), so the results below are to be treated as estimates rather than exact fact. Typical concentrations measured were around 2 µg/kg.

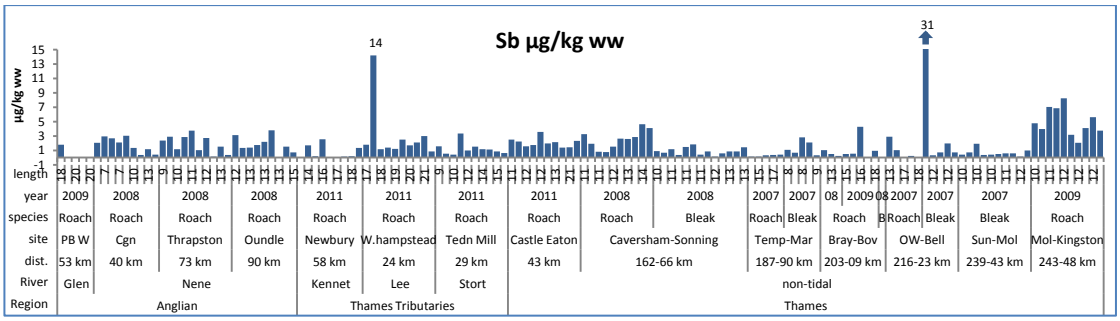


Figure 3.2-7 All antimon contents determined (caution: method reproducibility was poor for this metal, probably because nearly all values were below the official LOQ, so concentrations may not be completely reliable). Sorted by region, river, site (dist. refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

3.2.2.3 Arsenic (As)

Arsenic values were relatively uniform, with less than a factor 10 between the lowest value of 61 µg/kg ww and the highest one of 525 µg/kg ww (Figure 3.2-8). Despite this relatively narrow range, some site differences were apparent, for example Tednambury Mill, Castle Eaton, and the bleak (but not roach) from the Caversham to Sonning stretch having consistently low As concentrations.

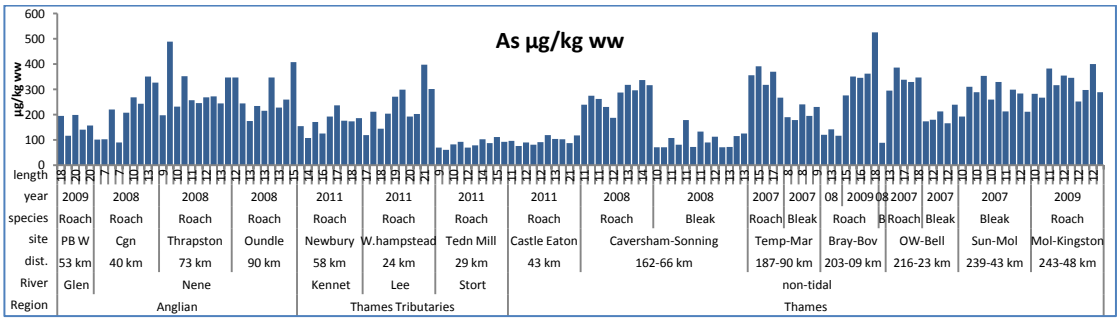


Figure 3.2-8 All arsenic contents determined. Sorted by region, river, site (dist. refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

3.2.2.4 Cadmium (Cd)

Cadmium levels varied about 36 fold from about 0.8 (<LOQ) to 27 µg/kg ww. The Castle Eaton site on the river Thames stands out for the roach having cadmium levels about 3-4 times as high as at the other sites, though still well within the allowable limits for human food.

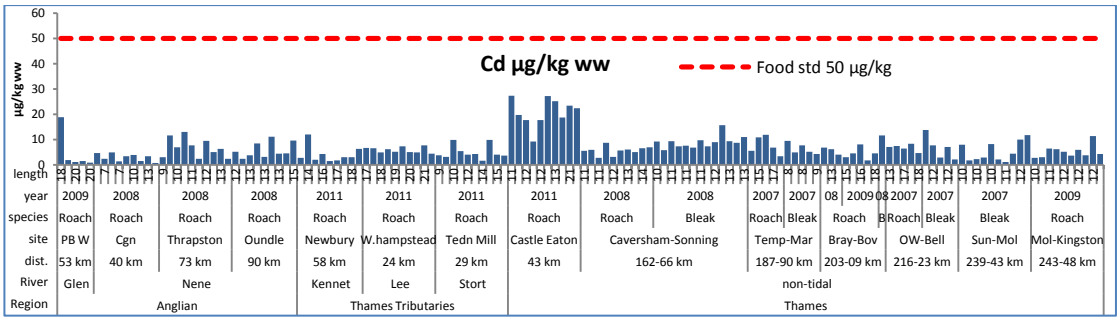


Figure 3.2-9 All cadmium contents determined. Sorted by region, river, site (dist. refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

3.2.2.5 Cobalt (Co)

Cobalt concentrations ranged from non-detectable (<blanks) to about 100 µg/kg, or about 100 times the limit of quantification with large variations both between and within sites.

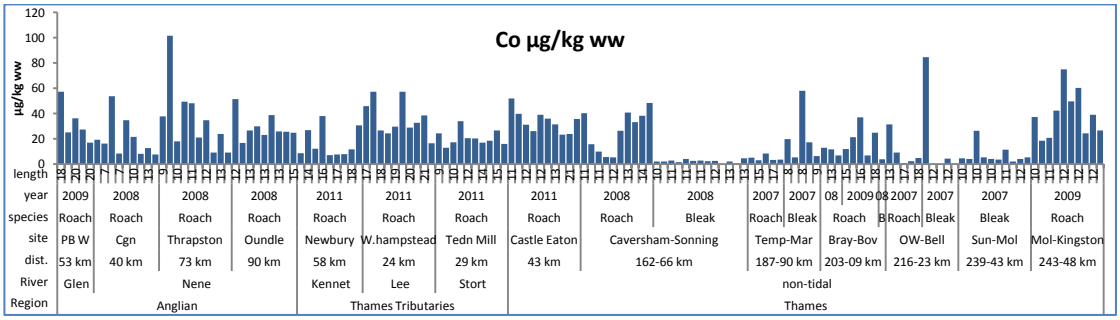


Figure 3.2-10 All cobalt contents determined. Sorted by region, river, site (dist. refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

3.2.2.6 Chromium (Cr)

The range of measured chromium concentrations is from 0.08 - 22 mg/kg, an almost 300-fold difference between the lowest and highest values. Most values (79%) however, were below 1 mg/kg, with some much higher.

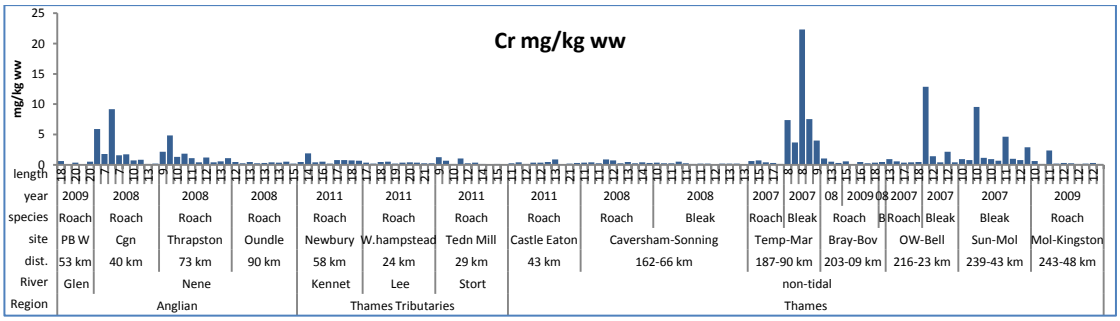


Figure 3.2-11 All chromium contents determined. Sorted by region, river, site (dist. refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length. Note that the y-axis in mg/kg not µg/kg.

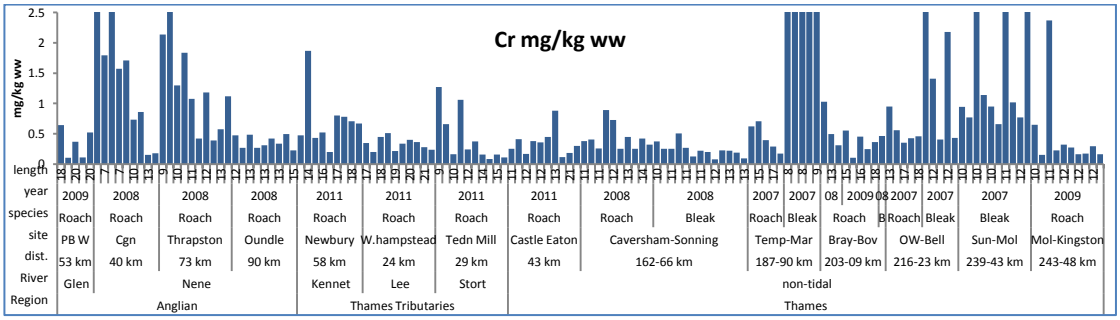


Figure 3.2-12 Detail of the lower concentrations of Figure 3.2-11.

3.2.2.7 Copper (Cu)

Measured copper concentrations ranged from 0.28 to 6.6 mg/kg, a 23 fold range. If the two highest values (both bleak, and much higher than any other bleak) are excluded, the range was only up to 2.4 mg/kg or 8.5 times the lowest value. Relatively high values were found at the Wheathampstead site (see also discussion in chapter 4.3).

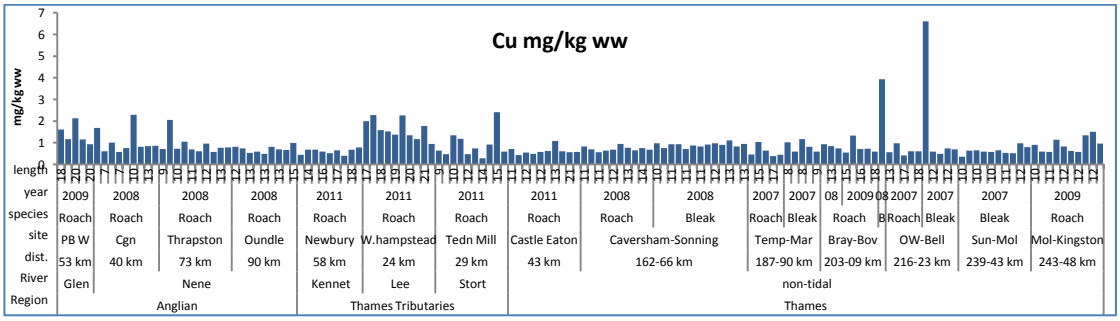


Figure 3.2-13 All copper contents determined. Sorted by region, river, site (dist. refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

3.2.2.8 Iron (Fe)

Iron contents measured were between 3.3 and 390 mg/kg a more than 100 fold difference, but most were less than about 50 mg/kg (Figure 3.2-14).

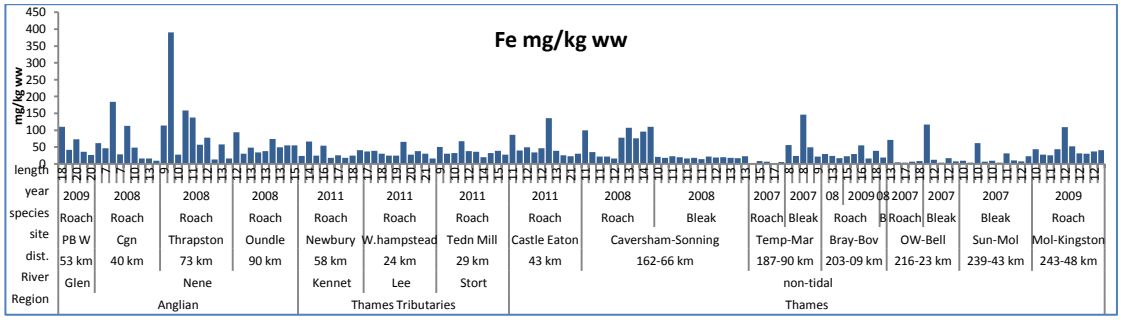


Figure 3.2-14 All iron contents determined. Sorted by region, river, site (dist. refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

3.2.2.9 Lead (Pb)

The lead concentrations in individual fish are shown in Figure 3.2-15. There were surprisingly large differences between some sites or between species at the same site. Ideally more studies should be carried out to ascertain that this is not an artefact of some aspect or measuring or processing. The picture looks overall quite similar to that for Cobalt.

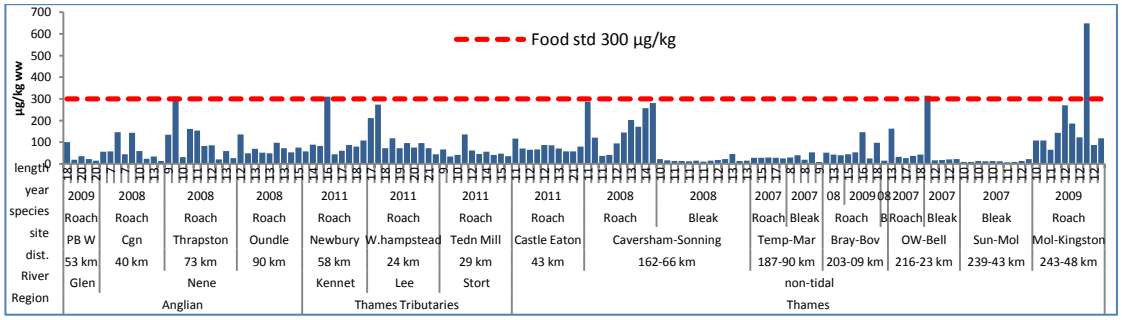


Figure 3.2-15 All lead contents determined. Sorted by region, river, site (dist. refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

3.2.2.10 Manganese (Mn)

Manganese concentrations varied between 0.9 and 24 mg/kg, a 27 fold difference. Most were within the 1-10 mg/kg order of magnitude. Differences between sites were not very strong but those from Newbury on the Kennet were

consistently low, whereas the ones from Oundle on the Nene were all on the high side (Figure 3.2-16).

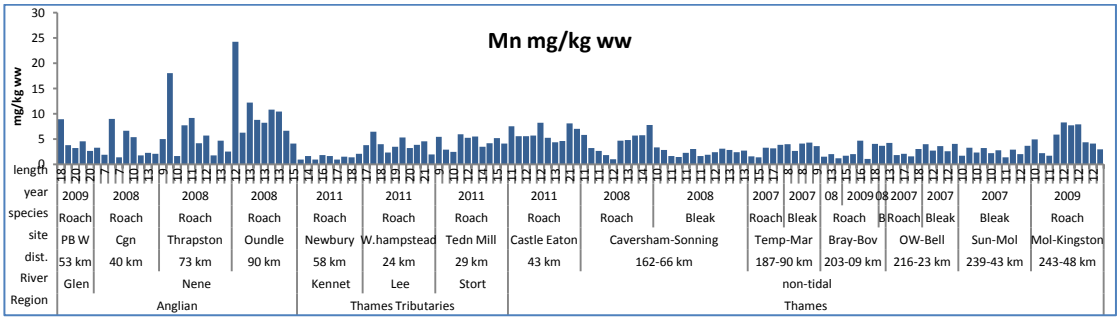


Figure 3.2-16 All Manganese contents determined. Sorted by region, river, site (dist. refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

3.2.2.11 Mercury (Hg)

Comparing the two methods for mercury

The first time samples were re-run on the Galahad mercury analyser, the Galahad results were always much higher (in the region of double) than those from the ICPMS analysis. However those digests had been stored for about 1 year between the two analyses, so there is a possibility that the storage or some other problem with the analysis caused an error. A selection of samples from a further batch of analyses was also repeated on the Galahad and in this case quite good agreement was achieved once the readings from both methods had been background corrected. For the following analyses only the ICP-MS method was used (Figure 3.2-18).

Overall measured mercury concentrations ranged from 6.2 to 68 µg/kg – only a factor of 11 between the highest and lowest values, and the majority of samples exceeded the 20 µg/kg European EQS (European Union 2013).

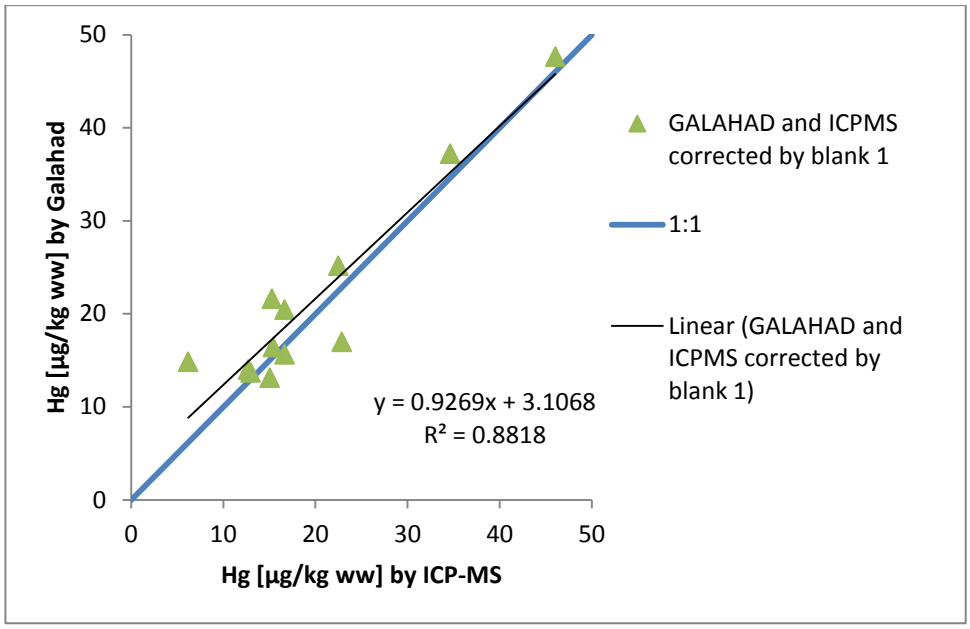


Figure 3.2-17 Comparison between the two methods for mercury analysis.

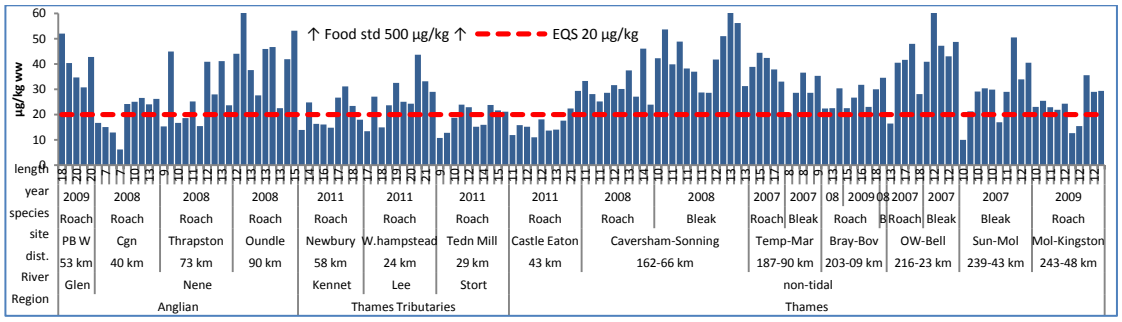


Figure 3.2-18 All mercury contents determined (ICPMS). Sorted by region, river, site (km refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length. The environmental quality standard (European Union 2013) is also shown.

3.2.2.12 Molybdenum (Mo)

The molybdenum concentrations measured were between 14 and 710 µg/kg, a 50-fold difference, with 81% of the values being within just a factor of three between 20 and 60 µg/kg.

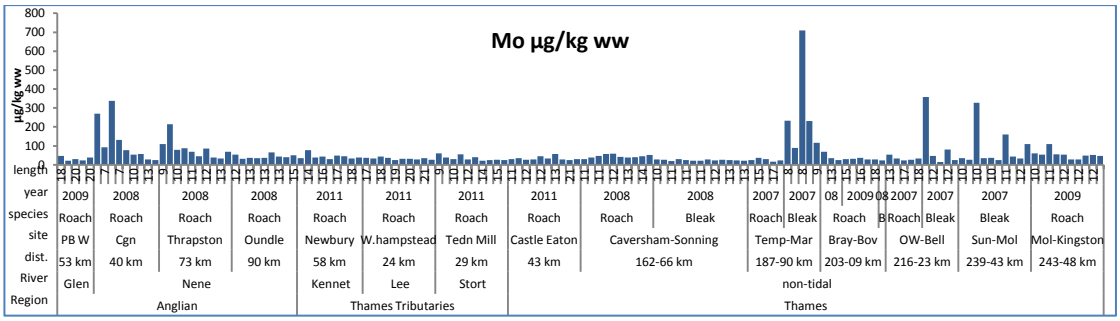


Figure 3.2-19 All molybdenum contents determined. Sorted by region, river, site (dist. refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

3.2.2.13 Nickel (Ni)

Measured nickel concentrations were from non-quantifiable (<blank) to 41 mg/kg, with only three fish having values above 1 mg/kg (maybe contamination?). Typical values are around 100 µg/kg (median 99 µg/kg). However, some caution is recommended when interpreting the nickel results as reproducibility for this metal was poor when several subsamples from the same homogenised fish were analysed separately (see section 3.2.1.1).

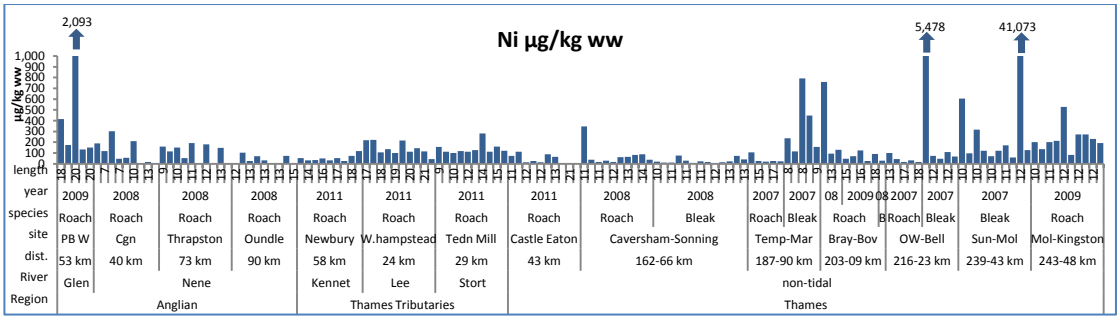


Figure 3.2-20 All nickel contents determined (caution: method reproducibility was poor for this metal, so the concentrations may not be completely reliable). Sorted by region, river, site (dist. refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

3.2.2.14 Selenium (Se)

Selenium concentrations occur in a fairly narrow range between 0.14 mg/kg and 2.2 mg/kg, or a 16 fold difference between the highest and lowest values.

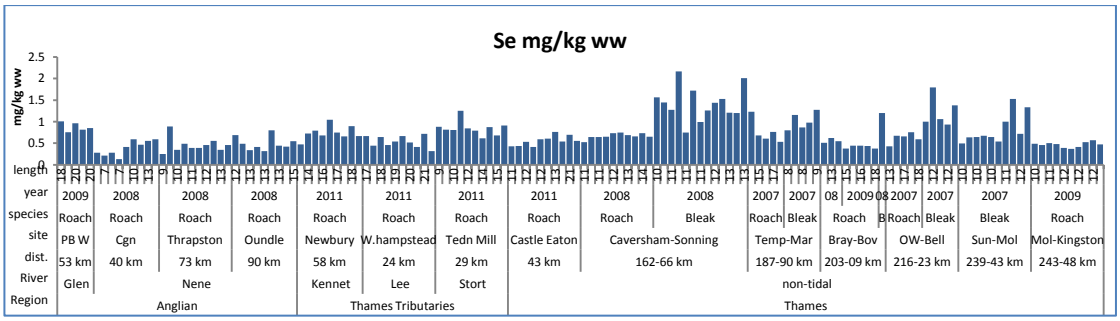


Figure 3.2-21 All selenium contents determined. Sorted by region, river, site (dist. refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

3.2.2.15 Strontium (Sr)

Measured strontium concentrations were from 5 to 28 mg/kg, only varying by a factor of 5.1.

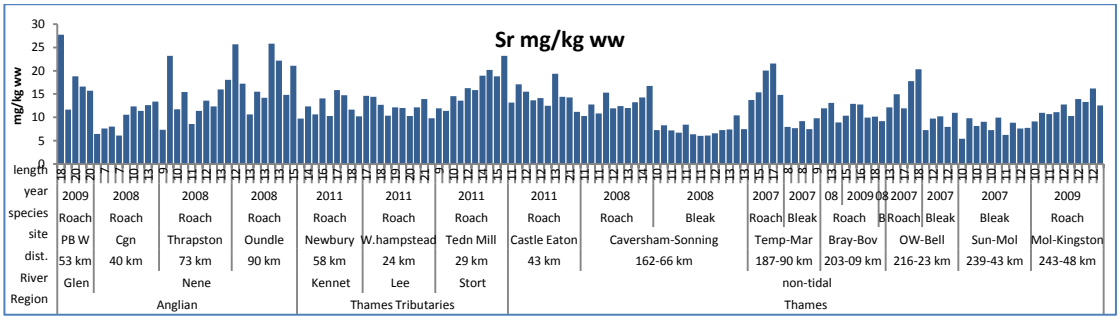


Figure 3.2-22 All strontium contents determined. Sorted by region, river, site (dist. refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

3.2.2.16 Vanadium (V)

Vanadium measurements had poor reproducibility in repeat analysis of subsamples from the same fish (see section 3.2.1.1), so the results below need to be treated with caution. Measured concentrations were in the non-detectable to low hundreds µg/kg fw and, while both low and relatively high concentrations occurred in roach, all bleak measured had low concentrations of vanadium.

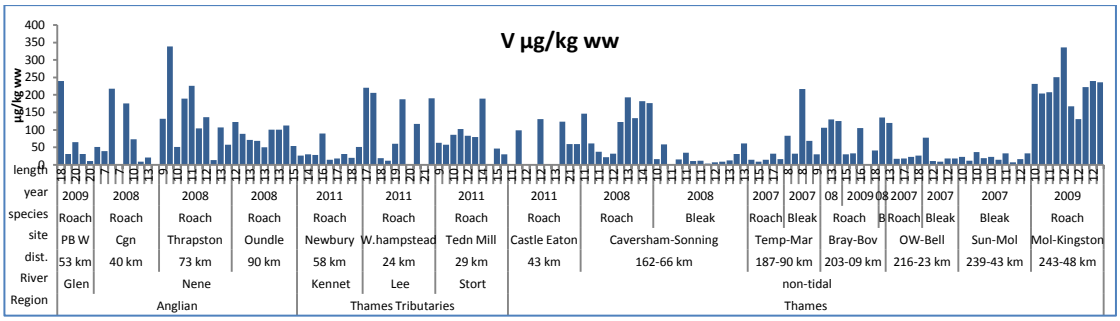


Figure 3.2-23 All vanadium contents determined (caution: method reproducibility was poor for this metal, so concentrations may not be completely reliable). Sorted by region, river, site (dist. refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

3.2.2.17 Zinc (Zn)

Zinc concentrations only varied in a very narrow range between 22 and 96 mg/kg or a factor of 4.4 between the minimum and maximum with 90% of the values between 24 and 55 mg/kg or just a factor of 2.3.

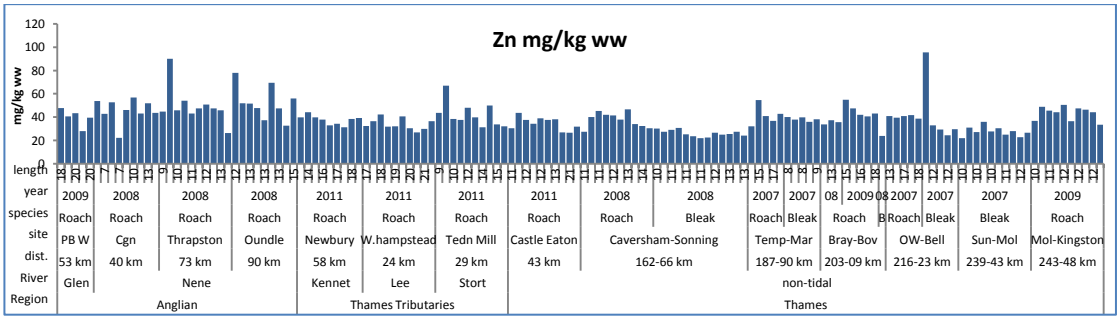


Figure 3.2-24 All zinc contents determined. Sorted by region, river, site (dist. refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

3.3 Persistent organic pollutants

Values recorded as <LOD (peaks not found) are plotted as 0. Values between LOD and LOQ (peak found, but less than lowest standard or less than 3*standard deviation of the blanks) were estimated from raw data, if available, but in most cases also plotted as 0.

3.3.1 Reproducibility: Analysis of two subsamples from the same fish

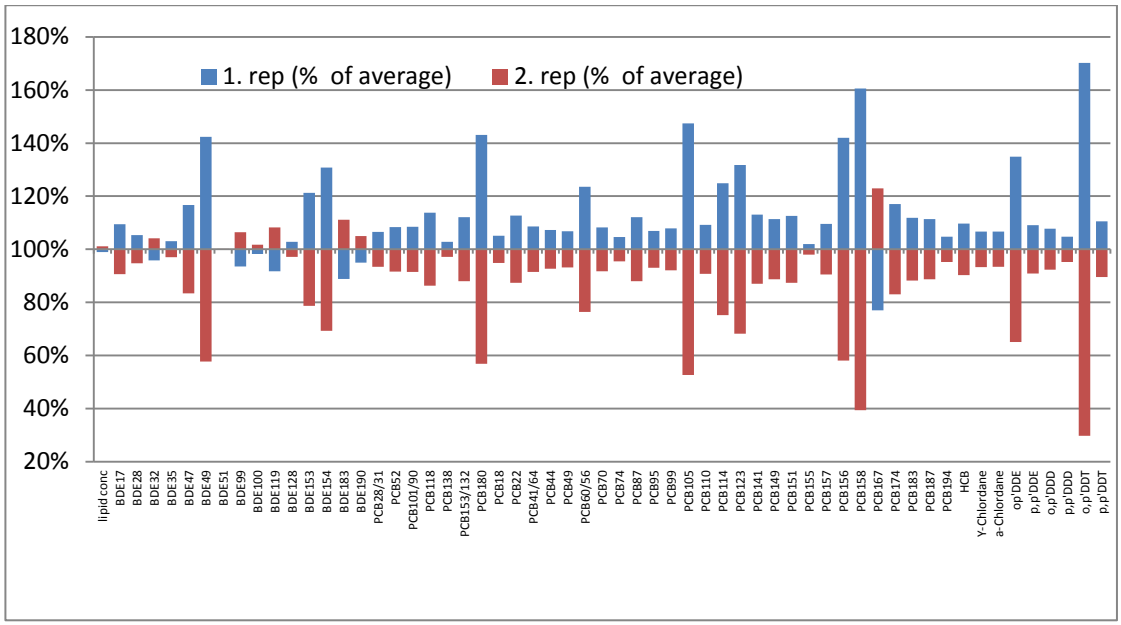


Figure 3.3-1 Repeat analysis of one roach sample from the river Stort 2011. All persistent organic pollutants that could be quantified both times are shown. The bars show the relative difference to the average, i.e. replicate 1 divided by average of replicates 1 and 2 etc.

The reproducibility for the concentration of organic pollutants extracted and measured twice in subsamples from the same fish (Figure 3.3-1) is quite reasonable for most POPs that were found in both subsamples, except for op'DDT and PCB 158. Replicate 2 was actually one of a small handful of samples were the peaks in the chromatogram were wider and less well resolved than in most other samples, making it more difficult to do accurate quantifications (Figure 3.3-2). Therefore, a) the results from replicate 1 are probably closer to the "real" concentrations than replicate 2 and b) this repeat analysis is likely to overestimate the uncertainty of the analysis.

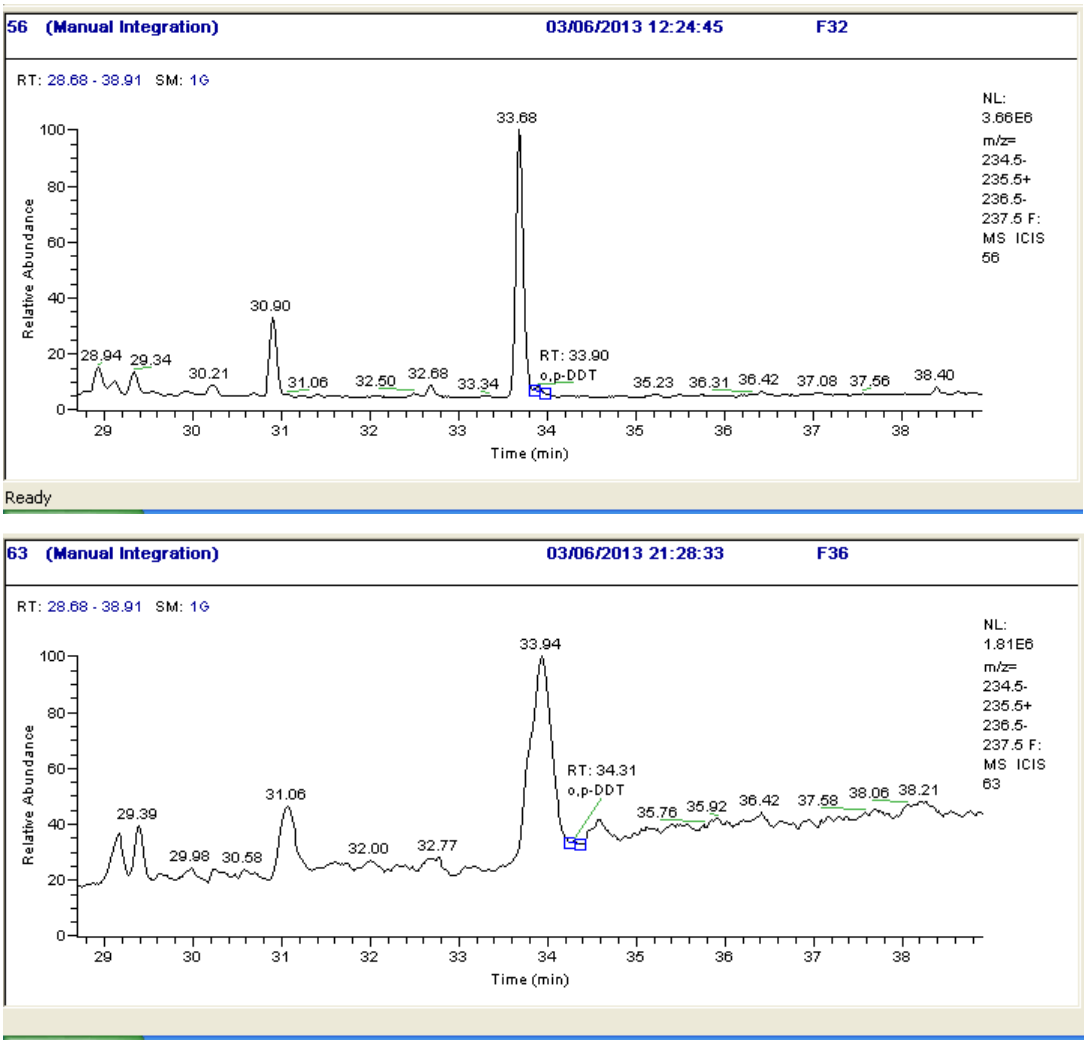


Figure 3.3-2 Example chromatograms of the two replicates. Most samples are more like the first one (i.e. narrow clear peaks with no change in baseline), but a handful — perhaps if there were problems with the clean-up — have the wider less well resolved peaks seen in the second replicate. The compound with particularly poor agreement between the two replicates, op'DDT is marked in the chromatograms: it is a tiny peak on the side of the pp'DDD peak.

3.3.2 Pesticides

3.3.2.1 DDT

Very large concentrations were found in Wheathampstead on the river Lee. The average total DDT concentration in roach from that site was 88 µg/kg (std dev. 70 µg/kg) or almost 20 times as much as the average concentration in roach from other sites, which was 4.8 µg/kg (std dev. 3.1 µg/kg). This is believed to be related to a former pesticide factory close to the site (see chapter 4.3.2). There is little difference between the other sites, but the two most upstream sites in the Thames catchment (Newbury on the Kennet and Castle Eaton on the Thames) seem to be a bit lower than the more downstream sites. The total DDT concentration is dominated by *pp'*DDE, the main degradation product of *pp'*DDT, which was the main component of technical DDT mixtures.

Comparing species is not so clear, because the numbers are very small. Bleak and eels caught at Sunbury to Molesey in 2007 had similar contamination whereas in roach caught at the same location in 2012 it was lower, but it is unclear whether that was due to the different year or different species (or even analytical issues).

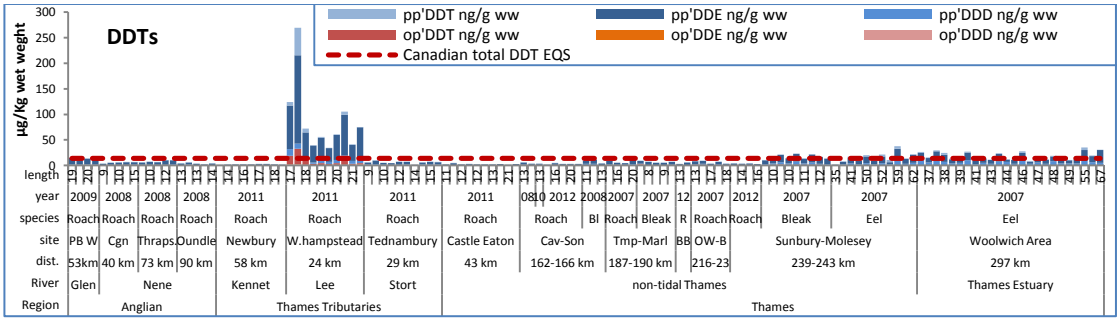


Figure 3.3-3 Concentration of DDT and its degradation and by-products DDE and DDD (op' and pp' congeners for all) of all fish analysed. Individuals at each site are ordered by species (roach, bleak, eel), year, and length (cm). Sites on each river are ordered by distance from the source (river-km). BB: Bray-Boveney 203-209 km. The Canadian Tissue Residue Guideline for the protection of wildlife consumers is also shown (there is currently no equivalent EU guideline).

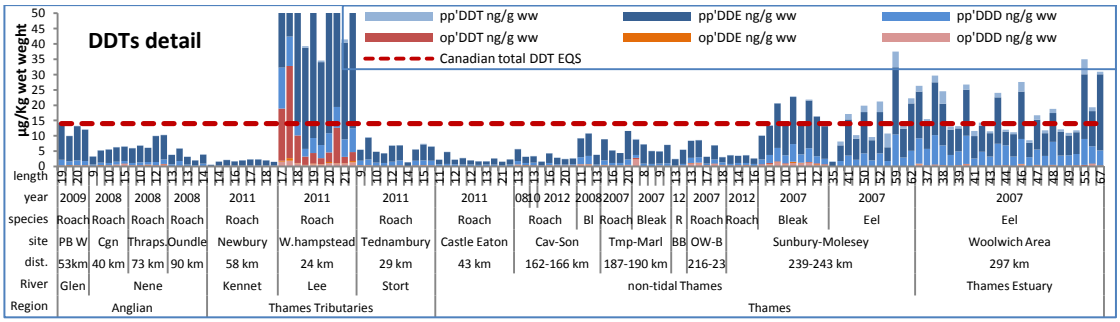


Figure 3.3-4 Detail showing the lower concentrations from Figure 3.3-3.

3.3.2.2 HCB

Hexachlorobenzene concentrations varied from 0.03 to 6.4 µg/kg, a 200 fold difference. The eels tended to have higher concentrations than roach or bleak, but no individual analysed exceeded the EU EQS of 10 µg/kg (European Union 2013).

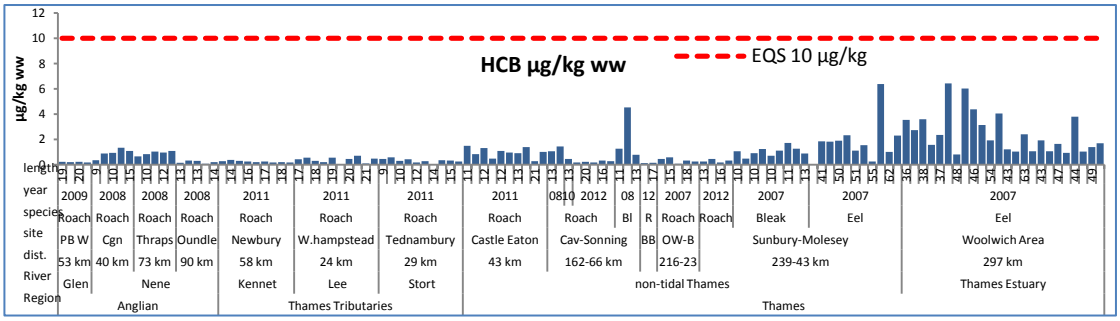


Figure 3.3-5 All HCB contents determined. Sorted by region, river, site (km refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

3.3.2.3 Chlordane

Chlordane (α+γ) concentrations ranged from 0.03 to 2.5 µg/kg, a 76 fold difference. Most eels and bleak had relatively high concentrations, while roach from some sampling occasions had fairly high concentrations and for others they were very low.

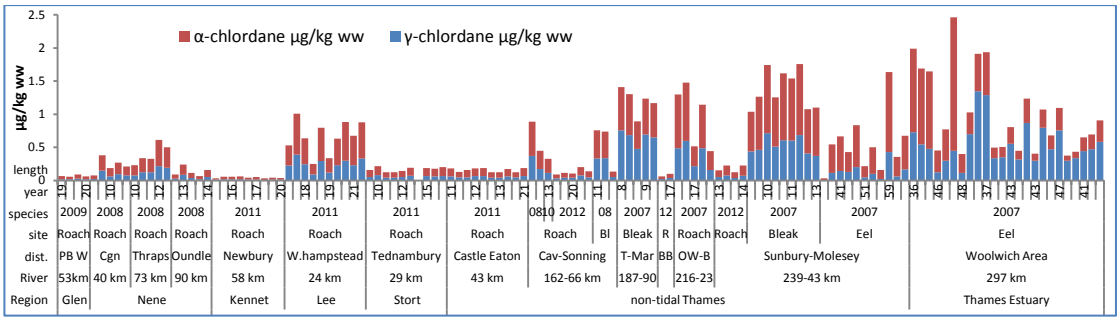


Figure 3.3-6 Chlordane α+γ. There is no EQS and the food standard is 50 µg/kg for the sum of the two congeners (for meat, none exists for fish) (European Commission 2005b).

3.3.2.4 HCHs (incl. lindane) and endosulfan

As with DDT, but to a much smaller extent the roach from the Wheathampstead site tended to have the highest concentrations of lindane and other HCHs. Overall the range of quantified values (a few could not be quantified) for lindane was 0.05-14 µg/kg or about a 250 fold difference, but without the Wheathampstead fish the maximum is only about half as much at 6.8 µg/kg.

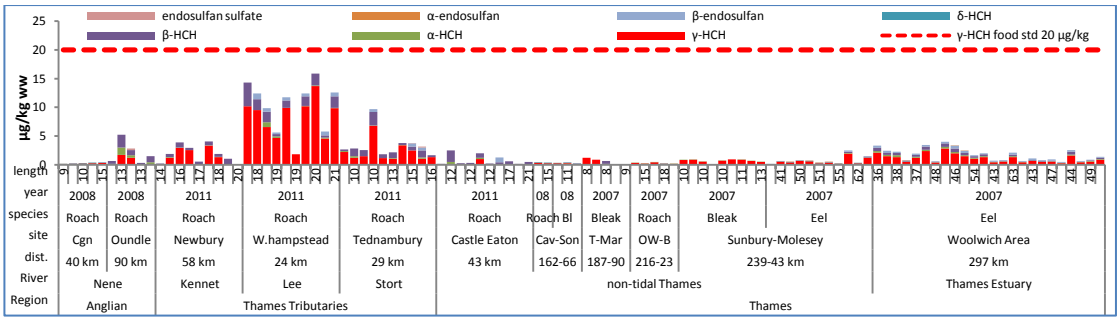


Figure 3.3-7 HCHs, including lindane (γ-HCH) and endosulfans. There are no EQS for these substances and the food standards (meat, none available for fish) are 20 µg/kg for γ-HCH and 50 µg/kg for endosulfan.

3.3.3 PCBs

About 40 PCBs were analysed. The total PCB contamination with those congeners ranged from 5 to 215 µg/kg. The ICES6 or ICES7 groups of indicator PCBs (see caption) contributed about half of that total. Eels were on the whole more contaminated than roach, but some of the bleak had similar levels to the eels.

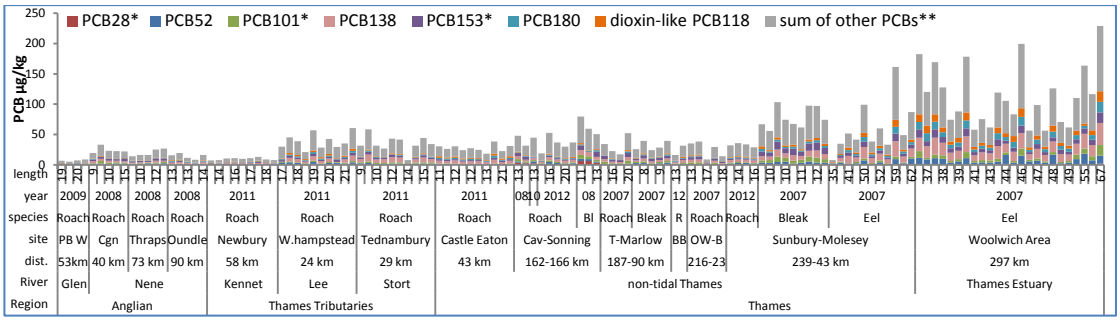


Figure 3.3-8 PCBs. ICES 7 indicator PCBs are marked individually (six non-dioxin-like PCBs (28, 52, 101, 138, 153, and 180 = ICES6, and dioxin-like PCB118), *may contain small amounts of other congeners, because 28/31, 90/101, 132/153 co-eluted), the other measured PCBs are plotted as a sum (see list in methods). Individuals at each site are ordered by species (roach, bleak, eel), year, and length (cm). Sites on each river are ordered by distance from the source (river-km). BB: Bray-Boveney 203-209 km.**

3.3.4 PBDEs

Overall the range for the sum of the 6 indicator BDEs was between 2.0 and 44 µg/kg, a factor of 22. BDE47 was the most common PBDE found. It normally contributed about 70% of the total. The roach at Castle Eaton on the Thames were an exception to that rule. The had much higher amounts of BDE 154 and other minor components than any other group and BDE 47 contributed only .about 30-40% to the total (Figure 3.3-9). Although some of the differences such as the fairly high concentrations at Wheathampstead can be explained by lipid content, the overall range of values was actually wider not narrower when they were lipid normalised. The highest concentration was 36 times as much as the lowest for lipid normalised data compared to only 22 times for the original data (Figure 3.3-10).

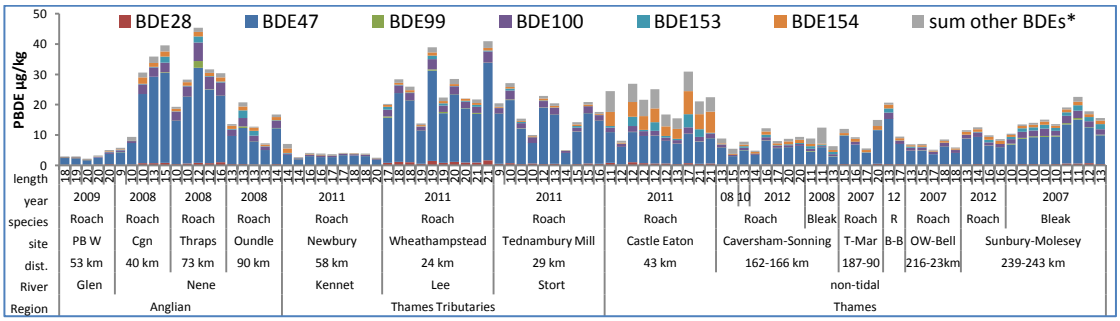


Figure 3.3-9 Indicator PBDEs and sum of other BDEs (* for list of other PBDEs analysed see methods section). Sorted by region, river, site, species, and year. Sites on each river are ordered by distance from the source (river-km). BB: Bray-Boveney 203-209 km. Within each of those groups the individuals are ordered by fork length.

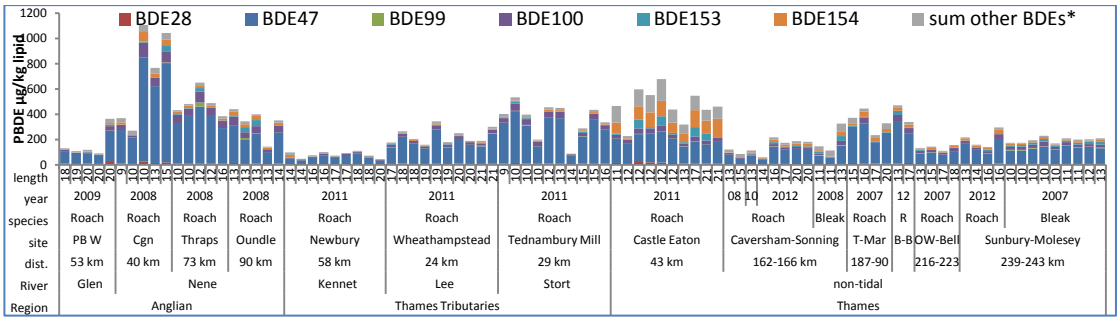


Figure 3.3-10 Lipid normalized concentrations of PBDEs (* for list of non-indicator PBDEs analysed see methods section). Sorted by region, river, site, species, and year. Sites on each river are ordered by distance from the source (river-km). BB: Bray-Boveney 203-209 km. Within each of those groups the individuals are ordered by fork length.

4 Discussion

A measured concentration on its own is only a number, it only become meaningful when it is put in context. Ways of providing context include comparisons to other recent or historic samples, to regulatory standards, or to harmful effect levels. The question of choosing appropriate representative samples is examined in In Chapter 4.1. In Chapter 4.2 toxic effects are discussed and the results from this study are compared to regulatory values concerning food and the environment. In chapter 4.3 patterns are found in data from within this study by comparing individual fish and individual chemicals with each other and properties of the chemical, the fish, and the sampling site are used to explain the observed patterns. The measured values are put into a geographical context in Chapter 4.4 by comparing them to similar recent studies from Europe, while in Chapter 4.5 the same is done on a temporal scale by focusing only on the UK, but going back further in time.

4.1 What part of the fish should be analysed to get a representative assessment of chemical contamination?

The choice of which part of a fish is to be analysed depends on the reasons why chemical contamination is to be investigated. If human consumption is the main concern, then the fillet which is the part most commonly eaten, is the most appropriate part to be selected but if the concern is for wildlife then whole body samples are more appropriate (see section 1.3.1.6). For chemicals that affect the development of offspring, such as selenium, eggs or ovaries have been recommended as the most appropriate body part to be monitored (US EPA 2014). Eggs also have the advantage that they may often be collected non-destructively. For fish this can be done by stripping them off their eggs at the right time of year, i.e. shortly before spawning, but at other times of year their collection is a lot more difficult (dissection of the ovary) or impossible (just after spawning).

Another approach is to collect and analyse the body part, in which the highest concentrations of the chemical of interest are expected. This is particularly suitable

when using large organisms where it would be impractical to store the whole body. as with monitoring schemes that use fat tissue from seals and whales (blubber), or livers and kidneys from other animals. Which body part is most contaminated. however, may depend on the chemical and its history. Mercury tends to accumulate in muscle tissue (fillet), for example, whereas hydrophobic persistent organic pollutants are associated with lipids and are, therefore, found in higher concentration in those parts of the body where the fat content is higher. In addition, pollutants are directed to the liver and kidneys for detoxification and if they cannot be efficiently removed they may accumulate there. The distribution of a chemical in the body of a fish (or other animal) may also depend on how recent the contamination was: as chemicals are initially taken up from food or water, they enter the body via the stomach or gills, which suggests that is where high concentrations may be found initially but over time the contaminants first enter the blood stream and are later deposited in various parts of the body, for example, in the fat tissue or in the bones.

The difference between analysing the liver and the carcass (rest of the fish after the liver, bile and some blood had been removed) was tested for a suite of POPs in some roach and bleak collected in 2007. Despite mostly generally higher concentrations in the liver the number of non-detects were higher in that organ because the sample size had to be reduced from the normal 5g wet weight to whatever was available, sometimes as little as 0.5 g.

The livers were **more** polluted with most, but not all, chemicals in most, but not all, fish. For example in the largest of the Temple-Marlow roach the liver is **less** contaminated than the carcass for nearly all the chemicals but for the other individuals it was the other way around for most compounds (Figure 4.1-1). The slope of the correlations was different for the different individuals. When both the liver and carcass concentrations were lipid-normalized, however, five of the seven individuals for which this was possible, had a similar relationship between the lipid normalized concentration in the liver and carcass. While a slope of around 1 would be expected if the lipid-normalization removed the difference between these body parts completely, the observed slope was only around 0.5, i.e. although the concentration in the liver was in most cases higher than in the carcass, when expressed with regards to lipid weight was it actually lower in the liver.

Lipid normalisation helps therefore to reduce the differences between the liver and carcass for the measured persistent organic pollutants, but doesn't eliminate them.

As much as possible comparisons between different studies should therefore be made on a like-for-like basis, ie comparing the same body parts. However, in the following chapters literature data from fillet measurements have been used to compare to the data for whole body homogenates from this study as excluding fillet data would have severely reduced the available literature.

When the graphs were plotted on a log-log scale to reveal more detail about the lower concentrations, the relationships more or less broke down for concentrations below about 0.5 µg/kg in the carcass (Figure 4.1-3 and Figure 4.1-4). Perhaps this was because, especially for the liver, these low concentrations were difficult to quantify accurately.

For the bleak the relationships between liver and carcass concentrations were much less obvious than for roach (Figures 4.1-5 and 4.1-6). This is probably because their smaller size made the quantifications more difficult, leading to fewer chemicals that could be quantified in both liver and carcass and more uncertainty in the values. Due to their small size, lipid contents were not determined for the bleak livers, so lipid-normalized values could not be compared.

Summary of the comparisons between liver and carcass concentrations of persistent organic pollutants (POPs):

- The POPs investigated (PCBs, PBDEs and some organochlorine pesticides) could be measured in the liver or carcass of roach and bleak but due to their small size measurements in the liver involved more uncertainty than in the carcass.
- Lipid-normalization made the difference between the liver and carcass measurements more reproducible but did not eliminate it: Before lipid-normalisation the correlations between the concentrations of individual chemicals in the liver and in the carcass varied a lot between individual fish, whereas for lipid normalised data the concentrations in the liver were around half of those in the rest of the fish, at least for those chemicals at high enough concentrations to be quantified with confidence.
- Due to the small available sample size, analysing the liver of small to medium sized fish is not recommended for routine monitoring. Rather, whole-body homogenates are the most appropriate where monitoring is done with the protection of wildlife in mind, while the fillet is the most appropriate where human consumers are of concern, e.g. for food standards (European Commission 2006a)

when fish is for sale or for those EQS (European Commission 2013) that are based on a potential risk to human consumers (presumably hobby fishermen, as the commercial ones are already covered by the food standards).

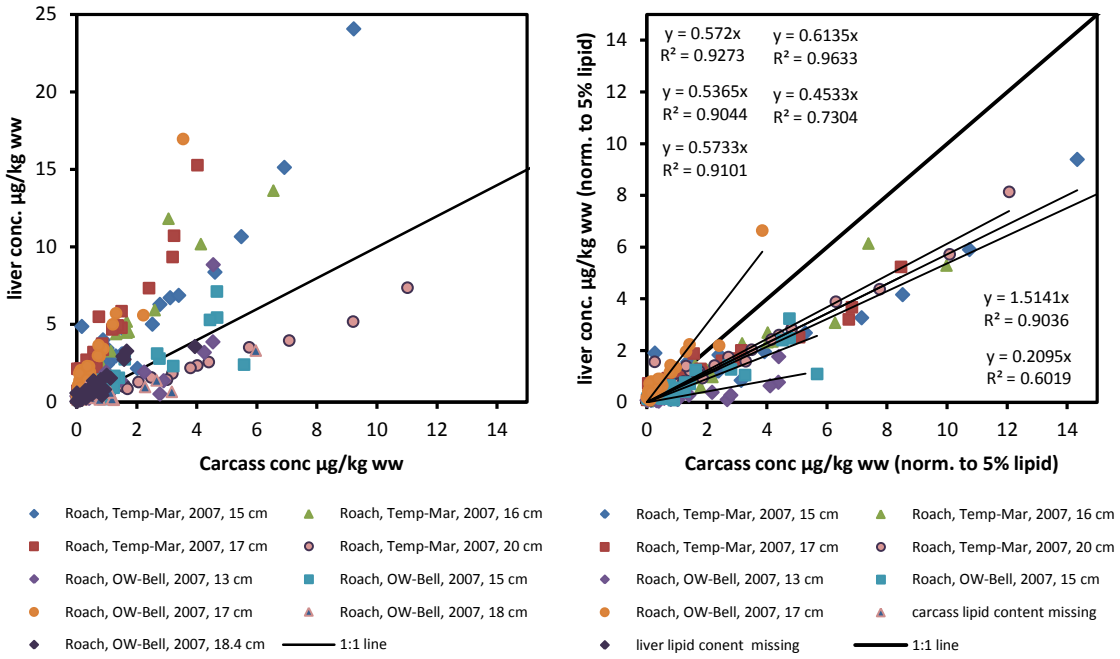


Figure 4.1-1 Roach: Concentration of POPs in the liver (y-axis) compared the carcass (x-axis) of 9 roach caught at two sites in 2007 (T-Mar: Temple-Marlow 187-190 km from the source and OW-Bell: Old Windsor-Bell 216-223 km from the source). Each individual fish is represented by a different colour and identified in the legend by the site and its fork length. Each dot represents a chemical. Only chemicals that were quantifiable in both liver and carcass were plotted.

Figure 4.1-2 Figure 4.1-1 normalized to 5% lipid content (only seven individuals can be displayed because for the other two one of the lipid contents is not known).
The trendlines for five of those seven are very similar (equations top left), but two show a different pattern (equations bottom right).

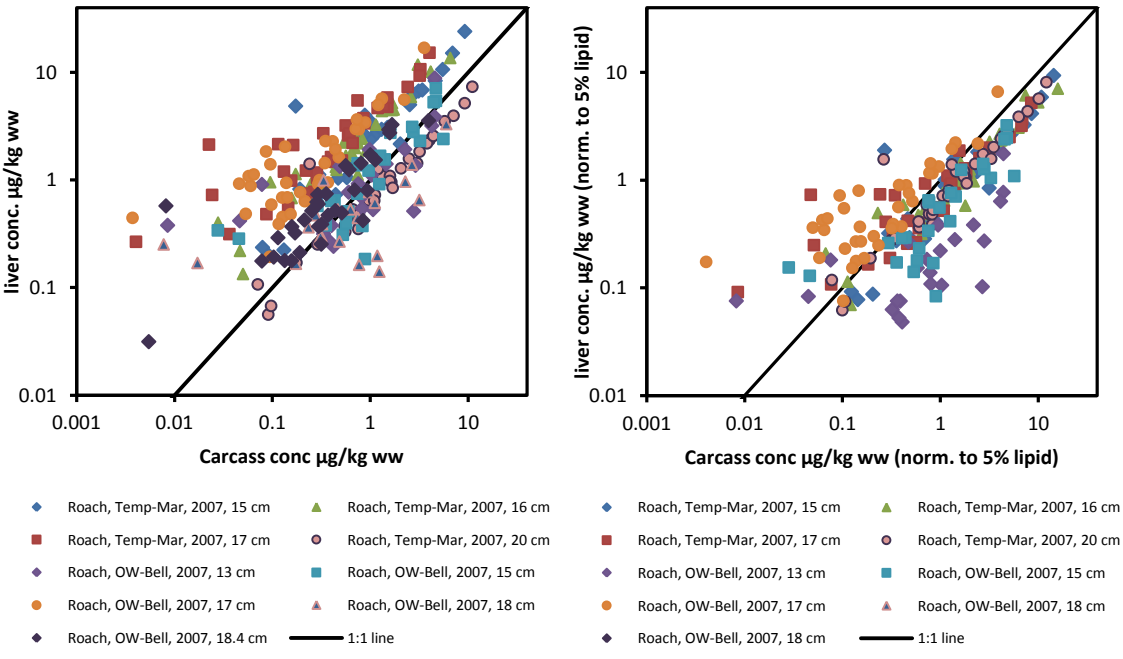


Figure 4.1-3 Figure 4.1-1 on logarithmic scales.

Figure 4.1-4 Figure 4.1-2 on logarithmic scales.

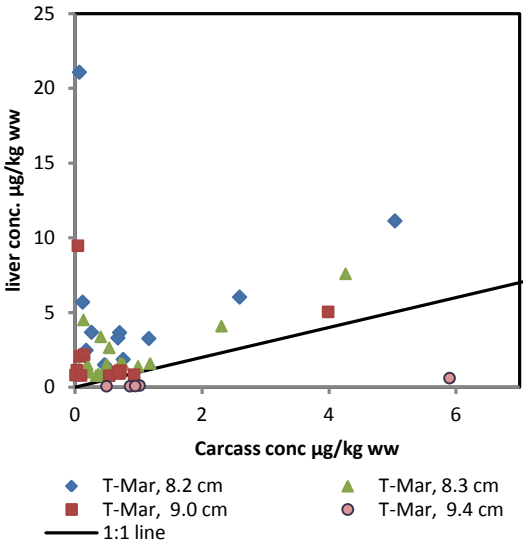


Figure 4.1-5 <u>Bleak</u>: Concentration of POPs in the liver (y-axis) compared the carcass (x-axis) of 4 bleak caught in 2007 (T-Mar: Temple-Marlow 187-190 km from the source). Each individual fish is represented by a different colour and identified in the legend by the site and its fork length. Each dot represents a chemical. Only chemicals that were quantifiable in both liver and carcass were plotted.

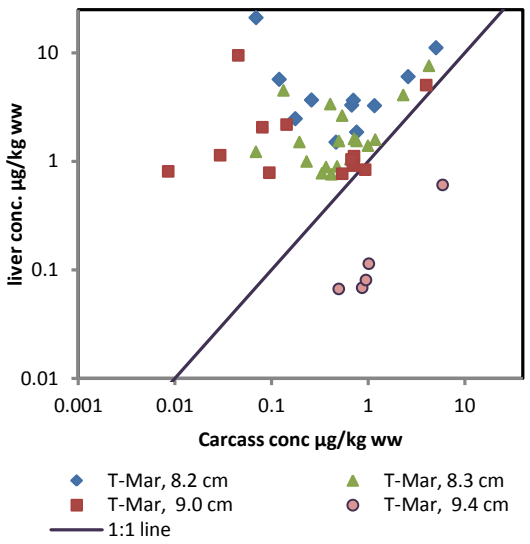


Figure 4.1-6 Figure 4.1-5 on logarithmic scales.

4.2 Chemical concentrations in the analysed fish compared to bio-monitoring limits and food standards

Given that this study is predominantly concerned with environmental quality rather than with food safety, food standards are only given for comparison and will be discussed relatively briefly.

4.2.1 Background to the European environmental quality standards (EQS)

The Water Framework Directive (European Union 2000) established the framework for setting environmental quality standards, which are applied either EU-wide or on a national basis (for pollutants that are only of concern in specific countries, e.g. due to the volumes of use or production). Annex V, section 1.2.6 of the Water Framework Directive describes in principle, how EQS should be set and a technical guidance document published later (European Commission 2011b) gives more detail to help practitioners to set national EQS in accordance with the guidance and to derive future EU-wide standards and review existing ones. The principles are:

- Standards may be set for water, sediment or biota
- Both chronic and acute toxicities should be taken into account
- The "base set" of taxa investigated to set water EQS should be: algae and/or macrophytes, daphnia (or representative organisms for saline water), and fish. Toxicity to humans, or other predators from eating contaminated fish as well as any available toxicity data for other aquatic species should also be considered.

For freshwater four different quality standards can be derived (European Commission 2011b):

- a water EQS based on direct ecotoxicity
- a water EQS for human consumption of drinking water

- a biota EQS based on secondary poisoning of predators (birds or mammals). As there is little data on aquatic predators, it is at present assumed that standards derived for the protection of birds and mammals would also protect benthic and pelagic predators, such as predatory fish.
- a biota EQS based on human consumption of fishery products

The last two points are relevant for this thesis as they are usually set for fish. In setting biota EQS, literature data is used to estimate a predicted no-effect level for the ingestion of food ($PNEC_{oral}$) and this applies to the prey of the organisms to be protected. The predators considered are, for example, fish-eating birds and mammals (e.g. otters) and their prey is fish. The relevant processes are illustrated in Figure 4.2-1 but if the toxicity studies are based on food intake, only the daily feeding rates need to be known to extrapolate from feed in laboratory studies to the prey of wild species. This is often called a diet-based approach (European Commission 2011b). Safety factors are applied to account for species or endpoints not investigated. The less data is available, the larger the uncertainty and the larger the applied safety factors. Recommended safety factors for deriving biota standards from NOECs are given in Table 4.2-1. Relatively new ("emerging") contaminants often have insufficient data, meaning that large safety factors are applied to the little data that is available. The lack of data for relatively new substances that have not yet been extensively studied can therefore lead in some cases to overly cautious quality standards and as more data becomes available, some standards are likely to be revised.

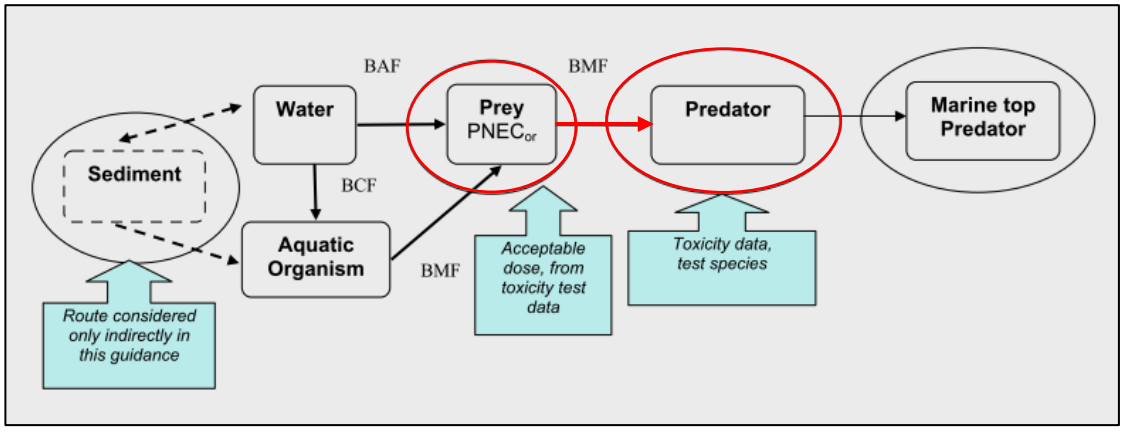


Figure 4.2-1 Steps involved in deriving a biota standard (from European Commission 2011b). If the standard is expressed for prey, only one extrapolation from prey to predator using daily feeding rates is necessary. In the freshwater environment "prey" would normally be fish, while "predator" could be fish-eating birds or otters. "Top predator" is only relevant for the marine environment.

Table 4.2-1 Assessment factors (safety factors) used to convert food based toxicity data into prey-based biota EQS (European Commission 2011b). If the most susceptible wild species is known, a refined assessment can be done specifically for that species by using its specific feeding rates laboratory data for the appropriate species group (birds or mammals) The assessment factor of 3 to account for the difference between lab and field can then be omitted, leaving a factor of 10 for species differences and 3 or 10 for non-chronic duration. Note that only medium to long-term studies (at least 28 days are considered to be suitable for deriving biota EQS.

Oral toxicity value	test duration	assessment factor	refined assessment factor[a]
$NOEC_{birds}$	Chronic	30	10
$NOEC_{mammals}$	Chronic	30	10
	90 days	90	30
	28 days	300	100

[a] if the risk assessment was specifically based on the wild species known to be the most susceptible

Standards for the quality of surface water with regards to "priority substances" were first introduced to EU legislation with the Priority Substances Directive (a "daughter directive" of the water framework directive, European Union 2008a), which entered into force in January 2009. Its objectives are protecting wildlife and humans from harmful effects of chemicals identified as priority substances in surface waters and monitoring trends of these chemicals. It aimed to set environmental quality standards (EQS) for a number of chemical pollutants, below which no harmful effects to wildlife or humans were expected. In the original version (European Union 2008a), EU member states had the option of setting biota, or sediment, standards which offer "at least the same level of protection" as the water standards and for mercury, hexachlorobenzene (HCB) and hexachlorobutadiene (HCBD), it was stated that water standards alone do not offer sufficient protection and therefore EU-wide limits were set for both water and biota for those substances. The legislation also specified that member states which chose not to apply the biota standard should set more stringent levels for the water standard than those set out in the directive. The EQS was set for prey tissue (wet weight) with member states being required to choose "the most appropriate indicator from among fish, molluscs, crustaceans and other biota;" (European Union 2008a, Article 3 (2a)). A requirement was set that where levels exceeded the EQS, downward trends should be demonstrated as "the Commission shall, by 2018, verify that emissions, discharges and losses as reflected in the inventory are making progress towards compliance […]" (European Union 2008a, Article 5(5)). The deadline for compliance with the standards in the 2008 version of

the Priority substances directive is "15 years after entry into force" of the water framework directive (European Union 2000). Compliance with the standards established in the 2008 Priority substances directive should therefore be achieved by 2015 (European Union 2013, preamble (9)).

In 2013 the priority substances directive was updated (European Union 2013) and now includes eight additional biota standards and states that, unless specified, the standards should be for fish rather than the more generic "prey" indicated in the old version. The specified exceptions are: crustaceans and mussels for fluoranthene and PAH's (benzo(a)pyrene monitored as a representative example of PAH's) and fish, crustaceans and mussels for dioxin-like toxicity (European Union 2013, Annex footnote 12). The "revised EQS for existing priority substances should be met by the end of 2021 and the EQS for newly identified priority substances by the end of 2027" (European Union 2013, preamble (9)).

The EQS have been derived by estimating which body burdens would not have negative effects on consumers of these fish (or crustaceans and mussels where applicable). For each priority substance a dossier has been prepared (https://circabc.europa.eu/faces/jsp/extension/wai/navigation/container.jsp, which after reviewing the literature suggests concentrations in the biota that would protect either humans or wildlife consumers from negative effects. In most, but not all, cases the lower one of the two has been chosen as the final EQS (Table 4.2-2).

For four or five of the 11 substances (HCB, HCBD, dicofol, PFOS and perhaps dioxin-like toxicity) the values derived for the protection of wildlife or human consumers are relatively similar (less than about a factor 5 different). In the case of mercury and HBCDD the value for the protection of wildlife is more than an order of magnitude lower, presumably because freshwater fish only makes up a relatively small part of the human diet whereas for some non-human predators, such as otters or birds, it can be close to 100%. More surprising are those chemicals for which the value for the protection of human health is much lower than that derived for wildlife consumers: fluoranthene, PBDEs, and heptachlor/heptachlor epoxide. While for example for mercury and dioxin-like toxicity the standard for human protection is the same as the food standard (European Commission 2005b), this is not the case for fluoranthene and PBDEs, for which a food standard was not deemed necessary, or for heptachlor/heptachlor epoxide, which has a food standard for meat (none exists yet for fish) of 200 µg/kg compared to the very much lower 0.0067 µg/kg EQS.

4.2.1.1 Chemicals with EQS measured in this study

Out of the current list of 11 chemicals (or chemical groups) that should be monitored in biota to compare to environmental quality standards (European Union 2013), large number of samples were analysed for three: mercury, hexachlorobenzene and polychlorinated di-phenylethers (PBDEs). Additionally, hexachlorobutadiene (HCBD) was measured in one batch of 40 samples, but problems with that run of the analysis mean that accurate values are not available. Nevertheless, is was clear that the HCBD concentrations were very low to non-detectable. This is in keeping with a recent study in France (Miege *et al.* 2012), which failed to detect HCBD in several species of fish and a study of Belgian eels, which found a median of only about 0.2 µg/kg ww and a maximum of 12 µg/kg ww (Roose *et al.* 2003), although much older studies in fish from the river Rhine found it at some sites above the current EQS in 1972/3 (Goldbach *et al.* 1976) and 1993 (Heinisch *et al.* 2004).

Table 4.2-2 gives an overview of the two sets of biota standards that were derived separately for the protection of human or wildlife consumers during the preparation of the Priority Substances Directive (European Union 2008a, 2013). The final EQS values are highlighted and represent usually - but not always - the lower one of the two.

Where no EU standards exist (yet), fish data were also compared to EQS from outside the EU. These are Canadian standards for total DDT (Canadian Council of Ministers of the Environment 1999) and PCBs and a proposed US standard for selenium (US EPA 2014). Table 4.2-3 gives an overview the relevant food and environmental standards and Table 4.2-4 compares them to the results from the fish in this study.

Table 4.2-2 Biota standards for the two protection goals: human health and protection of wildlife consumers summarized from the compound dossiers (https://circabc.europa.eu/faces/jsp/extension-/wai/navigation/container.jsp) in (European Commission 2014(draft)). The value that has been adopted as EQS is highlighted in orange. This is usually - but not always - the lower one of those derived for human or wildlife consumers.

Biota quality standards (QS_{biota}) derived for the two different protection goals.

Substance	$QS_{biota,\ hh\ food}$ [µg/kg ww]	$QS_{biota,\ sec\ pois}$ [µg/kg ww]
Brominated diphenyl ethers	0.0085	44
Fluoranthene	30	11522
Hexachlorobenzene (2005)	10	16.7*
Hexachlorobutadiene (2005)	12.2*	55
Mercury (2005)	500*	20
PAHs	5	No data available
Dicofol	134	33
PFOS	9.1	33
Dioxins dioxin-like compounds	0.0065 (TEQ)	For comparison purpose only: 0,0012 (TEQ)
HBCDD	6100	167
Heptachlor/-epoxide	0.0067	33

QSs were taken from Directive 2013/39/EU or EQS dossiers published in 2006 (*) and 2012 (cf. footnotes). [7]

Table 4.2-3 Overview of environmental and food quality standards in the EU applying to fish (and some EQS from Canada and the USA for comparison) for compounds measured in this study. Values are given in µg/kg ww unless specified

Contaminant	EU EQS (fish)[a]	other EQS (fish)	EU food std (fish)[b]
Metals			
lead	-		300
cadmium	-		50
mercury	20	Canada: 33[c]	most fish: 500 eel: 1000
selenium		USA proposed: 8.1 mg/kg dw[d]	
Organo-chlorine Pesticides			
HCB	10		meat[e]: 200
Chlordane (α+γ)			meat[e]: 50
Lindane (γ-HCH)			meat[e]: 20
Endosulfan			meat[e]: 50
Total DDT		Canada: 14[f]	meat[e]: 1000
PBDEs			
PBDEs ∑6 [g]	0.0085		
PCBs			
Non-dioxin-like PCB (ICES6)[h]			farmed or marine: 75 wild freshwater[i]: 125 wild eels: 300
Dioxins + furans + dioxin-like PCB as WHO 2005 TEQ[j]	EU: 0.0065		most fish: 0.0065 eel: 0.0010
Dioxin-like PCB as WHO 1998 (mammals)[k]		Canada: 0.00079[l]	
Dioxin like PCB as WHO 1998 (birds)[m]		Canada: 0.0024[l]	

[a] European Union (2013)
[b] European Commission (2006a)
[c] Canadian Council of Ministers of the Environment (2003)
[d] Proposed standard for whole body concentration to protect fish and their offspring. The consultation period ended 28.7.14 (US EPA 2014)
[e] meat standard used as no food standard is available for fish European Commission (2005b)
[f] Canadian Council of Ministers of the Environment (1999)
[g] sum of congeners 28, 47, 99, 100, 153, 154
[h] sum of PCBs 28, 52, 101, 153, 180 (ICES7 without 118).
[i] except eels, see below
[j]The 2005 updated toxic equivalency factors for dioxin-like toxicity to mammalian predators (including humans) (Van den Berg *et al.* 2006)
[k] Dioxin-like toxic equivalents to mammalian predators (incl. humans) (Van den Berg *et al.* 1998)
[l] Canadian Council of Ministers of the Environment (2001)
[m] Dioxin-like toxic equivalents to avian predators (Van den Berg *et al.* 1998)

4.2.2 Toxicity of the chemicals with food or environmental standards that have been measured in this study

N.B. More details about each of the chemicals are given in section 1.5.

4.2.2.1 Lead

Lead affects the central nervous system, especially during development leading to learning difficulties and similar impairments both in animal experiments and human epidemiological studies (EFSA 2010). Food it the major source of lead for humans with dietary intake estimated to be between 0.47 and 0.96 µg/kg body weight/d for average UK inhabitants (EFSA 2010), but fish only contributes a very small proportion to the total. The largest contributing group is vegetables, nuts and pulses, which contributes 14-19% of the total lead intake for average EU citizens (EFSA 2010).

4.2.2.2 Cadmium

Cadmium has a high toxicity. Long-term exposure leads to build-up in the kidneys, where many effects are found, but there are also negative effects on bones and cadmium is classed as a human carcinogen (Beauvais *et al.* 2001). A serious incident of human cadmium poisoning became known as the Itai Itai disease from the Japanese word for "pain" because the sufferers experienced intense pain in the bones. The cause was eventually found to be rice that had been irrigated with cadmium-contaminated river water (Tsuchiya 1969a, b). Food is thought to be the main source of cadmium for the general non-smoking population (Beauvais *et al.* 2001).

4.2.2.3 Mercury

Inorganic mercury has a low bioavailability and low toxicity but mercury found in biota is usually predominantly in the methylmercury or other organo-mercury forms, which are much more toxic. In common with most studies, total mercury was

measured in this study, so it is not possible to disambiguate which forms were present, but it is likely that most was methylmercury as that form bio-accumulates very strongly (Sandheinrich and Wiener 2011).

Mercury has a number of negative effects on fish and other wildlife at body-burdens in the hundreds of µg/kg fresh weight (reviewed in Wiener *et al.* 2003), which led Sandheinrich and Wiener (2011) to conclude that the threshold where negative effects happen to fish themselves is between 300 and 700 µg/kg for whole body homogenates or 500-1200 µg/kg if fillet is monitored and Boscher *et al.* (2010) proposed safe levels for mercury in fish in the diet of otters of between 100 µg/kg and 500 µg/kg (see the introduction chapter for more details). From the data given in Wiener *et al.* (2003), it can be estimated that the biomagnification factor of methylmercury between the contaminated food and the experimental fish is usually around 4, although none of the reviewed studies exposed fish for a full life cycle, so this may be an underestimate. Using a factor 4 or so for biomagnification and considering that the EQS needs to protect not only the species measured but also their predators and possibly further levels up in up in the food chain, therefore wanting to protect perhaps up to two trophic levels above the species measured, the safe body burden of 300-700 µg/kg mentioned above would translate to 1/16 of that 2 trophic levels lower i.e. 19-43 µg/kg. In that context the chosen value of 20 µg/kg ww seems entirely reasonable, even if it is difficult to achieve in many places (see chapters 4.4 and 4.5 on comparison to other studies to put the values measured here in context) and the measured concentrations of 6-68 µg/kg (Table 4.2-4) are unlikely to cause harm to the fish themselves, but may be of some concern to top predators.

4.2.2.4 Selenium

Selenium is an essential element needed in a number of enzymes, so there can be too little of it as well as too much and the difference between deficiency and toxicity is not actually that big: 1-2 orders of magnitude (US EPA 2014). It is a naturally occurring element but human activity can increase the amount available to aquatic wildlife mainly through mining and processing of metals, minerals and fossil fuels and through excess irrigation of soils that are naturally high in selenium (US EPA 2014). In the EU there are currently no food or environmental standards for selenium, but the US EPA has developed water quality standards for selenium which

are currently under review (US EPA 2014). In these it is recognised that the main risk to aquatic wildlife from selenium is due to its toxicity to developing fish embryos, while adult fish and other species appear to be much less sensitive.

Since the danger is to the developing embryo, it is best to monitor Se in the eggs or ovaries, because the concentration in the egg determines whether effects will occur in the developing larvae (deForest and Adams 2011). Reviewing the literature on selenium effects on fish development deForest and Adams (2011) calculated EC10 values for larval mortality as the threshold, but those were extrapolated values as they were always lower than the LOEC and often similar to the NOEC. Despite this uncertainty there was little difference in the EC10 values between the species investigated when Se was measured in the eggs or ovaries (deForest and Adams 2011, US EPA 2014). The egg or ovary based threshold was calculated for 10 % embryo mortality in the 5% most sensitive species as of 15.2 mg/kg dry weight, which is also the recommended EQS (US EPA 2014, p21). If egg or ovary concentrations are not measured deForest and Adams (2011) suggest that whole body concentrations can be used as a second-best alternative. For whole body concentration they calculated an EC10 of 8.1 µg/g dry weight based on larval mortality or oedema, but there were no data points between 7.5 (<5% effect) and 16 µg/g (>90 % effect), and lower EC10 values of 6.4 µg/g dry weight for mortality and 4.3 µg/g dry weight for growth were derived from a study on anadromous chinook salmon.

The US EPA also sees monitoring whole body or fillet concentrations as a second best option to monitoring egg or ovary concentrations, so an extrapolation was made from the above egg/ovary threshold to what would be the corresponding whole body or fillet concentration. They also recommend a threshold of 8.1 mg/kg dw for whole body or alternatively 11.8 mg/kg dw for the fillet. While reproductive effects were seen as most important, effects on growth were also sometimes observed at similar body burdens (US EPA 2014, p128).

Several incidents of fish population collapses have been (sometimes tentatively) linked to Selenium poisoning. In some of those selenium concentrations in fish were monitored and were between 8-38, 6-36 and 15-50 mg/kg dw in three separate incidents affecting lakes in the US and Sweden (reviewed in: deForest and Adams 2011), i.e. selenium concentrations in fish from the affected lakes was mostly above the threshold of 8.1 mg/kg dw but always by much less than an order of magnitude.

US EPA proposed water standards involve a further extrapolation into what concentration in the water would produce the threshold concentrations above in the fish. This is different for standing or flowing waters and divided into long-term average and maximum values. The water standards are only to be used if fish concentrations are not available (US EPA 2014).

4.2.2.5 Hexachlorobenzene (HCB)

The fungicide HCB's toxicity to humans was dramatically demonstrated in the late 1950s when thousands of people in Turkey suffered liver damage after eating HCB treated grains and many babies died as a consequence of feeding on contaminated breast milk (Gocmen *et al.* 1989). In terms of the toxicity to wildlife, EURO CHLOR, the trade organization of European chlorine producers, extrapolated from published water no observed effects concentrations (NOECs) to body burdens and calculated that the no observed effects level (NOEL) expressed as body burden for fish would be 7,500 µg/kg (Euro Chlor 2002a), but by extrapolating from the effects of food-borne HCB on animals in laboratory studies, the Niagara River Biota Project (Newell *et al.* 1987) derived much lower safe levels to protect fish-eating mink, estimating the NOEL for non-carcinogenic effects as 330 µg/kg in the prey fish and that a contamination of 20 µg/kg in the fish would give mink a lifetime cancer risk of 1/1000. The latter value is similar to recommendations by the US EPA which state that humans who eat food containing 29 µg/kg for 130 weeks may experience health effects (US EPA). The considerations of the cancer risk, for which there is no known threshold, i.e. no zero-risk, but where an **acceptable** level of risk can be defined, make the EU biota standard of 10 µg/kg seem in the right region, even though the food standard (for meat, none exists for fish yet) is much higher at 200 µg/kg (Table 4.2-3). One could argue over whether for example a 1/100 (additional) cancer risk is acceptable or only 1/1000 and the health risk from eating too much meat as such may well be higher than that from particular pollutants, such as HCB in the meat.

4.2.2.6 Hexachlorobutadiene (HCBD)

Studies in rats and humans show that HCBD undergoes several metabolization steps in the body forming the highly toxic trichlorovinyl-chlorothioketene (TCCT) in the kidney where it binds to adjacent tissue, causing toxic and carcinogenic effects (Staples *et al.* 2003). HCBD exposure was linked to effects on kidney function in humans in a recent case in the UK: In 2002, residents were moved to cleaner areas and 37 houses were demolished because of the unacceptably high atmospheric HCBD levels emanating from an industrial landfill in the Runcorn area near Liverpool. After relocation to cleaner areas, kidney function of the residents generally improved (Staples *et al.* 2003). There is little data on toxicity to wildlife but the Niagara River Biota Project (Newell *et al.* 1987) used the same approach as described above for HCB and concluded that 450 µg/kg HCBD in the diet would be associated with a 1/1000 cancer risk in mink. The EU EQS for HCBD has been set about an order of magnitude below that value at 55 µg/kg fresh weight, allowing for some bio-magnification.

4.2.2.7 DDT

Eggshell thinning in birds and subsequent reproductive failure, because the eggs tended to break, was linked to DDT, and this was the main driver for banning this pesticide (ATSDR 2002). Technical DDT consists of about 85% pp'DDT, the active insecticidal ingredient, and 15% op'DDT with minor contributions of pp' and op' DDEs and DDDs (ATSDR 2002).

The minor component op'DDT along with its degradation products op'DDE and op'DDD (marked in shades of red in the graphs in chapter 3) is estrogenic and pp'DDE, the compound most commonly found in the environment, is an anti-androgen (the pp'congeners are marked in blue shades in the graphs). These effects were initially noticed in humans and mammals but have also been shown for fish both in vitro and in vivo (Baatrup and Junge 2001, Bayley *et al.* 2002, Okoumassoun *et al.* 2002, Uchida *et al.* 2010). DDT was also related to effects on thyroid function in fish (Brar *et al.* 2010).

Lydy *et al.* (2011) reviewed the effects of DDT on fish with regards to the body burden. They list 11 papers, that studied the effects of DDT on fish and reported the body burdens in the experimental animals. The endpoint in eight of the studies was lethality and one study each observed effects on behavior, growth or reproduction. "Low effects" (LOEC?) were observed between 290 and 112,000 µg/kg DDT depending on the study. "DDT" in this context probably refers to op'DDT + pp'DDT.

4.2.2.8 Polybrominated diphenyl ethers (PBDEs)

Few studies on the toxicity of PBDEs to aquatic wildlife exist, but Muirhead *et al.* (2005) found a clear reduction in fertility and condition factor in male fathead minnows exposed to BDE-47 contaminated food. Extrapolating from studies on the neurodevelopment in mice the EFSA (2011) derived body burdens at which an effect might be expected in humans by calculating the $BMDL_{10}$ (bench mark dose, lower 95% confidence level for a 10% response) as 309 µg/kg for BDE-47; 12 µg/kg for BDE-99, 83 µg/kg for BDE-153 and 1,700 µg/kg for BDE-209. EFSA concluded that there was no need for risk management but recommended monitoring of PBDEs in food.

In deriving the EQS for PBDEs (European Commission 2011a) the EU advisors came up with 44.4 µg/kg (for the sum of 6 indicator PBDEs) to protect wildlife consumers. For the protection of human consumers of freshwater fish, however, they used data from the same studies that EFSA used, which showed exposure of rats to the most potent BDE-99 led to hyperactivity and altered anxiety behavior at 0.6 mg $kg^{-1}day^{-1}$ and by assuming that all 6 BDEs monitored would be as toxic as BDE-99 calculated an acceptable body burden for humans of 9 µg/kg (compared to 12 µg/kg, which EFSA calculated for the most potent BDE-99 alone). They then assumed the worst-case scenario of the maximum possible stability in the human body and lifelong intake, leading to high bioaccumulation, which (somehow) led to an allowable intake of only 4.2 ng $kg^{-1}day^{-1}$ (more than five orders of magnitude lower than the 600 µg $kg^{-1}day^{-1}$, that had an effect in rats) and with a further safety factor of 30 concluded that the amount in the fish should therefore be as low as 0.0085 µg/kg. Tomy et al. (2004) reported biomagnification factors between 35 and 45 for the six monitored PBDEs, when juvenile lake trout were fed PBDE spiked food at high

concentrations, but even such relatively high biomagnification values do not explain the need for such a low EQS .

4.2.2.9 PCBs and dioxin-like toxicity

Sures and Knopf (2004) found that the most potent dioxin-like PCB 126 completely suppressed the immune response of eels experimentally infected with the nematode *A. Crassus*, making them much more susceptible to this disease. The majority of the eels in this study were found to be moderately infected with A. Crassus (Thames Valley Aquatic Services 2007) (Table 4.2-2), but PCB126 has not been analysed. Van Ginneken *et al.* (2009) concluded that PCB contamination at environmentally relevant concentrations can have effects on eels' swimming performance. They furthermore state that PCBs reduce the amount of retinoids in the liver, which is a problem because these chemicals are essential for early larval development and the exposed females may not have sufficient amounts to pass on the eggs. Palstra *et al.* (2006) suggested that natural contamination with dioxin-like pollutants affects reproduction, but their conclusions were based on only a small number of data points and relied very heavily on one of those points, so may not be reliable.

Dioxin-like toxicity is assessed on the weighted sum of several groups of chemicals, which share some structural similarity with the most toxic dioxin 2,3,7,8-tetra-chloro-di-benzo-*p*-dioxin (TCDD). These include: 7 chlorinated dibenzo-*p*-dioxins (dioxins), 10 chlorinated dibenzo-furans (furans), 4 non-ortho-substituted PCBs (numbers 77, 81, 126, 169), and 8 mono-ortho-substituted PCBs (numbers 105, 114, 118, 123, 156, 157, 167, 189). Earlier, the inclusion of some di-ortho-substituted PCBs had also been suggested (Ahlborg *et al.* 1994), but was rejected by the expert group (Van den Berg *et al.* 1998).

Although, due to their structural similarity all these chemicals are expected to have the same mode of action, their potency varies greatly. To allow the calculation of the total toxic effects each of the substances has been assigned a toxic equivalency factor (TEF) relative to the most toxic one TCDD. These factors have been refined over time as more data became available and two versions endorsed by the World Health Organization (WHO) are currently in use:

- Van den Berg *et al.* (1998), known as WHO1998, gives TEFs separately for three groups of species: mammals (including humans), birds, and fish
- Van den Berg *et al.* (2006), or WHO2005, has updated values for the toxicity to mammals

It is important to remember that the relative toxicities between these different chemicals will vary between species or endpoints investigated and the TEFs are not to be seen as "absolute truth" but rather as an average estimate that allows to give a reasonable approximation of the total toxicity.

When comparing measured data to regulatory values it is important to ascertain which of the four versions (three WHO1998 + WHO2005), of the TEFs is to be used and whether the value is for the total toxicity of dioxins, furans, and dioxin-like PCBs or only some of these groups.

Of these dioxin-like substances only the mono-ortho substituted PCBs were included in the measurements in this study. Geeraerts *et al.* (2011) found that the mono-ortho PCBs contributed on average 47% of the calculated TEQs (WHO1998, presumably for mammals) in eels from Belgium. Assuming that this relationship also holds true in the UK, it can be estimated that the total dioxin like TEQ would be about twice of that measured for the mono-ortho PCBs alone. In a small study of Irish eels, however, (McHugh *et al.* 2010) the mono-ortho substituted PCBs contributed only 4-5% to the $WHO1998_{mammals}$ TEQ at two very dioxin contaminated sites and 14-41% at the four remaining sites, showing that total TEQ may also be more than double of the TEQ in the current study and that knowledge about all dioxin-like contaminants would be needed to accurately judge the risk from this group of chemicals.

4.2.3 Overview of measured concentrations compared to food and environmental quality standards

Table 4.2-4 Contaminant concentrations in fish from this study compared to environmental quality standards (EQS) and food standards for some metals and persistent organic pollutants. Where no EU EQS have been set, those from other countries are given. Unless specified, all concentrations are in µg/kg ww. To aid the reading of the table the cells are colour-coded by the number of exceedances: frequent exceedances are coloured red, rare exceedances yellow and no exceedances green with light green for those summary parameters where not all compounds contributing have been measured. For references and explanations of the summary parameters please refer to the footnotes in Table 4.2-3

Contaminant	Fish in this study [µg/kg ww]	EQS (fish) [µg/kg ww]	EU food std (fish[a]) [µg/kg ww]
Metals (not measured in eels)			
lead	7.6-650 (n=144)	-	300 **exceedances:** 3/110 (3%) roach, 1/34 (3%) bleak
cadmium	0.8-27 (n=144)	-	50 **no exceedance**
mercury	6.2-68 (normalised to 26% dw: 8.1-69)	EU: 20 **exceedances**: 79/110 (72%) roach, 32/34 (94%) bleak or normalised: 81 roach (74%), 32/34 bleak (94%)	500 **no exceedance**
selenium	135-2,164 (n=144) (0.68-8.4 mg/kg dw)	USA proposed: 8.1 mg/kg dw **exceedances:** no roach 1/34 bleak (3%)	
Organo-chlorine Pesticides			
HCB	0.03-6.4 (n=123) (normalised to 5% lipid 0.01-2.1)	EU: 10 **no exceedance**	meat: 200 **no exceedance**
Chlordane (α+γ)	0.03-2.5 (n=128)		meat: 50 **no exceedance**
Lindane (γ-HCH)	<LOQ-13.7 (n=108)		meat: 20 **no exceedance**
Endosulfan	<LOQ-0.9 (n=108)		meat: 50 **no exceedance**
Total DDT	0.6-265 (normalised to 5% lipid: 0.4-123)	Canada: 14 **exceeded:** 11/81 (14%) roach[b] 4/17 (24%) bleak 19/35 (54%) eel normalised to 5% lipid this would change to 15 roach (19%)[b], 2 bleak (12%), 4 eel (11%)	meat: 1000 **no exceedance**

Contaminant	Fish in this study [µg/kg ww]	EQS (fish) [µg/kg ww]	EU food std (fish[a]) [µg/kg ww]
PBDEs			
PBDEs ∑6	1.5-44 (n=99) (1.5-53 normalised to 5% lipid)	EU: 0.0085 all exceeded, but only 1 (or 2 if normalised to 5% lipid) of 99 individuals reached the proposed wildlife EQS of 44 µg/kg	
PCBs			
Non-dioxin-like PCB (ICES6)	eels: 4-104 (n=35) bleak+roach: 2-42 (n=98)		wild eels: 300 other wild freshwater: 125 no exceedance
Dioxins + furans + dioxin-like PCB as WHO 2005 TEQ	partial[c]: 0.000016-0.0010 (0.000013-0.00052 norm. to 5% lipid)	EU: 0.0065 no exceedance from partial toxicity measured	0.0065 (0.010 for eel) no exceedance from partial tox. measured
Dioxin-like PCB as WHO 1998 (mammals)	partial[d]: 0.00009-0.0048 (0.00006-0.0024 norm. to 5% lipid)	Canada: 0.00079 10/81 roach (12%) 12/17 bleak (71%) 33/35 eel (94%) exceeded, even though only partial toxicity was measured	
Dioxin like PCB as WHO 1998 (birds)	partial[d]: 0.000022-0.0013 (0.000015-0.00066 norm. to 5% lipid)	Canada: 0.0024 no exceedance by partial toxicity. measured	

[a] For the pesticides no fish standard was available, so the standard for meat was used (European Commission 2005b, 2006a).

[b] Without the 10 roach from Wheathampstead there is only 1/71 exceedance, this increases to 5/70 (7%) if normalised to 5% lipid content.

[c] The standard is for the sum of toxicity from dioxins, furans, and dioxin-like PCBs (non-ortho and mono-ortho substituted PCBs), but only the mono-ortho-substituted PCBs were measured

[d] The standard is for the sum of toxicity from non-ortho and mono-ortho substituted PCBs, but only the mono-ortho-substituted PCBs were measured

4.2.4 Are food standards exceeded?

Only four of a total of 144 fish measured exceeded the food standard for lead (Table 4.2-4, Figure 3.2-15) and none exceed the standards for any of the measured pesticides or non-dioxin-like PCBs.

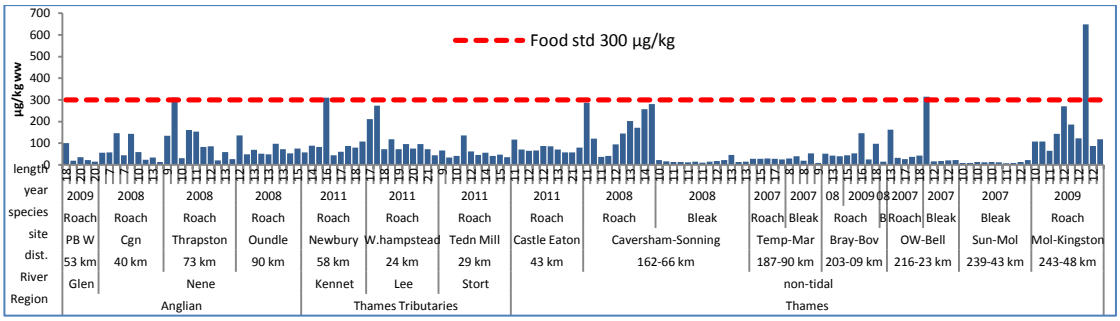


Figure 4.2-2 All lead contents determined. Sorted by region, river, site (dist. refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

The closest any of the measured organo-chlorine pesticides came to a food standard was Lindane in the roach from Wheathampstead on the Lee, where the measured concentrations were 1.8-13.7 µg/kg compared to the food standard for meat (none exists yet for fish) of 20 µg/kg (Table 4.2-4, Figure 4.2-3).

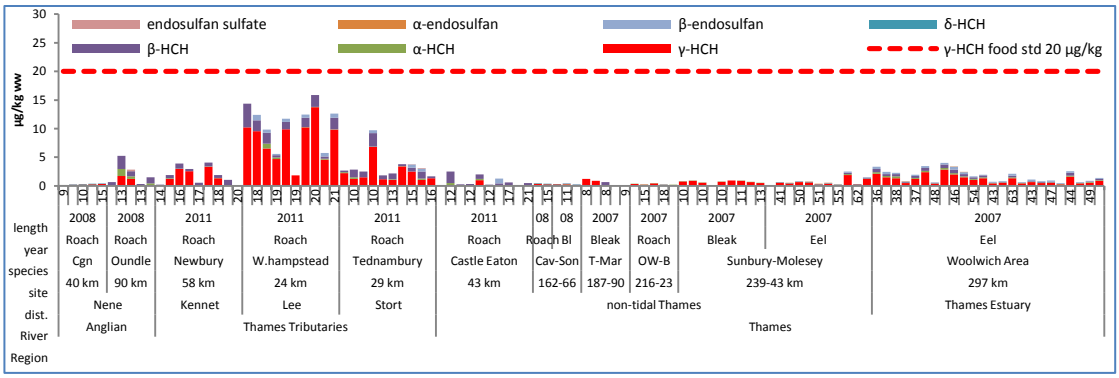


Figure 4.2-3 HCHs including lindane (γ-HCH) and endosulfans. The food standards (meat, none available for fish) are 20 µg/kg for γ-HCH and 50 µg/kg for endosulfan.

In the food standards for PCBs, the six non-dioxin-like congeners 28, 52, 101, 138, 153 and 180 were chosen as indicators, not due to their toxicity, but because they tend to occur in high enough concentrations to measure them reliably and they represent all relevant degrees of chlorination (Squadrone *et al.* 2015).

The measured concentrations compared to the relevant food standards (300 µg/kg for wild eels and 125 µg/kg for other wild freshwater fish (European Commission 2006a)) are plotted in Figure 4.2-4. None of the individuals tested exceeded those values. For roach and bleak the measured values were 2-23 and 11-42 µg/kg or 1.5-19% of their food standard of 125 µg/kg, while for eels the measured values were 4-104 µg/kg or 1.2-35% of their food standard of 300 µg/kg. A lipid normalised version of the figure is plotted in Figure 4.2-5 (see section 4.2.5, for explanation of normalisation).

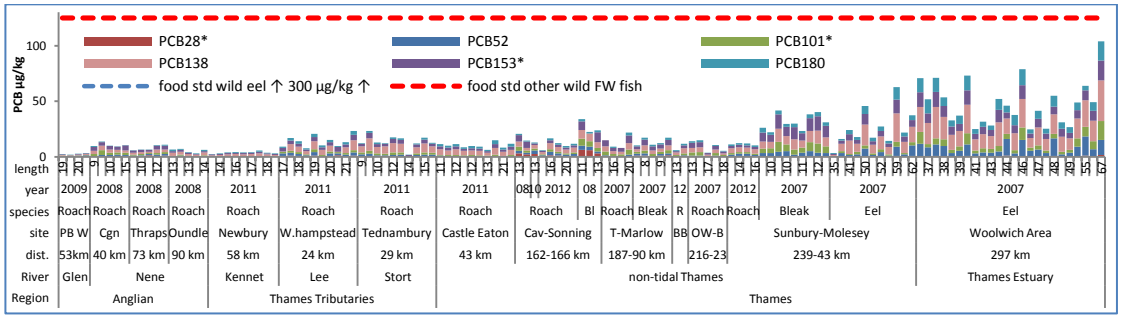


Figure 4.2-4 ICES6 PCBs and the food standards 125 µg/kg for wild freshwater fish and 300 µg/kg for wild eel, applicable to the sum of 6 non-dioxin-like indicator PCBs (ICES6, #28, 52, 101, 138, 153, 180) *co-eluted with another (minor) congener, so actual concentrations may be slightly different.

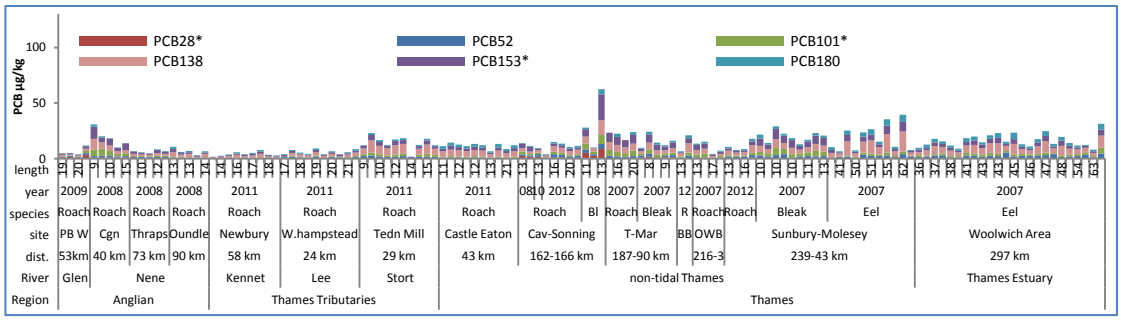


Figure 4.2-5 5% lipid normalised version of Figure 4.2-4. Lipid normalisation <u>isn't</u> a requirement for the food standards, but this graph is included to illustrate how lipid-normalisation reduces the differences between species for these chemicals.

Of the chemicals contributing to dioxin-like toxicity, as defined by the WHO 2005 (Van den Berg *et al.* 2006), only the 8 mono-ortho substituted PCBs were measured, leaving out the 7 chlorinated dibenzo-*p*-dioxins (dioxins), 10 chlorinated dibenzo-furans and 4 non-ortho-substituted PCBs. Although of those chemicals the measured mono-ortho substituted PCBs have been assigned the lowest TEQs relative to the most toxic dioxin 2,3,7,8 TCDD, a study of eels (Geeraerts *et al.* 2011) found that these PCBs contributed on average 47% of the WHO1998 TEQ (Van den Berg *et al.* 1998). Although most of the TEQs of the measured PCBs were higher in the WHO 1998 version than in the 2005 one relevant for the food standard, it is likely that the total dioxin-like toxicity would be in the region of 2-4 times that calculated for the mono-ortho PCBs alone, and less than the factor 10 needed to reach the food standard for the highest contaminated individuals (eels). Therefore, despite the uncertainty it is very likely that the food EU standards for dioxin-like toxicity would not be exceeded even if all compounds contributing to the TEQ were measured.

In summary, no food standards were exceeded for the chemicals measured with the exception of lead, which was above the threshold in 4 of 144 individuals (3%), but compliance for the dioxin-like toxicity cannot be ascertained with complete confidence because not all contributing compounds have been measured.

4.2.5 Are environmental quality standards exceeded?

For the EU environmental quality standards the exceedance of a value is recommended not to be judged on the individual samples (individual fish or composites for smaller species) but on averages (European Commission 2014(draft)). Because chemical contamination tends to be log-normal distributed the average is calculated from the logarithms of the concentrations and then converted back to the original format. Additionally a standardization step is recommended to account for the most important differences between individuals or species, which is to normalize the values to 26% dry weight in the case of mercury and to 5% lipid content for the organic pollutants (except PFOS, but that has not been measured in this study) (European Commission 2014(draft)).

Therefore the recommended data treatment is to :

1. normalise the data to 26% dry weight for mercury (would also make sense for the other metals for which there is a food std but no EQS) or 5% lipid content for organic pollutants
2. calculate Log_{10}(concentration)
3. average the Log_{10}(concentration) for each site/year combination
4. undo the log: therefore:
   concentration to compare to the standard = $10^{\text{average(Log(conc1), Log(conc2)…)}}$

While the normalisation is mainly done to allow better comparison between different data-sets, it also makes some sense from the predator's point of view, because a predator would likely need to eat less of prey with a high lipid or dry matter content than ones with lower contents, therefore higher pollution may be acceptable in such more "filling" food.

4.2.5.1 Mercury

The following graphs illustrate the calculations for mercury:

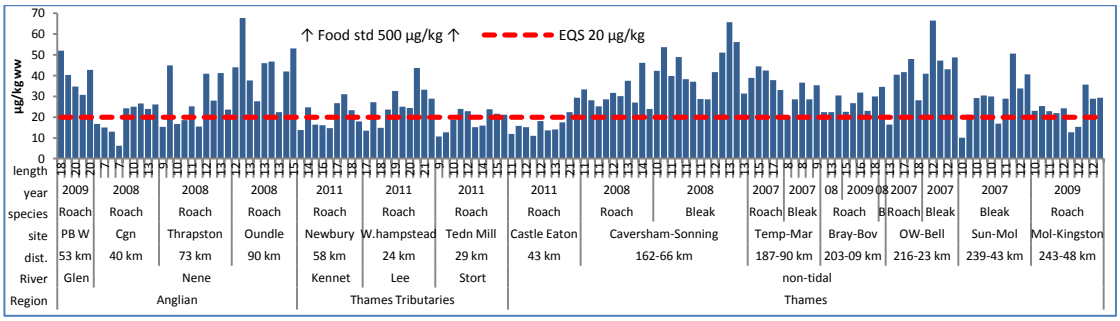


Figure 4.2-6 Raw data of all mercury contents determined as µg/g ww. Sorted by region, river, site (km refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length ↑. The environmental quality standard (European Union 2013) is also shown.

Figure 4.2-6 shows the wet weight concentration for all individuals where this parameter has been measured. 79 of 110 roach and 32 of 34 bleak exceeded the EQS. If Figure 4.2-6 is normalized to 26% dry weight it becomes Figure 4.2-7 and the number of individual exceedances of the EQS goes up from 79 to 81 of 110 for roach but stays the same at 32/34 for bleak. The changes are small because the actual dry weights are relatively close to 26% (see section 2.3.1).

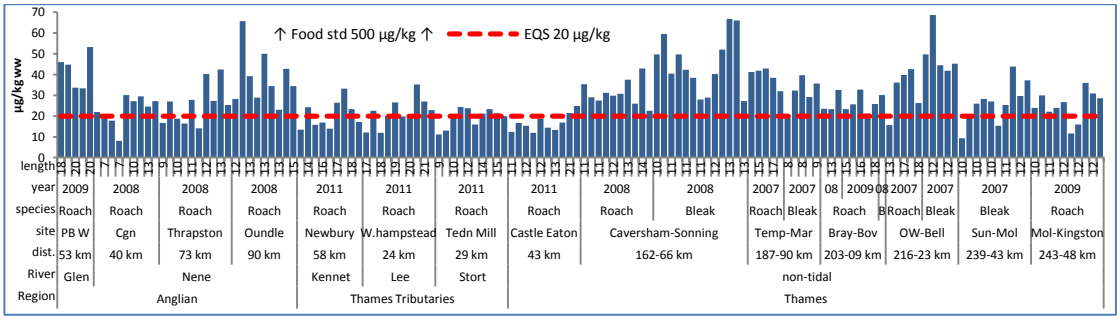


Figure 4.2-7 Figure 4.2-6 normalised to 26% dry weight.

When the log-converted average is calculated as described above, only three of the 14 groups of roach and none of the bleak pass the EQS (Figure 4.2-8) and even in those groups that pass on average there are several individuals that exceed the EQS. The three groups that pass are roach from the most upstream sites on the Thames as well as Newbury on the Kennet and Tednambury on the Stort, which are both on Thames tributaries, with very differing sewage impact. Tednambury was chosen as a

site that is heavily influenced by sewage treatment works effluents and Newbury as one with almost no known sewage discharges upstream. The relationships of mercury content with fish and site parameters are discussed in chapter 4.3

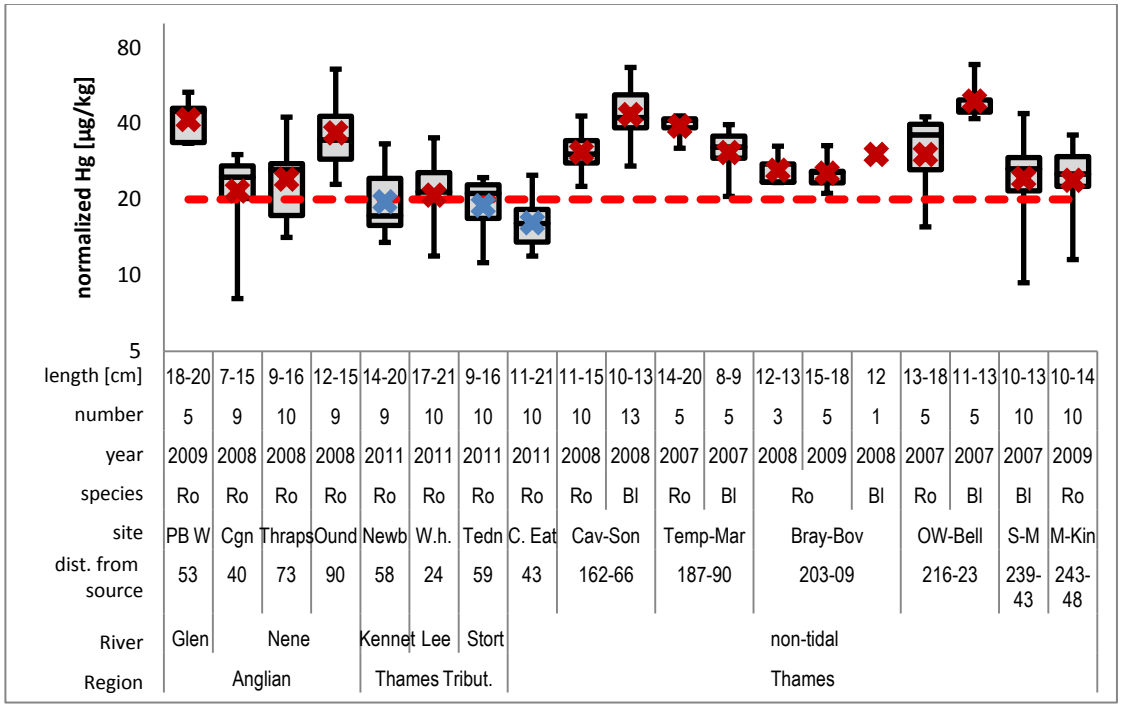


Figure 4.2-8 Mercury concentrations compared to the EQS of 20 µg/kg. Measured values have been normalized to 26% dry weight. The line represents the EQS, the crosses are the site-averages, which should be compared to the EQS (those below the EQS marked in blue and above in red). To give additional information on the spread of values, the quartiles of the distributions are shown as the box and whisker plots, with minimum and maximum as whiskers and 25, 50 and 75 percentiles as the boxes. The averages and percentiles were calculated on log-transformed data and then converted back as recommended in European Commission (2014(draft)). Note the logarithmic scale on the y-axis.

In short, therefore the mercury EQS was **exceeded at all but three sites** for the fish sampled in 2007-2011. It is therefore very unlikely that the standard will be met at most sites by the deadline of 2015.

4.2.5.2 Selenium

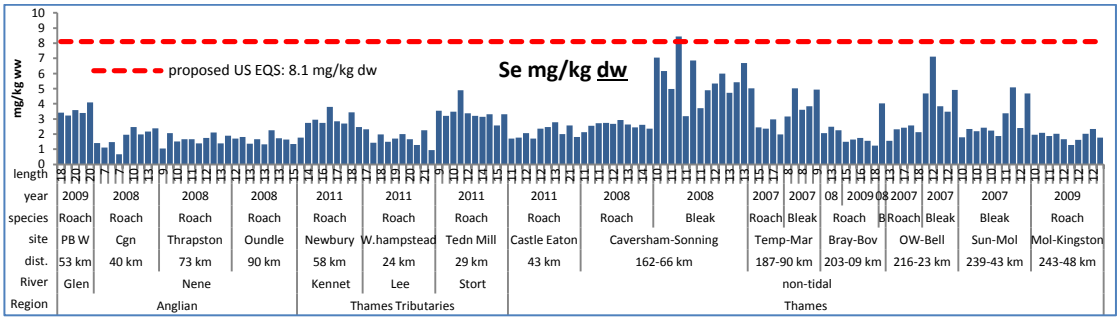


Figure 4.2-9 All Selenium contents determined as mg/kg dry weight. Sorted by region, river, site (km refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length ↑. The proposed US environmental quality standard (US EPA 2014) is also shown.

The levels measured in the fish ranged from 0.6 to 8.4 mg/kg dw (135-2,164 µg/kg ww), therefore spanning more or less the whole range of acceptable concentrations between deficiency (required levels for fish are 0.05-1 mg/kg dw, US EPA 2014) and toxic effects, with one individual (a bleak) narrowly exceeding the proposed US EPA whole body standard threshold of 8.1 mg/kg dw. This was a sample which had the liver, gall bladder and some blood removed before it was homogenised, but since bones, scales and other organs were still included it is appropriate to use the whole body standard and not the fillet standard.

The reproductive studies deemed to be of acceptable quality to be used to derive the selenium standard (deForest and Adams 2011, US EPA 2014) involved about a dozen species, but bleak and roach were not among them. The only member of the cyprinid family studied was fathead minnow which did not appear to be the most sensitive species. So while it is not clear whether roach or bleak would be more or less susceptible to selenium than other species it is likely that they are not the most sensitive species and therefore that the standard of 8.1 mg/kg would be sufficient to protect them and their offspring and that the one individual that narrowly exceeded that standard would probably be safe too. Therefore it does not seem likely that the fish analysed or their offspring would be adversely affected by the selenium concentrations in their bodies. As the margin is small, however, in some cases, their predators such as birds may be affected.

For domestic chickens selenium concentrations of 0.3-1.1 mg/kg dw in the diet are deemed adequate, below that supplements are recommended, 3-5 mg/kg is higher than necessary but not harmful, whereas above 5 mg/kg dw harmful amounts are

passed on to the eggs, leading to reduced hatchability and teratogenic effects in the embryos or chicks (Puls 1988, reviewed by Ohlendorf 2011). Thresholds for toxic effects on wild birds have been reported at 3-8 mg/kg dw in the diet (reviewed by Ohlendorf 2011). The higher end of that range is exceeded only once, but the lower end of 3 mg/kg dw is exceeded in 15% of roach and 79% of bleak measured. Eight of the top ten values were found among the 13 bleak from the Caversham to Sonning reach (162-166 km from the source) of the Thames. To estimate what dietary selenium concentration a predator eating bleak from this reach would receive I calculated the weighted average (taking into account the weight of the individuals), which is 5.62 mg/kg dw (the "ordinary" average is very similar at 5.65 mg/kg dw), which is above the value of 5 mg/kg dw above which (deForest and Adams 2011) expect "Elevated probability for reduced egg hatchability in sensitive [bird] species", but cautioning "effects down to this concentration may be measurable in the laboratory but unlikely to be detectable in the field unless dietary concentrations are considerably higher". This is because realistically a 10 or 20% reduction in reproductive success in the field is hard to detect against the background variability and even harder to ascribe to a cause, whereas in the controlled laboratory environment effects of that magnitude can be detected and if the experiment was done well should be caused only by the parameter studied- in this case selenium exposure.

4.2.5.3 Interaction between mercury and selenium

There can be an interaction between mercury and selenium, which is most commonly antagonistic, probably via the formation of mercury selenides which renders both of them inert (US EPA 2014, p21). Interestingly in the study of Swedish lakes, where selenium was implicated in perch population collapses in several lakes (see section 4.2.2.4), inorganic selenium had been deliberately added to mitigate high mercury levels (deForest and Adams 2011). As well as antagonistic effects, additive and synergistic effects between mercury and selenium have also been reported (US EPA 2014, p21). Additive effects may simply be due to mercury and selenium not binding to each other for whatever reason (maybe depending on what organic or inorganic form both of them are in), but the explanation for synergistic effects (if they are indeed real) is not known.

4.2.5.4 HCB

HCB values never exceeded the EQS, but some of the eels reached 60% when the individual raw values were considered (Figure 4.2-10). However, the values for most eels reduced when the 5% lipid normalisation was applied, which illustrates how normalisation reduces the difference between species (Figure 4.2-11). Therefore for the appropriately normalized data, all fish were about a factor 5 or more below the EQS of 10 µg/kg ww.

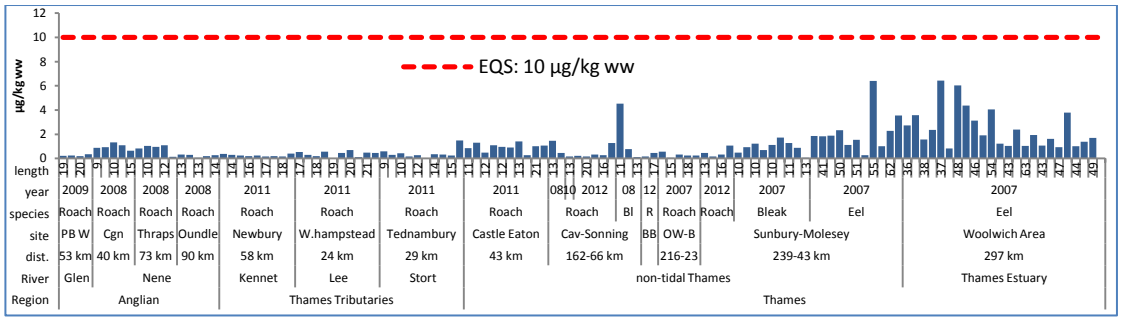


Figure 4.2-10 All HCB contents determined. Sorted by region, river, site (km refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

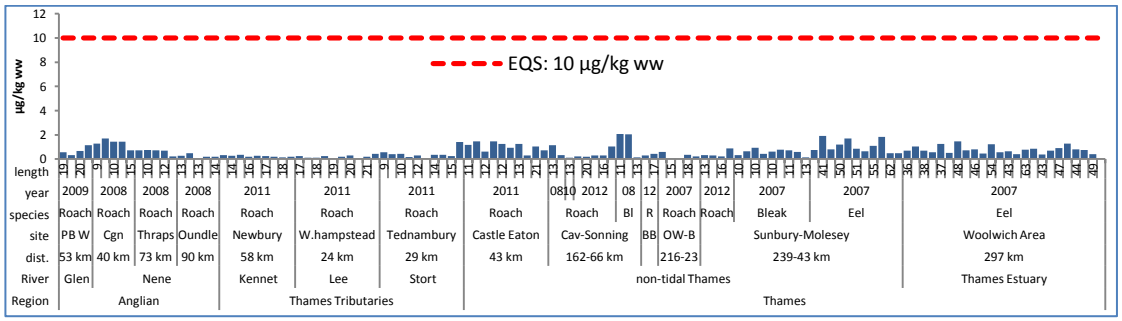


Figure 4.2-11 Figure 4.2-10, HCB concentrations, normalised to 5% lipid.

4.2.5.5 HCBD

Measurements of HCBD were attempted in one batch of 40 roach, but analytical problems meant that they could not be quantified accurately. Despite the uncertainties, it was clear that the values were very low and often below the detection limit. In a recent survey of eels in Scotland (Macgregor *et al.* 2010), HCBD was only detected in one of 150 samples at detection limits of either 1 or 3 µg/kg and the authors of a recent French study also failed to detect any HCBD at a detection limit of 2-3 µg/kg ww in fish and consequently questioned the need for a European EQS for this substance (Miege *et al.* 2012). In Belgium, Roose *et al.* (2003) found a maximum of 12 µg/kg, which is still well below the EQS of 55 µg/kg, in eel from an industrial

area. Therefore, except possibly in the vicinity of specific industries, there seems little worry about HCBD in fish.

4.2.5.6 DDT

There is currently no EU EQS for DDT, but Canada has one (Canadian Council of Ministers of the Environment 1999), so to put the measured concentrations in context they are compared to the Canadian standard. More than half the eels (19/35), 4/17 bleak and 11/81 roach exceeded this standard. 10 of the roach that exceeded the standard were from a site on the Lee that turned out to be close to a former pesticide factory, and those exceeded it by a very large margin (Figure 4.2-12).

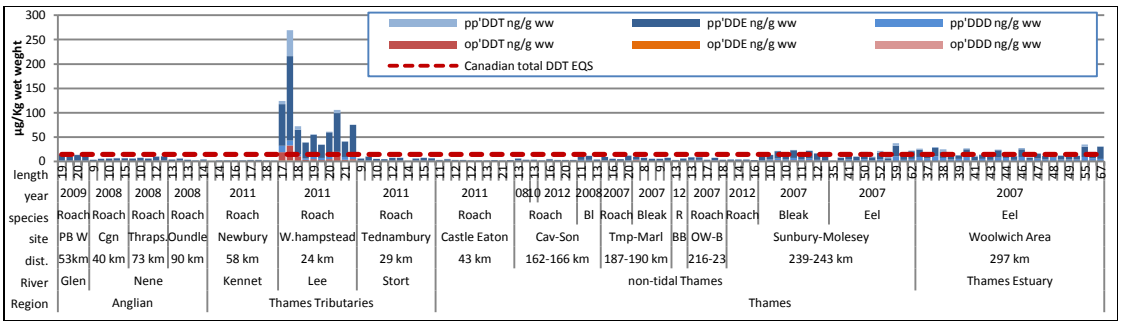


Figure 4.2-12 Concentration of DDT and its degradation and by-products DDE and DDD (*op*' and *pp*' congeners for all) of all fish analysed. Individuals at each site are ordered by species (roach, bleak, eel), year, and length (cm). Sites on each river are ordered by distance from the source (river-km). BB: Bray-Boveney 203-209 km. The Canadian Tissue Residue Guideline for the protection of wildlife consumers is also shown (there is currently no equivalent EU guideline).

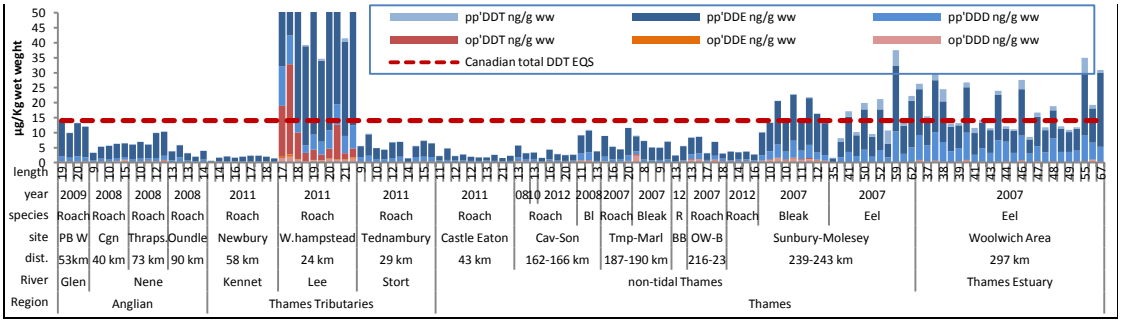


Figure 4.2-13 Detail showing the lower concentrations from Figure 4.2-12.

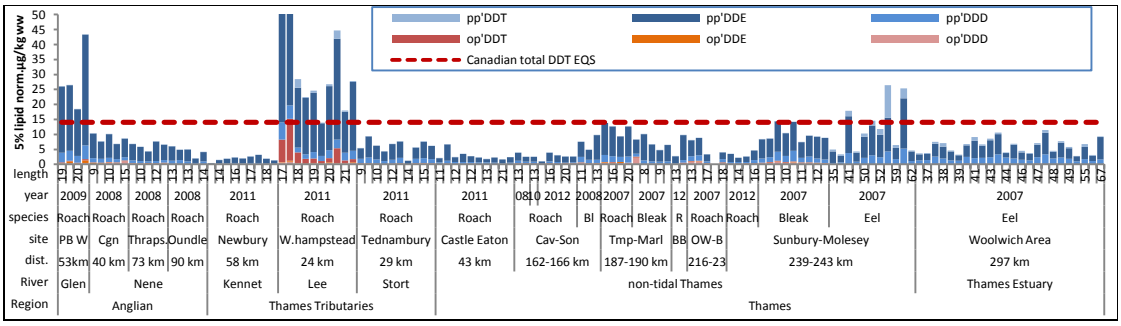


Figure 4.2-14 Figure 4.2-13 normalised to 5% lipid.

Although, a normalisation step is not specified in the Canadian monitoring, the effect of lipid-normalisation can be also illustrated for DDT. Looking at the "normal" sites for total DDT, by excluding the 10 roach from Wheathampstead on the Lee, gave exceedances of the Canadian EQS in 1/71 roach, 4/17 bleak, 19/35 eel, or 1%, 24% and 54% for the three species respectively, but once normalised to 5% lipid this changed to quite similar ratios, despite varying sites or years, of 7%, 12% and 11% failure for the three species respectively (Figure 4.2-14). The highly contaminated roach from the Lee were also more similar to some of the others once normalized, because they also had unusually high lipid contents, but the high lipid content could clearly not explain the whole difference. The likely cause for these results is discussed in section 4.3.

In terms of toxicity to the fish themselves, even the highest contaminated individuals were below the body burdens shown to have an effect on survival in the review by Lydy *et al.* (2011), but if total DDT is used in the assessment, some were not far off with the highest total DDT measured in our fish at 265 µg/kg and observed effects on survival at 290 µg/kg at least in one study (Berlin 1981, cited in Lydy *et al.* 2011).

4.2.5.7 PBDEs

All 99 individuals measured exceeded the very low EQS (0.0085 µg/kg ww), while only one individual roach (this parameter was only measured for bleak and roach, not for eel) reached the value that had been proposed for the protection of wildlife consumers. When the concentrations were 5% lipid normalised this rose to 2 individuals out of 99, which still means that on average all sites would have passed based on the wildlife EQS, but all failed by several orders of magnitude on the EQS

based on human risk (see discussion of the EQS values above). Therefore, there seems no risk to the fish themselves or their predators, while the interpretation of risk to humans is debatable.

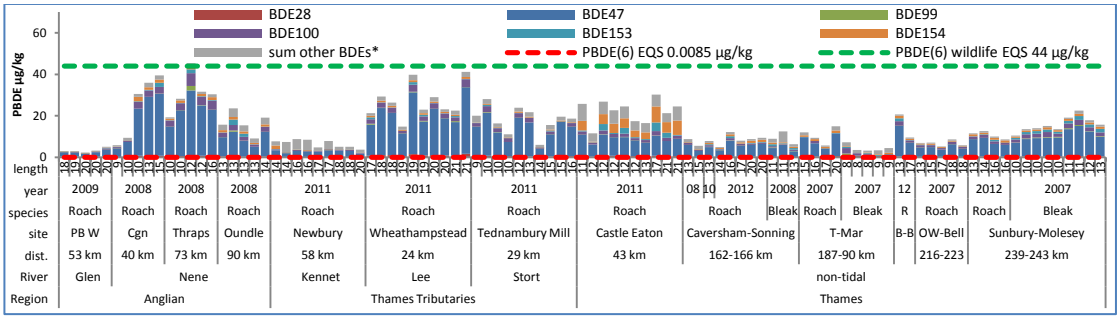


Figure 4.2-15 Concentrations of PBDEs. Individuals at each site are ordered by species (roach, bleak, eel), year, and length (cm). Sites on each river are ordered by distance from the source (river-km). BB: Bray-Boveney 203-209 km. The red line dotes the environmental quality standard of 0.0085 µg/kg (based on risk to humans) and the green line is the EQS that was proposed based on the risk to wildlife, but was not used because the one based on human risk is lower. Both are for the sum of the 6 indicator PBDEs.

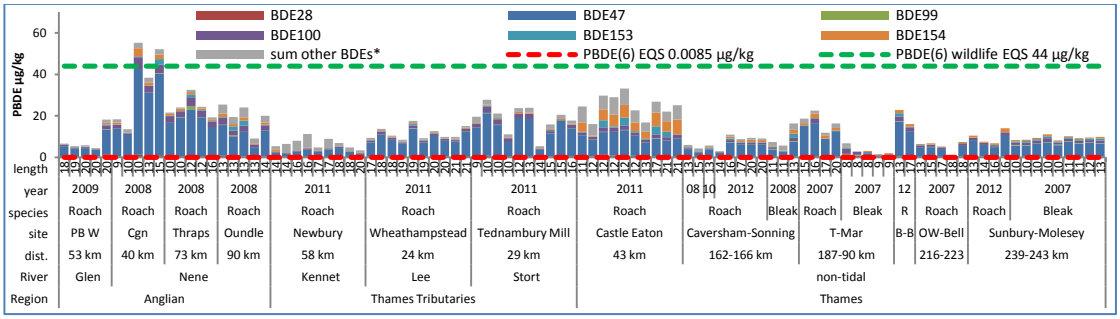


Figure 4.2-16 PBDEs 5% lipid normalised data of Figure 4.2-15.

4.2.5.8 PCBs and dioxin-like toxicity

Out of the groups contributing to dioxin-like toxicity (dioxins, furans, non-ortho- and mono-ortho-substituted PCBs, see above), only the mono-ortho-substituted PCBs were measured, so only a partial toxicity can be calculatde, but in eels analysed by (Geeraerts *et al.* 2011), those contributed about half of the calculated total $WHO1998_{mammals}$ toxicity. The 5% lipid normalised mono-ortho-PCB concentrations are 0.013-0.52 ng/kg TCDD equivalents, or less than 10% of the EU EQS. It is therefore likely (but as for the food standard, not certain), that even after including the missing chemicals the EQS would not be exceeded.

For comparison the EQS from Canada are also given. In the case of the EQS to protect mammalian predators, the majority of eels and bleak and some of the roach exceeded the Canadian EQS for dioxin-like PCBs even for the mono-ortho substituted

PCBs alone, while some of the eels had TEQs that exceeded half of the value for toxicity to avian predators, suggesting that they might exceed this value if all congeners contributing had been measured.

4.3 The influence of chemical, site and fish properties on chemical contamination in UK fish

4.3.1 Introduction: Factors that contribute to the concentration of a chemical found in a fish

4.3.1.1 Chemical discharge patterns

4.3.1.1.1 Production

Chemicals can be intentionally or accidentally produced, the latter includes for example combustion by-products. For combustion by-products existing models for classic air pollution can be adapted relatively easily, but for deliberately produced chemicals modelling is harder because release can happen during each stage of the life cycle (production, use, disposal) and to different compartments of the environment (Breivik *et al.* 2007 and references therein).

4.3.1.1.2 Release patterns

Chemicals can also be intentionally or unintentionally released to the environment. Pesticides, for example, are intentionally released to land at certain times in the year, but not others and tributyltin was intentionally released from ships hulls to water. Release of industrial chemicals by comparison is mostly unintentional and differs between the different stages in the life cycle: production, storage, use, and disposal. Additionally there are occasional uncontrolled, unintended events such as fires in industrial plants or spills of pesticides or other chemicals. Dioxins and furans for example have never been intentionally produced but are formed unintentionally

during combustion processes involving chlorinated products. Chemicals, that mainly enter the environment through treated wastewater can also be modelled relatively well (eg. Johnson *et al.* 2007, Johnson *et al.* 2008, Williams *et al.* 2009, Balaam *et al.* 2010, Johnson *et al.* 2013, Keller *et al.* 2014) and are of particular interest to the river environment. These include the many cleaning products, cosmetics and pharmaceuticals that are used in households as well as natural products, such as hormones, which are excreted by humans.

Which proportion of a compound is released to air, water or soil varies greatly between different pollutants and uses and the entry route has an influence on whether, where, and how much of it enters rivers and may become available to fish. Even pollutants initially released only to soil or air can enter watercourses later.

4.3.1.1.3 History/usage trends

Trends in usage patterns may be going down, or up or staying the same. Some examples from the different categories are below:

- banned a long time ago: PCBs and several of the pesticides measured
- banned or production ceased recently: e.g. endosulfan, Penta and Octa-PBDE mixtures, which have been banned since 2004 in textiles and upholstery (European Union 2003b) and 2006 in electronics (European Union 2003a).
- ongoing use, but severely restricted: e.g. mercury, most uses are no longer permitted in the UK, but it is still used in dentistry and in mercury cells in the Kastner-Kellner process at only one site (see introduction, section 1.5.1.1). It is also a trace constituent of other metals, fossil fuels, etc. so small amounts can be released, especially when the metals or ores are heated in smelters or when fossil fuels are burnt. Deca-BDE, which was not measured here due to needing a different instrument setup from the other PBDEs, is banned from use in electrical/electronic goods in the EU since 2008 (updated RoHS directive, European Union 2002), but the discussion over its use in plastics and textiles is still ongoing with a public consultation period concerning its possible restriction currently (9/14-3/15) underway (ECHA 2014)
- increasing use: e.g. nano-particles, certain pharmaceuticals (not measured here)

4.3.1.2 Chemical property factors

For the purpose of studying the (likely) environmental fate of chemicals, the following classifications (among others) can be useful:

4.3.1.2.1 Hydrophobicity/solubility

More hydrophobic/poorly water soluble chemicals are likely to accumulate in fats along the food chain, provided that they are soluble enough that they are bioavailable in the first place. By contrast hydrophilic/easily dissolved chemicals are generally easy to excrete and do not accumulate much.

4.3.1.2.2 Volatility

Some compounds are or have been primarily released to air, either because of their very high volatility as in the case of organic solvents or because they are released or produced during combustion, for example mercury as a trace component of fossil fuels, lead formerly added to petrol, or dioxins formed during combustion,

Even though the initial release to the environment is to air, they can also enter water courses by wet and dry deposition either directly or via runoff from soil where they have been previously deposited

4.3.1.2.3 Persistence

Chemicals can be divided into the following groups according to their persistence:

- Non degradable, such as heavy metals, ie. where the actual elements not their arrangement in a specific molecule are a problem for the environment
- Only very slowly degradable: POPs
- Degradable, but still a problem either because they form more toxic by-products, such as the alkylphenol polyethoxylates, which degrade to estrogenic alkylphenols, or because they are continuously released and therefore pseudo-persistant, such as hormones and pharmaceuticals

When assessing chemicals it is important to be clear on whether it is elements (e.g. heavy metals) or molecules (e.g. methyl-mercury, POPs), that are of concern. Elements can essentially not be lost or created (except in nuclear processes, which are irrelevant to the current study), only moved between different parts of the natural or man-made environment. However the molecules, that these elements are usually part of, are susceptible to many transformation processes that make them more or less toxic, more or less bio-available, more or less mobile etc.

While organic contaminants are always assessed on the basis of the molecules, contamination with heavy metals is conventionally assessed on the element basis, so the two groups are not always comparable.

4.3.1.3 River environmental factors

The factors above and others affecting transport to the rivers such as rainfall (for wet deposition and runoff, but also dilution) combine with river factors such as flow, temperature, organic carbon content of the water and the sediment, pH, hardness, alkalinity, etc. to determine both how much of a chemical is found in the water or sediment at a given river location and how bioavailable it is.

The concentration of a pollutant in a fish then depends on the bio-available concentration in its environment: water, sediment and food. All of them vary in space and time and react to changes in input at different speeds. When an input is removed or reduced, for example, with the banning of harmful chemicals, the water concentration reduces relatively fast. Sediments can store a large amount of persistent and hydrophobic chemicals, however, which are either re-released to the water where they are available to both fish and their food or taken up directly from the sediments by benthic invertebrates, which may then be eaten by fish. Therefore one would expect it to take far longer for the sediments and the tissue concentrations of animals to be returned to "clean" levels, than just the water. In the case of the sediments in particular some chemicals may be in a form that has a very low bioavailability, meaning that monitoring only sediments may overestimate the potential for harm.

4.3.1.4 Fish related factors

4.3.1.4.1 Age/size of the fish

Many authors have found larger/older individuals to be more polluted than smaller fish from the same site or species. There are several ways in which age can influence the concentrations of pollutants:

- **Different lipid content**: In the simplest scenario the concentration of a chemical is relatively constant and in equilibrium between the animal and the water. In this case the concentration in the animal would not directly depend on its size or age, but only on other factors, such as lipid content, which ,however, may be higher in larger well-fed individuals.
- **Declining environmental pollution over time**: Older individuals may still have residues of the past pollution.
- **Slow build-up of pollutant over time:** Particularly persistent hydrophobic pollutants that are mainly taken up with the diet are not very efficiently excreted or metabolised, but are instead stored in the lipids. So a proportion of each dose taken up with the diet remains in the body of the fish, leading to a gradual increase in the internal concentration.
- **Different feeding habits:** Generally larger individuals of a species can feed on prey that is on a higher level in the food web than that which is available to smaller members of their species, meaning for bioaccumulating substances that the food source of the larger individuals is likely to be more contaminated. Animals may also change their feeding habits in other ways with age, for example, switching between plankton and benthos which may be more contaminated as it is in contact with the sediment.
- **Different metabolism or use of energy**: With many metals, it has been observed that older specimen are less contaminated on a weight for weight basis than younger ones. A possible explanation of this is, that eliminating the metal from the body requires energy which a fast growing young specimen cannot afford as the majority of available resources is put towards growth.

Once growth slows down, the necessary resources become available to eliminate harmful metals (Merciai *et al.* 2014).

The effect of age or size (length or weight) has frequently been found to be a very significant factor in explaining the variation between individuals (for example Barak and Mason 1990a, b, c), but most data available is for the marine environment. Skåre *et al.* (1985) found a positive correlation between PCBs or Sum DDTs (*pp*'congeners of DDT, DDE and DDD) in the liver and weight in cod but not in other marine species analysed. Frantzen *et al.* (2009) measured a number of POPs (sum of 7 PBDE, a number of PCBs, dioxins and furans) in 800 herring caught off the Norwegian coast in 2006/2007. For all measured parameters the best correlation was with age (r= 0.54-0.77) followed by weight and length (r=0.41-0.57, r=0.39-0.60), with a poorer correlation with lipids (r= 0.17-0.32). This contrasts with the general perception that lipid content is the most important factor determining differences between individuals for POPs. Eljarrat *et al.* (2005) also found an increase of PBDE concentration with increasing size of the fish for PBDEs in bleak. Barak and Mason (1990a) found a good correlation between length and heavy metal contamination even across species. Once the size of the individuals was accounted for, there were no significant differences between sites or species in two rivers in Essex. For mercury concentrations in the current study it was also found that, while much of the literature reports higher concentrations, the few recent European data that are available for fish of a similar (small) size to those analysed here, were had comparable concentrations (Jürgens *et al.* 2013). Correlations between measured metal concentrations and fish size are discussed in detail in chapter 4.3.2.

4.3.1.4.2 Lipid content

Normalising to lipid content is often used to compare data from different individuals or different species. With hydrophobic chemicals, this often reduces the variability but it would only work *perfectly* if the pollutant was absorbed only into the lipid and not into any other part of the body *and* there was enough time for an equilibrium to be established.

4.3.1.4.3 Uptake, depuration and transformation

De Boer and Brinkman (1994) argue that, for large fish uptake of hydrophobic chemicals (log Kow>6.5) is quite fast, but release is very slow, so they do not clear the chemicals from their body even when the water is cleaner again. This means that for the uptake from water (not food) the concentration in the fish closely reflects that of the water so long as water concentration is *constant or increasing*. If water concentration is *decreasing*, however, the tissue concentration can't follow as fast, as the main way of reducing it is through growth dilution. In a simplified example, it could be assumed that uptake of a chemical is fast enough to reach equilibrium with the water before average water concentrations change significantly, but once taken up into the tissue the animal is unable to expel persistent hydrophobic pollutants, therefore, if the water concentration doubled, the concentration in the fish would also double, because it would take the chemical up both into existing and newly grown tissue, but if the concentration in the water halved, only the newly grown tissue would reflect that new lower concentration. So as an example, assuming the fish doubled in weight after the water concentration halved: the new tissue (1/2 of the total fish weight) would have the new concentration of 1/2 of the old concentration but the existing tissue would still hold on to the chemical, therefore making the average tissue concentration 3/4 of the old more contaminated value not 1/2 like the water.

These very hydrophobic chemicals are, however, also the ones where dietary uptake, not uptake via the water route, dominates and so there is an additional effect of biomagnification.

Thomann (1989) says:

$\text{Log } K_{ow} < 5$ only water phase is important,

$5 < \text{Log } K_{ow} < 6.5$ both water and food contribute to uptake,

$\text{Log } K_{ow} > 6.5$ food chain is the only determining factor

From this follows also: for log $K_{ow}<5$ it should not matter what size fish are collected (at least if the water concentration is relatively constant, otherwise smaller specimen will reflect changes in water concentrations faster), but for higher K_{ow} the concentration in larger fish would likely be higher, both because of accumulation from

food and because of the effect of growth dilution when the environmental concentration is decreasing.

The uptake from the water is mainly governed by the hydrophobicity of the dissolved chemicals which pass via the gills into the bloodstream and from there into the different tissues of the body. There are however cases where the fish has a specialised mechanism for removing a chemical from the water: Oxygen is an obvious and beneficial example of this. By binding the O_2 to haemoglobin the free O_2 is constantly removed from the blood stream, therefore the concentration of free O_2 in the blood is low and osmosis will drive O_2 from the water into the blood.[1] A similar effect happens with sex-hormones and chemicals that are structurally very similar, ie. xenoestrogens: Fish -and mammals- have so-called sex-hormone binding globulins, which constantly remove free sex hormones from the plasma therefore allowing more to be taken up from surrounding water. For this reason fish can accumulate a much higher concentration of sex hormones in their blood than would be expected from the K_{ow}.

Digestive fractionation: More hydrophobic chemicals accumulate more along the food chain than less hydrophobic ones, because the less hydrophobic chemicals can more easily be excreted, once taken up with the food. Therefore the pattern of contamination, for example with PCBs, would be expected shift towards the more hydrophobic ones when a predator is compared with its prey (Kucklick and Baker 1998).

[1] Fish with a swim bladder have an additional mechanism related to oxygen transport: they use the fact that haemoglobin binds less oxygen under acidic conditions. This effect is stronger in fish haemoglobin than in mammals and is called the Root effect in fish and the Bohr effect in other animals: Making the blood acidic with lactic acid and CO_2 (formed when glucose is converted anaerobically in special epithelial cells of the swimbladder) around the swim bladder releases oxygen into it when needed to increase the boyancy (Pelster and Decker 2004). The vessels for the incoming and outflowing blood are very close together allowing remaining free oxygen and acid to diffuse from the outflowing into the incoming blood thus making it an efficient counter flow system.

4.3.1.4.4 Effect of habitat, lifestyle and route of exposure

For the example of lead which was released into the atmosphere predominantly from leaded fuel used in internal combustion engines it can be shown, how the habitat in which an animal lives and therefore the exposure route can influence the response to changes in environmental concentrations. Data retrieved from the German environmental specimen bank (http://anubis.uba.de/wwwupb/servlet/upb) and Landesumweltamt Nordrhein-Westphalen (www.lanuv.nrw.de) show the effects regulations of lead in petrol had on lead concentration in air (fine particles), student's blood, freshwater fish and freshwater and marine mussels (zebramussel, *dreissena polymorpha* and common mussel, *mytilus edilus*) (Figure 4.3-1 and Figure 4.3-2).

Restrictions on the use of lead in fuels were first introduced in the 1970s and since then the laws have been tightened several times leading up to a total ban of leaded fuel in the UK from January 2000 in line with EU regulations (European Union 1998). Good monitoring data is available from Germany, which banned leaded fuel a few years before the UK in 1997. Due to the restrictions and eventually ban of lead in fuel the annual average lead concentration in air in the industrialised Rhine/Ruhr area in North Rhine Westphalia (NRW) has reduced from about 1 µg/m^3, when the monitoring started in the mid-seventies, to just 0.02 µg/m^3 in recent years (Figure 4.3-1). The lead content in the blood of students in the university town of Münster (NRW) closely followed the trend in air, indicating that air pollution was likely to be their main exposure route route and that, for the blood at least, the clearance is relatively fast. While the atmospheric lead has reduced to about 1/15 between 1981 and 2008, the lead content in students' blood has "only" reduced to about 1/6 in the same time, although the half-life for lead removal from blood is estimated to be only about one month (EFSA 2010). This could be either because of lead from earlier years with higher pollution still remaining in the 20-29 year old students' bodies, especially the bones, where the half-life is about 10-30 years (EFSA 2010) or because there are other sources of lead, notably the diet and drinking water (especially in houses with old lead pipes) (Figure 4.3-1).

These results can be contrasted with muscle samples from 8-12 year old bream taken from various locations along the River Elbe between 1993 and 2014. While the dataset is much shorter than the one for the human samples it shows a clear peak of

lead concentration in bream muscle at all sites roundabout the year 2000 with a possible downward trend before that between 1993 and 1998 though this period is too short to determine a clear trend. Bream feed predominantly on benthic organisms and are therefore exposed to contaminants from both the sediment and the water.

The dataset for mussels, on the other hand, has no discernible trend either in the freshwater or the marine species. The most likely explanation is that mussels being in close contact with sediments which act as a storage for heavy metal pollution, are still exposed to high lead concentrations. Note also that the absolute contamination of mussels is several mg/kg dw and much higher than for bream which always stayed below 200 µg/kg dw.

Different factors contribute to the faster response to a change in environmental concentrations in the human samples compared to the fish and mussels. Firstly, the sample type is different, for humans blood was analysed and for fish and mussels it was muscle tissue or soft tissue respectively. Blood is renewed much faster than muscle and can therefore respond much more quickly to changing input of chemicals. Secondly, the exposure route was different: for humans, at least in the earlier part of the time series, it was predominantly from air, whereas for the fish it was water and prey, which in turn was exposed to sediments, and for the mussels it was probably predominantly sediment. Since the release of lead to air has almost entirely ceased, the air exposure route has also reduced to very low levels, in sediments by contrast heavy metals remain for a long time – and are only removed either by getting dissolved in the water raising the concentration in that compartment again or by the sediments being physically removed during storm events or covered over by fresh less contaminated layers.

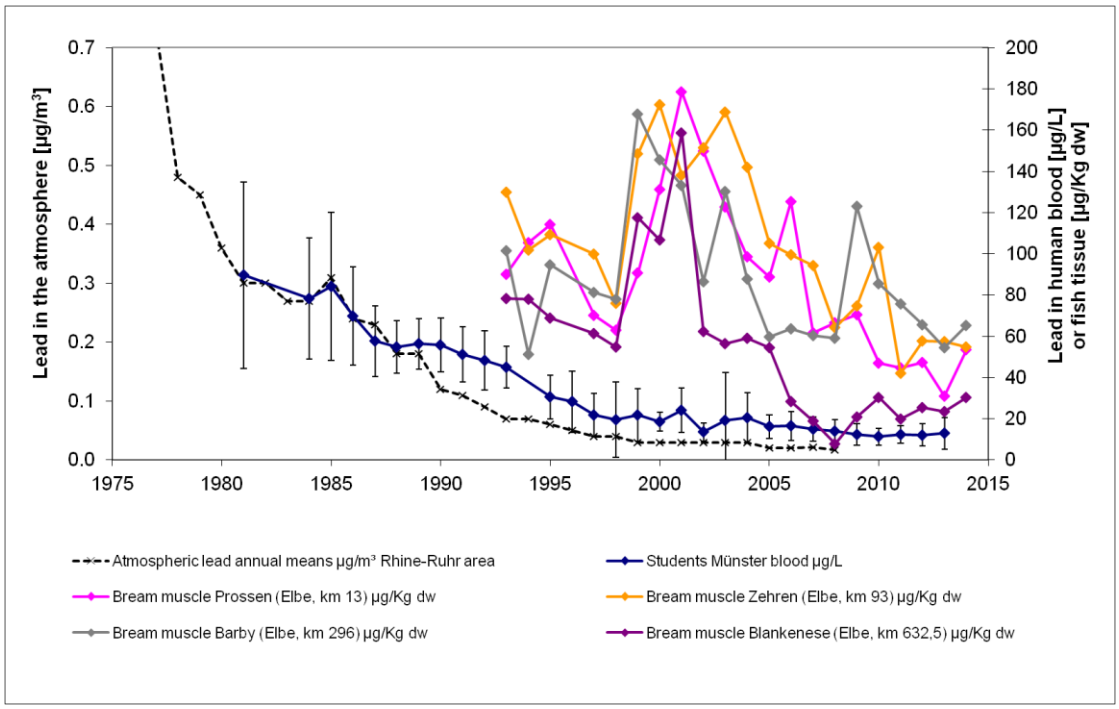


Figure 4.3-1 Atmospheric lead, compared to levels measured in human blood (arithmetric mean and standard deviation) and freshwater fish in Germany, atmospheric data from Landesamt für Natur, Umwelt und Verbraucherschutz Nordrhein-Westphalen (www.lanuv.nrw.de, retrieved 15.1.2010), fish data from German Environmental Specimen Bank (http://www.umweltprobenbank.de/en/documents, retrieved 27.5.2015) . The sampling sites are given together with their distance from the river source.

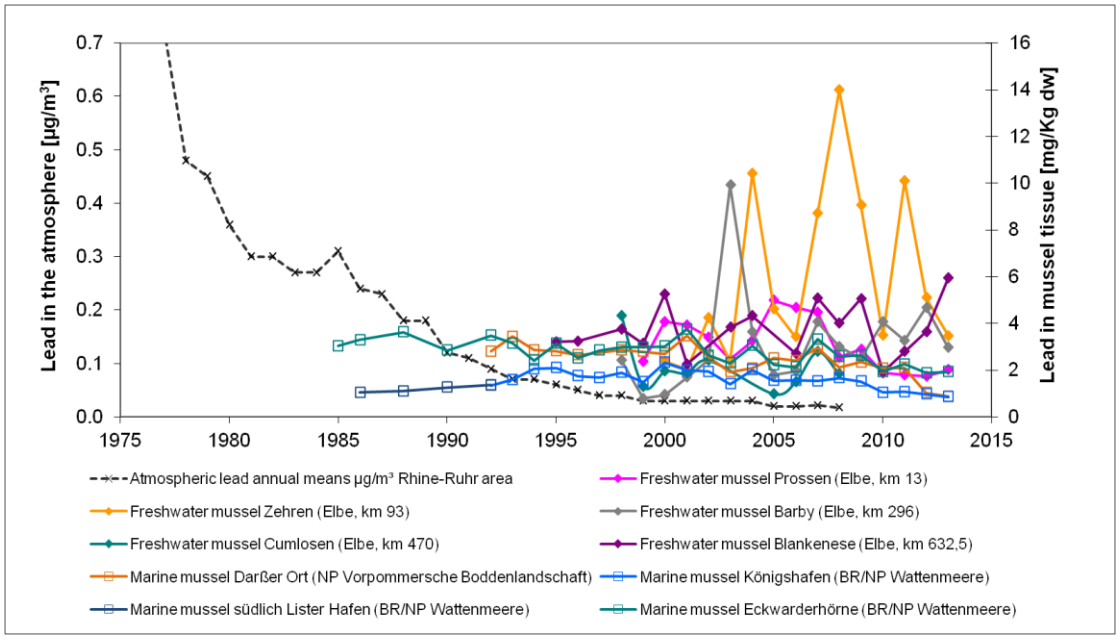


Figure 4.3-2 Atmospheric lead, compared to levels measured in soft tissue of freshwater (zebramussel, closed symbols) and marine (common mussel, open symbols) mussels in Germany. Freshwater mussels were taken at same sites as in Figure 4.3-1. Atmospheric data from Landesamt für Natur, Umwelt und Verbraucherschutz Nordrhein-Westphalen (www.lanuv.nrw.de, retrieved 15.1.2010), mussel data from German Environmental Specimen Bank (http://www.umweltprobenbank.de/en/documents, retrieved 27.5.2015).

4.3.1.4.5 Effect of season

Eggs and sperm contain relatively high levels of lipids. So fish loose proportionally more lipids with associated hydrophobic chemicals than they loose weight during spawning. Therefore, on a fresh weight basis one would expect animals after spawning to have a lower hydrophobic contaminant burden than just pre-spawning. Herrings, which spawn several times during their lifetime, had generally the highest POP levels (PCBs, PBDEs, dioxins, furans) before spawning and the lowest levels in young fish and in fish soon after spawning (Frantzen *et al.* 2009). A consistent sampling season is therefore important to determine year to year trends in the data. Most researchers suggest to sample before spawning when the highest concentrations of persistent and lipophilic chemicals can be expected. In the current setup of the Fish Archive, sampling is carried out between spring and autumn with the same sites generally being sampled in the same week each year. As the sampling is linked to the Environment Agency fish surveys, CEH has little influence on the timing, which may be after spawning at some sites, but is as much as possible at the same time of year each year for a given site. Therefore some caution must be taken, when comparing different sites, some of which are sampled before and others after spawning, but the temporal trends for a given site should generally not be affected. The majority of the sites, currently used, are routinely sampled in autumn, but some are sampled in spring close to the spawning time for roach. This brings the additional complication, that even if the sampling happens in the same week each year (as is intended but sometimes not possible due to bad weather or other external factors) exact time of spawning may vary slightly from year to year, mainly due to water temperature (which is a consequence of air temperature), so in some years most may not have spawned yet whereas in other years most have done so.

4.3.1.5 Summary of some of the parameters that may influence the concentration of a chemical in fish

The concentration of chemical pollutants in fish can be influenced by these major factors, some of which are summarized also in Figure 4.3-3:

- Chemical usage and discharge patterns, including their spatial and temporal changes (e.g. chemical use restrictions, changing types of industries and locations)
- Chemical properties, including hydrophobicity, volatility and persistence
- Local river factors affecting the concentration or bioavailability of chemicals, such as flow, proximity to sewage works or industries, pH, conductivity, sediment and water organic carbon contents, sediment and water oxygen concentrations
- Properties of the fish sample, for example: species, size (weight, length), condition factor, age, sex, whether they are pre- or post-spawning , whether the analysis is for whole body, fillet (muscle), or specific organs such as liver, kidney, heart, etc.

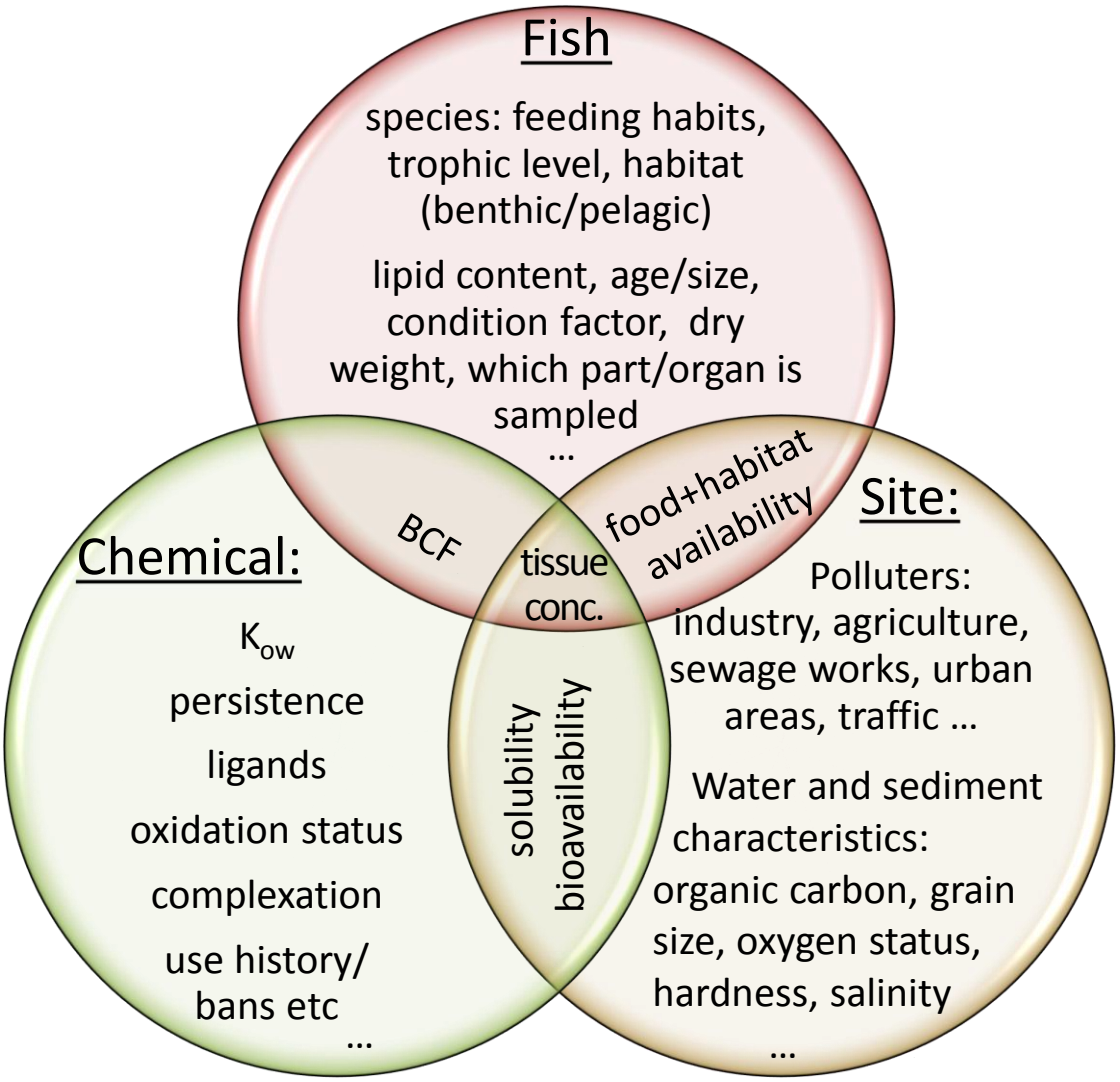


Figure 4.3-3 Schematic of some of the factors that influence the concentration of a chemical found in fish.

Figure 4.3-3 gives a schematic overview of some of the factors discussed above, that come together to determine the concentration of a chemical found in an individual fish. In the following sub-chapters, some examples from the fish in this study will be given, to illustrate instances where a particular one of these factors dominates.

4.3.2 Metal case studies

4.3.2.1 Do all metals have a similar distribution pattern?

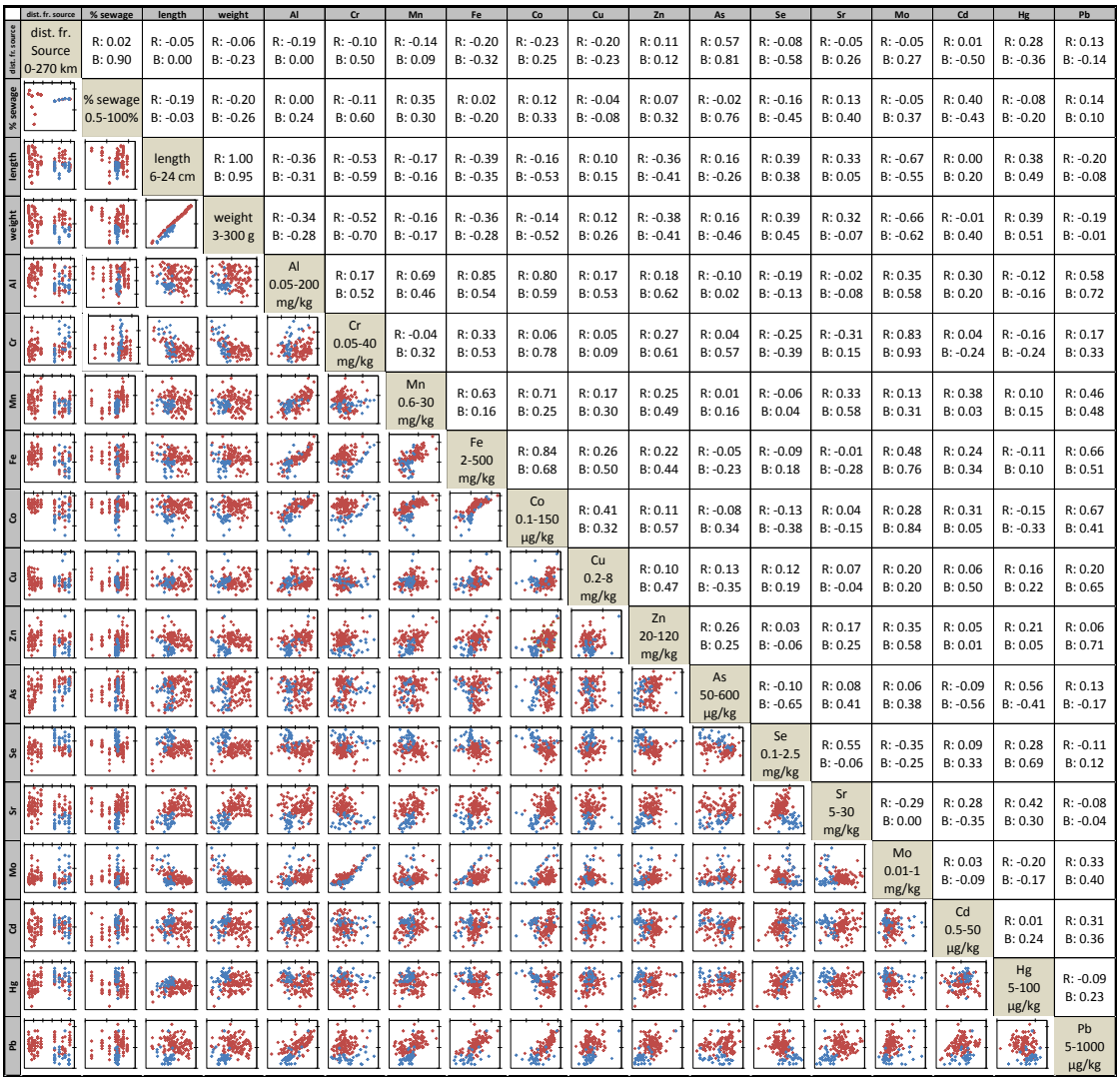


Figure 4.3-4 Correlation of all metals with each other and with size, distance from source and modelled sewage concentration. Red dots are for roach (R), blue for bleak (B). Distance from source is on a linear scale, all other parameters on logarithmic scales, with markers placed at 10 fold intervals. The range of the axes is given on the diagonal (note some are in mg/kg ww and others in µg/kg ww). For example, for iron the axis range is 2-500 mg/kg, meaning the left or bottom end of the axis is 2 mg/kg, the markers are at 20 and 200 mg/kg and the top or right end is 500 mg/kg. The range of values is a little bit less than the range given for the axes (3.3-390 mg/kg in the iron example). The top right half of the graph gives the correlation factors (Rs) for all the binary combinations of parameters plotted.

In Figure 4.3-4 the ww concentrations of all the measured metals/metalloids (except Ni, Sb, Va, because of their poor reproducibility, see section 3.2.1.1) are plotted against each other and against the site parameters distance from the river source and modelled average sewage content and the fish parameters length and

weight. This allows to spot visually which pairs of parameters seem positively or negatively correlated. The correlation coefficient R is also given for each pair of parameters, but while the R's give an indication of the goodness of fit of a linear regression, please note, that when comparing them, the different sample numbers (normally 110 for roach and 34 for bleak – see Table 4.3-1) and considerations whether linear regression on log-transformed data is the most appropriate data treatment also need to be taken into account.

Not surprisingly, there is a near-perfect correlation between length and weight of the individuals (R 1.00 for roach and 0.95 for bleak, or the more commonly used R^2 is 0.99 and 0.90 respectively), so it doesn't matter whether weight or length is used to describe "size", when looking for relationships between chemical concentrations and the size of the fish,.

The correlations between individual metals are quite variable. Strong correlations exist between chromium and molybdenum, which are frequently used together in lightweight and strong steel alloys, for example, for bicycle frames and between iron, cobalt and lead. Some of the stronger correlations are shown at a larger scale in Figure 4.3-5.

The fact that in most cases there **isn't** a strong positive correlation between the individual metals shows that there are differences between the metals that lead to different contamination patterns in the fish. These may relate to physico-chemical parameters such as K_{ow}, ionic form etc. influencing bioavailability or to release patterns such as diffuse (e.g. agriculture, roads) or point sources (e.g. sewage works, specific industries), increasing or decreasing use etc.

It is possible, that some correlations are due to some metals having been introduced together during the grinding process. Unfortunately the exact composition of the alloys used in the cryogrinding process are a trade secret. Knowing them would help ascertain whether some of the metals could have been introduced in the processing. The grinding tests (see section 3.2.1.3) did not indicate major problems, although some increase of chromium and maybe iron, manganese and arsenic was observed.

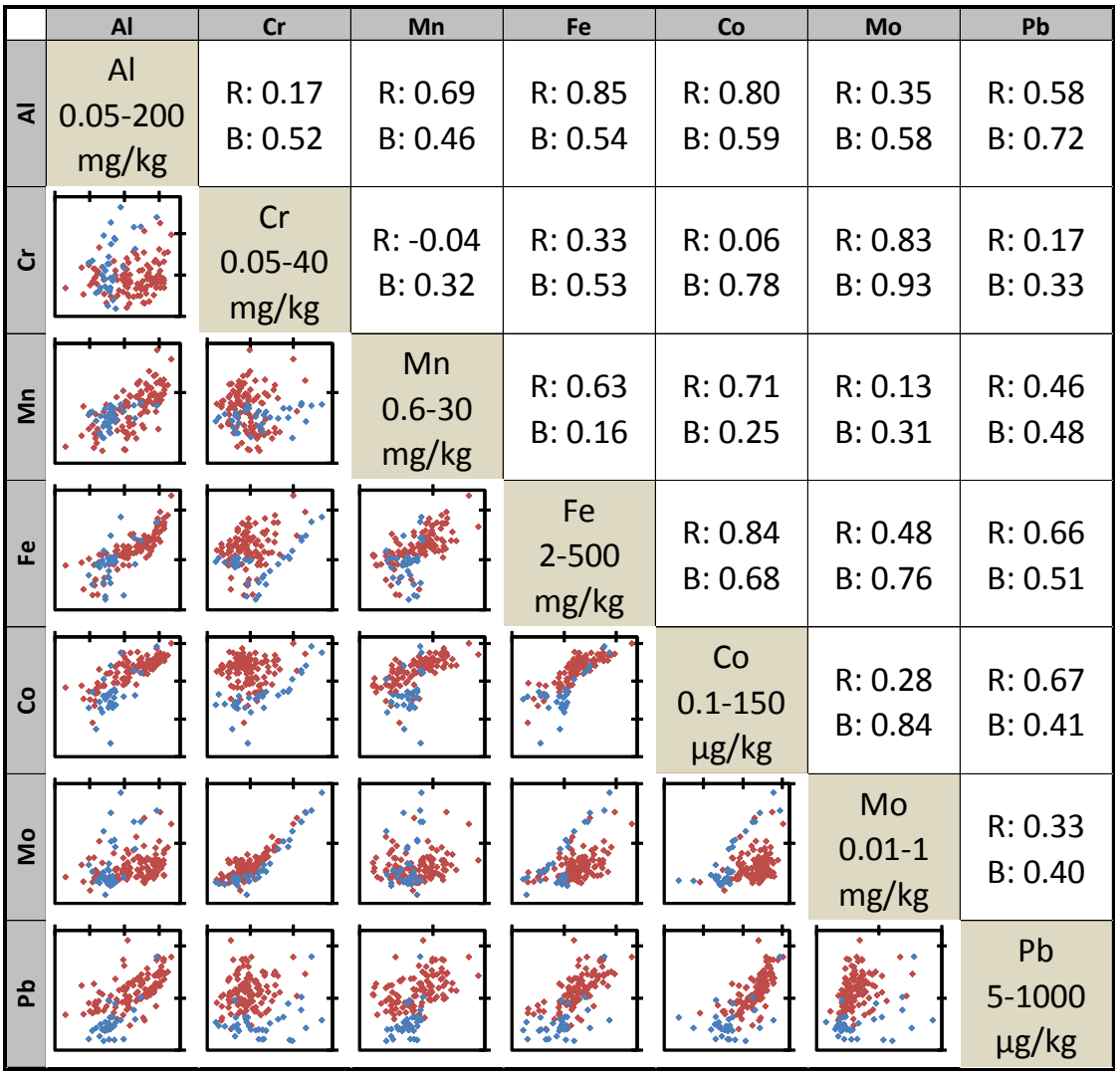


Figure 4.3-5 Excerpt of Figure 4.3-4 showing some of the stronger correlations between individual metals.

Some correlations in Figure 4.3-5 are strong for one species but not the other, for example, chromium and cobalt as well as iron and molybdenum are strongly correlated for bleak but not roach. The bleak all came from a relatively narrow region of the lower Thames, whereas the roach came from a much wider range of sites. To test whether these species differences were due to the smaller range of sites for the bleak, only the roach from the downstream Thames sites were considered in Figure 4.3-6. Removing the upstream roach did not change the correlations very much, except for those involving either lead or chromium. Compared to the previous figure all correlations for roach with chromium became less positive, i.e. a strong positive correlation (Cr-Mo) became weaker, a weak positive correlation (Cr-Fe) disappeared and no correlation became a negative one (Cr-Mn), conversely the positive

correlations with lead all became stronger (except with Cr because of all Cr correlations becoming more negative).

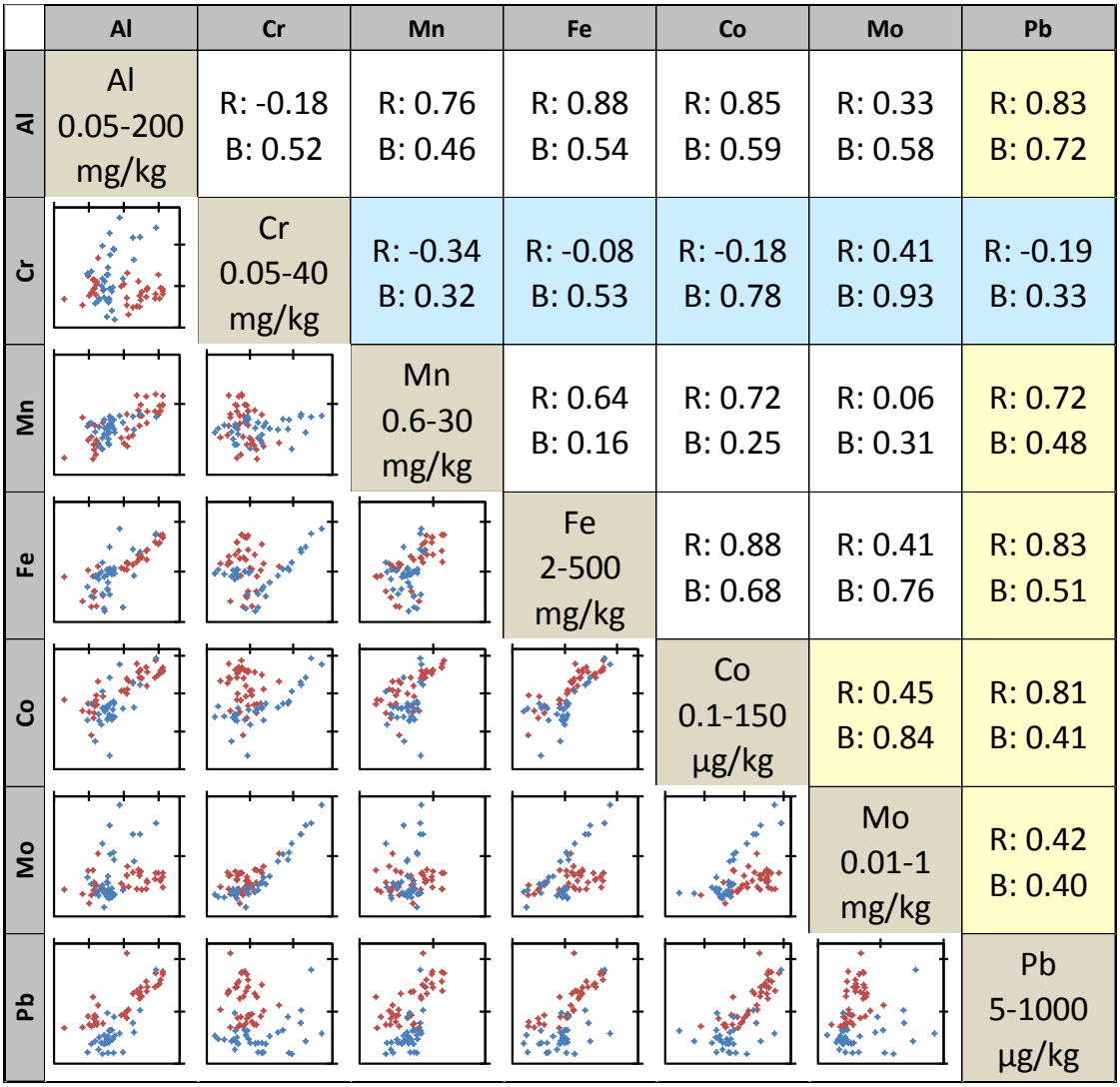


Figure 4.3-6 The same correlations as in the previous Figure 4.3-5, but only using roach from downstream Thames sites, i.e. the same area as the bleak were from. Coloured fields denote very different R for these censored data compared to the complete data in Figure 4.3-5.

Summary

There were positive correlations between **chromium and molybdenum** and between any combination of **aluminium, manganese, iron, cobalt, and lead** (except for iron or cobalt with manganese in bleak). Additionally molybdenum was positively correlated to cobalt and iron and selenium to mercury for bleak, but less so for roach.

To test whether any differences between the relationships for bleak and roach were skewed by the fact that bleak were sampled from a much smaller geographical range (lower Thames) than the roach, the correlation analysis was repeated for the

lower Thames only. This made little difference to most of the roach observations, apart from Cr-Mo, which reduced from a strong correlation (R=0.83) to a much weaker one (R=0.41) and Se-Hg which improved from a very weak correlation (R=0.28) to a stronger one (R=0.65) similar to that for bleak (R=0.69).

4.3.2.2 Do metals/metalloid concentrations correlate with the size of the fish?

As mentioned in the introduction to this section, contamination often increases with the size or age of the fish. For the metals measured (again leaving out Ni, V, Sb because they had very poor reproducibility), there was, however, more frequently a negative correlation with weight than a positive one (Table 4.3-1). Merciai *et al.* (2014) and other authors cited by them also found negative correlations between heavy metal concentrations and fish size for the three species for which they had a sufficient sampling size, which included bleak. They investigated, Al, As, Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn and found a negative correlation with size for all of them except perhaps As, which had no correlation for bleak and barbel and a negative one for gudgeon. They speculated that the higher metal contents in younger fish may have to do with their faster metabolism and growth, which may mean more uptake relative to their body size and because for the younger fish a larger proportion of the energy is invested in growth, less is available for depuration which is an active process (Merciai *et al.* 2014). In the fish from this study, only selenium and mercury show a statistically significant (α=5%) **increase** with weight of the fish for **both** roach and bleak, whereas a significant **decrease** for **both** species is observable for chromium, zinc and molybdenum and additionally cobalt if dry weight normalised data is used. Barak and Mason (1990b) also found a significant increase for mercury with the size of fish for both roach and eels, but for cadmium and lead there was no significant correlation for roach at most sites.

The increase with weight of mercury concentrations is used in the following section (section 4.3.2.3.1) to illustrate, how for this compound the influence of a fish parameter (weight) dominates over the site differences, but site differences can be uncovered if size related differences are accounted for.

Table 4.3-1 Regression parameters for Log(concentration) versus Log(weight) for metals/metalloids. Significant negative correlations are marked red and significant positive correlations green.

	Al	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Mo	Pb	Se	Sr	Zn
Roach (ww)														
n	110	110	110	110	110	110	108	110	110	110	110	110	110	110
slope	-0.63	0.10	-0.01	-0.14	-0.54	0.07	-0.35	0.20	-0.13	-0.40	-0.17	0.17	0.11	-0.10
intercept	4.95	2.14	0.73	1.53	3.51	2.79	5.12	1.08	3.78	2.26	2.12	2.47	3.95	4.78
R^2	0.11	0.03	0.00	0.02	**0.28**	0.02	0.13	***0.15***	0.03	**0.43**	0.04	***0.15***	0.10	**0.14**
p (slope)[a]	0.032%	9.1%	90%	13%	4.0E-09	20%	0.011%	2.7E-5	9.10%	4.9E-15	4.5%	2.4E-5	0.056%	4.3E-5
Bleak (ww)														
n	34	34	34	31	34	34	34	34	34	34	34	34	34	34
slope	-0.56	-0.52	0.58	-1.35	-2.35	0.30	-0.54	0.44	-0.12	-1.39	-0.02	0.38	-0.03	-0.25
intercept	3.95	2.79	0.14	2.12	5.56	2.58	4.84	1.06	3.56	3.23	1.25	2.61	3.93	4.75
R^2	0.08	0.21	0.16	0.27	**0.49**	0.07	0.08	***0.26***	0.03	**0.38**	0.00	***0.21***	0.00	**0.17**
p (slope)	11%	0.66%	1.8%	0.26%	3.6E-06	15%	11%	0.23%	35%	9.2E-5	95%	0.70%	70%	1.5%
Roach (dw)														
n	110	110	110	110	110	110	108	110	110	110	110	110	110	110
slope	-0.71	0.03	-0.09	-0.22	-0.62	-0.01	-0.43	0.12	-0.21	-0.48	-0.25	0.09	0.03	-0.18
intercept	5.66	2.85	1.44	2.24	4.22	3.50	5.82	1.78	4.48	2.97	2.83	3.18	4.66	5.48
R^2	0.14	0.00	0.01	0.05	**0.33**	0.00	0.20	0.06	0.07	**0.53**	0.08	0.05	0.01	**0.39**
p (slope)	4.9E-5	66%	27%	1.75%	3.6E-11	80%	1.5E-06	0.77%	0.53%	1.8E-19	0.24%	2.1%	30%	3.3E-13
Bleak (dw)														
n	34	34	34	31	34	34	34	34	34	34	34	34	34	34
slope	-0.59	-0.55	0.55	-1.38	-2.38	0.27	-0.57	0.40	-0.15	-1.42	-0.05	0.35	-0.06	-0.28
intercept	4.57	3.40	0.76	2.74	6.17	3.20	5.46	1.68	4.18	3.84	1.87	3.22	4.54	5.36
R^2	0.08	0.27	0.13	0.28	**0.50**	0.05	0.08	0.18	0.04	**0.39**	0.00	0.15	0.02	**0.15**
p (slope)	10%	0.16%	3.7%	0.22%	2.7E-06	22%	10%	1.2%	27%	8.4E-5	87%	2.5%	45%	2.4%

[a] probability that a such a slope (or steeper) would arise by chance when there is actually no correlation between x and y, i.e. the real slope is 0

4.3.2.3 Metals for which contamination <u>increased</u> with size of the fish: mercury + selenium

4.3.2.3.1 Mercury

The measured mercury concentrations are within a relatively narrow range of little more than one order of magnitude (highest/lowest concentration is 11 for mercury) and site differences are not very obvious from the bar graph reproduced here from chapter 3.

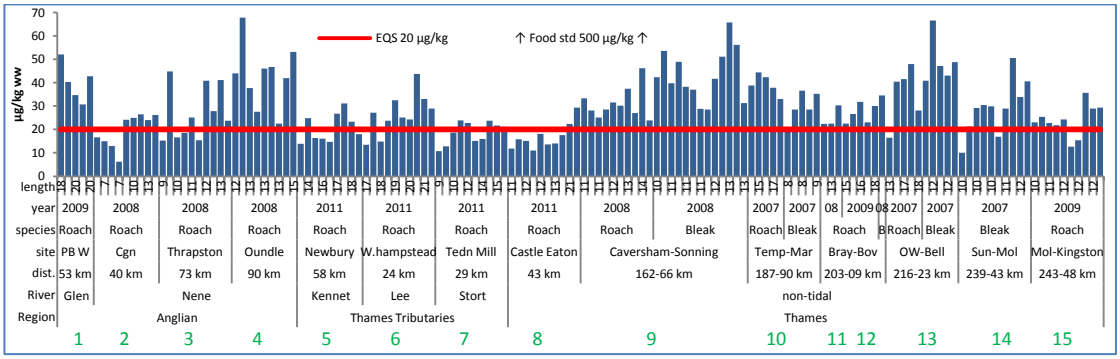


Figure 4.3-7 All mercury contents determined as µg/g ww. Sorted by region, river, site (km refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length. The environmental quality standard (European Union 2013) is also shown. The green numerals refer to the group numbers used in below in Figures 4.3-11 and 4.3-12.

Influence of the size of the fish on mercury concentrations

In Table 4.3-1 it was established that overall there was a statistically significant (α=5%) **increase with size** of the fish for mercury, shown in Figure 4.3-8 for weight. The graph would look very similar if length or age (estimated from length in most cases) were used instead, since those parameters are very strongly correlated.

This increase of mercury concentration with weight may be because older fish had more time to slowly accumulate mercury and larger fish of the same species tend to feed on larger prey, meaning they are effectively higher up in the food chain. Environmental mercury exposure is also reducing in most places (Lepom *et al.* 2012, UNEP 2013) but the difference in age of the fish was only a few years, during which the environmental concentrations would have changed very little.

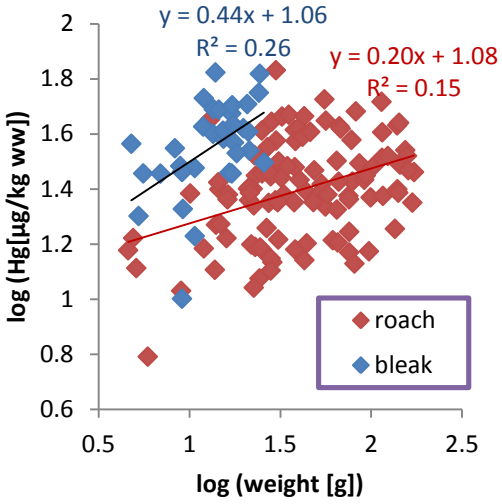


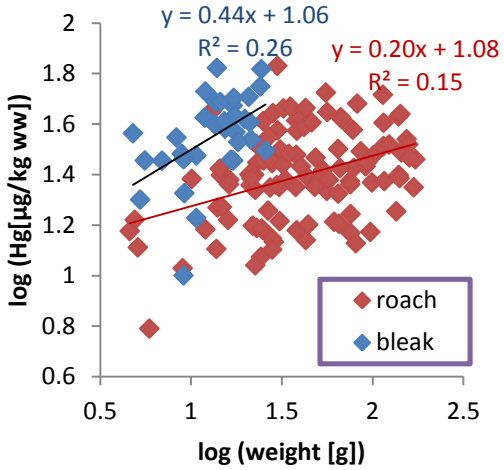
Figure 4.3-8 Linear regression of log-transformed data between mercury and fish weight - there is an increase of mercury concentration with weight.

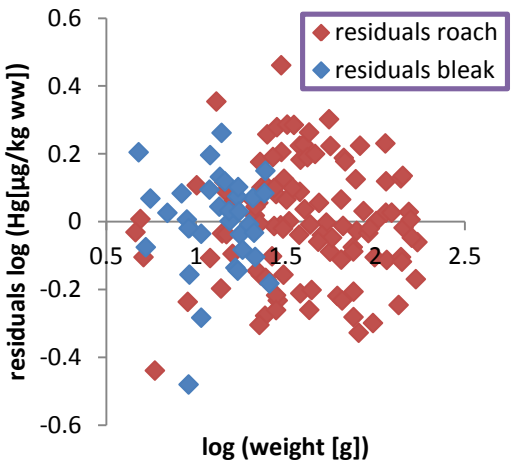
Species difference: roach versus bleak

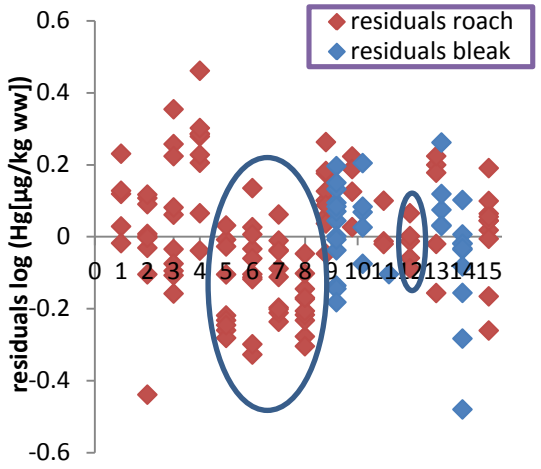
Figure 4.3-8 shows that, overall, bleak were about 70% more contaminated with mercury than roach of the same size. Since bleak are a smaller slower growing species than roach, the question was whether their higher contamination for a given size, could be explained by them being older. This was tested for the lower Thames data, by estimating the age for both bleak and roach from the median age-length relationships published by Britton (2007) and showed that bleak were about 30% more contaminated than roach of the same estimated age. All the differences were significant at the 10% level. Therefore age explains some, but not all, of the difference between mercury concentrations in roach and bleak of the same weight. Another contributing factor to the difference may be growth dilution. Individuals that grow faster because they eat more or more nutritious food than others tend to have a lower concentrations of mercury (Johnson *et al.* 2015). Even if the food has the same mercury content, in slower growing fish the amount of food ingested only leads to a smaller increase in their weight (the rest is used for "maintenance"), but all the mercury still remains, leading to a higher concentration altogether. Bleak are slower growing than roach.

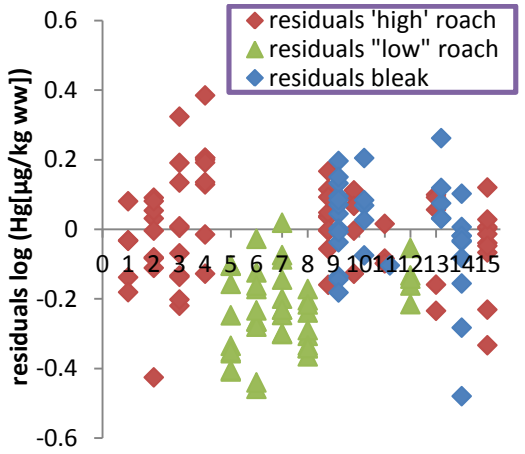
Is there a site difference "hiding" under the size influence?

For the example of mercury a method of uncovering site differences that are masked by another influence (dependence of contamination on weight) is explained below:

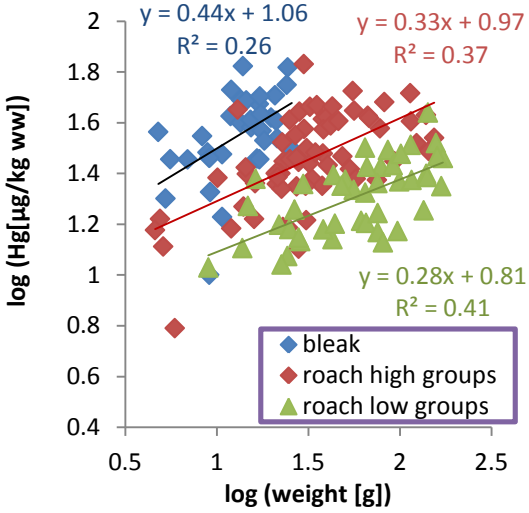
Method	Result/ Illustration
1. Calculate the linear regression between weight and mercury concentration for log-transformed data (Figure 4.3-9)	 **Figure 4.3-9 Linear regression of log-transformed data between mercury and fish weight.** ➔ there is an increase of Hg with weight
2. Check whether the slopes are significant	This was already established in Table 4.3-1, the probabilities of getting such slopes or steeper were less than 5% ➔ the increase of mercury with weight is significant

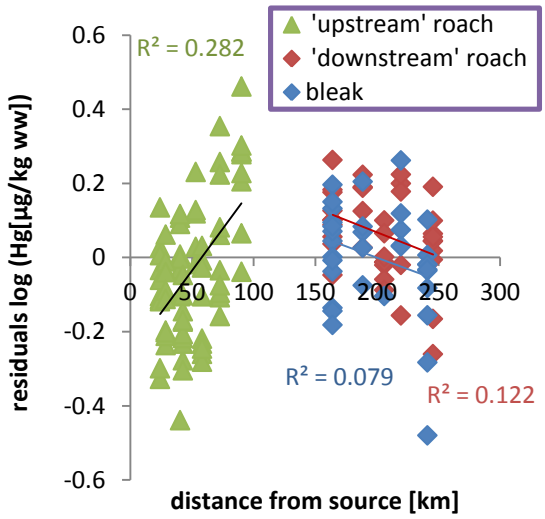
Method	Result/ Illustration
3. Is <u>linear</u> regression on <u>log-transformed</u> data an appropriate approach? ➔ Plot the residuals from the regression against weight of the fish (Figure 4.3-10) → If they follow a pattern such as a U-shape the relationship is not entirely linear and another regression (e.g. quadratic, or polynomial) is more appropriate. The residuals won't follow a linear trend because that has just been removed → If the scatter increases or decreases with weight, then log-transformation is not appropriate.	 **Figure 4.3-10 Residuals from the linear regressions of log Hg against log weight.** → Fairly even scatter means that the chosen regression (linear) and transformation (logarithmic) was appropriate. There is no further influence of weight either on the location or scatter of the residuals ➔ The residuals correctly represent weight-normalised concentrations

Method	Result/ Illustration
4. Plot the residuals grouped by sampling occasion (=site+fishing-date) 5. Do an ANOVA for the residuals to check for differences between groups 6. if there is a difference, try to guess where and divide the groups accordingly	 **Figure 4.3-11 Residuals by sampling occasion (see Figure 4.3-7 for the meaning of the numbers).** → ANOVA shows that there are significant differences (at α=5%) "somewhere" in the roach sampling occasions, but no significant differences for the bleak → Sampling occasions 5-8 and 12 are quite low compared to the rest. → Divide into "5-8+12" and "rest"

Method	Result/ Illustration
7. Calculate the linear regressions for both groups separately 8. Calculate ANOVAs for the residuals of both groups separately ➔ If there are still differences, either the division between the groups was in the wrong place or more than two groups are needed ➔ If the ANOVAs now say that within the two groups there is no significant difference between sampling occasions any more, then dividing the sampling occasions into two groups was enough to account for the differences	→ Now the ANOVA's show no significant differences between sampling occasions (at the 5% level) so all the roach in the "high" groups can be treated as one group and all the ones from the "low" ones as second group.  **Figure 4.3-12 Residuals of the <u>new</u> regression for "high" roach which excludes group 5-8 and 12. To show the differences, residuals for the "low groups" 5-8 and 12 are shown with respect to the "high" regression, not to their own one.** ➔ Dividing all the roach into just two groups was enough to account for the significant differences between the sampling occasions

Method	**Result/ Illustration**
➔ What do these results mean? → Which sampling occasions were grouped together? → What do the sampling occasions, that were grouped together have in common?	→ The sites/dates with lower Hg contamination for their size were: 5: River Kennet at Newbury, 2011 (n=9) 6: River Lee at Wheathampstead, 2011 (n=10) 7: River Stort at Tednambury, 2011 (n=10) 8: River Thames at Castle Eaton, 2011 (n=10) 12: River Thames Bray to Boveney, 2009 (n=5, but the previous year's 4 were in the "high" group, all were relatively close to the regression though) ➔ with the exception of the 5 fish from sampling occasion 12, the "low mercury" roach were all from sites relatively high up in their respective catchments

Method	Result/ Illustration
➔ Final picture of size dependence → The sampling occasions have been grouped so that the ANOVAs (see above) show that there is no longer a difference within the broad groups created → Check that the differences between groups are significant	 **Figure 4.3-13 Final picture. The "low roach" group are from the three Thames tributaries Stort, Lee, Kennet and the most upstream site analysed on the Thames itself (Castle Eaton), as well as 5 roach caught in the lower Thames (Bray-Boveney) in 2009.** → The three regressions ("high roach", "low roach" and "bleak") were tested for significant differences using the linear regression add-on in Microsoft Excel. → The slope for the three groups was similar but the offset was statistically significantly different at any sensible α chosen. ➔ Splitting the roach into two groups **improved the R^2** for roach from 0.151 overall (Figure 4.3-9) to 0.368 and 0.414 for the "high" and "low" groups respectively.

Method	Result/ Illustration
➔ Are there perhaps further relationships? → If the groupings arrived at hint towards another pattern, then it is worth checking that too	→ Since the lower mercury concentrations tended to be higher up in their catchments, it seemed worth plotting the residuals from the original regression by distance from the source  **Figure 4.3-14 Residuals from Figure 4.3-9, plotted against distance from the source – regardless of catchment.** ➔ For the roach from sites higher up in their catchments (several rivers) there was an increase of mercury contamination with distance from the source, but not for the roach and bleak from the lower Thames.

Method	Result/ Illustration
	→ Is there also a relationship with estimated sewage effluent content at the sampling site?

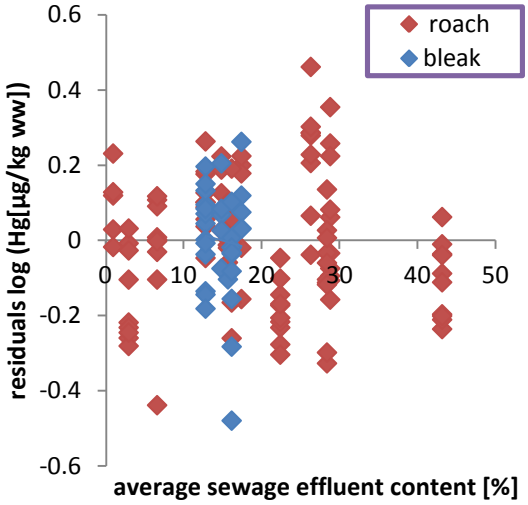


Figure 4.3-15 residuals from Figure 4.3-9, plotted against average sewage effluent content at the sampling site. Sewage effluent concentrations at the sites are given in Figure 2.2-2.

➔ Sewage effluent has **no** noticeable influence on mercury concentrations in fish

The calculations above show that **mercury concentrations depended** on **size** (measured as weight, but results are similar if length or estimated age are used instead), **species** (bleak or roach), and **site**. The site differences appeared to be related to their location in the catchment (close to the source or further downstream) and not to how much sewage effluent the rivers receive. By contrast, a much earlier study in the lower river Lee did find an effect of sewage with much higher mercury concentrations found in roach caught in a tertiary treatment lagoon of a sewage works than in those from further upstream in the river in 1974 (Bull *et al.* 1981). This may reflect a mercury problem specific to that sewage works in the 1970s.

Since the dry matter also increased with the size of the fish (see chapter 3.1.1), it was important to check whether the relationships above still hold true when the concentrations are given with regard to dry weight rather than wet weight. The correlation of mercury concentration with weight of fish remained (Figure 4.3-16), showing that there was an increase of mercury contamination with size of the fish over

and above the increase in dry weight content, but the fit of the regression lines (R^2) were less good because some of the size-effects were compensated for by the dry weight normalization.

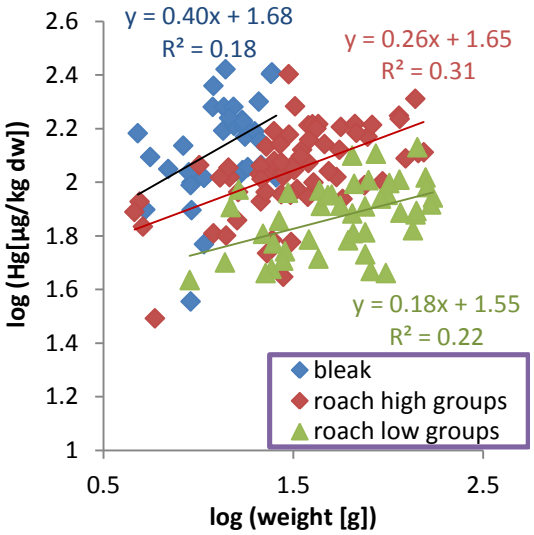


Figure 4.3-16 Same as Figure 4.3-13 but with regards to dry weight.

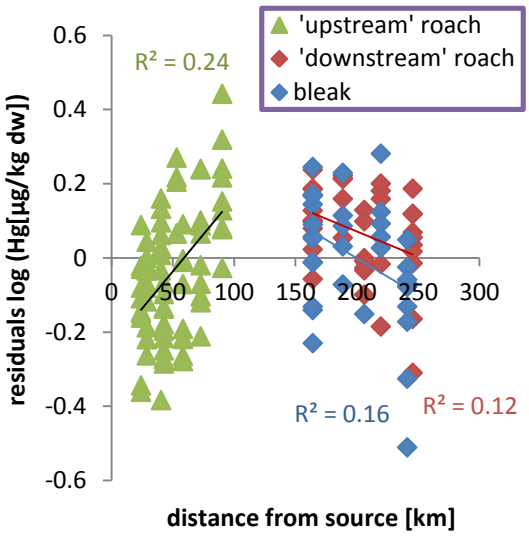


Figure 4.3-17 Figure 4.3-14 with regards to dry weight.

Mercury contamination therefore depends both on the fish (species and size) and on the site at which they had been caught (upstream or downstream). Having accounted for those factors by drawing 3 different regression lines, the R^2's for mercury content against weight were between 0.26 and 0.42 (Figure 4.3-13), so a large proportion of the variability was nevertheless unaccounted for.

What may explain the site differences in mercury concentration?

- Different concentrations in the environment:
  - A major source of mercury is released into the atmosphere from burning coal. This makes it a diffuse and almost evenly distributed source, but one would still expect higher concentrations nearer to urban or industrial areas than further away from them. This may be part of the explanation for having low concentrations high up in the catchments but doesn't explain why this relationship doesn't continue further downstream. The lower Thames is, however, largely groundwater fed at base flow conditions, maybe dilution with groundwater reduced contaminant concentrations.

- Different bioavailability:
    - As noted previously (section 1.5.1.1) mercury in the environment exists mainly in three forms: metallic mercury (Hg^0), inorganic mercury ions (Hg+ and Hg^{2+}) and organic mercury compounds (mainly methyl-mercury CH_3-Hg). Methyl-mercury is more bioavailable (eg. Wenning *et al.* 2011) and much more toxic than the inorganic forms and also bio-accumulates more readily. Mercury in fish (as opposed to sediment or water) measures essentially the bioavailable form, which the fish have likely taken up with their food, rather than from the water, so it is likely to be mostly in organic forms. Since a larger proportion of the mercury in the sediment is transformed to methylmercury under anaerobic conditions and since methylmercury bioaccumulates much more than inorganic mercury, higher body burden would be expected in lowland regions with anaerobic sediments than in upland regions if everything else was the same, but again this is not the case for the lower Thames sites. However mercury can also bind to the organic matter making it less bioavailable (see below). Therefore there is perhaps an optimum amount of organic carbon for the production of methylmercury: too little organic carbon and the bacteria don't find the right (anaerobic) conditions whilst too much binds some of the mercury in a form that is less bioavailable.
    - Despite decreasing atmospheric deposition, mercury concentrations in fish have recently increased rather than decreased in several places, for example in Norwegian lakes (Hongve *et al.* 2012) and Lake Erie in Canada (Sadraddini *et al.* 2011). This may be because of increased bioavailability of mercury in the sediments. According to Hongve *et al.* (2012) the explanation for this phenomenon may be that in the past there was atmospheric mercury deposition and acid rain, while today the water is less acid and contains fewer ions. This purer water is better at dissolving humus (dissolved organic matter, DOM) and mercury can be complexed with the DOM increasing its transport from soil into water courses during periods of higher DOM. Hongve *et al.* (2012) demonstrated a correlation between mercury in lake fish and DOM by comparing data nearly 20 years apart during which the acidification had greatly reduced, which increased the DOM, whereas Neal *et al.* (2011) showed the short term correlation between mercury and DOM in water with fortnightly or monthly samples over 2 years, where the DOM fluctuated in response to

flow (and season?). The in-lake methylation can also be increased both by the DOM, which helps to transport the mercury into cells (Graham *et al.* 2012, Hongve *et al.* 2012) and by sulphate left over from the acid rain which acts as a terminal electron acceptor for the microbial mercury methylation (Hongve *et al.* 2012). DOM can, however, also have the opposite effect of reducing the bioavailability of methylmercury in water (Tsui and Finlay 2011).

In future, it would be interesting to study samples from the middle reaches of the Thames, which have so far been missed, as well as a number of sites on other long rivers to establish whether the correlation between distance from the river source and mercury contamination is a general phenomenon.

Mercury summary

- Mercury concentration increased with the size or age of the fish
- Bleak had higher mercury contamination than roach of the same size or (estimated) age
- In the upper reaches of all rivers studied, size-adjusted mercury contamination of roach increased with distance from the source (no other species were *sample*d), but this trend did not continue for the bleak and roach collected in the lower Thames
- Sewage effluent content at the sampling sites had no noticeable influence on mercury contamination of fish

4.3.2.3.2 Selenium

Like mercury, the concentrations of selenium measured spanned little over one order of magnitude, but the concentrations were much higher than for mercury from 0.14 to 2.16 mg/kg (Figure 4.3-18).

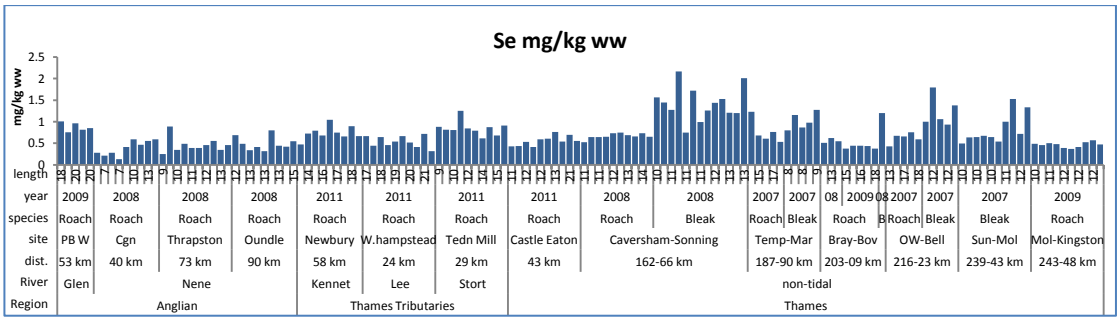


Figure 4.3-18 All selenium contents determined. Sorted by region, river, site (dist. refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

Influence of size for selenium

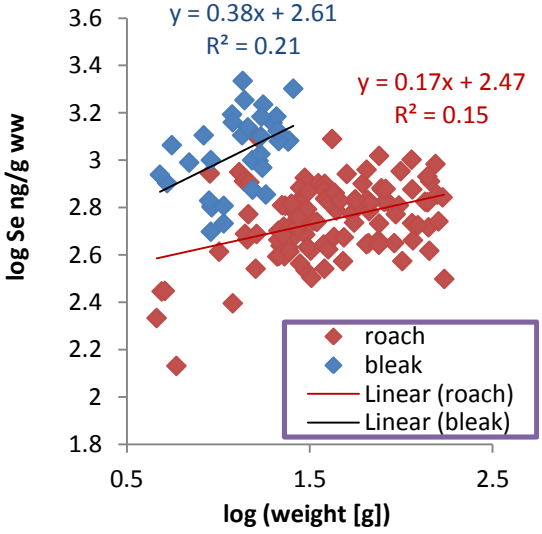


Figure 4.3-19 Linear regression of log-transformed data between selenium and fish weight - there is an increase of Se with weight.

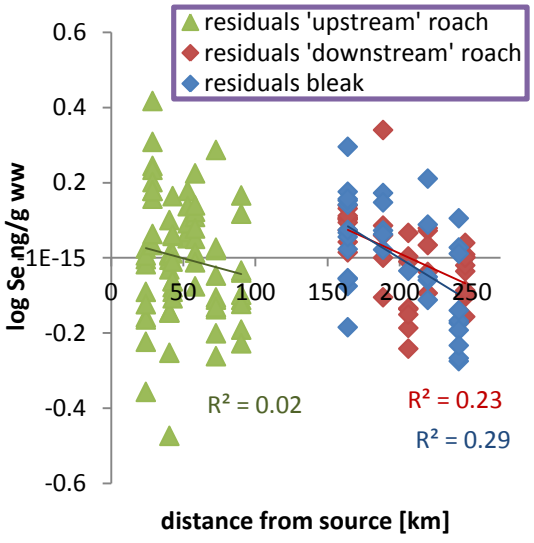


Figure 4.3-20 Residuals from Figure 4.3-19. There was a decrease of size-adjusted selenium with distance from the source for the lower Thames sites, but not for the more upstream sites in any catchment.

The patterns for selenium are very similar to those for mercury, which may be expected because they share similar mechanisms with inorganic forms being released into the environment and those being transformed into organic more bioavailable forms by microorganisms (US EPA 2014). However, reviewing the available literature deForest and Adams (2011) came to the conclusion that while there is a large increase of Se concentration between water and primary producers and a small further increase between plankton, invertebrates and forage fish, there is no further increase between forage and predator fish and that size or age of the fish has generally no influence on Se concentration or is negatively correlated. By contrast in the

current study a positive correlation between size of fish and selenium concentration (Figure 4.3-19, Table 4.3-1) was found, which was reduced but still significant at the 5% level if the concentrations were expressed with regards to dry weight rather than wet weight (Table 4.3-1), because dry matter content also increased with size.

Site differences for selenium

Once the size dependence was taken into account, a site dependence for selenium became visible: the residuals (i.e. size normalised Se concentrations) showed a similar but slightly different dependence on the distance from the source than for mercury, in that for the downstream Thames sites the decrease of contamination with distance from the source was clearer than for mercury, whereas for the upstream sites there was no clear trend (Figure 4.3-20). As for mercury, there was no obvious correlation with sewage content for the size adjusted selenium concentrations (Figure 4.3-21).

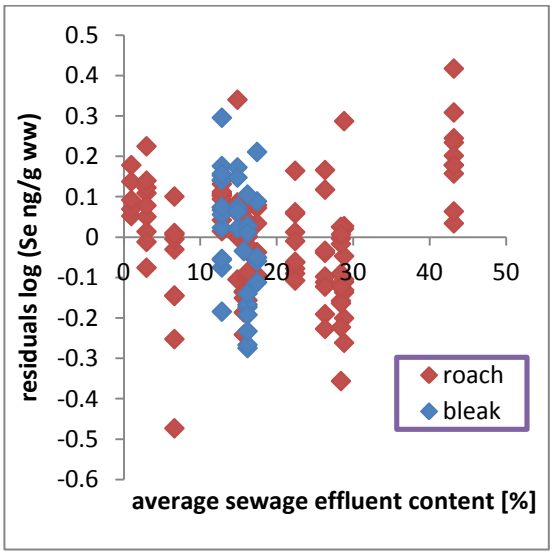


Figure 4.3-21 residuals from Figure 4.3-19, plotted against average sewage effluent content at the sampling site. Sewage effluent concentrations at the sites are given in Figure 2.2-2.

4.3.2.4 Metals where concentration <u>decreased</u> with the size of the fish: Cr, Zn, Mn, (+Co, if dry weight normalised)

4.3.2.4.1 Size and Site influences

Calculating the regression between weight and chemical contamination first and then looking at the residuals to establish any site differences in the weight-adjusted concentrations, works well where size is the dominant factor, as shown above for mercury and selenium.

Where the site differences dominate, this approach works less well: ideally any relationship with weight should be established for each sampling occasion separately – only pooling them if it can be established that there is no significant difference between sampling occasions, but in most cases there is not enough data or the data points span too small a weight range to do this efficiently. For example: if at one site only small fish were analysed and they have low contamination and at a second site all analysed fish are large and have high contamination, it is impossible to say whether the difference is due to the size or the site, but if all large fish are more contaminated than small fish regardless of site, then it is likely that the size is an important contributor. Despite the question-mark over the validity of the approach if site differences dominate, the log-linear regression with weight was calculated for all metals in the analysis suite (except Ni, Sb, Va, because of their poor reproducibility, see section 3.2.1) and summarized in Table 4.3-1 above.

Chromium, zinc, and molybdenum were significantly correlated with weight for both roach and bleak and regardless of whether the concentrations were dry weight normalised or not (Table 4.3-1). Additionally the correlations were significant for cobalt if dry weight normalised data was used. Unlike mercury and selenium, all of them had a negative slope and as dry weight tended to increase with weight most of these correlations were stronger when measured against dry weight rather than wet weight. The correlation between those four chemicals (ng/g dry weight) and weight of the individuals are plotted in Figures 4.3-22, 4.3-24, 4.3-26, and 4.3-28, while the residuals against distance from the sources of the rivers are plotted next to them in Figures 4.3-23, 4.3-25, 4.3-27, and 4.3-29. While the decrease of those metal contents with increasing size was significant in all cases, there wasn't an obvious influence of distance from the source as there was with mercury and selenium. The picture was

similar when the residuals were plotted against estimated sewage content instead of distance from the source (figures not shown): out of 8 regressions (2 species x 4 metals), 7 had an $R^2<0.1$, and the remaining one was for bleak, which were only caught at 3 sites with very similar estimated sewage contents, making any apparent trend unreliable. Therefore there was no discernible trend either with distance from the source or with estimated sewage content for chromium, zinc, molybdenum or cobalt.

For mercury and selenium, which increased with size, bleak had higher contamination for their size, in part because they are older at the same size. The concentrations of chromium. zinc, molybdenum and cobalt decreased with size and again the effect was stronger for bleak for the same reason.

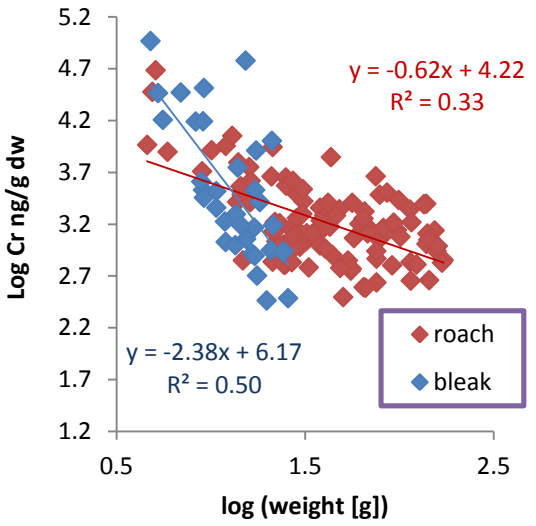


Figure 4.3-22 Chromium concentration (with regards to dry weight) compared to the weight of the fish.

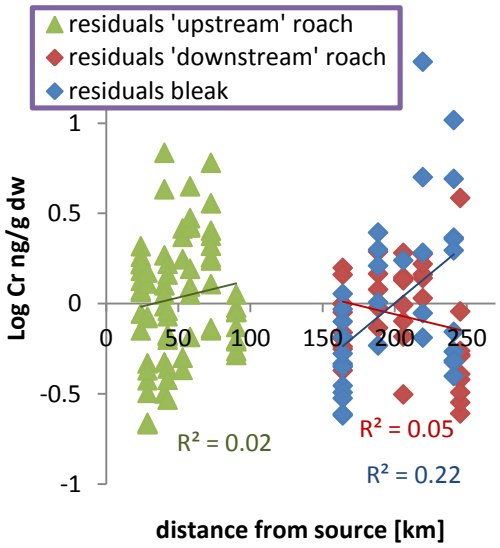


Figure 4.3-23 Residuals from Figure 4.3-22 plotted against the distance from the source (all catchments).

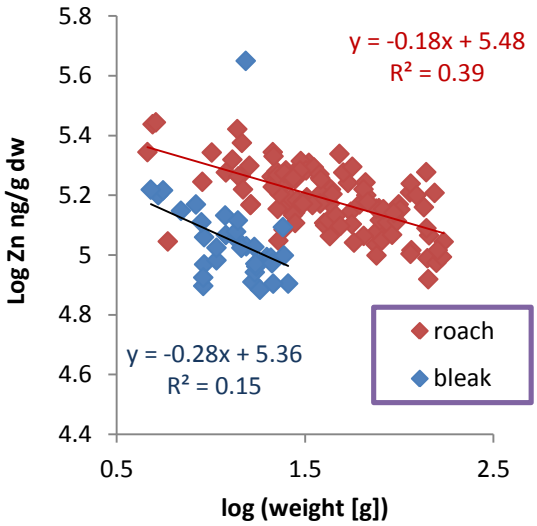


Figure 4.3-24 Zinc concentration (with regards to dry weight) compared to the weight of the fish.

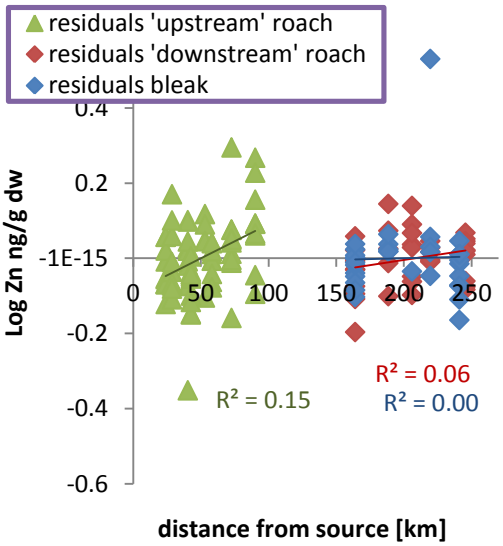


Figure 4.3-25 Residuals from Figure 4.3-24 plotted against the distance from the source (all catchments).

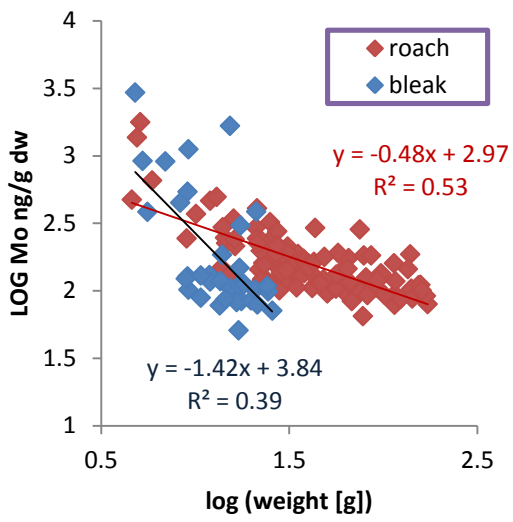


Figure 4.3-26 Molybdenum concentration (with regards to dry weight) compared to the weight of the fish.

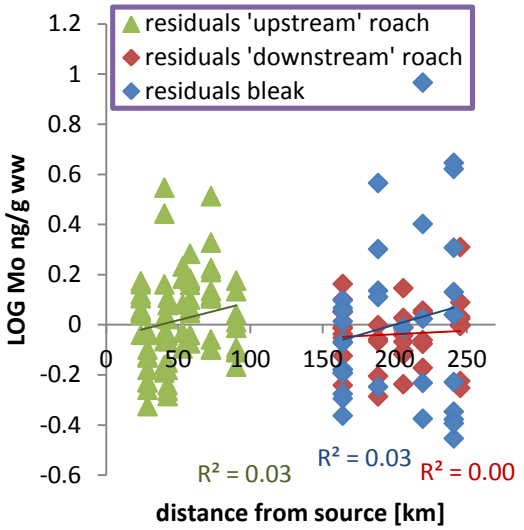


Figure 4.3-27 Residuals from Figure 4.3-26 plotted against the distance from the source (all catchments).

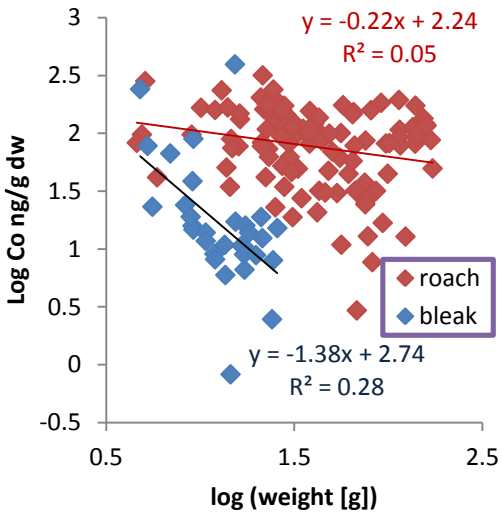


Figure 4.3-28 Cobalt concentration (with regards to dry weight) compared to the weight of the fish.

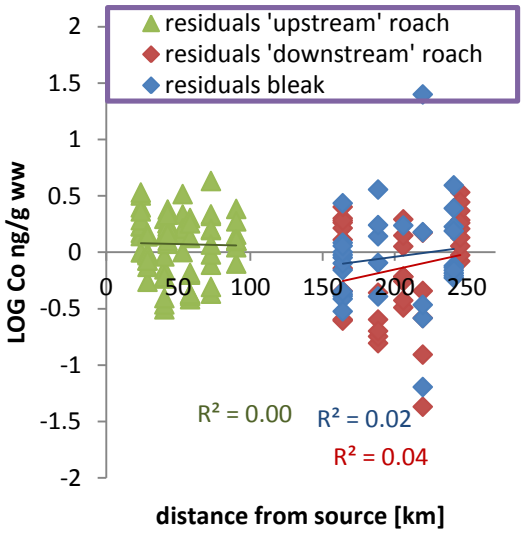


Figure 4.3-29 Residuals from Figure 4.3-28 plotted against the distance from the source (all catchments).

As these three metals are used in steel alloys or for steel surface treatment, it is a question whether contamination especially of the smaller individuals may be due to the metal tools used to homogenize the samples. However, if that was the case one would expect them to correlate strongly with iron, as that is the main component of all the tools used, but the correlation with iron is only strong for both species for cobalt (Figure 4.3-4).

4.3.2.4.2 Summary Cr, Zn, Mn, Co

- Concentrations of these 4 metals were negatively related with the size of the fish
- This effect was stronger if the data was dry-weight normalized
- There was no clear trend of the size-adjusted concentrations with regards to distance from the source or estimated sewage content at the sampling site.

4.3.2.5 A metal with a clear site difference: Cadmium

The Castle Eaton site on the river Thames stands out for the roach having cadmium levels about 3-4 times as high as at the other sites, although still well within the allowable limits for human food (Figure 4.3-30). The reason for this is not known. Maybe the cadmium contamination originates from industry in the town of Swindon. Swindon sewage treatment works discharges into the river Ray, which in turn joins the Thames a short distance upstream of the sampling site. Fish from both the Castle Eaton site and a site on the Thames upstream of the Ray (Cricklade) from other sampling years have been archived and should be tested for cadmium at the next opportunity.

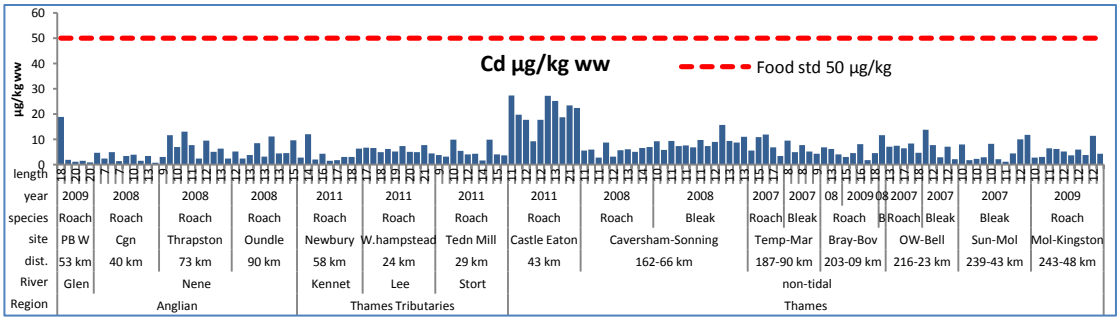


Figure 4.3-30 All cadmium contents determined. Sorted by region, river, site (dist. refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

4.3.2.6 Is metal contamination related to sewage effluents?

Many of the anthropogenic chemicals found in rivers get there mainly with sewage effluent: Hormones and drugs are excreted and flushed down the toilet;

cosmetics and personal care products also largely end up in the waste water when they are rinsed off the body in the shower; detergents and other cleaning products go into the waste water after use and even chemicals that are not so obviously associated with water such as flame retardants may be found in dirt and dust, some of which is caught on clothes or surfaces and washed off during cleaning and laundry (Schreder and La Guardia 2014). While sewage treatment effectively removes a large proportion of most of these chemicals it is never 100% efficient, so the rest still comes out in the treated sewage effluent and enters rivers.

Figure 2.1-3 shows the estimated treated sewage content of the rivers at the sampling sites (see chapter 2.1.2 for a description how the estimates were made). The mean, i.e. the concentrations fish would experience on average has been used for the correlations calculated in this chapter.

Metal concentrations compared to modelled sewage concentrations are shown graphically in the second column of Figure 4.3-4 and the second row shows the correlation coefficients between the log transformed estimated sewage content and metal concentrations. For roach none of the R's were better than 0.40. The correlation factors calculated for bleak are probably not very meaningful, because not only were far fewer bleak analysed, but they all came from the lower Thames with little variability of estimated sewage contents. For those metals where a significant positive or negative correlation between size of the fish and metal concentration was calculated (Hg and Se +, and Cr, Zn, Mn and Co -) the residuals, i.e. size adjusted concentrations, were also tested against estimated sewage content and did not show an effect of estimated sewage content on metal concentration. Overall, this shows little correlation between all the measured metals and sewage content and therefore that for the investigated metals, domestic sewage effluent is unlikely to be the major source.

4.3.2.7 Summary of all patterns found for metal contamination

Correlations between size of the fish and metal concentrations:

- Significant **positive** correlations with size were found for **mercury** and **selenium** in both roach and bleak, although the metal concentrations only varied by little more than an order of magnitude from 6.2 to 68 µg/kg for mercury and 0.14-2.2 mg/kg for selenium.

- Most other metals measured showed a **negative** correlation with fish size, which was significant at the 5% level in both roach and bleak, for **chromium, zinc** and **molybdenum,** whether wet weight or dry weight normalized data was used and additionally for **cobalt** if dry weight normalised data was used.
- The above positive or negative correlations with size tended to be stronger for bleak than for roach, presumably because as a small slow growing fish bleak are older for their size than roach. If estimated age rather than weight was used to relate to the metal contamination the species differences were reduced.

Effects of some site properties:

- None of the metals had a strong correlation with sewage content at the sampling site.
- When size-adjusted metal concentrations from the correlations above were used, patterns related to distance from the source emerged for mercury and selenium:
    - Size-adjusted mercury contamination increased with distance from the source in the upper reaches of the various rivers (only roach available), but not in the lower Thames (roach and bleak measured).
    - Size-adjusted selenium concentration was relatively constant in the upper reaches and decreased with distance from the source in the lower Thames.
    - No such patterns existed for chromium, zinc, molybdenum, or cobalt.

4.3.3 Persistent organic pollutants (POPs) case studies

4.3.3.1 POPs where the concentrations in fish are related to sewage effluents: PBDE flame retardants

PBDEs are members of the group of brominated flame retardants (BFR). They work by releasing Br atoms when heated. When solids burn, it is mainly flammable

gases that are released and mix with air that are responsible for the fire. The heat produced releases more gas from the solid, which burns to produce more heat etc. OH· and H· radicals are particularly reactive components of this mix. The Br atoms released from PBDEs and other BFRs when heated react with the OH· and H· radicals thus rendering them unreactive. Removing these reactive radicals starves the fire of the "best" fuel, and so slows or stops the spread. A main use for PBDEs was in soft furnishings such as polyurethane foam used in sofas and other upholstery. and also in the plastic casings of electrical and electronic equipment.

Schreder and La Guardia (2014) suggested that an important route for flame retardants to enter the aquatic environment is via sewage: wear and tear of the flame retardant containing items in the household creates dust some of which is trapped on clothing and gets washed off in the laundry. The waste water enters sewage treatment works where the flame retardants are only partially removed and so some proportion enters rivers with the treated effluent.

PBDEs are usually used "additive" which means that they are mixed into the material they are meant to protect rather than "reactive" flame retardants, which become part of the molecular structure of the polymer and are therefore far more difficult to release. PBDEs in small polymer fragments in dust are thus easily released to water, especially in the presence of detergents, that make lipophilic compounds easier to dissolve.

Figure 4.3-31 shows the sum of 6 indicator PBDEs compared to the estimated average sewage effluent concentration at the sampling sites. A regression has been calculated for roach and, on its own, it explains roughly half the variation on the log transformed data. It makes little sense to calculate the regression for bleak, because reliable data were only available for two sites but, as can be seen in the figure, the bleak data also fit quite well on the roach regression. Contrary to expectations, lipid-normalising the data didn't improve the relationships, in fact the R^2 reduced from 0.51 to just 0.25 (graph not shown).

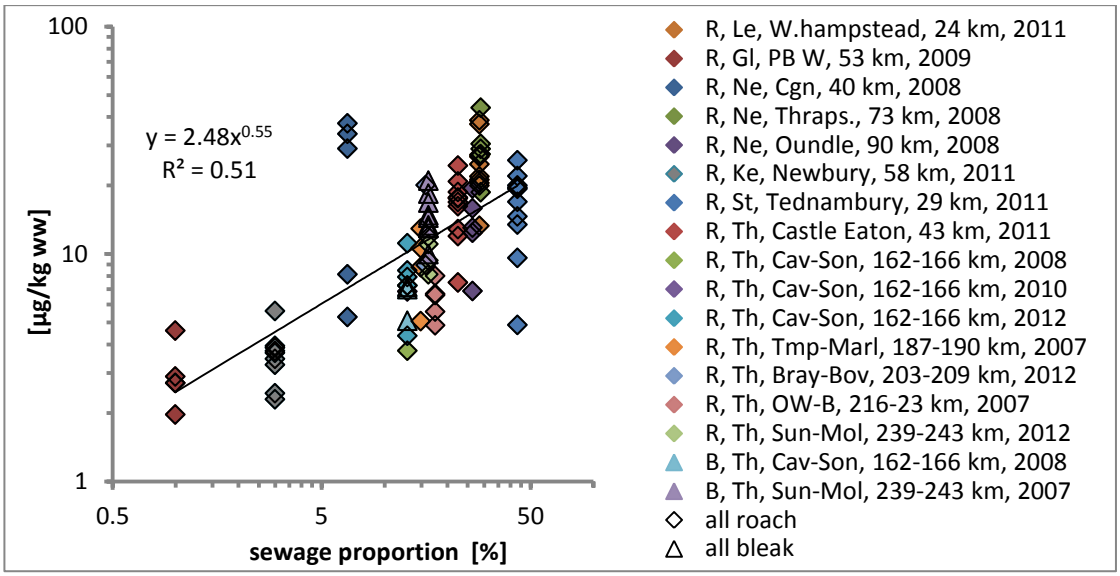


Figure 4.3-31 Sum of 6 indicator PBDE compared to the estimated average sewage content of the river. The regression is for roach (R, ◊). Bleak data (B, Δ) were only available from two sites, so it doesn't make sense to calculate a regression.

Contrary to the study of bleak by Eljarrat *et al.* (2005), size (age) of the fish in the current study did not seem to be important for PBDE concentration, either overall or for most individual sites (Figure 4.3-32). If trend lines are drawn for individual sites, some have a quite good positive or negative correlation, but there is no consistent picture, so those are more likely to be due to chance than showing a real site-specific relationship. The apparent trend towards more scatter for larger fish is mainly due to one of the groups of bleak being all very small and also within a relatively narrow range of PBDE concentrations, so is probably not due to real differences between smaller and larger fish. Similarly there was no clear pattern for PBDEs compared to the distance of the site to the river source (not shown).

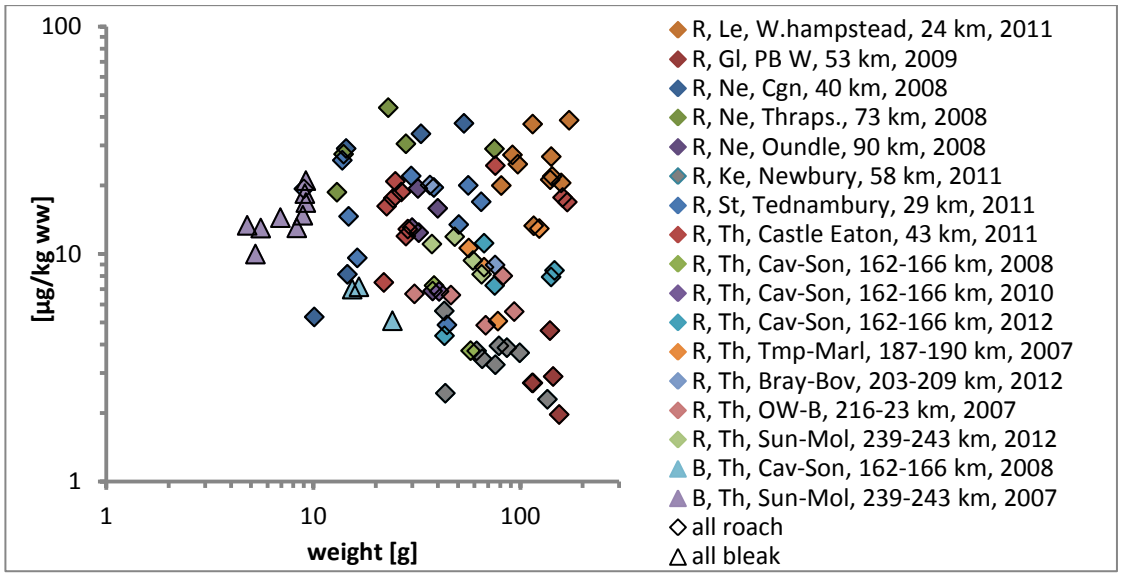


Figure 4.3-32 Sum of 6 indicator PBDE compared to the weight of the fish.

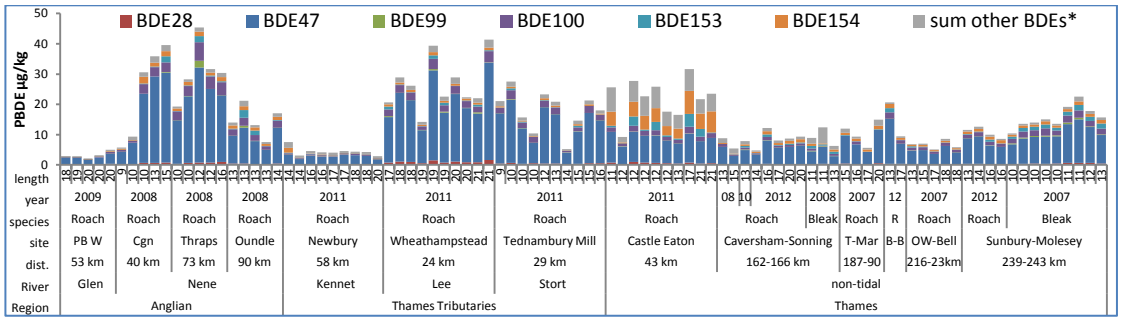


Figure 4.3-33 Indicator PBDEs and sum of other BDEs (* for list of other PBDEs analysed see methods section). Sorted by region, river, site, species, and year. Sites on each river are ordered by distance from the source (river-km). BB: Bray-Boveney 203-209 km. Within each of those groups the individuals are ordered by fork length.

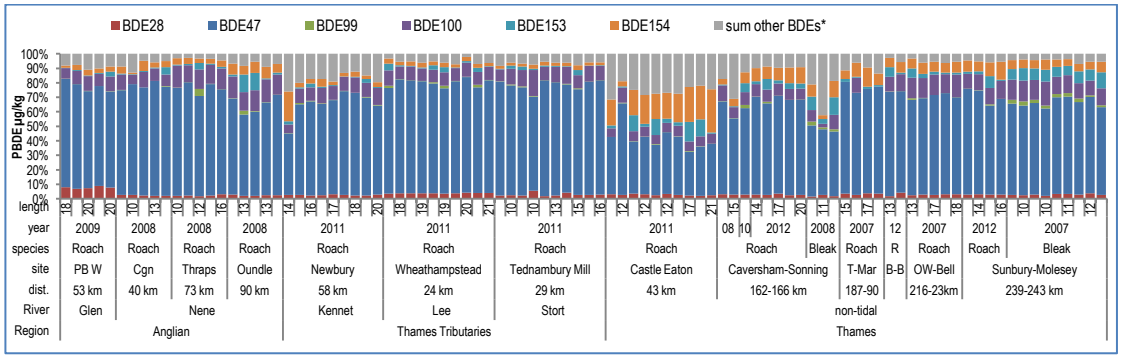


Figure 4.3-34 Relative contribution of indicator PBDEs and sum of other BDEs (* for list of other PBDEs analysed see methods section). Sorted by region, river, site, species, and year. Sites on each river are ordered by distance from the source (river-km). BB: Bray-Boveney 203-209 km. Within each of those groups the individuals are ordered by fork length.

4.3.3.2 POPs where the concentrations in fish may be indirectly related to sewage: PCBs

PCBs have been used as cooling fluids mainly in transformers and other large electrical equipment. They are therefore associated with industrial and urban areas where a lot of electricity was used, particularly before 1972 when the use of PCBs in open sources (i.e. open to the atmosphere, not sealed) was still permitted. Population density could be a good proxy for the electricity demand (and therefore transformer use) for urban areas, but large industries should be accounted for separately and since a lot of the release was likely before 1972, historic data would be useful. In a recent study of eels in Scotland (Macgregor *et al.* 2010), PCB contamination was indeed higher in urban than rural areas.

The modelled sewage content can be used as a proxy for urban population. This includes industry to some extent, but only with relation to their water use, while in this case electricity use is probably the more relevant factor. Furthermore, for PCBs aerial deposition is said to be the dominant transport pathway, therefore proximity to industrial or urban areas is likely to be important, and sewage discharge is related to that, but not always representative. As an example, one might imagine a town close to two rivers, and served by one sewage works discharging into one of them. Urban pollutants predominantly transported through air would affect both rivers, whereas those predominantly channelled through the sewage works would affect only one.

Despite these caveats it seemed worth checking whether there is a correlation between sewage content and PCB contamination (Figure 4.3-35). There is an increase in PCB contamination with increasing sewage content for the roach, but it is not as strong as for the PBDEs and without the two lowest sewage content sites there would essentially be no relationship. Surprisingly the correlation between PCBs and land cover by urban areas wasn't any stronger (Figure 4.3-36), but there was quite a good negative correlation with cereal production. Unfortunately the land cover information available from the RACQUEL program (http://wlwater.ceh.ac.uk/racquel/) does not show where heavy industry is or was, but none of the sites are in areas that are or were especially dominated by industry.

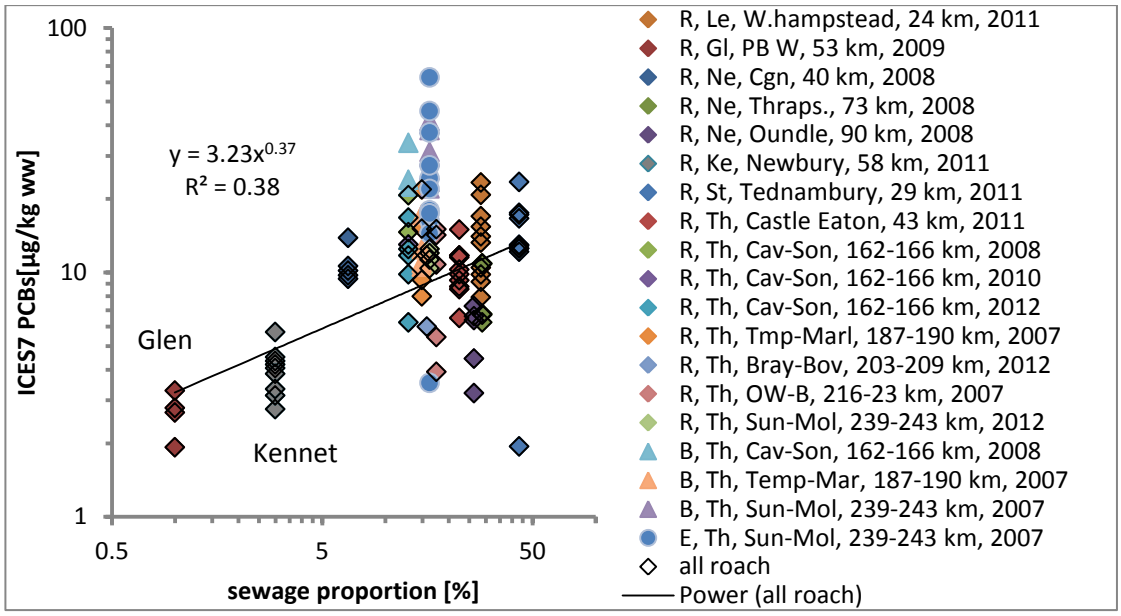


Figure 4.3-35 ΣICES6 in relation to estimated sewage content at the site. The regression is for roach. There were not enough sites sampled for bleak or eel to calculate a meaningful regression.

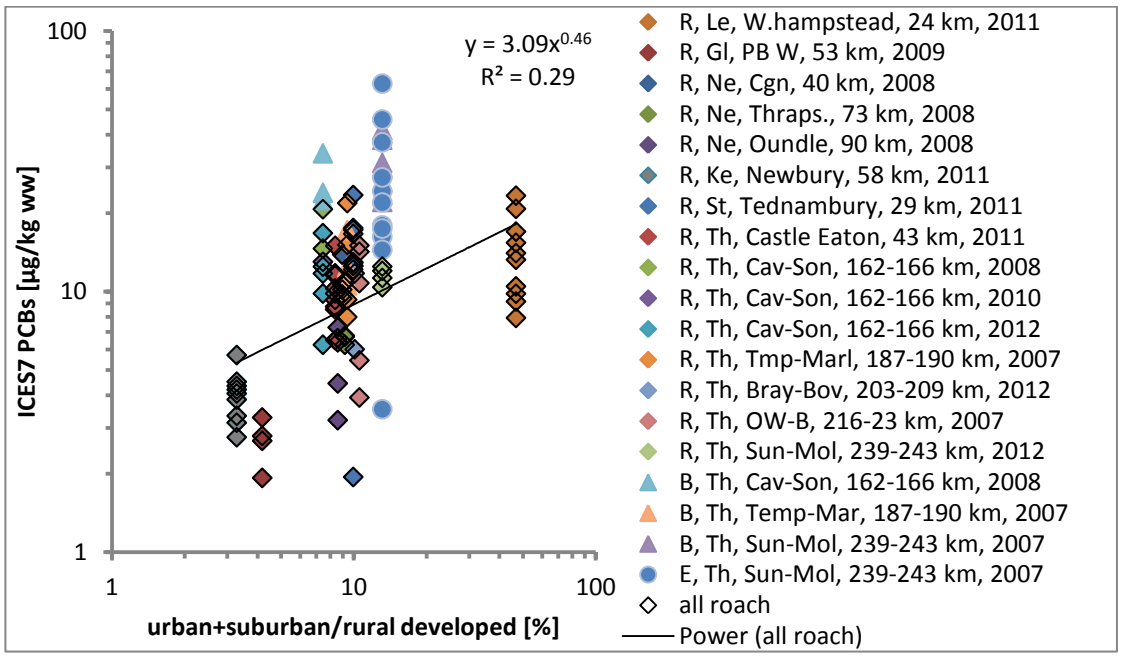


Figure 4.3-36 ΣICES6 in relation to the percentage of the catchment that is covered by urban or suburban/rural developed areas. The regression is for roach. There were not enough sites sampled for bleak or eel to calculate a meaningful regression.

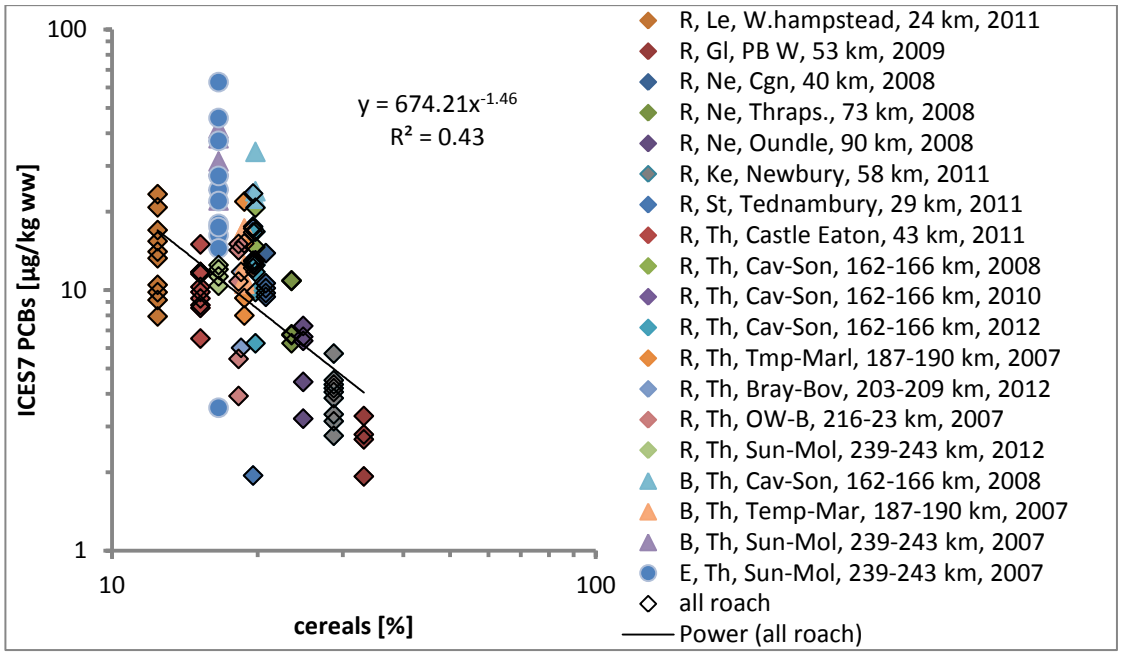


Figure 4.3-37 ΣICES6 in relation to the percentage of the catchment that is covered by cereal production. The regression is for roach. There were not enough sites sampled for bleak or eel to calculate a meaningful regression.

Fish size and distance from the source don't seem to be important in determining PCB concentrations in fish (graphs not shown).

Lipid content

For lipophilic chemicals the lipid content of the fish is very important. This is why often the concentrations are lipid normalized which essentially means pretending that the chemical is ONLY found in the lipid and giving the concentration in the lipid. The two graphs for the PCBs below show how lipid normalization reduced some of the differences. In particular the tidal eels' high concentration could be largely explained by their higher lipid content compared to the two other species and to the eels from the non-tidal reach.

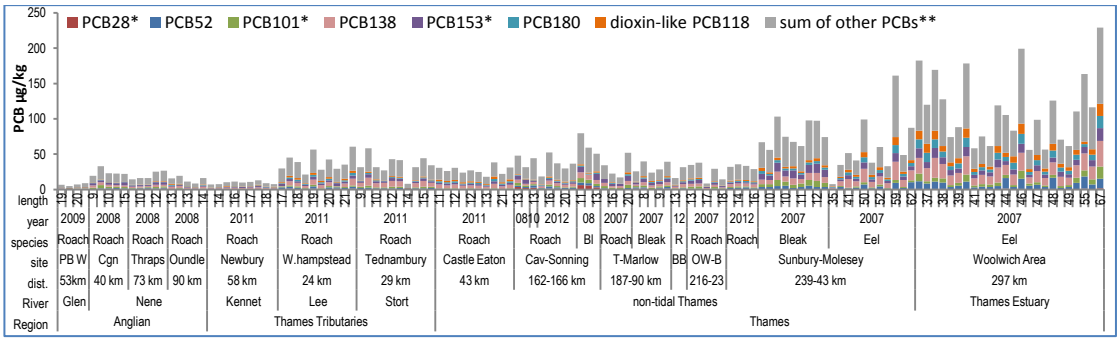


Figure 4.3-38 PCBs. ICES 7 indicator PCBs are marked individually (six non-dioxin-like PCBs (28, 52, 101, 138, 153, and 180 = ICES6, and dioxin-like PCB118, *may contain small amounts of other congeners, because 28/31, 90/101, 132/153 co-eluted), the other measured PCBs are plotted as a sum (see list in methods). Individuals at each site are ordered by species (roach, bleak, eel), year, and length (cm). Sites on each river are ordered by distance from the source (river-km). BB: Bray-Boveney 203-209 km.**

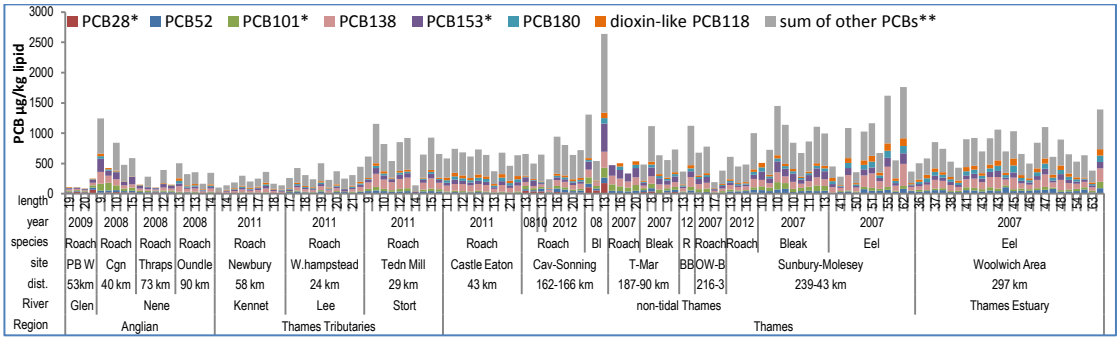


Figure 4.3-39 Lipid normalized PCBs (see caption from Figure 4.3-38).

4.3.3.3 POPs where the analysed fish pointed to a very local pollution source: DDTs and some other pesticides

The total DDT concentrations (sum of *op*'DDT, *pp*'DDT, *op*'DDE, *pp*'DDE, *op*'DDD, *pp*'DDD) at one particular site were much higher than at any of the other sites (Figure 4.3-40). These roach also had unusually high lipid contents, but that alone did not explain the difference (Figure 4.3-42). The few fish from the Glen, which had unusually low lipid contents but fairly normal DDT contamination (compared to the others in this study), were similar to some of those from the River Lee at Wheathampstead, (only) when the data was lipid normalised (Figure 4.3-42), otherwise — whether or not lipid normalised — the fish from the Wheathampstead group had much higher DDT contamination than any of the others. Such a large difference had to have a specific cause.

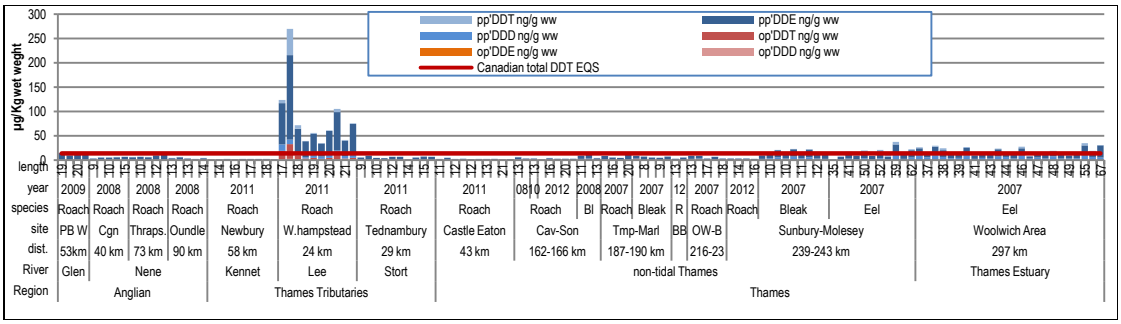


Figure 4.3-40 Concentration of DDT and its degradation and by-products DDE and DDD (*op*' and *pp*' congeners for all) of all fish analysed. Individuals at each site are ordered by species (roach, bleak, eel), year, and length (cm). Sites on each river are ordered by distance from the source (river-km). BB: Bray-Boveney 203-209 km. The Canadian Tissue Residue Guideline for the protection of wildlife consumers is also shown (there is currently no equivalent EU guideline).

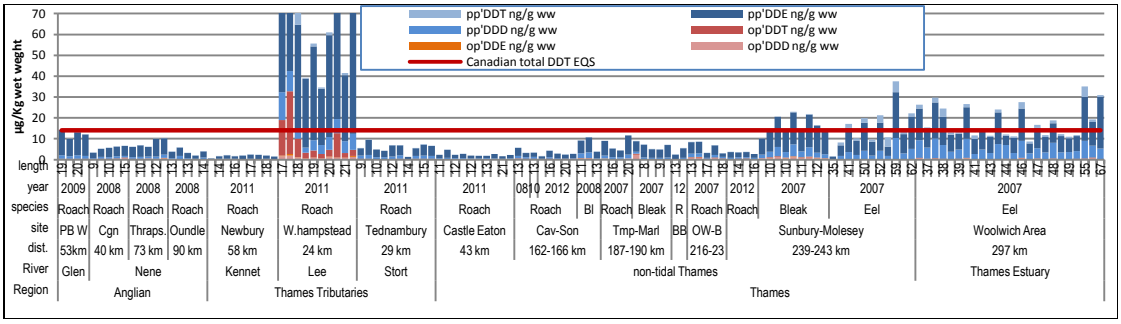


Figure 4.3-41 Detail of Figure 4.3-40.

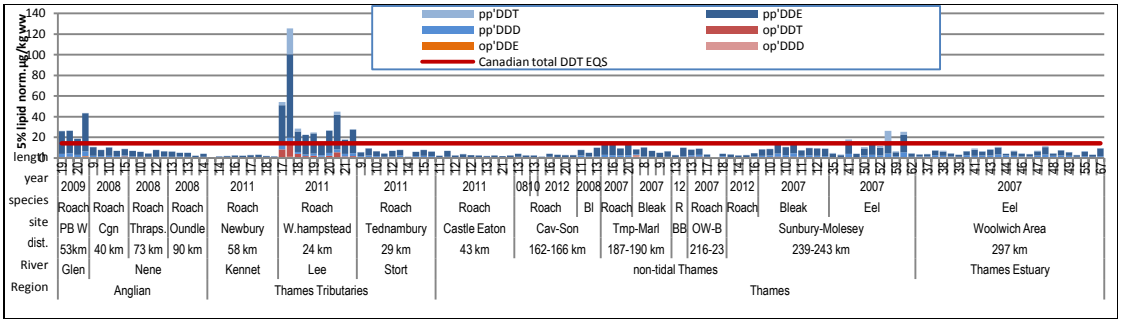


Figure 4.3-42 Figure 4.3-40 normalised to 5% lipid content.

4.3.3.3.1 Some background of the Wheathampstead site

The EA fisheries report for the River Lee (also commonly spelled "Lea") mentions that back in 1967 all fish were wiped out between Wheathampstead and Hereford (about 20 km) and fish kills were observed as far as Stanstead Abbots (about 30 km from Wheathampstead) due to a spill of the pesticide MECARBAM (UK Environment Agency 2010). Mecarbam has not been measured in this study, but it

would be worth testing for it in future studies. Another less serious fish kill affecting the sampled area was recorded in 1991 and was caused by sewage from East Hyde sewage works about 7 km upstream of the site.

A study of the genetic diversity of roach at a large number of sites in the Thames catchment, which included fish caught at the Wheathampstead site in 2010, revealed a genetic bottleneck at that site and also for roach caught at a site further upstream (Hamilton *et al.* 2014b). The EA fisheries surveys for 2003-2009 (UK Environment Agency 2010) found no roach at the Wheathampstead site before 2006, but good numbers since then, and as a weir a short distance upstream restricts movement the roach have most likely moved in from downstream.

The roach from Wheathampstead were among the largest in the whole data set and had higher lipid contents than most. To check whether the growth rate of roach at Wheathampstead is different from other rivers, the EA fisheries report was consulted (UK Environment Agency 2010), this and the superimposed ages of our own fish showed that the growth rate for roach at the Wheathampstead site was fairly standard (Figure 4.3-43).

A possible cause for the high DDT levels in this group of fish was found in an advertisement for the Murphy Chemical Company published in 1946 (Figure 4.3-44). A look into the history of this company found that it started off as Murphy and Son in 1887 selling brewing supplies, in 1928 the Wheathampstead site was acquired and the company branched out into agricultural chemicals with both research and development and production at the Wheathampstead site. While the brewery supplies firm "Murphy and Son Ltd" is still in business, but now based in Nottingham, the agro-chemicals arm "Murphy Chemical Company Ltd" in Wheathampstead was sold to Glaxo in 1956 (http://www.murphyandson.co.uk/heritage/index.html) and then changed hands a few more times (Dalgety, Dow, Fions), before eventually closing around 1990. Since the factory closed an attempt has been made to clean up the considerable pesticide contamination of the ground by removing soil for treatment and treating contaminated ground water on site in reed beds which were completed in 1998 and are, to my knowledge, still operating http://www.oceans-esu.com/case-studies/.

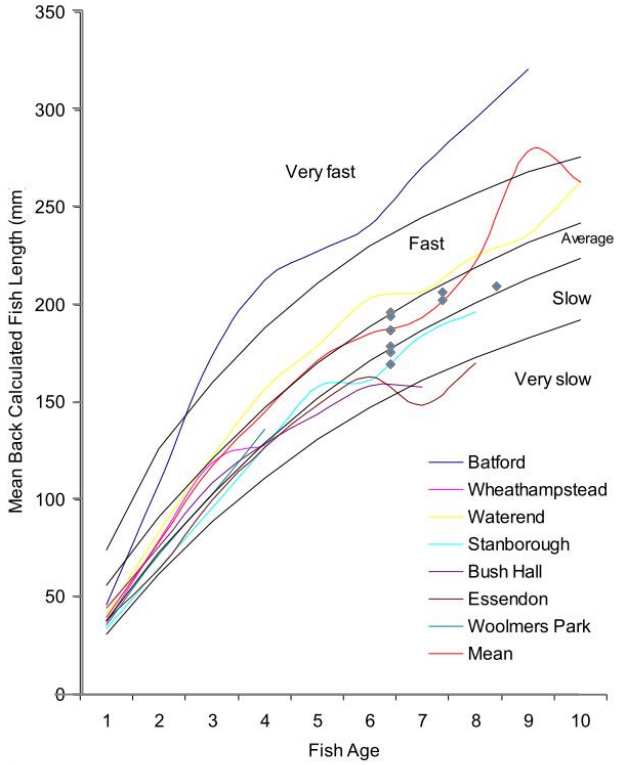


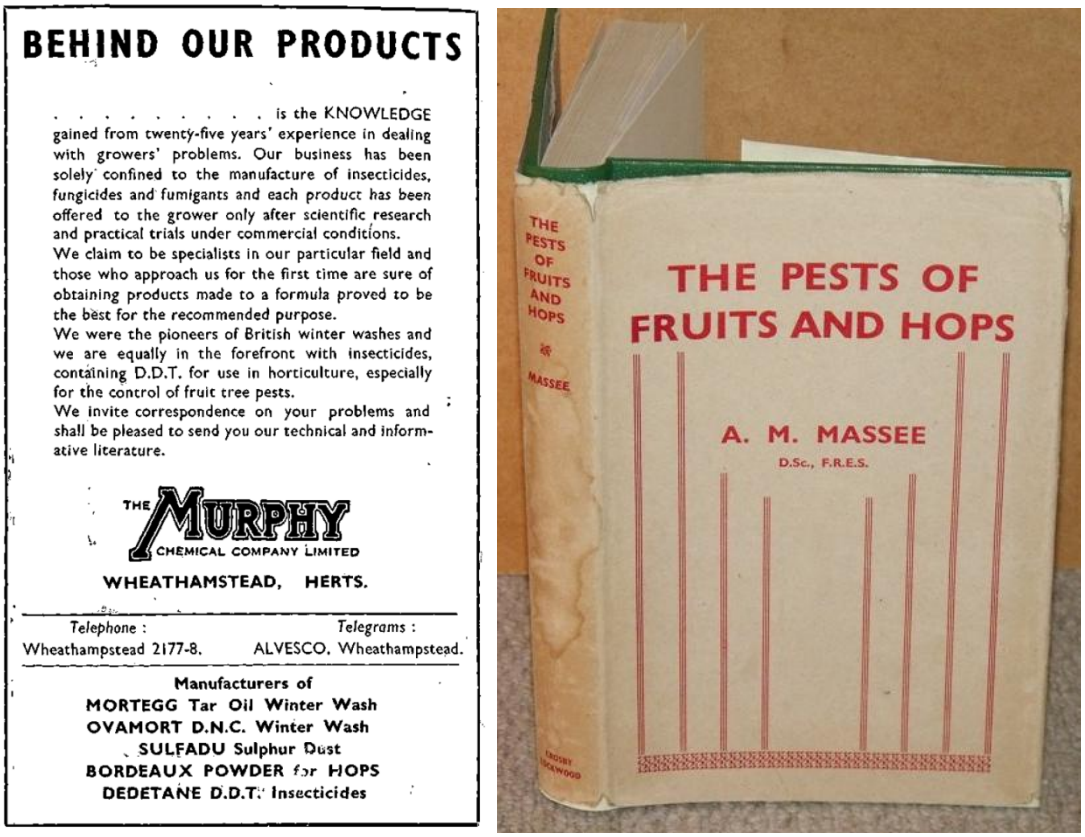
Fig 77. Graph showing the growth of roach in the Upper Lee compared to the standard growth of roach in 'southern' rivers (National Fisheries Laboratory, unpublished data)

Figure 4.3-43 Growth rates for roach in the river Lee (from 2009 fisheries report (UK Environment Agency 2010)). Roach from Wheathampsted show average growth for 1-4 year old fish (pink line). No older fish had been found at that site at that time. The ages and lengths of the 10 roach from Wheathampstead analysed here, have been marked on this older picture (ages from personal communications from Liz Nicol, Brunel University) and also show mostly average growth rates.

The case of the high DDT concentrations in fish can serve as an example how monitoring chemicals in fish tissue can be useful to spot previously unknown problems. A spike in a temporal or spatial series would indicate that something unusual happened, which warrants further investigation. Ideally more samples would be taken from the same site and sites upstream and downstream to determine how localised the problem is and whether improvements over time are evident. Also comparing the fish results with sediments and/or water would be useful, and given that a wide range of pesticides were produced and tested at the site it would be good to widen the scope from the few organochlorine pesticides currently measured.

In this case it was surprising to find total DDT concentrations to be so much higher than in any of the other samples and trying to discover the likely cause led eventually to the history of Murphy Chemical Company. Of course had we had better

knowledge of the local area we could have expected to find pesticide residues in Wheathampstead, but we didn't know about the factory. The site had been chosen on the grounds of having restricted fish movement because of weirs and relatively high sewage content due to the two sewage works upstream and to the river being quite small.



BEHIND OUR PRODUCTS

. . . . . is the KNOWLEDGE gained from twenty-five years' experience in dealing with growers' problems. Our business has been solely confined to the manufacture of insecticides, fungicides and fumigants and each product has been offered to the grower only after scientific research and practical trials under commercial conditions.
We claim to be specialists in our particular field and those who approach us for the first time are sure of obtaining products made to a formula proved to be the best for the recommended purpose.
We were the pioneers of British winter washes and we are equally in the forefront with insecticides, containing D.D.T. for use in horticulture, especially for the control of fruit tree pests.
We invite correspondence on your problems and shall be pleased to send you our technical and informative literature.

THE MURPHY CHEMICAL COMPANY LIMITED
WHEATHAMSTEAD, HERTS.

Telephone : Wheathampstead 2177-8.
Telegrams : ALVESCO, Wheathampstead.

Manufacturers of
MORTEGG Tar Oil Winter Wash
OVAMORT D.N.C. Winter Wash
SULFADU Sulphur Dust
BORDEAUX POWDER for HOPS
DEDETANE D.D.T. Insecticides

THE PESTS OF FRUITS AND HOPS
MASSEE

THE PESTS OF FRUITS AND HOPS

A. M. MASSEE
D.Sc., F.R.E.S.

Figure 4.3-44 Advert in Massee (1946).

Apple Blossom Weevil.—The control of the Apple Blossom Weevil is at last a reality, thanks to the two recently introduced insecticides D.D.T. and Benzene Hexachloride ("666").

The correct time to dust or spray against this pest is just before egg-laying begins at the "bud burst" stage, for by then the greatest number of weevils will be on the trees without causing any damage, and the persistent nature of D.D.T. will account for those which arrive afterwards.

Figure 4.3-45 Excerpt from Massee (1946), showing how what we today see as a main problem with DDT, namely its persistency, was seen as an asset back in the 1940s.-It also mentions Benzene hexachloride, which is another name for hexachlorocyclohexane or technical HCH.

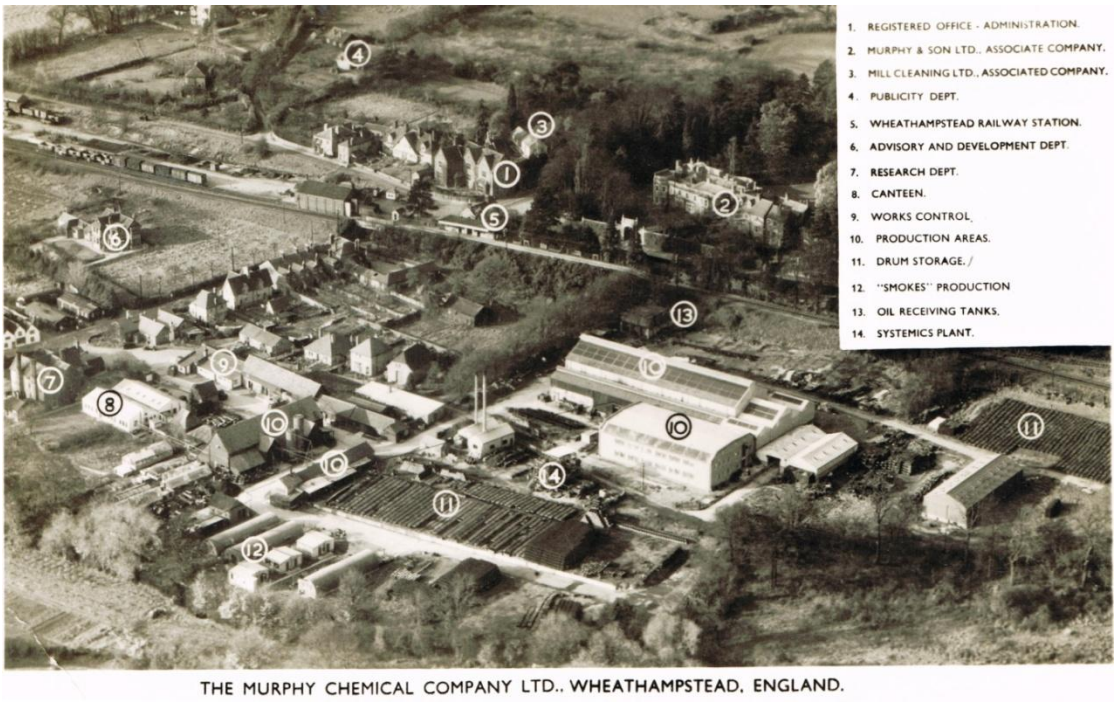


Figure 4.3-46 Postcard showing the Murphy Chemical Company in 1952 (https://www.flickr.com/photos/47716665@N02/6867783700/, the originial aerial photo is also at http://www.britainfromabove.org.uk/image/eaw047661). Building number 2 still remains, see Figures 4.3-47 and 4.3-48. The light coloured trees at the bottom of the picture are growing on the banks of the river Lee.

Figure 4.3-47 The Murphy's site in 2000, ready for housing to be built. The remaining Murphy and Son Ltd building is marked in green and the approximate area used by the Murphy Chemical Company in orange (© Google).

Figure 4.3-48 The site in 2006 (© Google).

4.3.3.3.2 Relative contributions of the constituents of "total DDT"

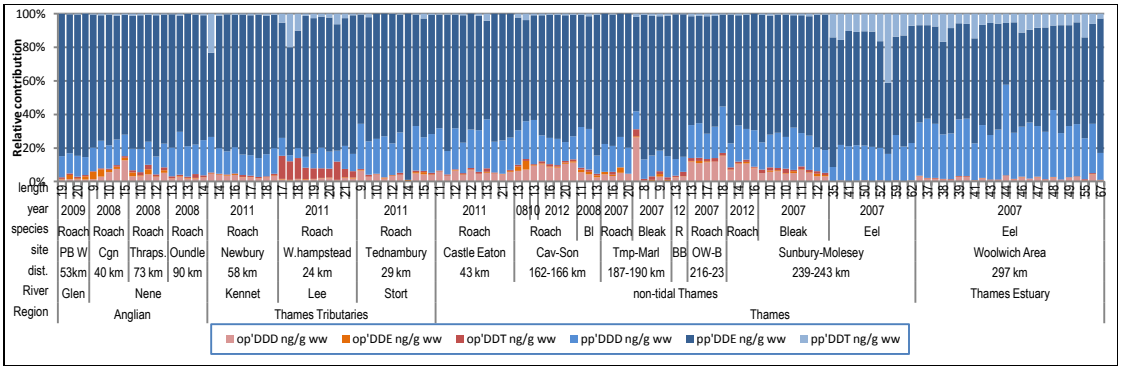


Figure 4.3-49 Relative contribution of the components of "total DDT".

The relative contribution of the 6 components of "Total DDT" (Figure 4.3-49) is roughly similar for most of the roach and bleak measured, but the eels show a slightly different pattern with very low levels of all the *op*' congeners and relatively high levels of *pp*'DDT, the main untransformed product. Maybe this is because eels are more in contact with anaerobic sediments than roach or bleak and DDT is likely to be more stable under these conditions. The roach from the contaminated Wheathampstead site also have a slightly higher relative contribution of *pp*'DDT and a particularly noticeable contribution of *op*'DDT compared to the other samples. This may reflect their closeness to the source with more of the untransformed DDTs still available. Technical DDT consists of about 85% *pp*'DDT and about 15 % *op*'DDT

(ATSDR 2002, p.2), so one would expect the ratios in fish to be similar. However while the overall ratio between the sum of all *op*' and *pp*' congeners is in some cases close to the 15:85 ratio, in most cases less of the *op*' congeners were detected. This may in part be an artefact of the methods where small amounts below the LOD were recorded as 0, but may also reflect different stability in the environment. From Figure 4.3-49 it looks like the *op*' and *pp*' DDT congeners don't break down in exactly the same way in the environment: for the *pp*' congeners *pp*'DDE is the largest contributor with *pp*'DDD and the untransformed *pp*'DDT playing only a minor role, whereas for the *op*' congeners DDD is generally more prominent than DDE.

The Wheathampstead roach have an unusual congener distribution with relatively high levels of *op*'DDT, and proportionally lower levels of both *op*'DDD and *pp*'DDD, than other fish in the study. This may reflect differences in degradation patterns perhaps triggered by the high contamination of the soil and sediment with this and perhaps other pesticides or it may reflect a difference in the original formulation used. Murphy's factory had a development department for improving pesticides, so it is likely that some formulations or varieties of formulations that were not or not yet on the market were tested on the fields close to the river Lee.

4.3.3.4 Other pesticides

The fish from the contaminated Wheathampstead site also had elevated concentrations of the insecticide lindane (γ-HCH), but not as dramatic as for DDTs (Figure 4.3-50). The situation is less clear-cut for chlordane which was higher than at the other three sites investigated for a specific project in 2011 (Kennet, Stort and Castle Eaton on the Thames, Hamilton *et al.* 2014a), but similar to some other fish caught earlier (Figure 4.3-51). The fungicide hexachlorobenzene by comparison doesn't have elevated levels at Wheathampstead, so this was perhaps not something they produced or tested there (Figure 4.3-52). Another compound mentioned in the advertisement (Figure 4.3-44), Bordeaux powder, is based on copper sulphate and copper concentrations are also slightly elevated in fish from the Wheathampstead site (Figure 4.3-53).

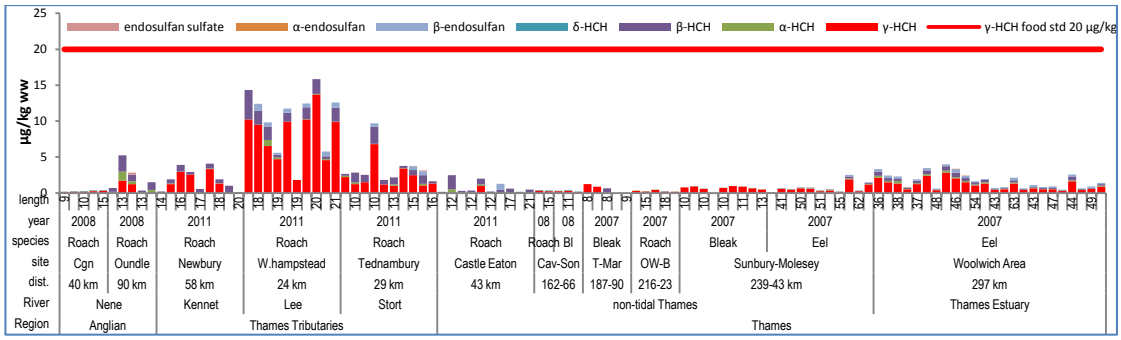


Figure 4.3-50 HCHs including lindane (γ-HCH) and endosulfans. There are no EQS for these substances and the food standards (meat, none available for fish) are 20 µg/kg for γ-HCH and 50 µg/kg for endosulfan.

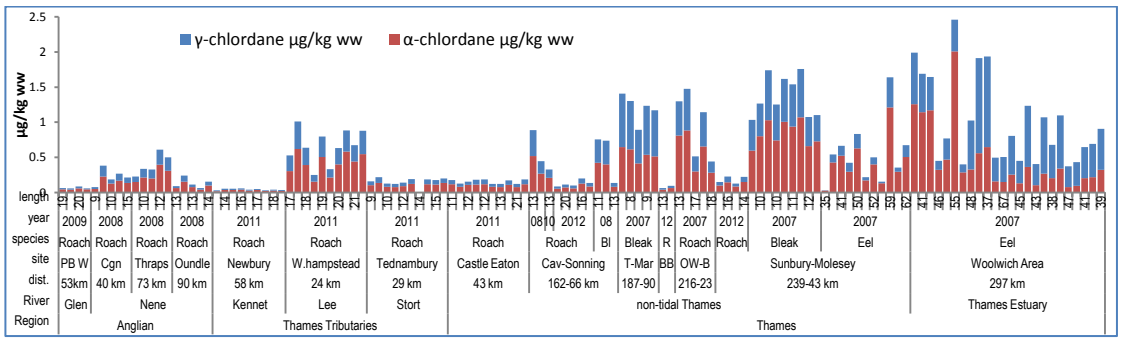


Figure 4.3-51 Chlordane α+γ. The food standard of 50 µg/kg for the sum of the two congeners (for meat, none exists for fish) (European Commission 2005b) is well outside the range of this graph.

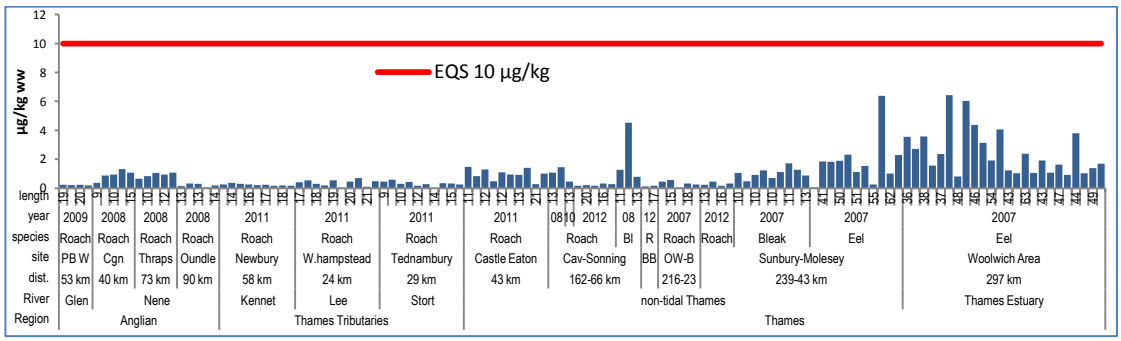


Figure 4.3-52 All HCB contents determined. Sorted by region, river, site (km refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

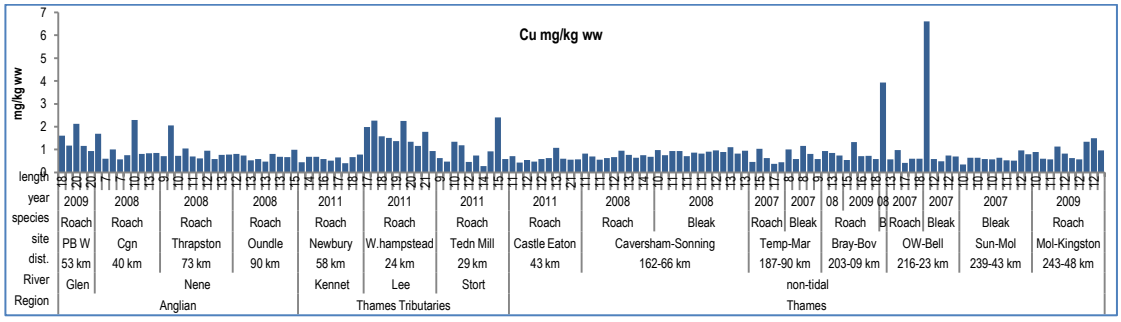


Figure 4.3-53 All copper contents determined. Sorted by region, river, site (dist. refers to distance downstream of the source), species and year. Within each of those groups the individuals are ordered by length.

4.3.3.4.1 Correlations of pesticides with fish or site parameters

Total DDT, chlordane (α+γ), lindane and HCB were checked against weight of the fish, distance from the source, and estimated sewage content at the site, and none showed a clear trend. There was a weak correlation between chlordane (α+γ) and estimated sewage content (Figure 4.3-54), but this was mainly influenced by the two sites with the lowest sewage content. Total DDT in roach compared to size of the fish, distance of the sampling site from the source of the rivers, and average proportion of treated sewage the fish experience at that site are shown as examples for those parameters that do not seem to have an influence in Figures 4.3-58 - 4.3-60.

Other than the special case of the former factory and test beds at Wheathampstead, pesticides would be expected to be associated with agricultural areas and sometimes specific crops, so it is not very surprising that there is no particular link with sewage content of the river or even whether the site is more upstream or downstream, but there are links with land cover. It was expected that despite having been banned some time ago, organochlorine pesticide concentrations would be positively correlated to the percent of land covered by cereals or horticulture/non-rotational agriculture, but surprisingly, for chlordane this correlation was negative Figure 4.3-55, while it was positively correlated with percentage urban area (Figure 4.3-56) and slightly less strongly (R^2=0.48) suburban/rural developed. The association between urban areas and sewage may be the reason that it also had a positive correlation with modelled % sewage (Figure 4.3-54). No correlations with land cover were found for HCB. For DDT (excluding the special case of the Wheathampstead site) there was some correlation with the percentage of the catchment covered by horticulture and other non-rotational agriculture.

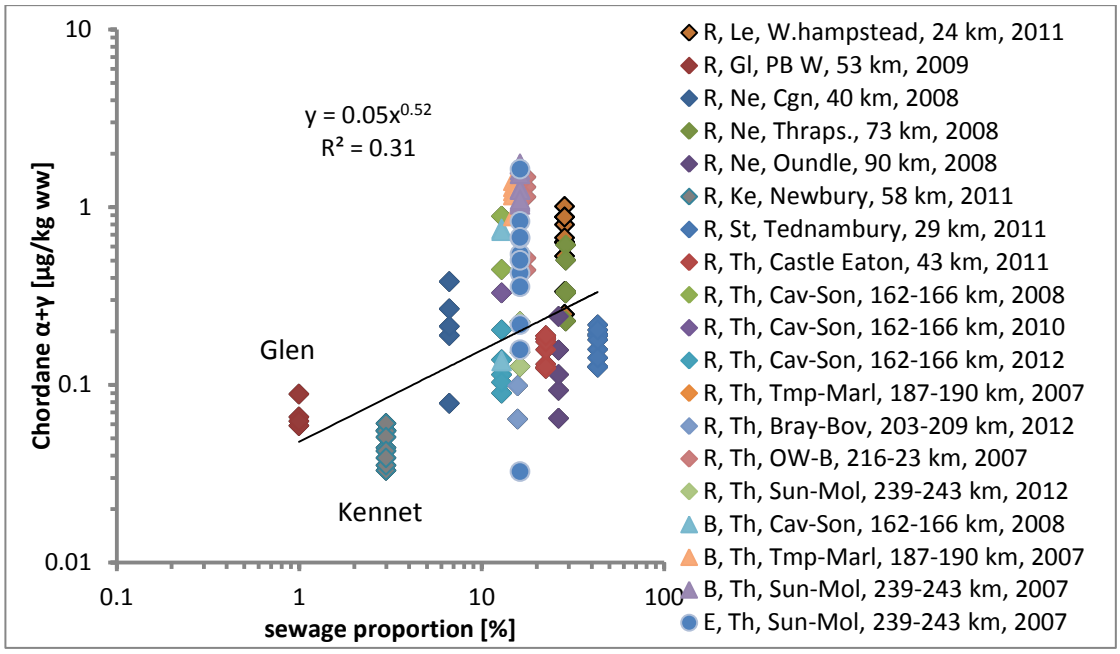


Figure 4.3-54 Sum of α+γ chlordane compared to the estimated average sewage content of the river. The regression is for roach (R, ◊). Bleak data (B, Δ) were only available from three very similar sites and eel data (E, ○) only from one, so it doesn't make sense to calculate their regressions, but they are plotted for information. Rivers: Lee (Le), Glen (Gl), Nene (Ne), Kennet (Ke), Thames (Th).

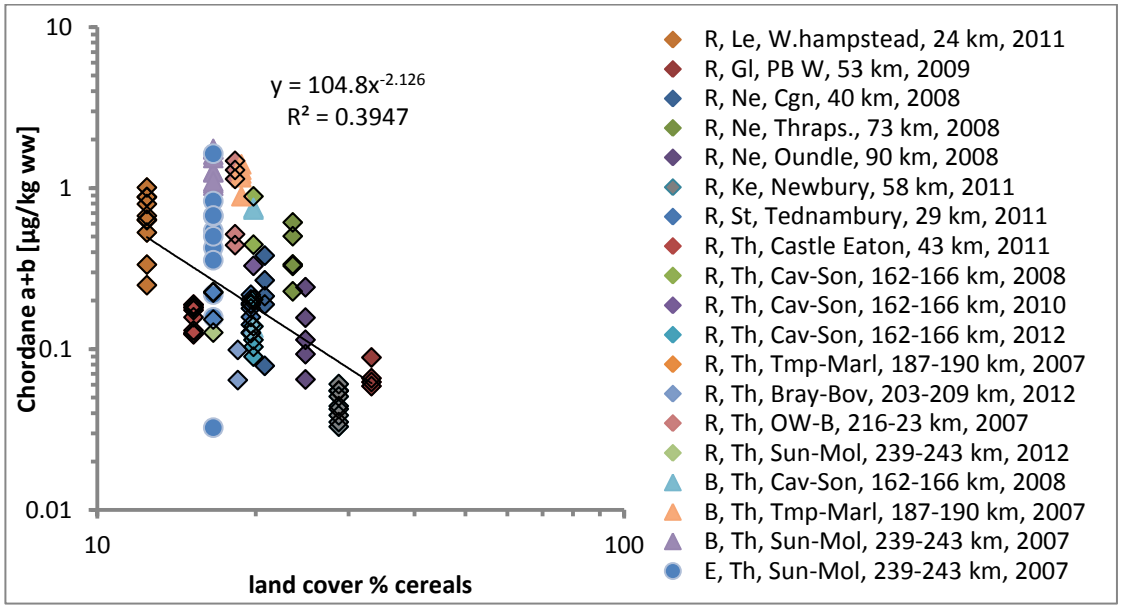


Figure 4.3-55 Sum of α+γ chlordane compared to the percentage of cereals in the landcover of the catchment. The regression is for roach (R, ◊). Bleak data (B, Δ) were only available from three very similar sites and eel data (E, ○) only from one, so it doesn't make sense to calculate their regressions, but they are plotted for information. Rivers: Lee (Le), Glen (Gl), Nene (Ne), Kennet (Ke), Thames (Th).

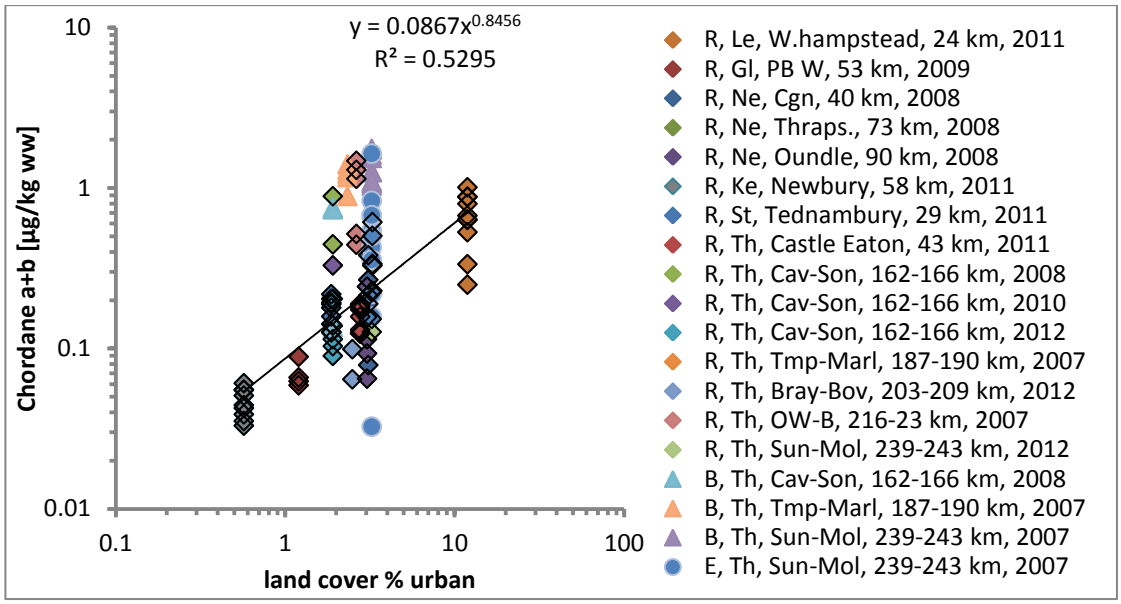


Figure 4.3-56 Sum of α+γ chlordane compared to the percentage of urban areas in the landcover of the catchment. The regression is for roach (R, ◊). Bleak data (B, Δ) were only available from three very similar sites and eel data (E, ○) only from one, so it doesn't make sense to calculate their regressions, but they are plotted for information. Rivers: Lee (Le), Glen (Gl), Nene (Ne), Kennet (Ke), Thames (Th).

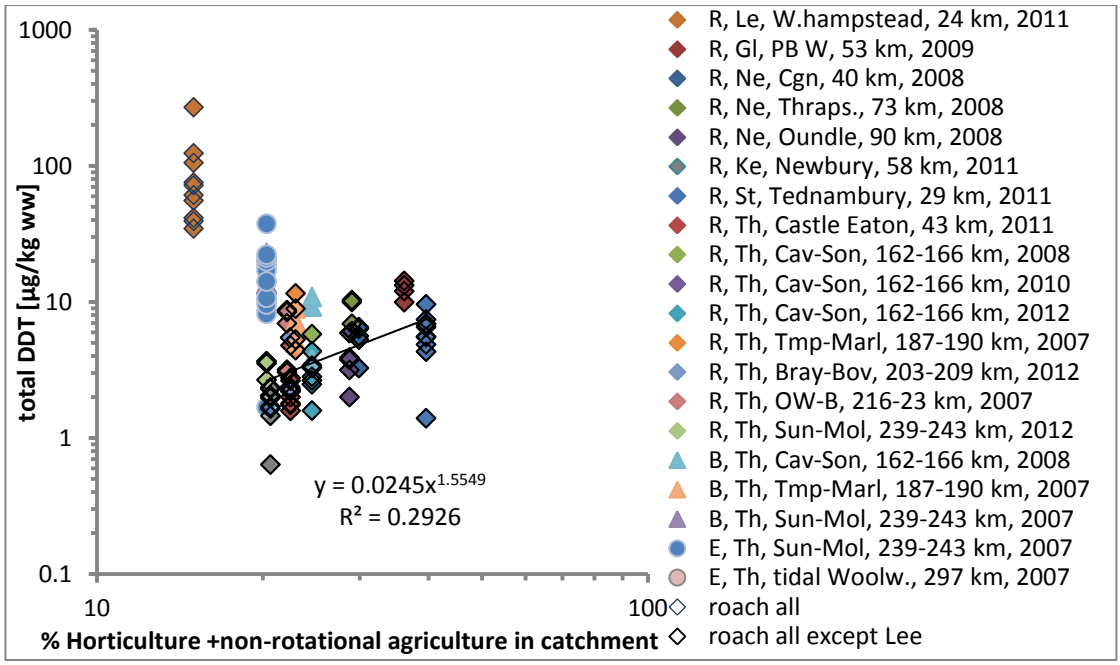


Figure 4.3-57 Sum of DDTs compared to the percentage of horticulture/other non rotational agriculture in the landcover of the catchment. The regression is for roach (R, ◊). Bleak data (B, Δ) were only available from three very similar sites and eel data (E, ○) only from one, so it doesn't make sense to calculate their regressions, but they are plotted for information. Rivers: Lee (Le), Glen (Gl), Nene (Ne), Kennet (Ke), Thames (Th).

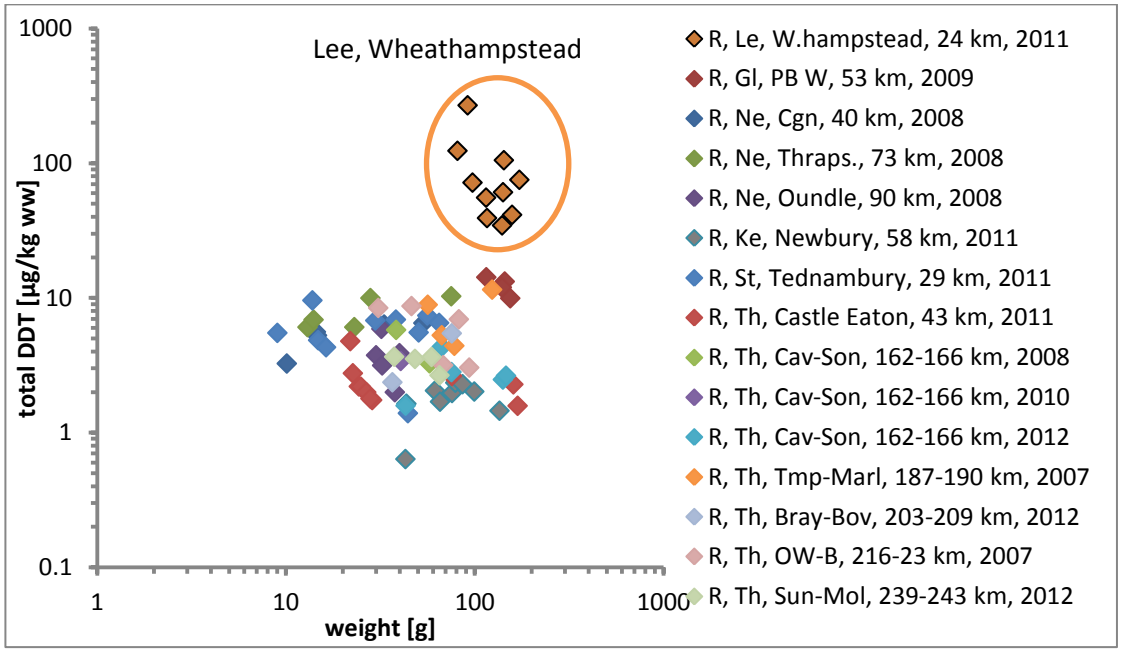


Figure 4.3-58 Total DDT concentration compared to the weight of fish (only roach plotted for simplicity). Rivers: Lee (Le), Glen (Gl), Nene (Ne), Kennet (Ke), Thames (Th).

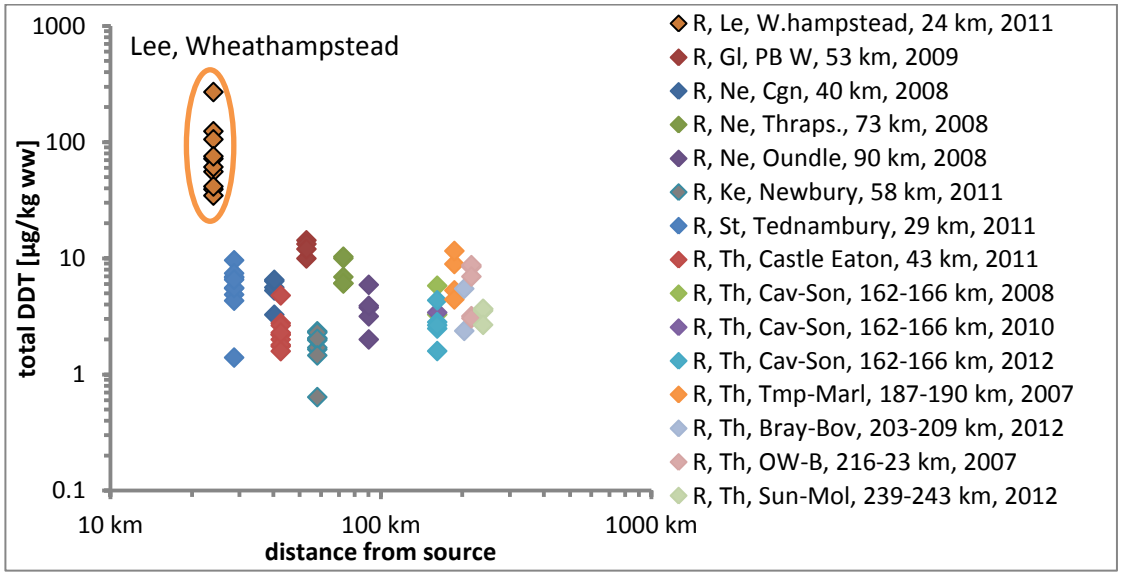


Figure 4.3-59 Total DDT concentration compared to the distance of the site from the source of the river (only roach plotted for simplicity).

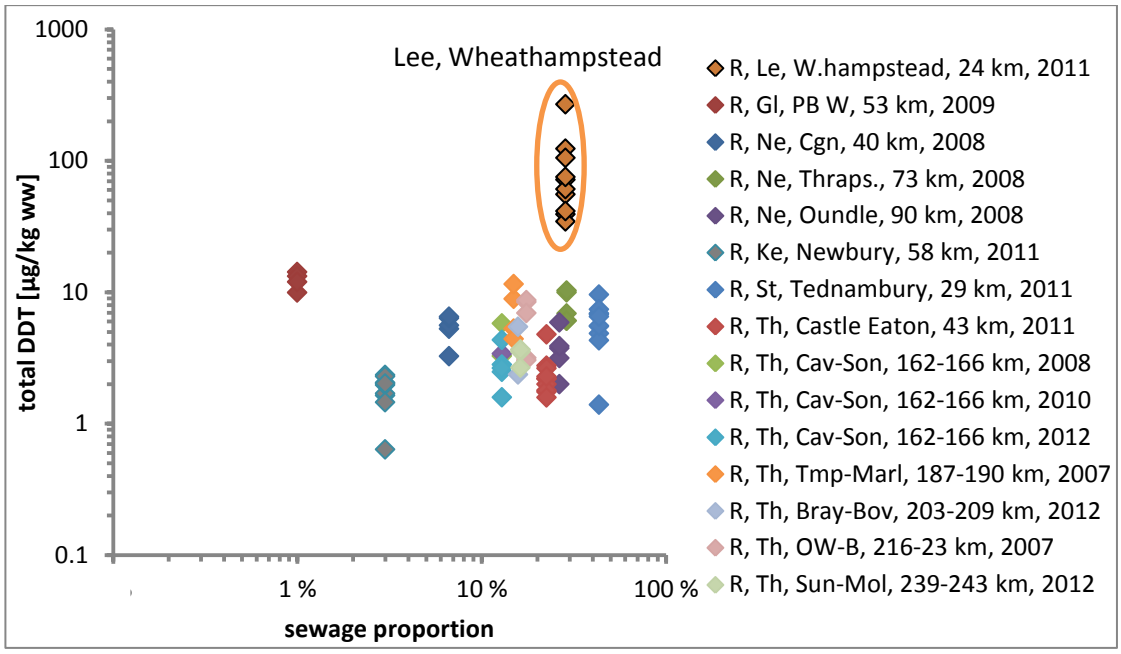


Figure 4.3-60 Total DDT concentration compared to the average proportion of treated sewage at the site (only roach plotted for simplicity).

4.3.3.5 Summary of patterns found for contamination with persistent organic pollutants

- PBDE concentration in the fish was correlated to the estimated sewage content at the sampling sites, confirming the previous observations that a major route for brominated flame retardants to enter the aquatic environment is through domestic sewage
- PCB contamination was also correlated with sewage content but more weakly than PBDE. This probably reflects the fact that PCBs are associated with pollution from (former) industrial and urban areas and sewage content can be seen as a proxy for population or industrial densities
- The pesticide DDT and its degradation and by products DDE and DDD (=total DDT) and to a lesser extent lindane, chlordane, and copper were found at high concentrations in the 10 fish from the Wheathampstead site on the river Lee, compared to the other fish analysed. The cause is likely to be found in a pesticide factory and research unit which occupied an area close to the site for much of the 20th century.

- The DDT example shows how unexpected “spikes” in the spatial or temporal monitoring data can pinpoint to a previously unknown (at least to us) issue, that warrants further investigation.

4.4 The Fish Archive samples in a European context

Most of the monitoring data for contamination in fish concerns marine species, probably because humans consume far more marine than freshwater fish and a lot of the fish monitoring is done for food safety reasons. Even, where the primary reason for monitoring marine or freshwater species is for environmental trend monitoring or concerns for the health of fish or their predators, species commonly consumed by humans are often chosen. Perhaps this is for practical reasons, such as availability, experience with fishing these species, or the possibility of combining monitoring for food safety and environmental monitoring in the same samples. Species that are of interest for human consumption are also often (top) predators, which are often more contaminated than their prey, therefore representing a worst-case scenario.

On the other hand humans tend to consume only the fillet of most fish and therefore the monitoring often focuses on that, while most other predators would eat the whole animal, although sometimes bones are regurgitated. In this study we measured whole body homogenates, which is most appropriate if the concern is for wildlife, but most literature studies measured chemicals only in the fillet. For mercury, a published conversion between whole-body concentrations and fillet concentrations is available (see Chapter 4.4.1.1), but this information is lacking for other chemicals, so the only choice is between disregarding most of the data or treating both sample types the same, i.e. using an arbitrary factor of 1.

As it is not always appropriate to compare the freshwater and marine environment, the focus of this chapter is as much as possible on the same species that we investigated in this study and on freshwater, but in the case of eels also including estuary/lagoon data.

For the German Environmental specimen bank, which collects large bream "reference" values have been published (Paulus *et al.* 2005). These represent the 25 percentile and 75 percentile of recent data. Values between those percentiles are seen as within the "normal" range, while values above or below that are either high or low. How many years have been included in the calculation of the percentiles depends on whether there was a temporal trend. If there was no trend then all data was used, and

otherwise from whatever time the trend seems to have flattened (and therefore only the last year if the trend was still ongoing at the time of setting the reference values?).

This system has since been updated and refined into 4 reference values which define the boundaries between 5 reference ranges (RR): exceptionally low, low. medium, elevated, exceptionally elevated - and are defined for 2 year periods (Teubner 2010, Teubner *et al.* 2013). Table 4.4-1 shows the reference ranges for the years 2007/2008 (the latest range given in Teubner 2010).

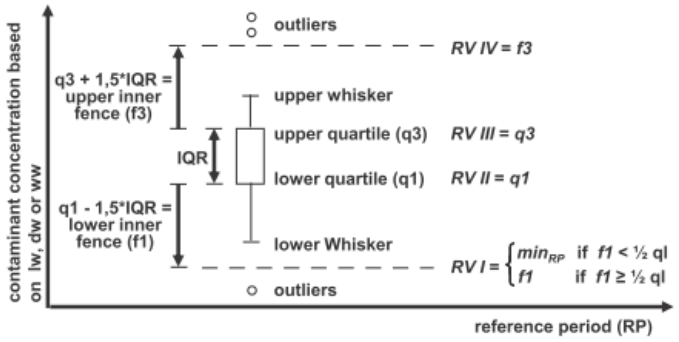


Fig. 1. Scheme for derivation of the reference values (RV): lw = lipid weight, dw = dry weight, ww = wet weight, IQR = inter quartile range, min = minimum, ql = quantification limit.

Figure 4.4-1 Scheme for deriving 5 categories for pollution or biometric parameters in the German ESB (Teubner *et al.* 2013). (It isn't mentioned what the whiskers in this graph represent, eg. 10%ile and 90%ile or 5%ile and 95% etc. but this doesn't matter as this value is not used in the calculations).

Table 4.4-1 Some reference values (RV) from the German ESB for 8-12 year old bream for the years 2007/08 (Teubner 2010, Teubner *et al.* 2013). RV1 is either 25%ile-1.5*interquartile range or minimum value measured (see Figure 4.4-1), RV2 is the 25%ile, RV3 75%ile, RV4 75%ile+1.5*interquartile range. Concentrations are for muscle tissue. Chemicals that were only measured in bream liver such as cadmium and cobalt are not included.

compound or parameter	Unit	very low <RV1	low RV1-25%ile	normal 25-75%ile	high 75%ile-RV4	very high >RV4
weight	g	561	561-1099	1099-1638	1638-2445	>2445
fork length	cm	<33	33-41	41-46	46-53	>53
condition factor	g/cm^3	<0.83	0.83-1.05	1.05-1.20	1.20-1.42	>1.42
water content	%	<74.7	74.7-76.2	76.2-79.9	79.9-81.1	>81.1
fat content	%	<1.79	1.79-2.62	2.62-6.56	6.56-7.51	>7.51
copper	mg/kg dw	<0.910	0.910-1.21	1.21-1.40	1.40-1.70	>1.70
mercury	µg/kg dw	<106	106-534	534-1492	1492-2929	>2929
lead	µg/kg dw	<5.69	5.69-22.9	22.9-63.5	63.5-124	>124
arsenic	mg/kg dw	<0.112	0.112-0.333	0.333-0.592	0.592-0.980	>0.980
selenium	mg/kg dw	<1.13	1.13-2.83	2.83-3.97	3.97-5.68	>5.68
HCB	ng/g lipid	<13.0	13.0-59.5	59.5-512	512-1190	>1190
α-HCH	ng/g lipid	<0.884[a]	<0.884a	0.884a-17.1	17.1-41.3	>41.3
β-HCH	ng/g lipid	<0.356a	0.356a-0.933	0.933-24.8	24.8-60.5	>60.5
γ-HCH	ng/g lipid	<4.09a	<4.09a	4.09a-17.9	17.9-38.6	>38.6
pp'DDE	ng/g lipid	<84.4	84.4-192	192-2962	2962-7117	>7117
pp'DDD	ng/g lipid	<11.7	11.7-42.2	42.2-1679	1679-4134	>4134
pp'DDT	ng/g lipid	<0.515a	0.515a-1.52	1.52-34.3	34.3-83.4	>83.4
op'DDT	ng/g lipid	<0.620a	0.620a-5.83	5.83-214	214-527	>527
PCB 28	ng/g lipid	<56.7a	<56.7a	<56.7a	56.7a[b]	>56.7a
PCB 52	ng/g lipid	<7.26a	7.26a-48.0	48.0-263	263-587	>587
PCB 101	ng/g lipid	<58.1	58.1-150	150-497	497-1016	>1016
PCB 118	ng/g lipid	<23.3	23.3-94.4	94.4-257	257-502	>502
PCB 138	ng/g lipid	<216	216-408	408-1126	1126-2202	>2202
PCB 153	ng/g lipid	<217	217-423	423-1256	1256-2507	>2507
PCB 180	ng/g lipid	<104	104-165	165-553	553-1135	>1135

[a] ½ LOD

[b] RV3(75%ile) was 130 ng/g lipid in 2005/08, making RV4 240 ng/g lipid

4.4.1 Selected metals

Metals were only measured in roach and bleak, but a lot of the available literature data is for eels. For mercury, food legislation takes into account that eels are often more contaminated than other species, but consumption of eels is relatively low, by allowing twice as much mercury in eels for human consumption than in other freshwater fish.

Since no recent data for roach or bleak from other European countries was found, the data for some particularly toxic metals, mercury lead and cadmium from this study was compared to other species such as eels, but it has to be remembered that there may be significant species differences related, for example, to the fact that eels are much more associated with the sediment than other fish species.

4.4.1.1 Mercury

The mercury concentrations in the current study were almost a factor 10 lower than those found in Germany in 8-12 year old bream where the muscle tissue Hg values were mostly around 200 µg/kg in the most recent (2009) samples (Lepom *et al.* 2012). Most of the literature data is for muscle (fillet) samples rather than whole body homogenates and since mercury accumulates mainly in the muscle, the fillet concentrations tend to higher than the whole body homogenates (Peterson et al. 2004). Peterson et al. (2007) found an excellent regression when the whole body and fillet concentrations of 208 fish from 13 species with a wide range of mercury concentrations were compared (Figure 4.4-2). Using the equation given by (Peterson *et al.* 2007) whole body mercury concentrations can be converted to estimated fillet concentrations or vice versa.

log (fillet Hg [µg/g]) = 0.2545 + 1.0623 log (whole-fish Hg[µg/g])

or

log (whole-fish Hg [µg/g]) = 0.9414 log fillet Hg[µg/g]) -0.23396

The relative amounts of mercury in the fillet and whole fish depend on the concentration. Therefore it is important to enter the concentrations into the equation in the correct units. Converting the above equations to µg/kg, to facilitate the conversion of values in the current study gives:

log (fillet Hg [µg/kg]) = 0.0676 + 1.0623 log (whole-fish Hg[µg/kg])

or

log (whole-fish Hg [µg/kg]) = 0.9414 log fillet Hg[µg/g]) – 0.063635

According to these equations, the concentration in the fillet is between 1/3 and 3/4 higher than in the whole body for realistic concentrations between 10 and 1000 µg/kg ww.

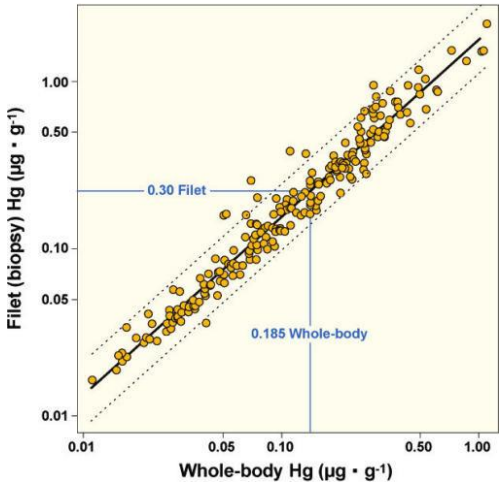


Figure 4.4-2 Correlation between muscle and whole body mercury concentration in 208 fish (reproduced from Figure 2 in Peterson et al. 2007 which is Figure 3 in Peterson *et al.* 2004 without two outliers). The regression is log [fillet biopsy Hg] = 0.2545 + 1.0623 log [whole-fish Hg]. R^2=0.957. Dotted lines are the 95% confidence limits on the prediction for an individual fish.

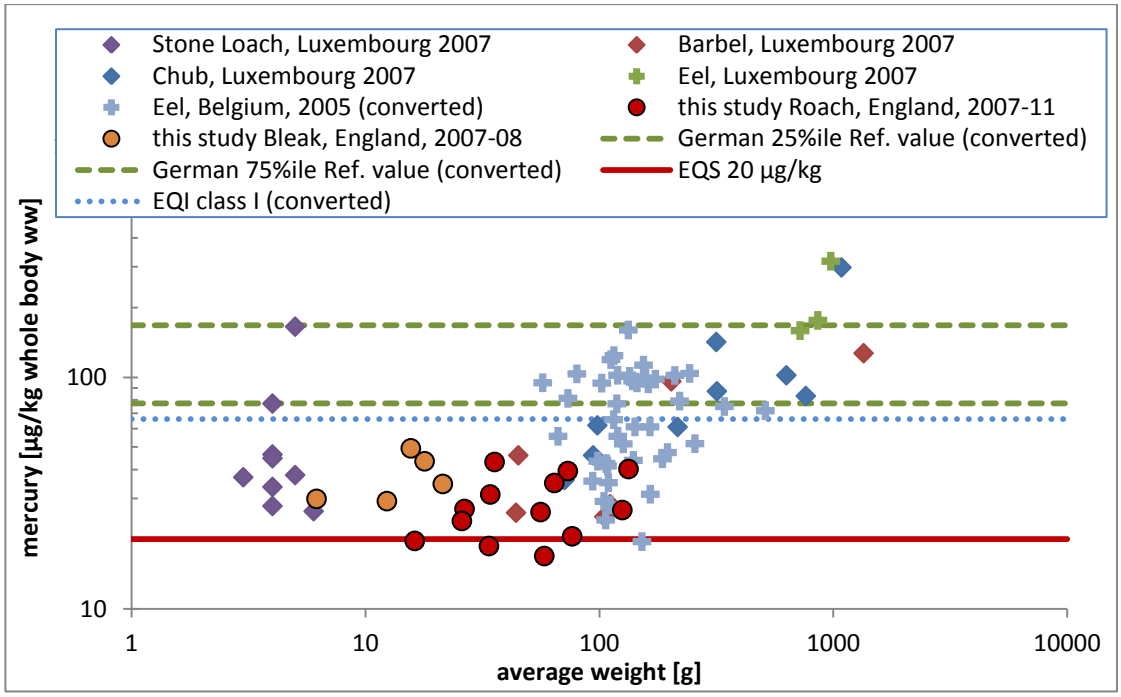


Figure 4.4-3 Mercury data from whole body homogenates compared to recent European literature data for a number of species, plotted against the weight of the fish. Where the literature data was given for muscle tissue, it was converted to whole body concentrations using the relationships published by Peterson *et al.* (2007). The Belgian data are taken from Belpaire (2008), choosing only samples from 2005 (the last year available) and the values for Luxembourg are from Boscher *et al.* (2010). The area between the dashed green lines is regarded as "normal" concentrations in the German ESB for 8-12 year old bream caught in 2007/08 (Teubner 2010). The eel quality index value (EQI, see chapter 4.4.2.1) is from Belpaire and Goemans (2007) The EQS of 20 µg/kg is marked with a red line.

Mercury concentrations tend to increase with age (Boscher *et al.* 2010) and trophic level, so the lower values found for the relatively small roach and bleak collected in this study compared to the much larger bream in Germany may reflect this.

The values measured in the present study are indeed in the same range as those measured in 2007 in whole body homogenates of chub and barbel of a similar size from Luxembourg: their concentrations ranged from 10-68 µg/kg for the sites where all analyzed fish were small (27-120 g), whereas several hundred µg/kg were found in larger (1-2 kg) chub, barbel and eels (Boscher *et al.* 2010) and there was an overall trend towards higher values for larger fish even with different species and studies (Figure 4.4-3).

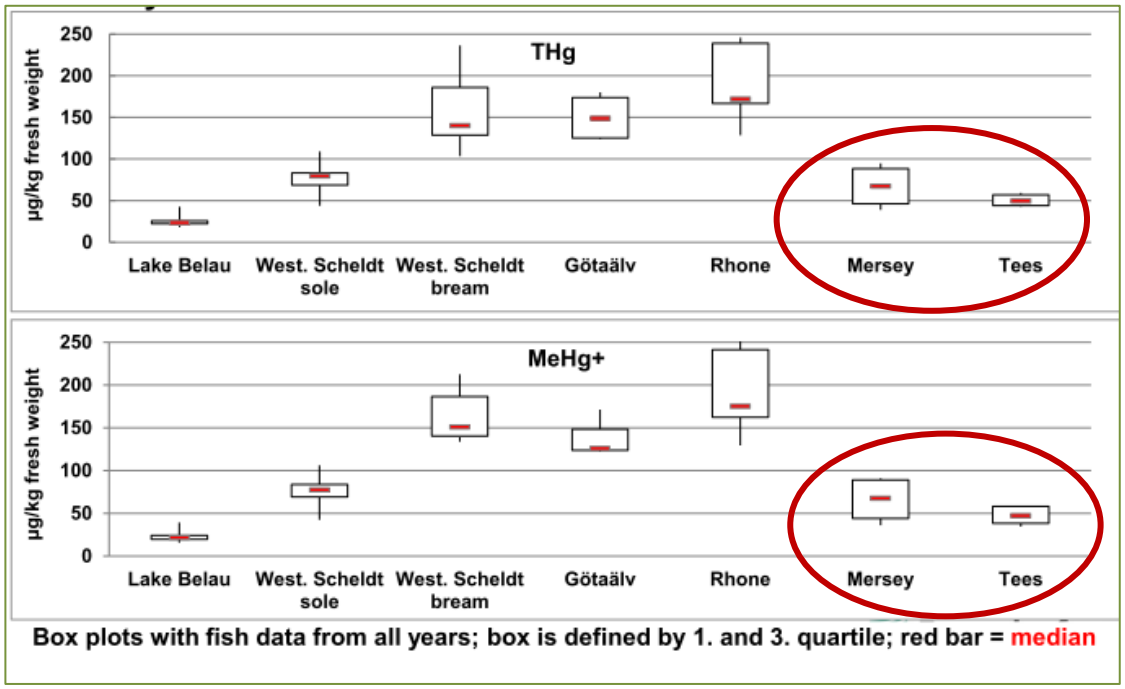


Figure 4.4-4 Comparison of recent mercury data (THg = total mercury, MeHg = methyl mercury) in Bream and sole from a number of European sites (Knopf *et al.* 2014): Lake Belau, a clean lake in Germany, Western Scheldt (Netherlands), Götaälv (Sweden), Rhone (France), Mersey and Tees (England). All results are for large 8-12 year old bream except for the samples of sole additionally collected in the Western Scheldt.

In a recent study of mercury concentrations across Europe (Knopf *et al.* 2014), the mercury concentrations in bream at the two English sites were low compared to those from the other European rivers. Only bream from the control site Lake Belau had lower contamination. The last site in the UK where mercury is still used at a large scale is located in Runcorn (just outside Liverpool) on the river Mersey, but the site where the bream were caught is about 20 km upstream from there, so it is unlikely that the bream have been influenced by any possible contamination from Runcorn.

4.4.1.2 Lead

Lead concentrations in the roach from this study were mostly in the medium and high categories according to the German ESB standards for bream (Table 4.4-1), but all within the allowed range for human food, but of course roach or bleak are not entirely comparable to bream which are also cyprinid but much larger (about 1.1-1.6 kg, see Table 4.4-1) than roach or bleak.

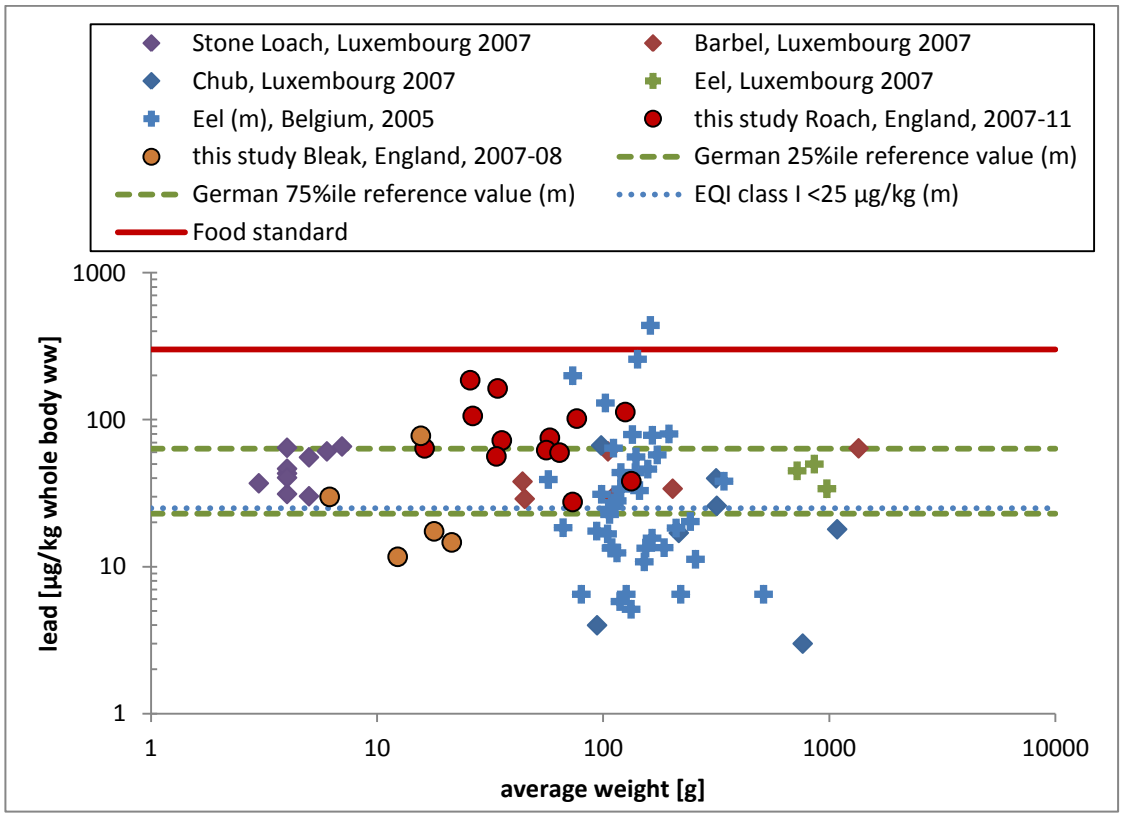


Figure 4.4-5 Lead concentrations compared to recent European literature data, plotted against the weight of the fish (Belgium: Belpaire 2008, only samples from 2005 chosen, Lux: Boscher *et al.* 2010). Whole body concentrations unless marked (m) in the legend. The area between the dashed green lines is regarded as "normal" concentrations in the German ESB for 8-12 year old bream caught in 2007/08 (Teubner 2010). The eel quality index value (EQI, see chapter 4.4.2.1) is from Belpaire and Goemans (2007) The food standard of 300 µg/kg is marked with a red line.

4.4.1.3 Cadmium

The average cadmium concentrations for the bleak and roach were relatively low compared to the fish from Luxembourg and the Netherlands plotted in Figure 4.4-6.

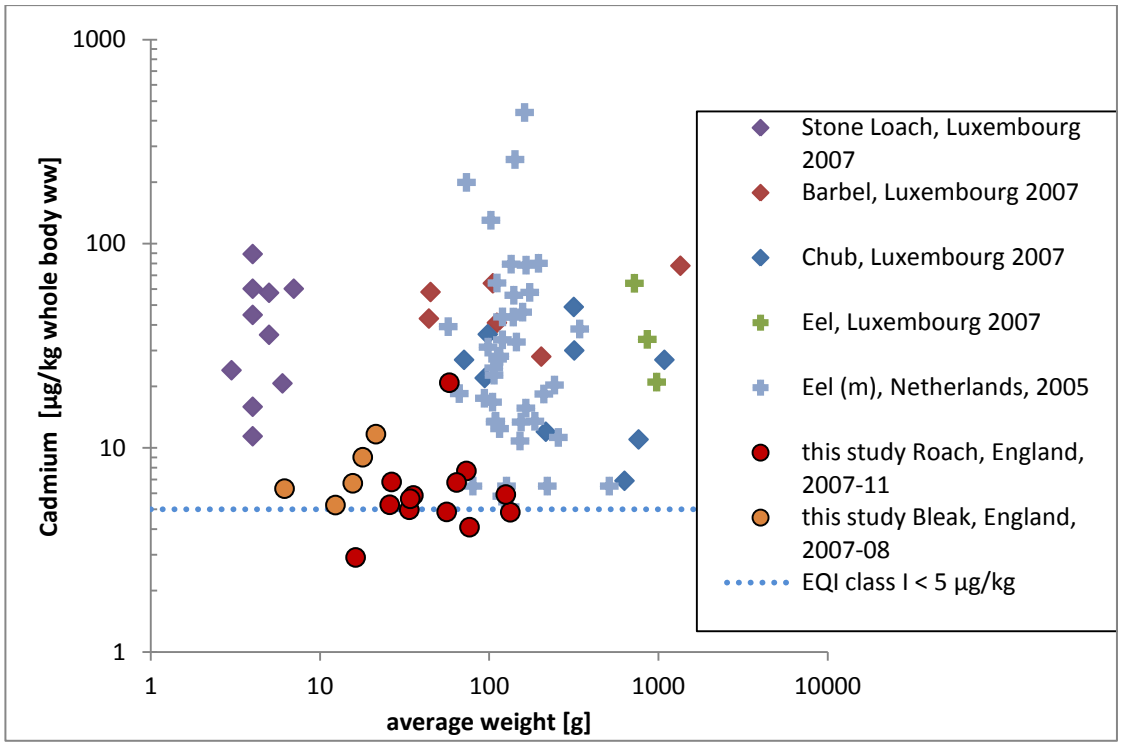


Figure 4.4-6 Cadmium concentrations compared to recent European literature data, plotted against the weight of the fish (NL: Belpaire 2008, only samples from 2005 chosen, Lux: Boscher *et al.* 2010). Whole body concentrations unless marked (m) in the legend. The area between the dotted green lines is regarded as "normal" concentrations for bream in the German ESB (Paulus *et al.* 2005, converted from dw to ww using the water content above).

4.4.2 Organochlorine pesticides and PCBs in eels

Eels are very suitable for monitoring because their long life and high lipid content mean they accumulate more persistent hydrophobic chemicals than other species. Furthermore, during the yellow eel phase they tend to spend many years in the same area, making them a representative sampler for the water bodies in which they reside.

For this reason and because the relatively high contamination compared to other species may be of concern to human health, there is more data on contamination of eel than perhaps any other freshwater species. Eels are therefore very suitable for an international comparison and have been chosen to use for comparing data from the current study to literature values from other countries. However, when comparing data from different studies, ideally eels of a similar maturation stage should be compared. Eels that are about to start the spawning migration need to have a very high fat content

but those that are still several years away from setting off have a lower fat content. Migrating eels are known as silver eels (see introduction) While eels in their continental growth phase are called yellow eels. Ideally the gender should also be known, because males mature much earlier and at a smaller size than females, so two eels of the same length could be a male which is about to start its spawning migration and needs to have a considerable fat content to achieve that and a female, that will spend perhaps another 5 or 10 years in freshwater building up fat reserves before she starts her migration. Gender information is, however, rarely published along with the chemical analysis, perhaps because eels in the yellow stage are difficult to sex. Regrettably this information was not available for the present study either, because the data supplied included some implausibly large "males" casting doubt over the reliability of the information.

We received 24 eels from the Thames estuary and 11 from the non-tidal part of the lower Thames from the Environment Agency and analysed them for PCBs and organochlorine pesticides (Table 4.4-3). Of these, the more commonly analysed POPs were compared to recent European studies in Table 4.4-4 and Figures 4.4-7 to 4.4-12.

4.4.2.1 The Eel Quality Index (EQI)

To facilitate comparison and interpretation of concentrations of contaminants in eels and in recognition that, for successful reproduction, the quality of potential spawners is as important as their quantity, an eel quality index (EQI) has been developed in Belgium (Goemans *et al.* 2003, Belpaire and Goemans 2007). This is based on an original dataset of eels from 303 Belgian sites and is now also used in other countries (eg. Amilhat *et al.* 2014, Couderc *et al.* 2015). For each of the Belgian sites the mean concentrations were calculated for a number of chemicals; for each compound these means were then ranked and the 5%ile defined as background or reference value (RV). Eels are classed depending on how much they deviate from that value with log(conc/RV) <0.4, classed as "I: not deviating" 0.4-0.8 "II: slightly deviating", 0.8-1.2 "III: deviating" and >1.2 "IV: strongly deviating" (on a linear scale the limits translate to <2.5, 2.5-6.3, 6.3-15.8 and >15.8 times the reference value).

For example, the total DDT RV is: 16 µg/kg, so less than $16*10^{0.4}$=40 µg/kg is class I, and therefore high quality. The original published boundaries from Belpaire and Goemans (2007) are reproduced in Table 4.4-2. Although this is a purely statistical approach and does not indicate whether the observed concentrations are toxic, it helps to compare data from different studies. An average classification can then also be derived across different chemicals and with appropriate extensions to the published reference values even including non-chemical parameters, for example indicators of fish health and condition, such as infection rates (Amilhat *et al.* 2014).

According to the EQI, 91% of the upstream and 75% of the estuary eels were class I with the rest class II for ΣICES7 PCBs and for the individual PCBs classified the majority of the eels were also in class I, except for PCB52 where almost half were in class 3 and 4.

With regards to pesticides the Thames eel were all in class I for total *pp*'DDTs, *pp*'DDE, and lindane and most were in class I for α-HCH and *pp*'DDD. For HCB the largest number (16) were in class II with 11 and 8 in classes I and III respectively. The only poor performance seemed to be with regards to *pp*'DDT which has the lowest RV of the compounds investigated (by a factor of 10), although for total *pp*'DDTs all the eels were all class I. It would be worth checking whether or how that RV may have been influenced by non-detects. Overall this shows that the observed concentrations of most of the measured chemicals in the lower Thames eels are comparable to those from some of the less contaminated sites in Belgium.

Table 4.4-2 Reference values for the eel quality standard (Belpaire and Goemans 2007). "log RV", should really be log(conc./RV) and sum PCBs refers to ICES7 (Goemans *et al.* 2003).

Table III. – Reference values and boundary values of the quality classes for a series of heavy metals, PCB congeners and organochlorine pesticides as defined in the EPMN. Values are expressed in ng.g^{-1} wet weight of muscle tissue, unless indicated as * in ng.g^{-1} lipid weight or ** in µg.g^{-1} wet weight of muscle tissue.

Contaminant	Reference value (RV)	Not deviating log RV < 0.4	Slightly deviating 0.4 ≤ log RV < 0.8	Deviating 0.8 ≤ log RV < 1.2	Strongly deviating log RV ≥ 1.2
Mercury	40	< 100	100 - < 252	252 - < 634	≥ 634
Cadmium	2	< 5	5 - < 12.6	12.6 - < 31.7	≥ 31.7
Lead	10	< 25	25 - < 63	63 - < 158	≥ 158
Cupper**	0.25	< 0.6	0.6 - < 1.6	1.6 - < 4	≥ 4
Zinc**	14	< 35	35 - < 88	88 - < 222	≥ 222
Nickel	14	< 35	35 - < 88	88 - < 222	≥ 222
Chrome	96	< 241	241 - < 606	606 - < 1521	≥ 1521
Arsenic	41	< 103	103 - < 259	259 - < 650	≥ 650
Selenium	205	< 515	515 - < 1293	1293 - < 3249	≥ 3249
PCB 28	0.12	< 0.3	0.3 - < 0.8	0.8 - < 1.9	≥ 1.9
PCB 31	0.1	< 0.3	0.3 - < 0.6	0.6 - < 1.6	≥ 1.6
PCB 28+31	0.25	< 0.6	0.6 - < 1.6	1.6 - < 4	≥ 4
PCB 52	1	< 2.5	2.5 - < 6.3	6.3 - < 15.8	≥ 15.8
PCB 101	2.5	< 6	6 - < 16	16 - < 40	≥ 40
PCB 105	1.2	< 3	3 - < 7.6	7.6 - < 19	≥ 19
PCB 118	3.5	< 9	9 - < 22	22 - < 55	≥ 55
PCB 138	7.7	< 19	19 - < 49	49 - < 122	≥ 122
PCB 153	10	< 25	25 - < 63	63 - < 158	≥ 158
PCB 156	0.6	< 1.5	1.5 - < 3.8	3.8 - < 9.5	≥ 9.5
PCB 180	4.5	< 11	11 - < 28	28 - < 71	≥ 71
Sum PCBs	29	< 73	73 - < 183	183 - < 460	≥ 460
Sum PCBs*	240	< 603	603 - < 1514	1514 - < 3804	≥ 3804
α–HCH	0.05	< 0.1	0.1 - < 0.3	0.3 - < 0.8	≥ 0.8
γ–HCH	1.3	< 3.3	3.3 - < 8.2	8.2 - < 20.6	≥ 20.6
Dieldrin	1.1	< 2.8	2.8 - < 6.9	6.9 - < 17.4	≥ 17.4
HCB	0.5	< 1.3	1.3 - < 3.2	3.2 - < 7.9	≥ 7.9
p.p'-DDD	2.5	< 6	6 - < 16	16 - < 40	≥ 40
p.p'-DDT	0.005	< 0.01	0.01 - < 0.03	0.03 - < 0.08	≥ 0.08
p.p'-DDE	13	< 33	33 - < 82	82 - < 206	≥ 206
Sum DDTs	16	< 40	40 - < 101	101 - < 254	≥ 254

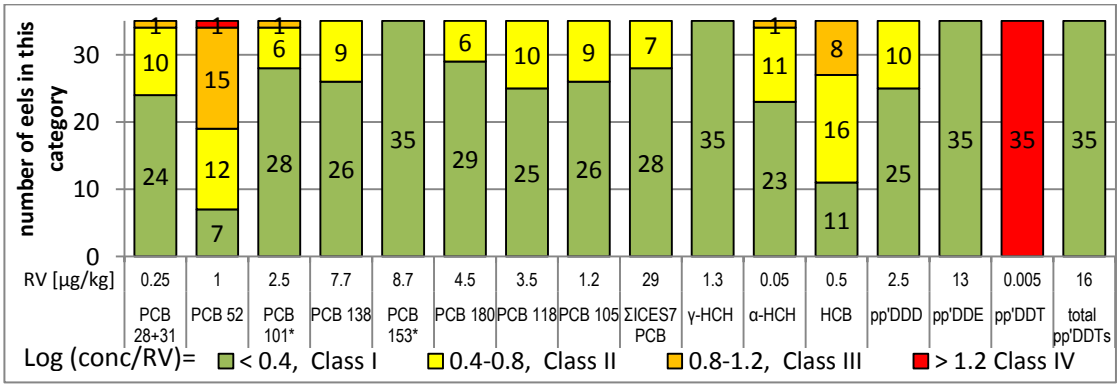


Figure 4.4-7 All 2007 Thames eels from both sites compared to the Eel Quality Index (EQI, Belpaire and Goemans 2007). Reference Values (RV) are the 5%ile of sites of a large Belgian dataset and quality classes are defined as:

Class I: log(concentration/RV) < 0.4 (conc/RV <2.5): not deviating from RV (i.e. high quality)
Class II: log(concentration/RV) 0.4-0.8 (conc/RV 2.5-6.3): slightly deviating from RV
Class III: log(concentration/RV) 0.8-1.2 (conc/RV 6.3-16): deviating from RV
Class IV: log(concentration/RV) > 1.2 (conc/RV >16): strongly deviating from RV (i.e. poor quality)
*** these PCBs co-eluted with another PCB and were quantified together.**

4.4.2.2 DDT/DDE

Out of the "total DDTs" (*op*'+*pp*'DDT. *op*'+*pp*'DDE, and *op*'+*pp*'DDD) *pp*'DDE was chosen for comparison with other studies as it is usually the dominant compound and therefore most frequently detected. The contamination of eels with *pp*'DDE in this study was lower than most of the recent European eel data summarized in Table 4.4-4 and Figure 4.4-9. All individuals were also within the definition of class I of the Eel Quality index (Figures 4.4-7- both for total *pp*'DDTs and for the main component *pp*'DDE, despite exceeding the Canadian EQS (see also chapter 4.3).

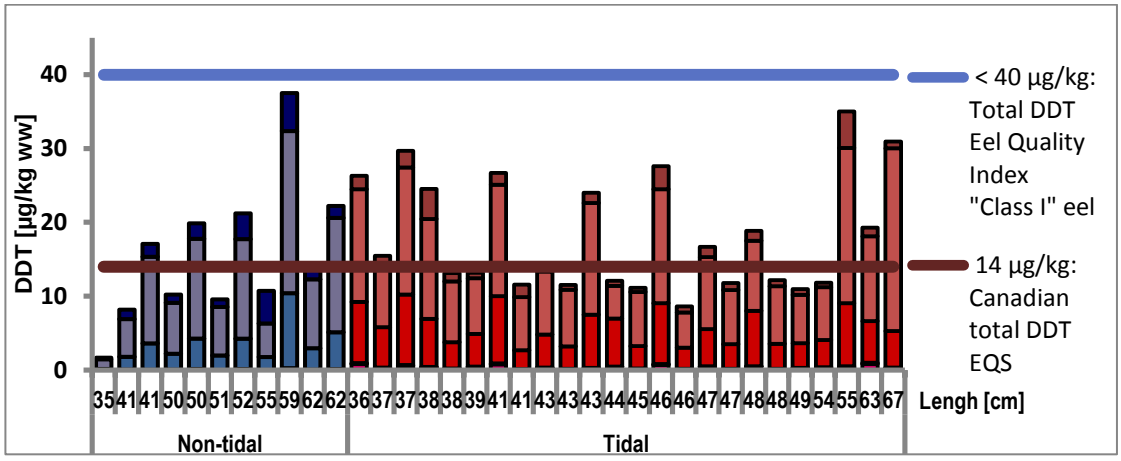


Figure 4.4-8 Total DDT concentrations in the individual 35 lower Thames eels compared to the Canadian EQS and eel quality index (EQI). The bars show negligible contributions of op' congeners at the bottom followed by pp'DDD, pp'DDE, pp'DDT. The EQI is based on a large dataset from Belgium, where the 5%ile concentration is set as the reference values (RV) and concentrations less than 2.5 times are classed as high quality "class I" eels.

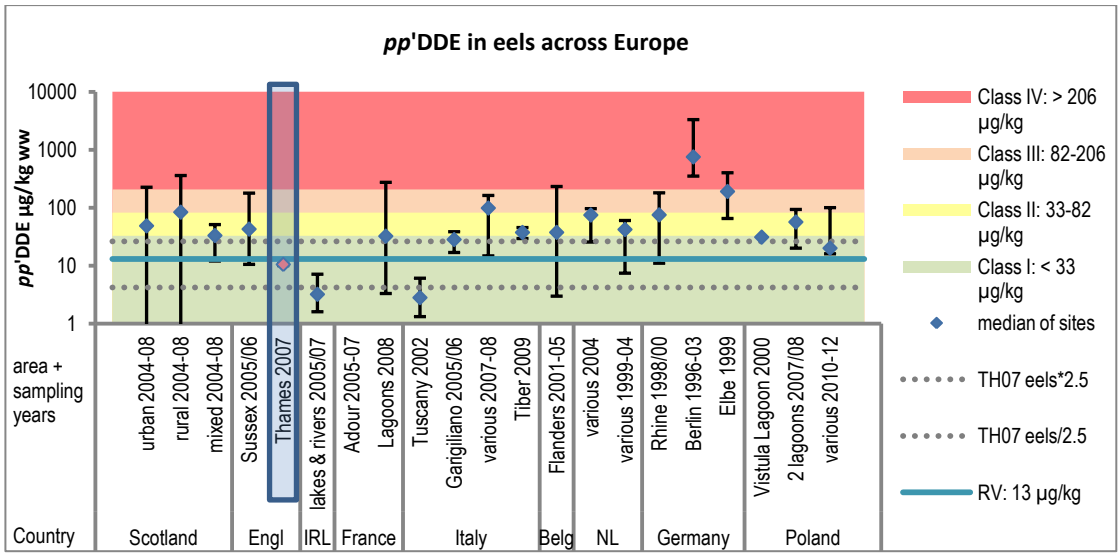


Figure 4.4-9 Graphical representation of the recent European data for pp'DDE in eels. Compared to the eel quality index (EQI, Belpaire and Goemans 2007). The median, minimum and maximum of the site averages are given. Normally data is from 2000 onwards was considered, but some data from the late 1990s was included where it was part of a longer study. The studies are presented in the same order as in Table 4.4-4 (without the separate Santillo entry for England as it was for a single sample, and without the silver eel groups). Please refer to Table 4.4-4 for references. Values between the dotted lines are within a factor of 2.5 of our results. This factor was used as it is the definition of "not deviating" in the EQI (Goemans *et al.* 2003). See also Figure 4.4-7 for more information on the EQI.

4.4.2.3 Lindane (γ-HCH)

Concentrations of the pesticide lindane (γ-HCH) were comparable to some recent studies from Scotland, France, Italy and Poland, but lower than recent studies from Germany and the Benelux countries.

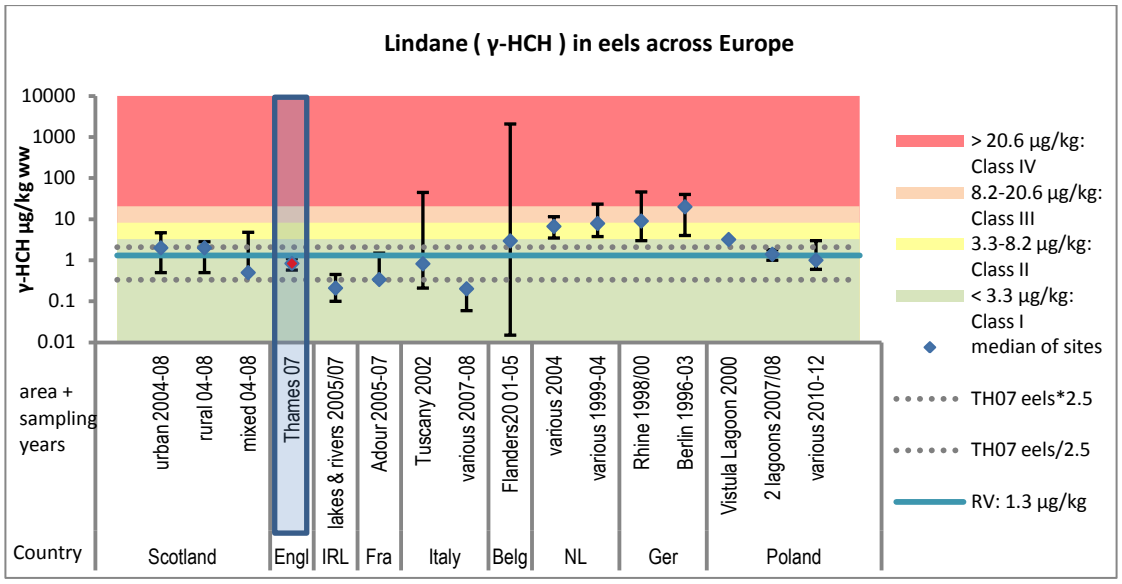


Figure 4.4-10 Graphical representation of the recent European data for γ-HCH (lindane) in eels compared to the eel quality index (EQI, Belpaire and Goemans 2007). The median, minimum and maximum of the site averages are given. Normally, data is from 2000 onwards, but some data from the late 1990s was included, where it was part of a longer study. The studies are presented in the same order as in Table 4.4-4 (without the separate Santillo entry for England as it was for a single sample, and without the silver eel groups). Please refer to Table 4.4-4 for references. Values between the dotted lines are within a factor of 2.5 of our results. This factor was used as it is the definition of "not deviating" in the EQI (Goemans *et al.* 2003). See also Figure 4.4-7 for more information on the EQI.

4.4.2.4 HCB

Concentrations of HCB in Thames eels were in a similar range as in most recent European studies that measured this chemical Figure 4.4-11. High concentrations above the EQS of 10 µg/kg were mainly found in Belgium and the Netherlands and also in the Rhine in France and Germany (as well as the Netherlands). For example in the French (ONEMA 2012) study 58 of 399 eels (15%) overall were above the 10 µg/kg EQS threshold, but for the Rhine this rose to 44/54 or 81%. In the Flanders data (Belpaire 2008) 15% of site averages collected between 2001 and 2004 were above the EQS and in 10 of 17 Dutch sites, including one of two on the Rhine the EQS was still exceeded in eels in 2011, despite a clear downward trend over time in the concentrations (van Leeuwen *et al.* 2013).

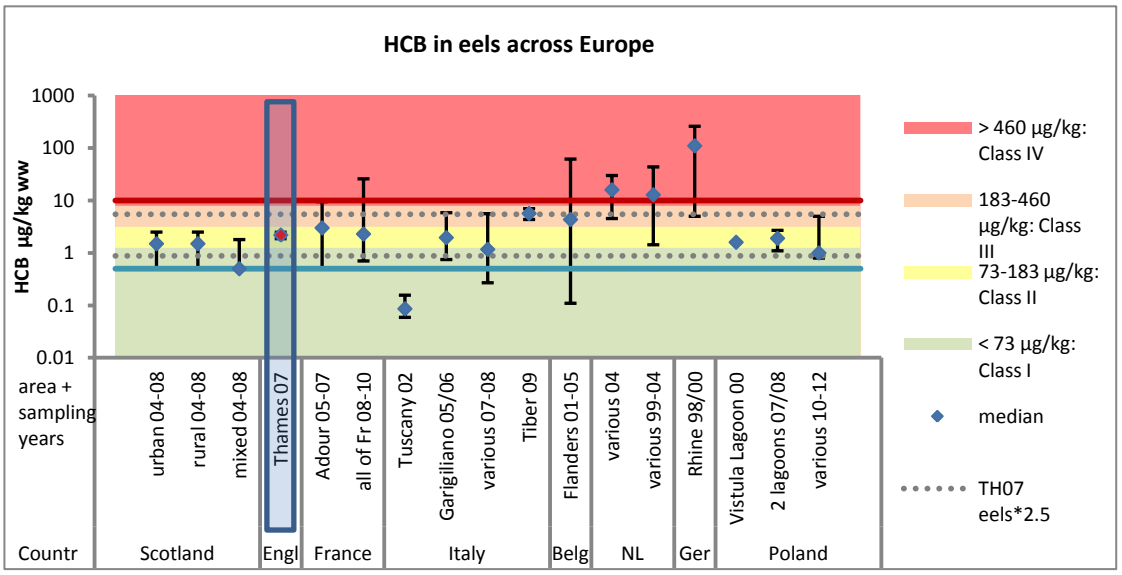


Figure 4.4-11 Graphical representation of the recent European data for HCB in eels. Compared to the eel quality index (EQI, Belpaire and Goemans 2007). The median, minimum and maximum of the site averages are given. Normally, data is from 2000 onwards, but some data from the late 1990s was included, where it was part of a longer study. The studies are presented in the same order as in Table 4.4-4 (without the separate Santillo 2005 entry for England as it was for a single sample, and without the silver eel groups). Please refer to Table 4.4-4 for references. Values between the dotted lines are within a factor of 2.5 of our results. This factor was used as it is the definition of "not deviating" in the EQI (Goemans *et al.* 2003). See also Figure 4.4-7 for more information on the EQI.

4.4.2.5 PCBs

Total PCB levels (46 congeners) ranged from 7 to 232 µg/kg, fresh weight with the ICES7 indicator PCBs providing about half of that (Table 4.4-3). The ICES7 values were towards the lower end of recent European measurements and fairly typical for recent UK data.

Compared to a recent Europe-wide survey (Santillo *et al.* 2005), the PCB contamination found in the eels in this study was approximately in the lower third of values. In that study, some sites in the Netherlands, Germany, and Italy had approximately 10 fold higher PCB contamination. Other studies also found quite high PCB values in the Benelux countries, Germany and some of the French studies (Figure 4.4-12 and Table 4.4-4).

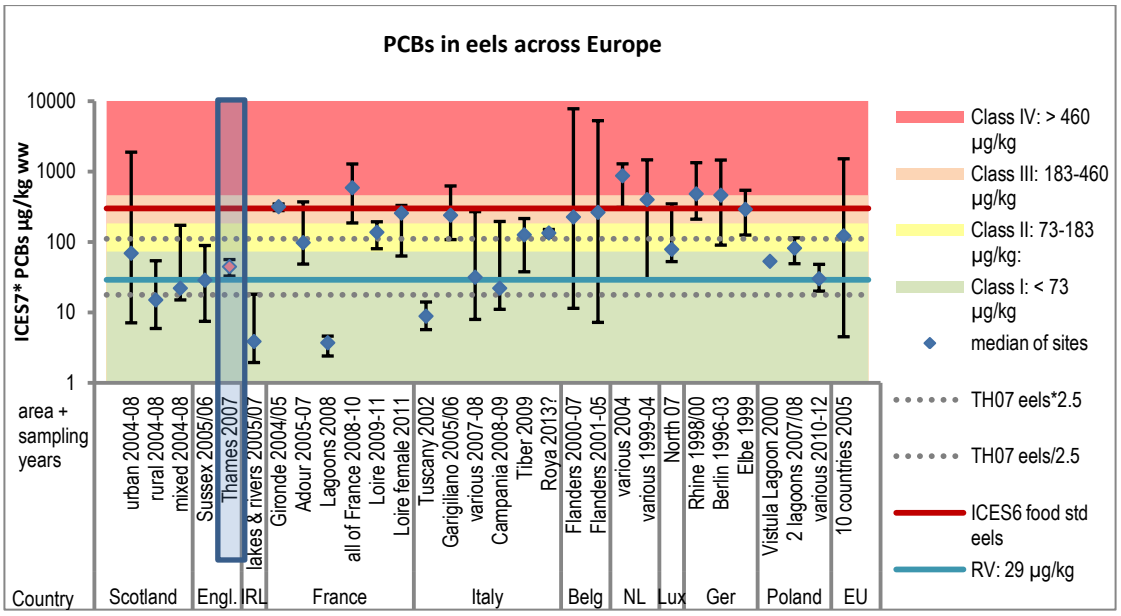


Figure 4.4-12 Graphical representation of the recent European data for ICES7 PCB in eels. Compared to the eel quality index (EQI, Belpaire and Goemans 2007). The median, minimum and maximum of the site averages are given. Normally Data is from 2000 onwards, but some data from the late 1990s was included where it was part of a longer study. The studies are presented in the same order as in Table 4.4-4 (without the separate Santillo entry for England as it was for a single sample, and without the silver eel groups). Please refer to Table 4.4-4 for references. The red line shows the ICES6 food standard. Values between the dotted grey lines are within a factor of 2.5 of our results. This factor was used as it is the definition of "not deviating" in the EQI (Goemans *et al.* 2003). See also Figure 4.4-7 for more information on the EQI.

***The data is for ICES7 pesticides where available, but sometimes using ICES6 instead – for our eels ICES6 was 85% of ICES 7 on average, so whether ICES6 or ICES7 is plotted would make little difference on a logarithmic scale.**

Table 4.4-3 Summary of the main determinants in eels in this study. All values given as mean (standard deviation, range) (Jürgens *et al.* 2015).

Determinand	unit	Non-tidal Thames [fresh weight]		Thames estuary [fresh weight]		sig. diff?[a]	Non-tidal Thames [lipid weight]		Thames estuary [lipid weight]		sig. diff?[a]	banned in UK[b]
Fishing date		13.9.2007		1.10.2007		-						
Number	-	11		24		-						
Length	cm	51	(9.0, 35-62)	46	(7.9, 36-67)	10%						
Weight	g	228	(133, 60-482)	186	(142, 75-667)	n.s.[c]						
Age[d]	y	12	(3, 7-18)	9	(2, 6-14)	5 %						
Fulton's condition factor[e]	-	0.15	(0.03, 0.12-0.20)	0.18	(0.03, 0.12-0.26)	10%						
Lipid content	%	10.0	(9.1, 1.7-29)	16.5	(8.3, 5.1-36)	5%						
number of *A. crassus*[f]	-	2.6	(2.7, 0-10)	1.0	(1.7, 0-7)	10%						
PCBs (Sum 46)[g]	µg/kg	63	(43, 7.3-166)	113	(50, 56-232)	5%	877	(540, 303-1854)	746	(239, 408-1408)	n.s.	from 1972[i]
Sum ICES7 PCBs[i]	µg/kg	33	(21, 4.2-79)	56	(24, 28-124)	5%	472	(295, 166-1007)	375	(132, 200-753)	n.s.	
Sum ICES6 PCBs[j]	µg/kg	26	(17, 3.5-63)	48	(20, 25-104)	5%	380	(235, 132-789)	325	(112, 172-630)	n.s.	
mono-ortho PCBs as partial WHO1998 TEQ (mammals) [kl]	ng/kg	1.6	(1.1, 0.2-4.1)	1.9	(0.9, 1.0-4.8)	n.s.	22	(14, 8.0-49)	13	(5.1, 6.5-29)	10%	
mono-ortho PCBs as partial WHO2005 TEQ [km]	ng/kg	0.32	(0.22, 0.035-0.83)	0.39	(0.19, 0.19-1.0)	n.s.	4.6	(3.0, 1.7-10)	2.6	(1.1, 1.3-6.1)	10%	
total DDT[n]	µg/kg	15.7	(9.6, 1.7-38)	18.2	(7.8, 8.6-35)	n.s.	236	(167, 66-528)	124	(48, 57-229)	10%	1981[o]
op'DDT	µg/kg	0.047	(0.046, 0.001-0.14)	0.059	(0.050, 0.01-0.23)	n.s.	0.57	(0.49, 0.04-1.5)	0.37	(0.23, 0.09-0.91)	n.s.	
pp' DDT	µg/kg	2.2	(1.5, 0.24-5.2)	1.5	(1.1, 0.57-4.9)	n.s.	43	(60, 6.7-217)	10	(6.3, 2.9-27)	1%	
pp' DDE	µg/kg	10.0	(5.9, 1.3-22)	10.9	(5.2, 4.4-25)	n.s.	147	(95, 41-336)	76	(35, 30-150)	1%	
α-chlordane	µg/kg	0.42	(0.32, 0.03-1.2)	0.46	(0.47, 0.08-2.0)	n.s.	5.3	(3.2, 1.8-11)	2.7	(1.8, 0.65-7.8)	0.5%	1981[o]
γ-chlordane	µg/kg	0.13	(0.12, 0.003-0.43)	0.54	(0.31, 0.11-1.3)	0.5%	1.4	(0.78, 0.16-3.0)	3.6	(1.9, 1.1-7.0)	0.01%	1981[o]
γ-HCH (Lindane)	µg/kg	0.58	(0.54, 0.05-1.9)	1.1	(0.71, 0.27-2.8)	1%	6.0	(1.9, 3.2-8.9)	6.4	(2.3, 3.5-14)	n.s.	2002[p]
β-endosulfan	µg/kg	0.06	(0.06, <0.02-0.23)	0.22	(0.11, 0.09-0.50)	0.05%	0.71	(0.29, 0.33-1.1)	1.4	(0.40, 0.82-2.2)	0.01%	2007[q]
HCB	µg/kg	1.9	(1.7, 0.05-6.4)	2.5	(1.6, 0.82-6.4)	n.s.	21	(12, 2.8-38)	15	(5.9, 7.7-29)	n.s.	1981[o]

[a] significance level in Student's t-tests (for equal or unequal variance as determined with F-test (5% level)), on log transformed data for the chemical analysis, and on untransformed data for the other parameters

[b] or severely restricted (de-facto ban)

[c] n.s.: not significant at 10% level

[d] years continental age, determined by researchers from CEFAS from stained otolyths. In a few cases the age could not be accurately determined and was for statistical purposes instead estimated from the linear length/age relationship of these eels

[e] weight[g]/(length[cm])^3*100

[f] juveniles+adults, no larval stages were found

[g] 46 PCBs (see section 2.1)

[h] open uses prohibited 1972, ban in all new systems 1986, most existing equipment with > 5 L 2000 (DEFRA 1997, 2002)

[i] commonly found congeners 28,52,101,118,138,153, and 180.

[j] ICES7 without the dioxin-like congener 118

[k] to calculate the complete TEQ, dioxins, furans, and non-ortho-substituted PCBs would also need to be measured

[l] Van den Berg *et al.* (1998)

[m] Van den Berg *et al.* (2006)

[n] sum of *pp*'DDT, *op*'DDT, *pp*'DDE, *op*'DDE, *pp*'DDD, *op*'DDD

[o] EEC (1978)

[p] European Commission (2000), technical HCH, which is typically dominated by the α-congener was already banned 1981 EEC (1978)

[q] European Commission (2005a)

Table 4.4-4 Recent European literature data for selected contaminants in yellow or silver eel [µg/kg fw], >30cm length if possible. Median and range of site averages. Sorted by country and sampling date. Some data was estimated from graphs or calculated from values given by lipid content or dry weight (updated from table in Jürgens *et al.* (2015)).

Year(s) of capture	locations	number sites	samples per site	t[a]	DDE	γ-HCH (lindane)	HCB	ICES7 PCB	reference
	Scotland								
2004-08	urban sites in Scotland	12	5	m	49 (<1-225)	<3.9 (<1-4.68)	ca. 1.5 (≤1-ca. 2.5)	69 (7.1-1878)	(Macgregor *et al.* 2010)
	rural sites in Scotland	14	5	m	84 (<1.5-358)	<3.9 (<1-2.82)	ca. 1.5 (≤1.1-ca. 2.5)	15 (5.9-54)	
	mixed u/r sites in Scotland	3	5	m	33 (12-51)	<1 (<1-4.79)	<1 (<1-1.8)	22 (15-172)	
	England								
2005	Thames estuary, SE England	1	1 pooled	m	-	-	-	136	(Santillo *et al.* 2005)
2005/06	contaminated sites Sussex, S England	21	5	m	43 (11-178)	<1.5 (<1-<25)	-	29 (7.5-89)	(Foster and Block 2006)
2007	**Thames, near London SE England**	**2**	**11, 24**	**s**	**10 (10,11)**	**0.84 (0.58,1.1)**	**2.2 (1.9,2.5)**	**44 (33, 56)**	**current study**
	Ireland								
2005/07	Lakes and rivers	5-7	1 pooled	m	3.2 (1.6-7.1)	0.21 (<0.2-0.45)	<0.9 (<0.5-<2)	3.9 (1.9-18.1)	(McHugh *et al.* 2010)
	France								
2004/05	Gironde	4	13-58b	m	-	-	-	316 (278-345)	(Tapie *et al.* 2011)
2005-07	Adour estuary	3	3-7	m	0.48 (0.43-0.57)	0.34 (0.33-1.49)	total range <1-9.1[b]	98 (48-370)	(Tabouret *et al.* 2011)
2008	3 lagoons, male silver eels	3	12-22	m	32 (3.3-273)	-	-	3.7 (2.4-4.6)	(Amilhat *et al.* 2014)

Year(s) of capture	locations	number sites	samples per site	t[a]	DDE	γ-HCH (lindane)	HCB	ICES7 PCB	reference
2008-10	all of France grouped into 6 major basins	6	16-160	m	-	-	2.3 (0.7-26)	587 (186-1276)	(ONEMA 2012)
2009-11	Loire estuary, yellow eels	3	11-16b	m	-	-	-	137 (80-193)	(Blanchet-Letrouvé *et al.* 2014)
2009-11	silver eels (>50 cm, female?)	1	13		-	-	-	229 ± 130	
2011	Loire estuary, female yellow eels > 40 cm	3	10	m	-	-	-	256 (63-329)[c]	(Couderc *et al.* 2015)
2012	female silver eels	1	15	m	-	-	-	190 ± 35	
	Italy								
2002	Tuscany	7	15	m	2.8 (1.3-6.1)	0.82 (0.21-45)	0.09 (0.06-0.16)	8.8 (5.7-14)[d]	(Corsi *et al.* 2005)
2005/06	Garigiliano estuary	1x3[e]	10	m	28 (17-38)	-	2.0 (0.75-5.9)	239 (138-622)	(Ferrante *et al.* 2010)
2007/08	river, lake, lagoon	3	15-23	m	98 (15-162)	0.20 (0.06-0.20)	1.2 (0.27-5.6)	32 (7.9- 269)[d]	(Quadroni *et al.* 2013)
2008/09	Campania region	7	1-2	m	-	-	-	22 (11-195) [c]	(Pacini *et al.* 2012)
2009	polluted R. Tiber + clean Lake Bolzena	2	30,6	m	37 (29, 45)	-	5.7 (4.4, 7.0)	126 (38, 214)	(Pujolar *et al.* 2012)
2013?	river Roya, Northern Italy	2	9,11	m	-	-	-	150, 117 [c]	(Squadrone *et al.* 2015)
	Belgium[f]								
2000-07	Flanders	48	1 pooled	m	-	-	-	226 (11-7753)	(Belpaire *et al.* 2011)
2001-05	Flanders	261[g]	1-21[h]	m	37 (3.0-232)	3.0 (<0.03-2,076)	4.3 (0.11-62)	263 (7-5252)	(Belpaire 2008)
2000-09	Flanders	60	1 pooled	m	24 (4.3-436)[i]	-	-	75 (5.0-2600) [c]	(Malarvannan *et al.* 2014)
	The Netherlands								
2004	Lakes, rivers and canals[j]	8	1 (6) pooled[k]	m	75 (25-96)	6.7 (3.5-11)	16 (4.5-30)	869 (308-1281)	(de Boer *et al.* 2010)

Year(s) of capture	locations	number sites	samples per site	t[a]	DDE	γ-HCH (lindane)	HCB	ICES7 PCB	reference
1999-04	Lakes, rivers and canals	14	6 pooled[l]	m	42 (7.4-60)	7.9 (3.8-23)	12.8 (1.4-44)	398 (30-1461)	(Kotterman and Pieters 2003, Pieters and Kotterman 2005)
	Luxembourg								
2007	North Luxembourg	3	3-9	w	-	-	-	78 (53-346)	(Boscher *et al.* 2010)
	Germany								
1998/00	River Rhine	15-25	3-25		75 (11-180)[m]	9 (3-46)	110 (5-260)	480 (210-1330)[c]	(Heinisch *et al.* 2004, 2005a, b, 2006a,b, 2007)[n]
1996-03	Berlin area	10-11	3-20		750 (350-3300)	20 (4-40)	-	460 (90-1450)	
1999	River Elbe	7-8	3-20		190 (65-400)	-	-	290 (125-540)	
	Poland								
2000	Baltic Sea lagoon (Vistula)	1	7 (1-2 eels)	m	31[i]	3.2[o]	1.6	53	(Szlinder-Richert *et al.* 2010)[p]
2007/08	2 Baltic Sea lagoons (Vistula+Szczecin)	2	14, 2 pooled	m	20, 93[i]	1.0, 1.8[o]	1.1, 2.7	49, 114	
2010-12	same 2 lagoons, Baltic sea, Vistula river, lakes	5[q]	5-46	m	20 (16-100)[i]	1 (0.6-3)[o]	1 (0.8-5)	30 (20-48)	(Szlinder-Richert *et al.* 2014)
	Europe-wide								
2005	10 European countries	20	1 pooled	m	-	-	-	122 (<7-1512)	(Santillo *et al.* 2005)

[a] type of sample: m: muscle, s: section, w: whole body

[b] site averages were not calculated due to non-detects

[c] only 6 congeners (usually the non-dioxin like ICES6)

[d] includes additional congeners

[e] one area three times

[f] the different entries for Flanders may be referring to some of the same eel samples

[g] only samples from 2001 onwards chosen: 261 sampling occasions from 219 sites

[h] typically 5

[i] results were converted to *pp*'DDE from the reported Σ(*pp*'DDT, *pp*'DDE, *pp*'DDD), using the estimate of 66% being *pp*'DDE according to the results from our eels (chapter 4.2), which compare very well with Belpaire (2008), where the average for all 2001-2005 sampling occasions was 67%

[j] There is some overlap between the two Dutch studies with four or five locations reported in both

[k] 6 annual pooled samples from 2001 to 2006 chosen for PCBs, but only one of those (2004) supplied for the other chemicals

[l] 1 pooled sample, usually of 25 eels. per year and site. Site averages were calculated from the 6 annual samples.

[m] sum of *op'* and *pp*' DDE

[n] only eels>10% lipid

[o] Σ(α,β,γ-HCH). In our eels γ-HCH was on average 78% of the total but in the Baltic Sea region of Poland β-HCH (not γ-HCH) was dominant and γ-HCH only contributed 10-30% (Szlinder-Richert *et al.* 2010, Szlinder-Richert *et al.* 2014)

[p] site averages were calculated from individual results weighted by number of eels in composite samples.

[q] 8 sites but the three lakes were reported together

4.4.2.6 Summary: POPs in eels compared to other European studies

- Organic pollutants in eels were compared to the Eel Quality Index: For most compounds, where the EQI was defined, most or all of the Thames eels were in Class I (not deviating from the reference value = high quality) or Class II (slightly deviating from the reference value). The only exception to this was *pp*'DDT, which has a very low RV (possibly due to frequent non-detects?). Therefore the Thames 2007 eels can be seen as of good quality with regards to organic pollutants.
- **PCB** concentrations were comparable to recent UK data. There were big differences between sites and studies across Europe, some averages were much higher than ours, others much lower, without a clear separation by country or region
- **DDE** was less than most recent UK and European data
- **Lindane (γ-HCH)** was less than most recent data from the Netherlands and Germany and comparable to most other recent European data
- **HCB** values were comparable to most recent EU data, but values in the Netherlands and Germany were higher and in one of the Italian studies (Corsi *et al.* 2005) they were much lower.

4.5 Is chemical contamination of UK freshwater fish improving?

Can the data be used to demonstrate whether voluntary or legislative measures have been successful in reducing harmful contaminants in fish? Our own data doesn't cover the time scale needed but it can be compared to literature data.

4.5.1 Some metals

Table 4.5-2 shows literature data for some metals in roach in the UK (or England, as no reports were found for Scotland and the data for Wales is restricted to just three individuals). Only mercury, cadmium and lead were measured frequently in roach before and one reference was found that also measured zinc. Therefore those four metals, which are also particularly harmful, have been chosen for comparison with literature data.

Table 4.5-1 Comparison of metal concentrations in roach to literature data

year(s)	area	site	n	type	ave length [cm]	ave weight [g]	Hg [µg/kg]	Cd [µg/kg]	Pb [µg/kg]	Zn [mg/kg]	reference
1974	River Lee	STW lagoon	23	m		50[a]	165				Bull *et al.* (1981)
		River Lee	30	m		50[a]	77				
1980?	nr Manchester	Rostherne Mere		w		120-220		5,678	1690	93	Badsha and Goldspink (1982)
	nr Manchester	Pond in Lyme Park		w		25-80		2,428	2839	85	
1980/81+ 84	Southwest England		31	m			66	120	1570		Mason (1987)
	Wales		3	m			72	100	320		
	East Anglia		29	m			53	90	1110		
	Northeast England		16	m			67	50	890		
1985-87	Eastern	R. Brett us of town	108	m	17.4	123	120	20	70		Barak and Mason (1990b)
		R. Brett ds of town	103	m	18.2	127	90	30	50		
		R. Chelmer us of town	95	m	22.7	286	180	30	70		
		R. Chelmer ds of town	111	m	17.8	125	130	30	60		
1992?	River Wey nr London	R. Wey Waverley Abbey	5(4)[b]	m	15.6	63	72	19	89		Gazzard and Yorke (1993)
		R. Wey Eashing Br.	5	m	16.5	69	38	5	25		
1995/96	South	R. Ray	5	m	21.2	160		67			Yamaguchi *et al.* (2003)
		R. Windrush	5	m	27.3	241		86			
		R. Thames Hannington	6	m	20.2	131		55			

year(s)	area	site	n	type	ave length [cm]	ave weight [g]	Hg [µg/kg]	Cd [µg/kg]	Pb [µg/kg]	Zn [mg/kg]	reference
1996	East Anglia	R Ant	28	m	18.3	113	26				Downs *et al.* (1999)
	East Anglia	R. Yare	28	m	17.4	112	27				
	East Anglia	R. Waveney	32	m	17.8	107	28				
	East Anglia	R. Colne	30	m	19.9	175	104				
	East Anglia	R. Pant	35	m	18.7	138	41				
1971	East Anglia	R Yare	13	m			713				Edwards *et al.* (1999)
1986	East Anglia	R Yare	9	m			197				
1991	East Anglia	R Yare	17	m			106				
1993	East Anglia	R Yare	17	m			171				
1994	East Anglia	R Yare	40	m	19.2	132	55				
1995	East Anglia	Ormsby Broad (control site)	49	m	14.8	51	54				
2009	Anglian	R. Glen Pinchbeck West	5	w(m)	19	133	40 (59)	4.8	38	40	This study.
2008		R. Nene Cogenhoe	9	w(m)	10	16.2	20 (28)	2.9	64	46	Mercury muscle concentrations estimated from whole body concentrations using the relationship in (Peterson *et al.* 2007)
2008		R. Nene Thrapston	10	w(m)	11	26.5	27(39)	6.8	106	50	
2008		R. Nene Oundle	9	w(m)	13	35.6	43(64)	5.8	72	52	
2011	Thames Tributary	R. Kennet Newbury	9	w(m)	17	76.5	21(29)	4.1	102	38	
2011		R. Lee Wheathampstead	10	w(m)	19	125	27(38)	5.9	113	34	

year(s)	area	site	n	type	ave length [cm]	ave weight [g]	Hg [µg/kg]	Cd [µg/kg]	Pb [µg/kg]	Zn [mg/kg]	reference
2011		R. Stort Tednambury Mill	10	w(m)	12	33.7	19(26)	5.0	56	42	
2011	Thames	R. Thames Castle Eaton	10	w(m)	14	58.1	17(24)	20.9	75	35	
2008		R. Thames Caversham-Sonning	10	w(m)	12	34.1	31(45)	5.6	164	38	
2007		R. Thames Temple-Marlow	5	w(m)	16	73.3	39(58)	7.7	28	41	
2008		R. Thames Bray-Boveney	8	w(m)	15	56.0	26(38)	4.9	62	42	
2007		R. Thames Old Windsor-Bell	5	w(m)	16	64.1	35(51)	6.8	60	40	
2009		R. Thames Molesey-Kingston	10	w(m)	12	25.8	24(34)	5.3	186	43	

[a] this study focused on the correlation between mercury and weight, so the values given are using the regressions to calculate the concentration in a 50g roach

[b] one very high value excluded for Hg. Non-detects used at ½ detection limit

While the reductions in metal concentrations in roach in the UK (Figure 4.5-12, Figure 4.5-8) are not very obvious (yet), partly due to the scarcity of previous data, water concentrations of the metals where good data is available have reduced clearly over recent years (data from the Environment Agency, Figure 4.5-2 to Figure 4.5-6).

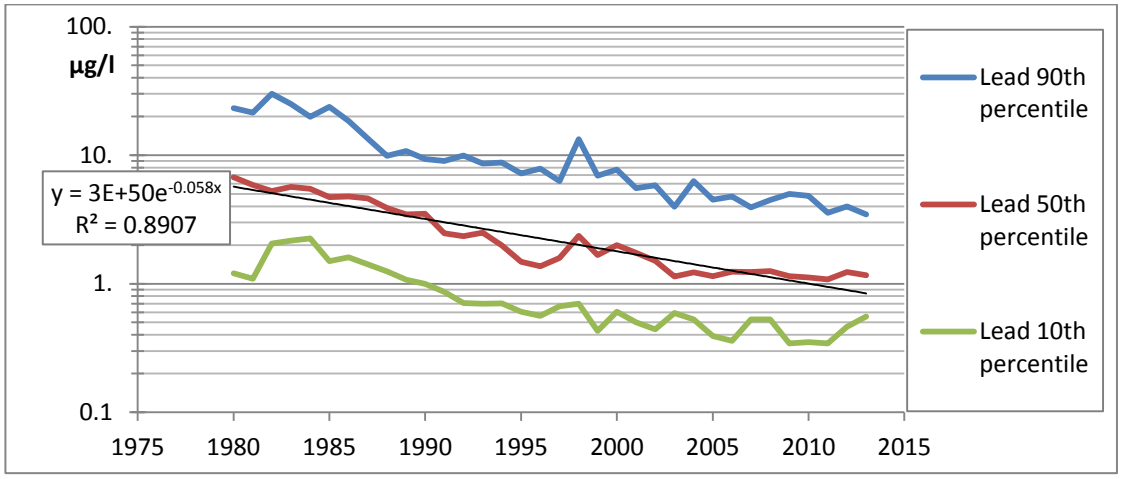


Figure 4.5-1 Lead concentrations in UK rivers - 1980-2013. Median, 10-percentile, and 90-percentile of the annual average concentrations of about 200 sites (Environment Agency Harmonised Monitoring Scheme (HMS) summary data (http://www.geostore.com/environment-agency).

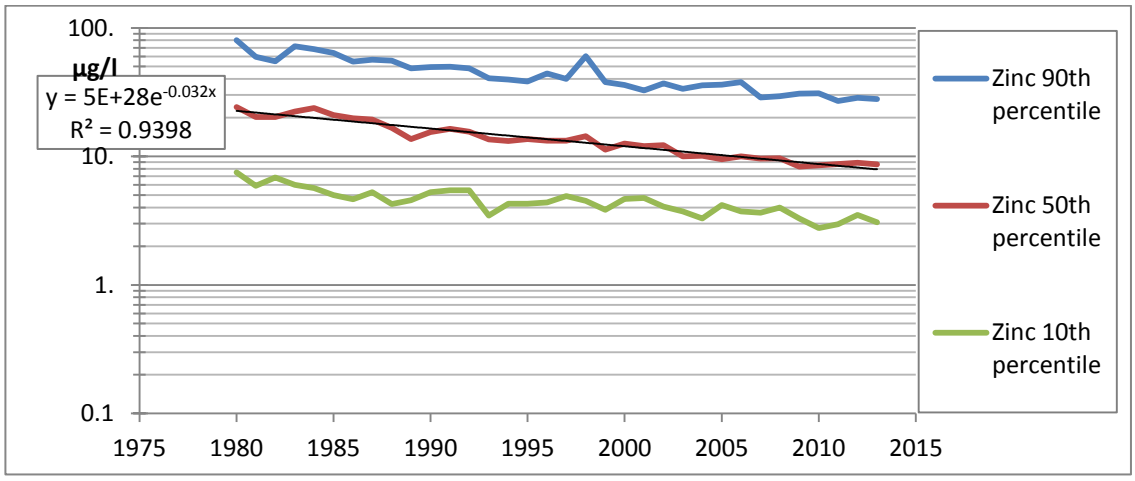


Figure 4.5-2 Zink concentrations in UK rivers - 1980-2013. Median, 10-percentile, and 90-percentile of the annual average concentrations of about 200 sites (Environment Agency Harmonised Monitoring Scheme (HMS) summary data (http://www.geostore.com/environment-agency).

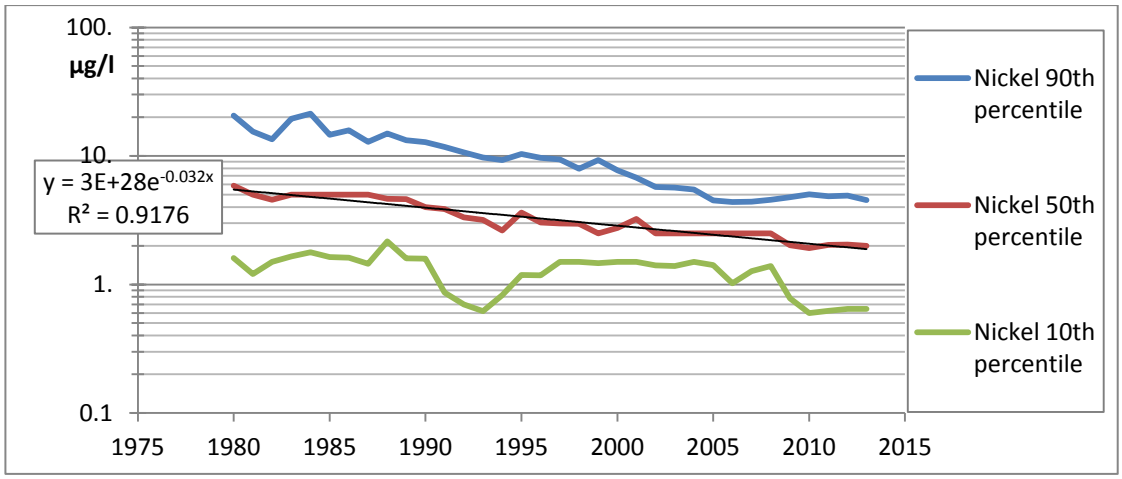


Figure 4.5-3 Nickel concentrations in UK rivers - 1980-2013. Median, 10-percentile, and 90-percentile of the annual average concentrations of about 200 sites (Environment Agency Harmonised Monitoring Scheme (HMS) summary data (http://www.geostore.com/environment-agency).

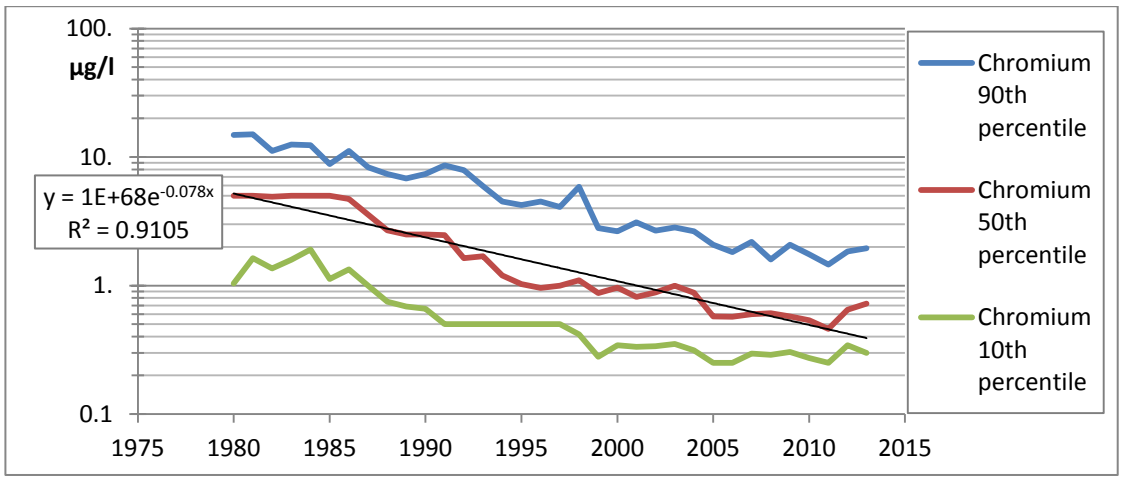


Figure 4.5-4 Chromium concentrations in UK rivers - 1980-2013. Median, 10-percentile, and 90-percentile of the annual average concentrations of about 200 sites (Environment Agency Harmonised Monitoring Scheme (HMS) summary data (http://www.geostore.com/environment-agency). Some of the 10th percentiles reflect the LOQ at the time of sampling (<LOQ being assigned the value of ½ LOQ).

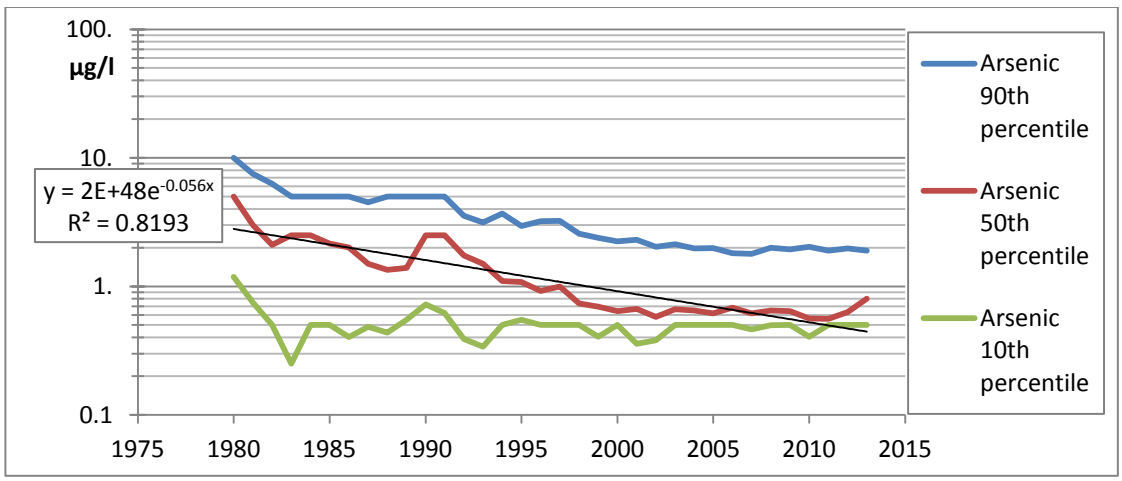


Figure 4.5-5 Arsenic concentrations in UK rivers - 1980-2013. Median, 10-percentile, and 90-percentile of the annual average concentrations of about 200 sites (Environment Agency Harmonised Monitoring Scheme (HMS) summary data (http://www.geostore.com/environment-agency). Fewer sites (around 100) were monitored before 1995).

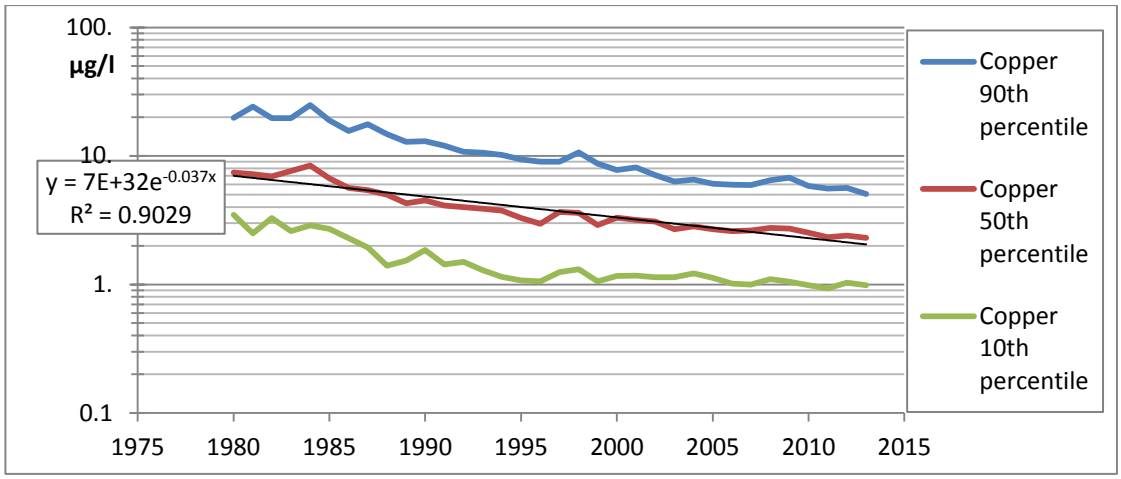


Figure 4.5-6 Copper concentrations in UK rivers - 1980-2013. Median, 10-percentile, and 90-percentile of the annual average concentrations of about 200 sites (Environment Agency Harmonised Monitoring Scheme (HMS) summary data (http://www.geostore.com/environment-agency).

4.5.1.1 Mercury in roach

The mercury values measured in the present study, while often exceeding the 20 µg/kg biota EQS, are lower than some have been 20 or 30 years ago in England (Barak and Mason 1990a,b,c). However, in studies that monitored mercury concentration in the same species of fish systematically, trends were not always clear or still going up until quite recently despite measures to reduce the available mercury in the environment (e.g. Figure 4.5-7) and comparing values from different studies is complicated by the fact that there is a strong size dependence of mercury concentrations. Mercury may be higher in muscle samples than in whole body homogenates, but Goldstein *et al.* (1996) found this difference to be usually less than a factor 2 and Peterson *et al.* (2004, 2007) developed an equation to estimate whole body concentrations from fillet concentrations or vice versa, which works out as about a factor 1.5 at realistic concentrations (see chapter 4.4, Figure 4.4-2).

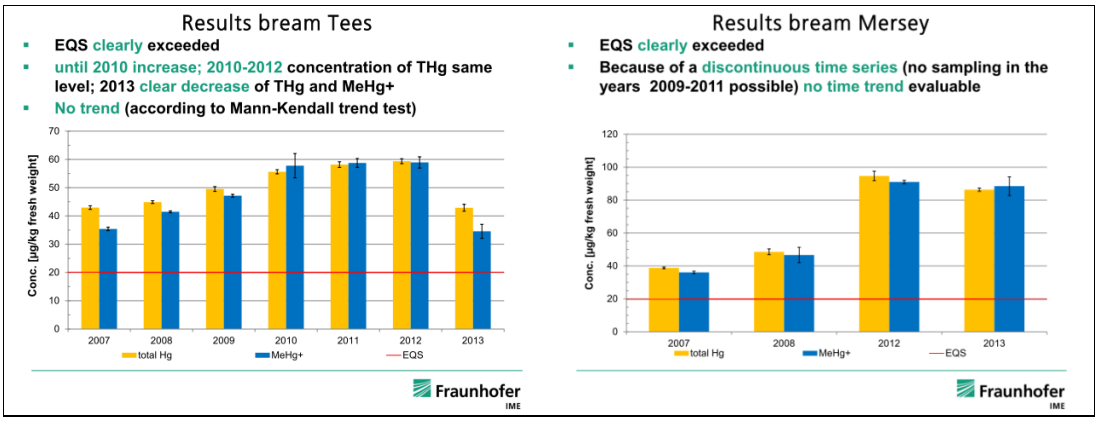


Figure 4.5-7 Mercury in bream from two sites in England (Knopf *et al.* 2014). Sampling sites are in the tidal areas but the Mersey site is about 20 km upstream of Runcorn where liquid mercury is still used at a large scale.

Although Figure 4.5-8 appears to show that the mercury concentrations measured in roach in this study are lower than those observed in the past, this picture changes when the difference between measuring the whole body homogenate or the fillet and the size influence is accounted for. Figure 4.5-9 shows that the mercury concentrations measured in this study are very similar to those of roach measured in the past when fish of similar sizes are compared.

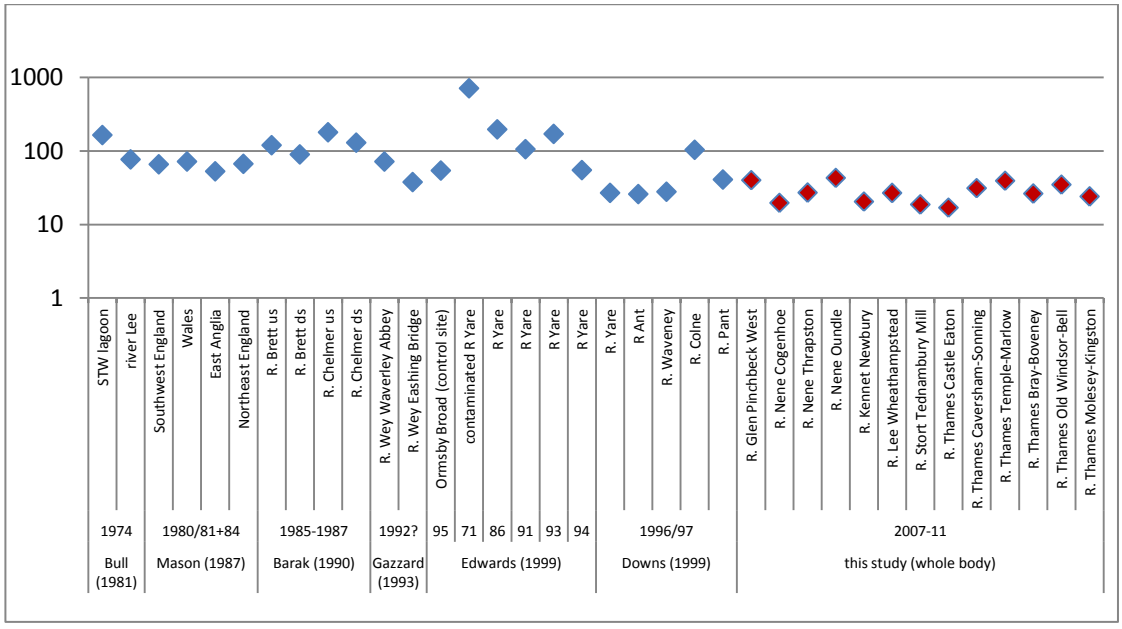


Figure 4.5-8 Mercury in roach. Literature data compared to results from the current study (data in Table 4.5-1).

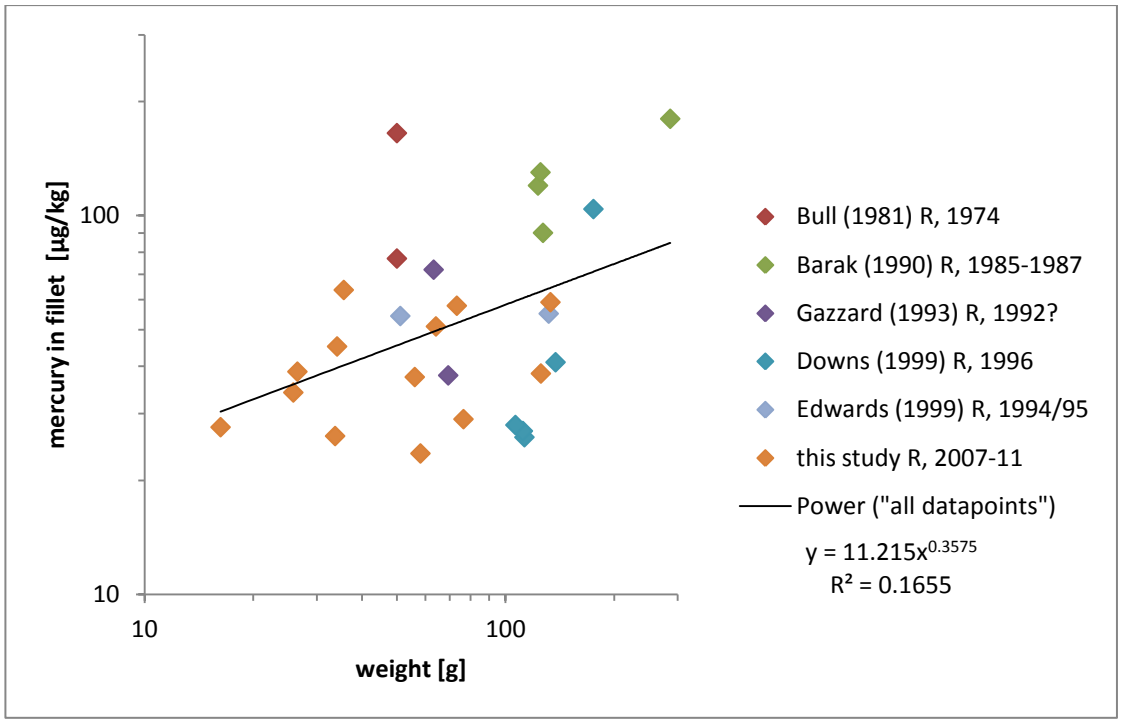


Figure 4.5-9 Mercury concentrations in roach fillets, site averages plotted against average weight (data in Table 4.5-1). Whole body concentrations from the current study were converted to estimated fillet concentrations using the equation given by (Peterson *et al.* 2007).

Although general trends may not yet be obvious for mercury, encouraging downward trends have been observed where there was a specific local problem such as in the river Yare (Figure 4.5-10). This river is influenced by a sewage treatment works which received significant amounts of mercury with industrial effluent in the 1960s and 1970s. When mercury concentrations exceeding the food standard were observed in fish, the discharge consents were reduced eventually leading to an improvement in the Hg concentrations which for roach were indistinguishable to those from a control site by 1994, although they were still elevated in eel (Edwards *et al.* 1999).

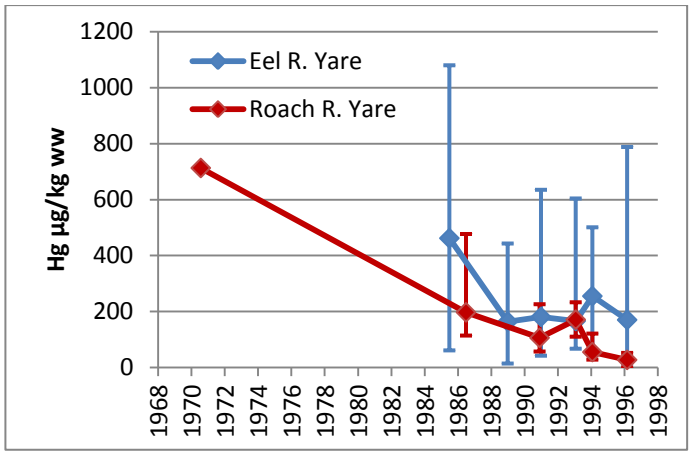


Figure 4.5-10 Mercury in eel and roach from the river Yare (Norfolk) over time. Data from (Downs *et al.* 1999, Edwards *et al.* 1999). Average, min and max plotted. Mercury contamination from chemical industry in the late 1960s/early 70s entering via sewage discharge was documented in this river (Downs *et al.* 1999, Edwards *et al.* 1999).

Figure 4.5-7 shows mercury contamination in large bream collected in two English estuaries (Knopf *et al.* 2014). Although the time series is very short (7 years) and in the case of the Mersey incomplete, there appears to be an increasing trend until 2012 with a small decrease in 2013. The protocol and species used in (Knopf *et al.* 2014) was the same as those monitored routinely in German rivers where reducing Hg concentrations in bream have been found over the last 20 years at many but by no means all sites. At some German sites Hg concentration in bream was still increasing and at most sites it was higher than at the two English sites measured (Lepom *et al.* 2012) (see also chapter 4.4).

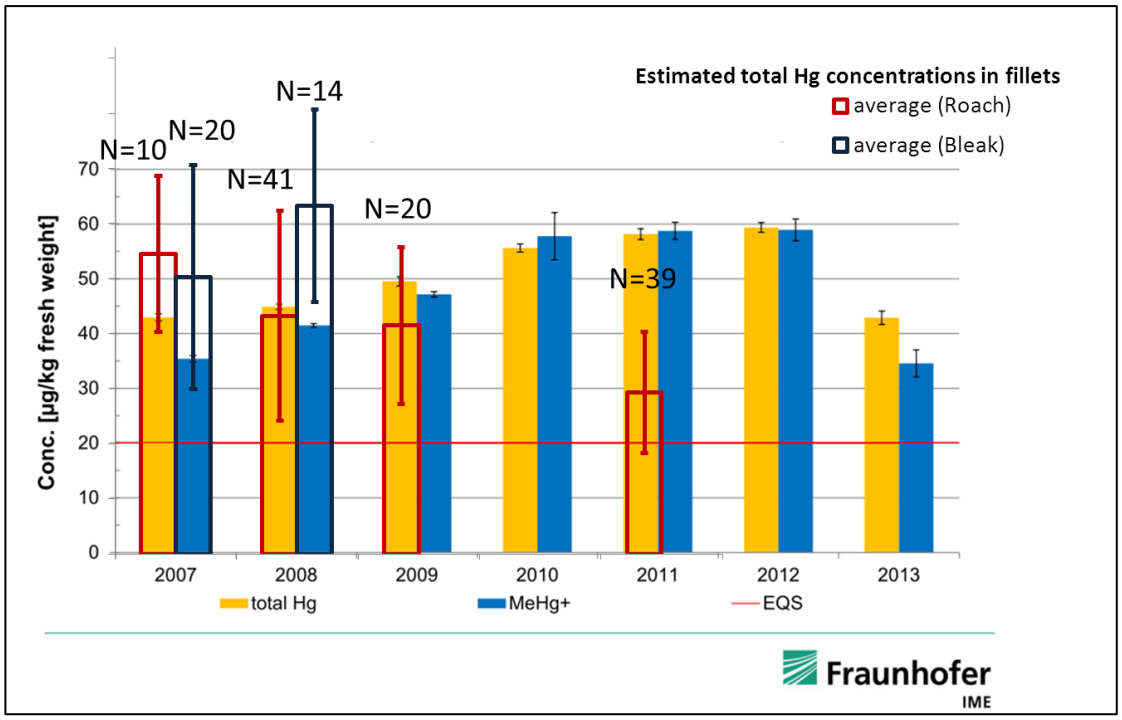


Figure 4.5-11 Mercury concentrations in fish from this study (average and std. dev. of all individuals analysed from that year) superimposed on the bream data from the river Tees (UK) from Knopf *et al.* (2014). Fillet concentrations for the current study were estimated from whole body concentrations using the equation from Peterson *et al.* (2007).

In summary, there is not yet sufficient data to show whether mercury contamination of freshwater fish in the UK is declining as has been shown in other countries, for example Germany (Lepom *et al.* 2012). On the whole the concentrations found in roach and bleak in the current study are similar to comparable samples previously measured

4.5.1.2 Cadmium in roach

The cadmium concentrations in roach from the present study, are generally lower than most of those previously reported in the UK (Figure 4.5-12).

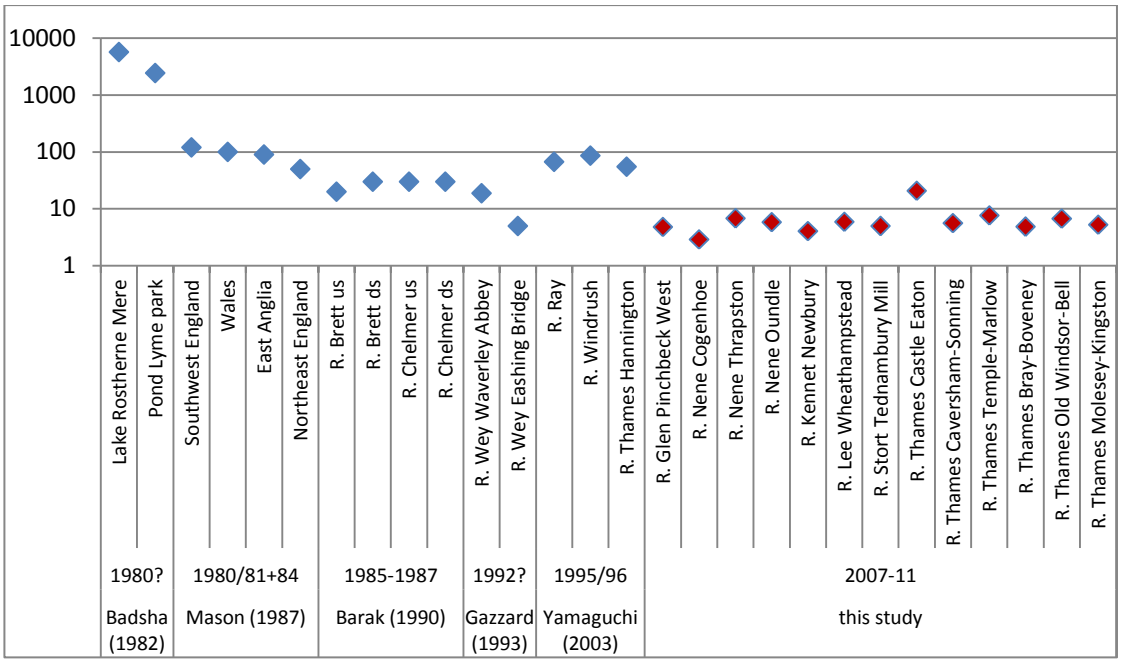


Figure 4.5-12 Cadmium concentrations in roach compared to literature data.

4.5.1.3 Lead

The lead concentrations found in this study were comparable to those reported by Barak and Mason (1990b) and Gazzard and Yorke (1993) in the late 1980s and early 1990s, but clearly lower than the ones Mason (1987) measured in the early 1980s. The quite marked difference between the lead concentrations measured by Mason (1987) and the much lower ones in the other two studies is unlikely to be due to the time difference of just 5 years between them and reflects probably site differences.

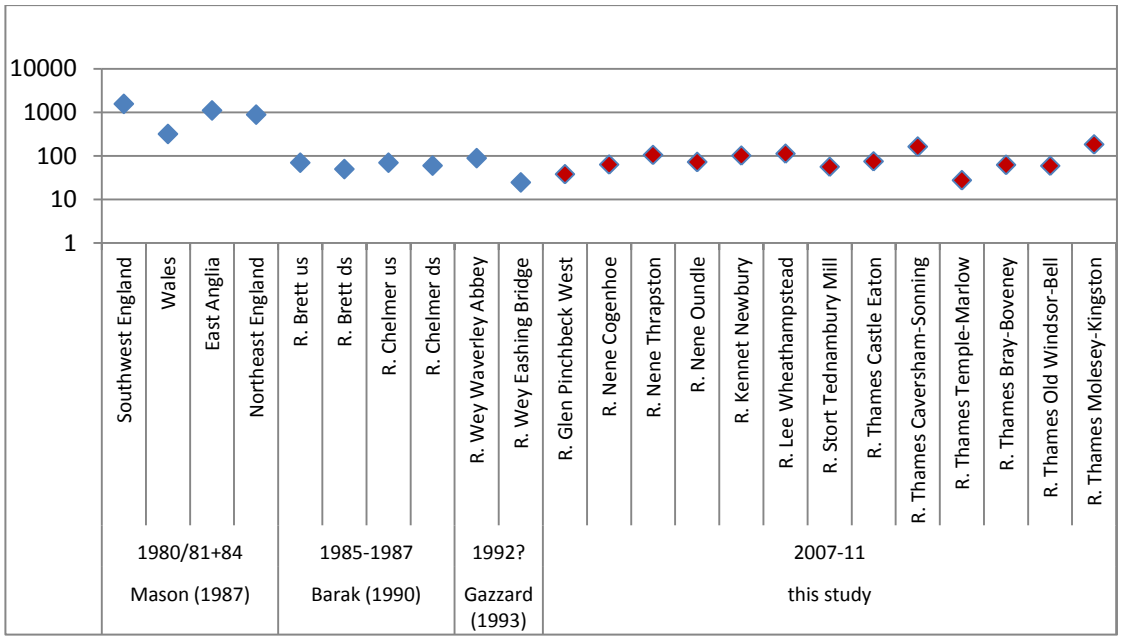


Figure 4.5-13 Lead concentrations in roach compared to literature data.

4.5.1.4 Zinc

Only one previous study reporting zinc concentrations in roach was found (Badsha and Goldspink 1982). This reported zinc concentrations in roach caught at two sites near Manchester which were about twice as high as those measured in this study. By comparison the lead and cadmium concentrations reported by (Badsha and Goldspink 1982) were more than one or two orders of magnitude higher respectively than the ones in the currents study (Table 4.5-1). This may reflect a generally low variability in zinc concentrations. In our samples zinc was among the least variable chemicals measured with the highest values for an individual fish just 4.4 times as much as the lowest and 90% of values within a factor 2.3.

4.5.1.5 Other metals

No other data for metals in roach or bleak in the UK has been found.

4.5.2 Organochlorine pesticides and PCBs in eels

Since eels have been monitored frequently for organic pollutants in the past it was decided to use the eels data rather than the larger number of roach measured in this study for comparison to previous literature.

The following graphs summarize UK literature data ordered by year the eels were caught. Although the spread of values is very large, the highest values seem to be in the earlier studies for pp'DDE (main degradation product of DDT) and lindane, while PCBs have not been measured in the earlier studies.

Table 4.5-2 Past UK literature data for selected contaminants in yellow or silver eel [µg/kg fw], >30cm length if possible. Median and range of site averages. Sorted by country and sampling date. Some data was estimated from graphs or calculated from values given by lipid content or dry weight (updated from table in (Jürgens *et al.* 2015)

Year(s) of capture	locations	number sites	samples per site	t[a]	DDE	γ-HCH (lindane)	HCB	ICES7 PCB	reference
	United Kingdom								
1983	sheep dip impacted sites, SW England[bc]	4	6-8	m	245 (77-298)	58 (30-79)	-	-	(Hamilton 1985)
	unimpacted sites, SW England[b]	3	7-8	m	54 (51-83)	48 (21-171)	-	-	
1984	sheep dip impacted sites, SW England[b]c	5	n.a.	m	<14 (<5-230)	-	-	-	
	unimpacted sites, SW England[b]	3	n.a.	m	<15 (<5-<36)	-	-	-	
1985	sheep dip impacted sites, SW England[b]c	3	n.a.	m	<190 (<47-209)	-	-	-	
	unimpacted sites, SW England[b]	1	n.a.	m	40	-	-	-	
1986	urban sites in Scotland	8	1 pooled		186 (43-557)	45 (25-63)	-	-	cited in (Macgregor *et al.* 2010)
	rural sites in Scotland	10	1 pooled		322 (33-994)	33 (2.8-1413)	-	-	
	mixed u/r sites in Scotland	2	1 pooled		91 (61, 120)	56 (11,100)	-	-	
1991	Scottish Reed beds	11	1 pooled	w	60 (<10-270)	-	-	ca. 20 (ca.3-ca. 250)[d]	(Mason 1993)
1994/95	contaminated sites Sussex, S England	18	5	m	79 (18-635)	16 (<0.1-60)	-	26 (6.8-383)[e]	(Foster and Block 2006)
1995/96	Rivers Thames & Windrush SE England	2	2	m	-	3.3 (1.6,4.9)	-	<13[f]	(Yamaguchi *et al.* 2003)
1996	River Severn, W England/Wales	2	5 pooled	m	-	-	-	100 (92,109)	(Harrad and Smith 1999)
2004-08	urban sites in Scotland	12	5	m	49 (<1-225)	<3.9 (<1-4.68)	ca. 1.5 (≤1-ca. 2.5)	69 (7.1-1878)	(Macgregor *et al.* 2010)
	rural sites in Scotland	14	5	m	84 (<1.5-358)	<3.9 (<1-2.82)	ca. 1.5 (≤1.1-ca. 2.5)	15 (5.9-54)	
	mixed u/r sites in Scotland	3	5	m	33 (12-51)	<1 (<1-4.79)	<1 (<1-1.8)	22 (15-172)	

Year(s) of capture	locations	number sites	samples per site	t[a]	DDE	γ-HCH (lindane)	HCB	ICES7 PCB	reference
2005	Thames estuary, SE England	1	1 pooled	m	-	-	-	136	(Santillo *et al.* 2005)
2005/06	contaminated sites Sussex, S England	21	5	m	43 (11-178)	<1.5 (<1-<25)	-	29 (7.5-89)	(Foster and Block 2006)
2007	Thames, near London SE England	2	11, 24	s	10 (10,11)	0.84 (0.58,1.1)	2.2 (1.9,2.5)	44 (33, 56)	current study

[a] type of sample: m: muscle, s: section, w: whole body

[b] only eels >30 cm

[c] includes a site that was thought to be un-impacted, but had high levels of dieldrin and DDE

[d] estimated using the conversion arochlor1260=3.6*ICES7 PCB (Weatherley *et al.* 1997)

[e] calculated from the individual PCB concentrations given in that report

[f] only 6 congeners, usually the ICES6 which are on average 85% of ICES7 in our eels

4.5.2.1 Pesticides

The burden of organo-chlorine pesticides measured in the Thames eels from this study is lower than some of the previous measurements from the UK, suggesting that there may be a downward trend in the environment as would be expected after a ban. As the sites, sizes and methods vary between studies such conclusions are only tentative. In Belgium, however large numbers of eels were analysed over 11 years allowing for trends to be determined at those sites that were sampled at least twice. For lindane the Belgian trend was very clear showing a reduction by almost 2 orders of magnitude during the 11 year period (1 order of magnitude per 6 years), whereas the reduction was slower for HCB, α-HCH and total DDT (estimated to take between 20 and 25 years to reduce by a factor 10).

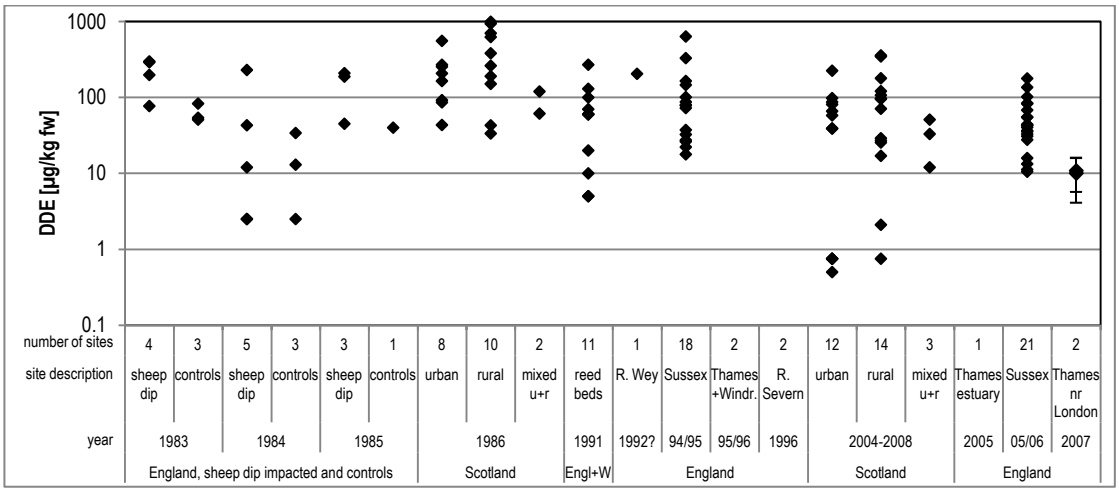


Figure 4.5-14 Historic pp'DDE concentrations in UK eels, site averages sorted by date of capture. Where some or all values were <LOQ or only given in graphs, a best estimate was made. References and more details are given in Table 4.5-2. The results from the current study are plotted in red with error bars showing the standard deviation.

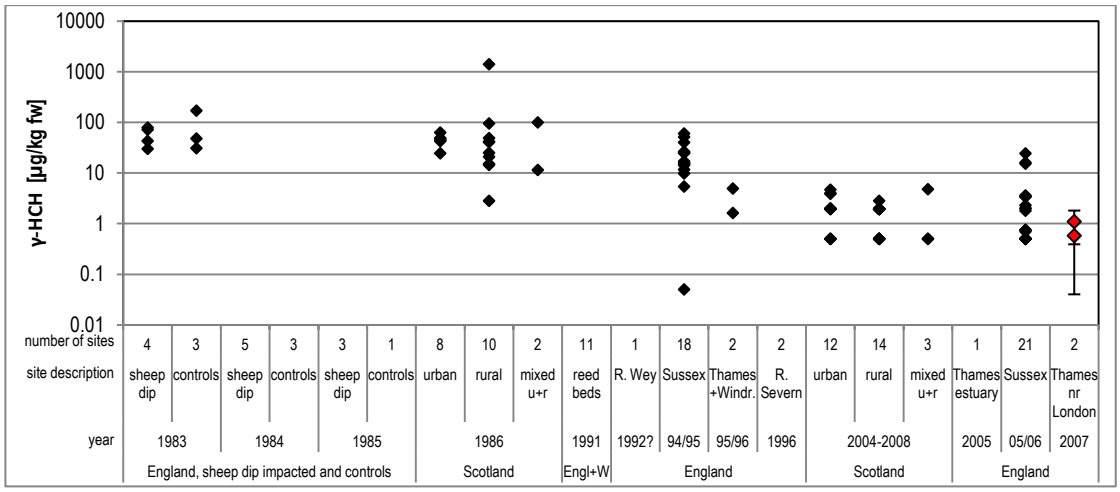


Figure 4.5-15 Historic lindane (γ-HCH) concentrations in UK eels, site averages sorted by date of capture. Where some or all values were <LOQ or only given in graphs, a best estimate was made. References and more details are given in Table 4.5-2. The results from the current study are plotted in red with error bars showing the standard deviation.

4.5.2.2 PCBs

Although the high PCB values reported in some UK sites in the 1990s (Gazzard and Yorke 1993, Mason 1993, Harrad and Smith 1999, Foster and Block 2006, see also Table 4.4-2), were not repeated in this and other recent studies, there is not a very clear downward trend over time. Foster *et al.* (2006) argued that PCB contamination of Sussex (UK) eels had reduced between 1994/95 and 2005/06, but there is a discrepancy between the values for individual ICES7 PCBs and the published sums for the 1994/95 data in that report. When the individual values are used to derive the ΣICES7 (as done in Figure 4.5-16) there is no obvious difference between the two data sets. For Belgium more comprehensive data than for the UK is available and Maes *et al.* (2008) could show in an extensive dataset of eels caught in Flanders between 1994 and 2005 that PCB contamination has gone down recently (at least in Flanders) at a rate which would take about 14 years to reduce by an order of magnitude.

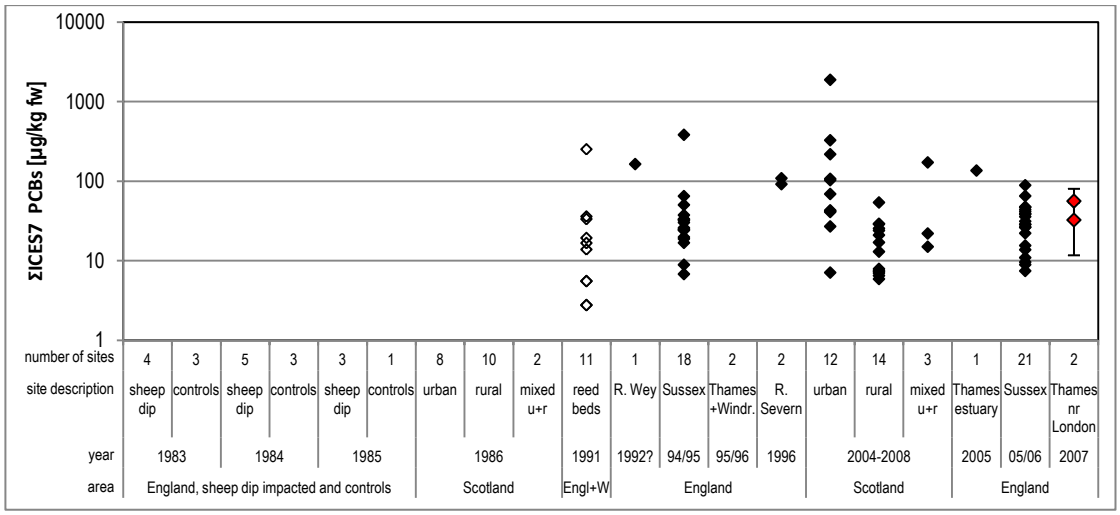


Figure 4.5-16 Historic PCB concentrations in UK eels, site averages sorted by date of capture. Where some or all values were <LOQ or only given in graphs, a best estimate was made. The 1991 reed bed values were estimated from published Arochlor concentrations using the conversion Arochlor1260=3.6*ICES7 PCB suggested by (Weatherley *et al.* 1997). References and more details are given in Table 4.5-2. The results from the current study are plotted in red with error bars showing the standard deviation.

5 Conclusions

Use of the Fish Tissue Archive

- Using fish tissue burdens is a practical and sensible approach to monitoring the pollution of freshwater systems with both organic and inorganic pollutants. Compared to water the contaminant levels in fish are:
    - less variable because they integrate contaminant burdens over their life time
    - often easier to measure despite the more difficult matrix, because the concentrations can be much higher
    - more relevant with regards to potential harm both to the species sampled and to their predators (including humans), as only the bioavailable fraction is measured
- Three species of fish were considered for this study: eels, bleak, and roach
    - Eels are very suitable for monitoring water quality where they reside, but few are found in the upper reaches of rivers and due to them being now classified as critically endangered, their routine use for monitoring cannot be recommended.
    - Due to their small size, limiting the amount of material available for analysis, bleak are less suitable
    - Therefore roach are recommended as a common species suitable for monitoring river water quality in the UK environment. If resources allow, it would also be beneficial study more than one species - ideally with differences in feeding habits, habitat use etc.
- Whole body homogenates are suitable for monitoring the chemicals investigated so far, but fillets or specific organs can also be used where that is more appropriate (though the small size of organs may limit what can be analysed)
- Storing samples long term at -80°C allows for retrospective monitoring of a wide range of parameters

More than 100 roach, 34 bleak and 35 eels caught in English rivers between 2007 and 2011 were analysed for a suite of metals, organochlorine pesticides, PCBs

and PBDEs (metals and PBDEs in roach and bleak only), allowing to address the aims of this study.

- Are food standards exceeded in any of the samples?No food standards were exceeded, except for lead, which was measured above the limit of 300 µg/kg wet weight in 3% of individual fish, but for dioxin-like toxicity only some of the compounds contributing to the standard have been measured.

Are environmental quality standards exceeded in any of the samples?

- The environmental quality standard (EQS) for hexachlorobenzene (HCB) of 10 µg/kg was never exceeded. The maximum concentration was 6 µg/kg (or only 2.1 µg/kg if normalised to 5% lipid as advised by the EU).
- The EU EQS for mercury (20 µg/kg) was exceeded in more than ¾ of fish where it was measured.
- The EU EQS of 8.5 ng/kg for PBDEs was exceeded by several orders of magnitude in every sample where it was measured, but the value proposed to protect wildlife consumers (44 µg/kg) was only reached in one of 99 individual roach and bleak measured, suggesting that, despite exceeding the EQS, PBDE concentrations were unlikely to be high enough to harm those fish or their predators (including humans).The EU EQS for dioxin-like toxicity is the same as the food standard (6.5 ng/kg TEQ) and was not exceeded, but not all compounds contributing have been measured, so the actual values would be higher. 12% of roach, 71% of bleak and 94% of eels exceeded a Canadian EQS for dioxin-like toxicity for the measured compounds alone.
- 15% of roach, 24% of bleak and 54% of eels exceeded a Canadian EQS for total DDT of 14 µg/kg (no EU standard exists).
- A proposed US selenium EQS of 8.1 µg/kg dw was narrowly exceeded in only one individual.

Are the contamination levels likely to have negative effects on the fish themselves or their predators (including human consumers)?

- None of the chemicals measured were at levels likely to cause problems for the fish themselves, but some of those where environmental quality standards were

frequently exceeded (mercury and perhaps DDT and dioxin-like toxicity especially in eels) may be of concern to their predators.

Are the differences in chemical contamination between individual fish samples related to other fish parameters, such as size/age, lipid content, species, etc. and can normalisation to account for those differences make values more comparable?

- Mercury and selenium levels depended primarily on the size of the fish with larger individuals being more contaminated, but once that size dependence was taken into account, site patterns related to the distance of the sampling sites to the river sources emerged.
- The concentrations of most other metals measured decreased with increasing size of the fish. The negative correlation with size was significant at the 5% level for both roach and bleak for chromium, zinc, and molybdenum and additionally for cobalt if dry-weight normalised data was used.
- For some, but not all, persistent organic pollutants, lipid-normalising the measured concentrations reduced the variability between individuals and the difference between analysis of liver samples and carcass samples.

Are different or similar patterns observed with different compounds?

- Strong correlations were found between some individual metals, for example, aluminium, iron, and cobalt or chromium and molybdenum. This may be because they tend to be used together in alloys.

Are there spatial patterns in the results from this study and what may have caused them?

- Comparing the contamination between different sites, **very high DDT** concentrations and also elevated concentrations of the pesticides lindane and chlordane and copper, which is the active ingredient in some fungicides, were found in fish from a site on the river Lee. This site had been chosen because it has high input of sewage treatment works effluent. A closer look at the history of the

area revealed that the fish were caught very close to the site of a former pesticide factory with associated beds for testing the effectiveness of their products. This provides a plausible explanation for the very high levels of some (but not all) pesticides. This can be seen as an example how unexpected results in the fish data can point towards a previously unknown problem, which warrants further investigation and also shows the long legacy persistent chemicals can leave decades after their production and use has stopped.

- Cadmium levels were about 3-4 times higher in roach from the Castle Eaton site on the upper Thames than any other site monitored. The reason for this is not known, but may be do with the town of Swindon and its sewage works being on a tributary (River Ray) a short distance upstream of that site.
- Size-adjusted mercury concentrations increased with distance from the river source in the upper reaches of the various catchments, but not in the lower Thames.
- Size-adjusted selenium concentrations decreased with distance from the river source in the lower Thames.
- PBDE concentrations in the fish were correlated to the estimated average proportion of treated sewage contributing to the flow in the rivers where they were caught. This may be because PBDEs can enter the aquatic environment with domestic waste water when PBDE containing house dust, mainly from soft furnishings, is caught on clothes and subsequently washed off in the laundry.

Are there regional trends when compared to other European data?

Metal concentrations were measured in roach and bleak, and could be compared to recent literature data for mercury, lead, and cadmium.

- Mercury concentrations were lower than most of those reported for freshwater fish from other European countries, but comparable to some other data for small fish.
- Lead concentrations were mostly in the medium to high category compared to reference values established by the German environmental specimen bank, but were overall in a typical range for recent European studies.
- Cadmium concentrations were relatively low compared to available data from Luxembourg and the Netherlands.

- Eels were compared to other recent European studies for PCBs and those pesticides for which sufficient literature data was found. The contamination of Thames eels with organochlorine pesticides was relatively low for *pp*'DDE and fairly typical for HCB across Europe. For lindane, the concentrations were similar to those measured in Scotland and Southern Europe, but lower than most of the values from the Netherlands and Germany. PCB concentrations in European eels varied wildly between and within studies, but the Thames eels in this study were within the lower part of that range.

Are there temporal trends when compared to previous UK data?

- Concentrations in UK roach have previously been reported for a few metals, allowing some comparisons.
- Although mercury concentrations were lower than in many previous UK studies, it is unclear, whether this reflects a trend or can be explained by different sizes of fish and sample types (fillet, compared to whole body homogenate in the current study).
- Lead concentrations measured were comparable to literature data from the late 1980s and early 1990s, but lower than those reported in a study from the early 1980s.
- Cadmium concentrations were generally lower than most of those previously reported in the UK.
- Zinc concentrations were about half of those reported in the only previous UK study that reported this parameter in roach
- Concentrations of some organochlorine pesticides and PCBs in Thames eels were compared to previous UK data. The main DDT degradation product *pp*'DDE and lindane (γ-HCH) and were lower than in most previous studies. For PCBs, only relatively recent data from the 1990s onwards was available for the UK and was comparable to the concentrations measured in the present study.

Overall, the fish measured were relatively clean by comparison to previous UK and international data although high pesticide levels were measured at one site (Wheathampstead on the river Lee, close to a former pesticide factory).

6 Recommendations

Our understanding of environmental pollution is often hampered by insufficient knowledge of the past. Collecting samples and storing them for future use can help to address that issue, allowing spatial and temporal trends to be determined, even for chemicals which were not measured at the time of sampling. Provided the storage conditions are suitable, measuring both old and recent samples at the same time and with the same methods reveals trends more reliably than comparing recent measurements to published data (which may not be available anyway). Having "before" samples available is essential to monitor the impact of new industrial activities or accidents, such as oil or other chemical spills, but also to ascertain how successful attempts to improve the environment are, such as major upgrades to sewage treatment works or restrictions on chemicals or activities. Thus the benefits of an environmental specimen bank can be summarized as follows:

Archiving allows today's samples to be used to answer tomorrow's questions.

For the freshwater environment, biota samples are particularly useful, because they concentrate bioaccumulative substances and are very relevant in terms of potential harm to the environment as they represent the bioavailable fraction. Different parts of the aquatic food web could be monitored, but choosing fish over invertebrates or plants has the advantage of allowing for reasonably large sample sizes and also being relatively high in the aquatic food web, they integrate the chemical pollution from the trophic levels below. Although for these reasons top-predators would be desirable species to monitor, it would be both difficult and unsustainable to collect and monitor them routinely, since they tend to occur in smaller numbers than animals lower in the food web. Therefore it is recommended to use a common medium-sized species, such as the roach, keeping as much as possible to a consistent size or age.

Collection and storage of individual whole fish is recommended. If the whole fish are archived then it can still be decided at a later stage whether to measure contaminants in whole body homogenates, or whether to monitor the fillet or specific organs such as the liver and if individual fish are stored rather than pooled samples, subsamples can be pooled later to reduce the cost of analysis or achieve the required

sample size. For example, in the case of the present study, the cost per sample for the analysis of metal content and the amount of material needed was much lower than for organochlorine compounds, so more samples (individuals or pools) could be analysed for metals at an acceptable cost.

Ideally, fish should be collected annually in autumn, thus avoiding the variability around the spawning period, which is introduced by fish losing some of the chemicals in their bodies with the eggs and sperm, and reducing the impact of the sampling on the populations as the collected individuals would have already produced a new generation, but the most cost-effective sampling strategy is to take advantage of the Environment Agency fish population monitoring. This takes place between spring and autumn with each site being visited at the same time each year (weather permitting). Although autumn sampling is preferable for the reasons abov, sampling shortly before spawning has the advantage that the sex can be determined very easily by stripping a small amount of eggs or sperm during sampling. For sites on smaller rivers where a removal of 10 roach each year is not sustainable, less frequent sampling is recommended.

Ideally subsamples of fish from all sampling years at all sites would be analysed to monitor trends, but as that would be too expensive, it would be sensible to choose a subset of sites and perhaps analyse 5 fish from every third year for an initial screening. This has less statistical power than analysing fish from every year (Bignert 2003), but if fish are collected annually, even if they are not analysed, then samples from the intervening years can be analysed later, if the findings of the initial screening suggest that more detail is required.

Both results of any analyses and details of what samples are stored in the archive and may be available for research should be made available to other researchers to maximise the usefulness of both samples and data. While such information would ideally be available in a searchable form online, the tables in the appendix of this thesis are intended to be at least a start, encouraging collaboration with colleagues in the UK and abroad.

The updated version of the Priority Substances Directive (European Union 2013) now requires biota (usually fish) to be monitored for a number of chemicals and the use of environmental specimen banks is recommended in the accompanying guidance document (European Commission 2010). The Fish Archive is very suitable for this and has the advantage that it was already started **before** the regulations came

into force, therefore allowing not only to comply with the future monitoring requirements but also to compare those samples to the ones from the recent past. However, the number of sites from which fish are collected is still relatively small and doesn't cover the whole country, so if the Fish Archive is to become part of the required biota monitoring of the Environment Agency, it will need to expand geographically.

Recommendations summary

The recommendations for the continuation of the Fish Archive are:

- Collect and store individual samples of whole fish
- Storage at -80°C or even in liquid nitrogen minimizes changes over time and maximises the number of parameters for which samples can be analysed in the future.
- Unless the available sample is so small that all of it is needed for the intended analysis, the intended sample (whole fish or organ) of an individual fish should be homogenised and divided into sub-samples prior to analysis, so that remaining sub-samples can be stored for other analyses in the future.
- For trend monitoring of chemicals where the analysis is a very large cost factor compared to the cost of collecting and preparing samples (such as the organochlorine contaminants measured here), **several** composite samples from **sub-samples** of the individual homogenised samples should be prepared. As 10 fish have generally been collected per site and year, two pooled samples of five fish each is the minimum. To allow for easy division into 3 or 4 subsamples the target number of fish collected per site and year should perhaps be increased to 12 in future.
- Where the cost of analysis is relatively low, where variability between individuals has not been tested recently or where the analysis of composite samples yielded unusual or unexpected results, individual samples should be analysed.
- Results should be made available to other researchers to maximise the usefulness of the data.

- Samples should also be shared with other researchers, but since the available material is limited, decisions have to be made considering on a case by case basis, whether the expected knowledge increase justifies the number and amount of samples required.

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8 Appendix

8.1 Tables of raw data

8.1.1 Overview of what fish have been collected and what -if anything- has been measured

Table 8.1-1 All fish sampled so far (December 2014) and what -if anything- has been measured [abcd]

Region	River	site	km ds of source	year	fish caught	dry weight	lipid content	metals	pesticides (HCB, DDTs, +Chlordanes)	pesticides (HCHs + endosulfans)	PCBs	PBDEs	EDCs in bile[e]	pharmaceuticals in plasma[f]
Anglian	Glen trib.	Bourne Eau	5	2009	10 R	-	-	-	-	-	-	-	-	-
	Glen	Pinchbeck W.	53	2009	30 R	5 R	5 R	5 R	4 R	-	4 R	4 R	-	-
	Welland	Stamford Meadows	67	2008	10 R	-	-	-	-	-	-	-	-	-
				2009	30 R	-	-	-	-	-	-	-	-	-
				2011	12 R	-	-	-	-	-	-	-	-	-
				2013	26 R	-	-	-	-	-	-	-	-	-
		Deeping St. J.		2014	20 R	-	-	-	-	-	-	-	-	-
	Nene	Clifford Hill	38	2010	14 R	-	-	-	-	-	-	-	-	-
				2012	20 R	-	-	-	-	-	-	-	-	-
		Cogenhoe	40	2008	10 R	10 R	5 R	10 R	5 R	5 R	5 R	5 R	-	-
				2009	30 R	-	-	-	-	-	-	-	-	-
				2012	20 R	-	-	-	-	-	-	-	-	-
		Thrapston	72	2008	10 R	10 R	10 R	10 R	5 R	-	5 R	5 R	-	-
				2009	14 R	-	-	-	-	-	-	-	-	-
		Oundle	90	2008	9 R	10 R	10 R	10 R	5 R	5 R	5 R	5 R	-	-
				2009	18 R	-	-	-	-	-	-	-	-	-
				2010	27 R	-	-	-	-	-	-	-	-	-
		Elton	101	2008	10 R	-	-	-	-	-	-	-	-	-

Region	River	site	km ds of source	year	fish caught	dry weight	lipid content	metals	pesticides (HCB, DDTs, +Chlordanes)	pesticides (HCHs + endosulfans)	PCBs	PBDEs	EDCs in bile[e]	pharmaceuticals in plasma[f]
Midlands	Anker	Leather Mill	20	2012	11 R	-	-	-	-	-	-	-	-	-
				2014	10 R	-	-	-	-	-	-	-	-	-
		Ratcliffe Bridge	25	2013	13 R	-	-	-	-	-	-	-	-	-
				2014	21 R	-	-	-	-	-	-	-	-	-
		Fieldon Bridge	27	2014	20 R	-	-	-	-	-	-	-	-	-
		Polesworth	35	2013	16 R	-	-	-	-	-	-	-	-	-
				2014	10 R	-	-	-	-	-	-	-	-	-
		Tamworth	44	2012	11 R	-	-	-	-	-	-	-	-	-
				2014	10 R	-	-	-	-	-	-	-	-	-
Thmaes trib.	Kennet	Newbury	58	2011	9 R	9 R	9 R	9 R	9 R	(9 R)	9 R	9 R	-	-
	Lee	Wheathampstead	24	2011	10 R	10 R	10 R	10 R	10 R	(10 R)	10 R	10 R	-	-
	Stort	Tednambury Mill	29	2011	10 R	10 R	10 R	10 R	10 R	(10 R)	10 R	10 R	-	-
Thames	non-tidal Thames	Cricklade	36	2008	9 R, 1 B	-	-	-	-	-	-	-	-	-
				2009	20 R	-	-	-	-	-	-	-	-	-
				2010	13 R	-	-	-	-	-	-	-	-	-
				2013	10 R	-	-	-	-	-	-	-	-	-
		Castle Eaton	43	2009	11 R	-	-	-	-	-	-	-	-	-
				2011	10 R	10 R	10 R	10 R	10 R	(10 R)	10 R	10 R	-	-
				2013	12 R	-	-	-	-	-	-	-	-	-
		Sandford-Abingdon	106-113	2011	11 R	-	-	-	-	-	-	-	-	-
				2012	10 R	-	-	-	-	-	-	-	-	-
				2013	7 R	-	-	-	-	-	-	-	-	-
				2014	10 R	-	-	-	-	-	-	-	-	-
		Caversham-Sonning	162-166	2008	10 R, 13 B	10 R, 13 B	10 R, 13 B	10 R, 13 B	2 R, 3 B	2 R, 3 B	2 R, 3 B	2 R, 3 B	-	-
				2009	20 R	-	-	-	-	-	-	-	-	-
				2010	26 R	-	1 R	-	1 R	-	1 R	1 R	-	-
				2011	10 R	-	-	-	-	-	-	-	-	-
				2012	10 R	-	5 R	-	5 R	-	5 R	5 R	-	-
				2013	10 R	-	-	-	-	-	-	-	-	-

Region	River	site	km ds of source	year	fish caught	dry weight	lipid content	metals	pesticides (HCB, DDTs, +Chlordanes)	pesticides (HCHs + endosulfans)	PCBs	PBDEs	EDCs in bile[e]	pharmaceuticals in plasma[f]
Thames	non-tidal Thames	Shiplake-Marsh	170-175	2010	10 R	-	-	-	-	-	-	-	-	-
				2011	10 R	-	-	-	-	-	-	-	-	-
				2012	10 R	-	-	-	-	-	-	-	-	-
				2013	11 R	-	-	-	-	-	-	-	-	-
		Temple-Marlow	187-190	2007	5 R, 12 B	5 R, 5 B	4 R, 4 R liver, 5 B	5 R, 5 B	4 R (only DDTs), 4 R liver (only DDTs), 5 B, 4 B liver	5 B (only HCH), 4 B liver	4 R, 4 R liver, 5 B, 4 B liver	4 R, 4 R liver, 5 B, 4 B liver	4 R	
				2008	5 R, 5 B	-	-	-	-	-	-	-	-	-
				2009	10 R	-	-	-	-	-	-	-	-	-
				2010	10 R	-	-	-	-	-	-	-	-	-
				2011	10 R	-	-	-	-	-	-	-	-	-
				2012	10 R	-	-	-	-	-	-	-	-	-
				2013	13 R	-	-	-	-	-	-	-	-	-
				2014	8 R	-	-	-	-	-	-	-	-	-
		Marlow-Cookham	190-196	2007	4 R, 11 B	-	-	-	-	-	-	-	3 R	
				2008	5 R, 5 B	-	-	-	-	-	-	-	-	-
				2009	10 R	-	-	-	-	-	-	-	-	-
				2010	10 R	-	-	-	-	-	-	-	-	-
				2011	9 R, 1 D	-	-	-	-	-	-	-	-	-
				2012	10 R	-	-	-	-	-	-	-	-	-
				2013	16 R	-	-	-	-	-	-	-	-	-
		Cookham-Boulters	196-200	2007	5 R, 10 B	-	-	-	-	-	-	-	5 R	
				2008	6 R, 4 B	-	-	-	-	-	-	-	-	-
				2009	8 R	-	-	-	-	-	-	-	-	-
				2010	10 R	-	-	-	-	-	-	-	-	-
				2012	10 R	-	-	-	-	-	-	-	-	-
				2013	11 R	-	-	-	-	-	-	-	-	-
		Boulters-Bray	200-203	2007	6 R, 12 B	-	-	-	-	-	-	-	5 R	
				2010	10 R	-	-	-	-	-	-	-	-	-

Region	River	site	km ds of source	year	fish caught	dry weight	lipid content	metals	pesticides (HCB, DDTs, +Chlordanes)	pesticides (HCHs + endosulfans)	PCBs	PBDEs	EDCs in bile[e]	pharmaceuticals in plasma[f]
Thames	non-tidal Thames	Bray-Boveney	203-209	2007	8 R, 10 B	-	-	-	-	-	-	-	8 R	
				2008	11 R, 6 B	3 R, 1 B	3 R, 1 B	3 R, 1 B	-	-	-	-	-	-
				2009	10 R	5 R	5 R	5 R	-	-	-	-	-	-
				2011	11 R	-	-	-	-	-	-	-	-	-
				2012	10 R	-	2 R	-	2 R	-	2 R	2 R	-	-
				2013	22 R	-	-	-	-	-	-	-	-	-
				2014	9 R	-	-	-	-	-	-	-	-	-
		Boveney-Romney	209-211	2007	6 R, 12 B	-	-	-	-	-	-	-	6R	
				2008	5 R	-	-	-	-	-	-	-	-	-
				2009	10 R	-	-	-	-	-	-	-	-	-
				2011	10 R	-	-	-	-	-	-	-	-	-
				2012	10 R	-	-	-	-	-	-	-	-	-
				2013	10 R	-	-	-	-	-	-	-	-	-
				2014	10 R	-	-	-	-	-	-	-	-	-
		Romney-Old Windsor	211-216	2007	5 R, 10 B	-	-	-	-	-	-	-	5 R	
				2008	5 R, 7 B	-	-	-	-	-	-	-	-	-
				2009	10 R	-	-	-	-	-	-	-	-	-
				2010	10 R	-	-	-	-	-	-	-	-	-
				2011	10 R	-	-	-	-	-	-	-	-	-
				2012	10 R	-	-	-	-	-	-	-	-	-
				2013	18 R	-	-	-	-	-	-	-	-	-
				2014	8 R	-	-	-	-	-	-	-	-	-
		Old Windsor-Bell	216-223	2007	5 R, 10 B	5 R, 5 B	5 R, 4 R livers, 5 B, 5 B livers	5 R, 5 B	5 R, 5 R livers, 5 B livers	5 R, 5 R livers, 5 B livers	5 R, 5 R livers, 5 B livers	5 R, 5 R livers, 5 B livers	5 R	
				2008	1 R, 9 B	-	-	-	-	-	-	-	-	-
				2010	10 R	-	-	-	-	-	-	-	-	-
				2011	10 R	-	-	-	-	-	-	-	-	-
				2012	10 R	-	-	-	-	-	-	-	-	-
				2014	10 R	-	-	-	-	-	-	-	-	-

Region	River	site	km ds of source	year	fish caught	dry weight	lipid content	metals	pesticides (HCB, DDTs, +Chlordanes)	pesticides (HCHs + endosulfans)	PCBs	PBDEs	EDCs in bile[e]	pharmaceuticals in plasma[f]
Thames	non-tidal Thames	Bell-Penton Hook	223-228	2007	10 B	-	-	-	-	-	-	-	-	-
				2008	5 R, 5 B	-	-	-	-	-	-	-	-	-
				2009	10 R	-	-	-	-	-	-	-	-	-
				2010	10 R	-	-	-	-	-	-	-	-	-
				2011	10 R	-	-	-	-	-	-	-	-	-
				2012	10 R	-	-	-	-	-	-	-	-	-
				2013	10 R	-	-	-	-	-	-	-	-	-
		Penton Hook-Chertsey	228-231	2007	10 B	-	-	-	-	-	-	-	-	-
				2008	9 R, 1 B	-	-	-	-	-	-	-	-	-
				2009	8 R	-	-	-	-	-	-	-	-	-
				2010	10 R	-	-	-	-	-	-	-	-	-
				2011	10 R	-	-	-	-	-	-	-	-	-
				2012	10 R	-	-	-	-	-	-	-	-	-
				2013	10 R	-	-	-	-	-	-	-	-	-
		Chertsey-Shepperton	231-234	2010	10 R	-	-	-	-	-	-	-	-	-
				2011	10 R	-	-	-	-	-	-	-	-	-
				2012	10 R	-	-	-	-	-	-	-	-	-
				2013	10 R	-	-	-	-	-	-	-	-	-
		Shepperton-Sunbury	234-239	2007	10 B	-	-	-	-	-	-	-	-	-
				2008	5 R, 5 B	-	-	-	-	-	-	-	-	-
				2010	10 R	-	-	-	-	-	-	-	-	-
				2011	10 R	-	-	-	-	-	-	-	-	-
				2012	20 R	-	-	-	-	-	-	-	-	-
				2013	10 R	-	-	-	-	-	-	-	-	-
				2014	10 R	-	-	-	-	-	-	-	-	-
		Sunbury-Molesey	239-243	2007	10 B, 12 E	10 B	10 B, 11 E	10 B	9 B, 11 E	9 B, 11 E	9 B, 11 E	9 B	-	-
				2010	10 R	-	-	-	-	-	-	-	-	-
				2011	10 R	-	-	-	-	-	-	-	-	-
				2012	10 R	-	4 R	-	4 R	-	4 R	4 R	-	-
				2013	6 R	-	-	-	-	-	-	-	-	-
		Molesey-Kingston	243-251	2009	10 R	10 R	10 R	10 R	-	-	-	-	-	-
				2013	10 R				-	-	-	-	-	-

Region	River	site	km ds of source	year	fish caught	dry weight	lipid content	metals	pesticides (HCB, DDTs, +Chlordanes)	pesticides (HCHs + endosulfans)	PCBs	PBDEs	EDCs in bile[e]	pharmaceuticals in plasma[f]
	Thames Estuary	Woolwich area	297	2007	24 E	-	24 E	-	24 E	24 E	24 E	-	-	-

[a] invalid measurements where something went wrong during the process were not included

[b] R: roach, B: bleak, E: eel, D: dace

[c] HCBD was only attempted in one batch (analysed by Lancaster University). Problems with the analysis prevented accurate quantification, but it was clear that HCBD concentrations were very low, mostly non-detectable

[d] The 2011 fish that were given to Danielle Ashton from the Environment Agency have not yet been considered or entered into the database

[e] Bile from a small number of fish from 2007 was analysed by Sue Jobling's team from Brunel University for estrogens and some xeno-estrogens

[f] Plasma from some of the same fish was analysed by Jerker Fick from Umeå University, Sweden for about 100 pharmaceuticals, but most were below detection limit

8.1.2 Eels

Table 8.1-2 Details of the eel samples analysed. Numbers E201-212 from non-tidal reach at Sunbury-Molesey, numbers E213-236 from tidal reach at Woolwich. (Sample number E204 was not supplied)

Sample ID	Fishing date	Fork Length [mm]	Live weight [g]	lipid content	condition factor[a]	number of AC parasites[b]	age[c]
E201	13/09/2007	505	199.0	3.29 %	0.155	2	13
E202	13/09/2007	550	234.4	2.03 %	0.141	2	n/a
E203	13/09/2007	624	481.7	23.99 %	0.198	3	18
E205	13/09/2007	408	86.0	4.78 %	0.127	10	n/a
E206	13/09/2007	503	207.4	9.63 %	0.163	3	n/a
E207	13/09/2007	350	60.4	1.69 %	0.141	4	7
E208	13/09/2007	621	338.4	2.78 %	0.141	2	15
E209	13/09/2007	592	394.8	29.24 %	0.190	2	n/a
E210	13/09/2007	407	82.6	12.35 %	0.123	0	n/a
E211	13/09/2007	520	193.1	9.00 %	0.137	0	n/a
E212	13/09/2007	501	231.9	11.73 %	0.184	1	11
E213	01/10/2007	357	90.6	36.14 %	0.199	1	6
E214	01/10/2007	405	94.2	19.79 %	0.142	0	9
E215	01/10/2007	375	81.6	17.21 %	0.155	2	7
E216	01/10/2007	462	182.2	11.27 %	0.185	7	n/a
E217	01/10/2007	369	99.2	20.60 %	0.197	0	7
E218	01/10/2007	547	191.4	25.70 %	0.117	5	14
E219	01/10/2007	482	176.0	7.87 %	0.157	0	7
E220	01/10/2007	479	224.7	20.66 %	0.204	0	n/a
E221	01/10/2007	460	166.5	30.33 %	0.171	0	n/a
E222	01/10/2007	374	112.6	19.84 %	0.215	2	9
E223	01/10/2007	537	312.4	20.78 %	0.202	0	n/a
E224	01/10/2007	670	553.8	16.49 %	0.184	0	12
E225	01/10/2007	425	139.4	10.74 %	0.182	1	8
E226	01/10/2007	447	151.7	8.08 %	0.170	0	n/a
E227	01/10/2007	633	667.4	30.45 %	0.263	2	12
E228	01/10/2007	430	121.2	6.74 %	0.152	1	n/a
E229	01/10/2007	432	109.1	11.26 %	0.135	0	9
E230	01/10/2007	380	74.7	13.98 %	0.136	0	n/a
E231	01/10/2007	466	156.2	11.71 %	0.154	1	10
E232	01/10/2007	472	172.8	5.14 %	0.164	1	7
E233	01/10/2007	439	140.5	15.03 %	0.166	0	10
E234	01/10/2007	414	133.3	6.33 %	0.188	1	n/a
E235	01/10/2007	485	193.1	9.46 %	0.169	0	8
E236	01/10/2007	386	114.8	20.49 %	0.200	1	8

[a] Fulton's condition factor: K= weight/length^3 x 100 [g/cm^3]

[b] *Anguillicola crassus* nematodes. All were found in the swim bladder and were either adult or juvenile stages. No larval stages were found

[c] refers to continental age and was determined from stained otoliths by Alan Walker et al from CEFAS

Table 8.1-3 PCBs in individual eel carcasses [µg/kg fresh weight]

Eel / PCB	Sunbury, non-tidal											Woolwich, tidal																								
	E201	E202	E203	E205	E206	E207	E208	E209	E210	E211	E212	E213	E214	E215	E216	E217	E218	E219	E220	E221	E222	E223	E224	E225	E226	E227	E228	E229	E230	E231	E232	E233	E234	E235	E236
18	0.02	0.01	0.06	0.02	0.02	0.01	0.01	0.05	0.03	0.02	0.02	0.05	0.03	0.02	0.02	0.02	0.09	0.01	0.06	0.03	0.03	0.02	0.03	0.02	0.01	0.04	0.04	0.02	0.02	0.02	0.02	0.05	0.01	0.01	0.03
22	0.01	0.01	0.07	0.01	0.01	0.01	0.01	0.04	0.02	0.01	0.01	0.06	0.04	0.02	0.01	0.02	0.11	0.04	0.08	0.05	0.04	0.02	0.04	0.02	0.01	0.07	0.03	0.01	0.01	0.03	0.01	0.08	0.01	0.01	0.02
28/31	0.11	0.03	0.87	0.25	0.23	0.01	0.12	0.80	0.23	0.23	0.30	0.64	0.82	0.64	0.20	0.33	1.34	0.21	1.05	0.66	0.80	0.49	1.93	0.31	0.20	0.62	0.28	0.24	0.35	0.37	0.12	1.32	0.08	0.21	0.31
41/64	1.28	0.44	5.27	1.71	2.83	0.10	1.34	7.49	1.52	2.09	1.71	4.69	5.09	4.15	2.30	3.27	11.1	1.34	6.91	6.09	4.61	2.10	7.11	2.13	1.45	2.90	1.82	2.51	1.74	2.75	1.51	7.15	1.23	1.54	2.24
44	0.15	0.12	1.32	0.27	0.54	0.01	0.14	1.28	0.37	0.31	0.49	2.34	2.81	1.65	0.98	1.42	3.53	0.63	3.04	3.83	1.76	1.47	2.72	0.98	0.50	1.50	0.50	0.48	0.65	1.11	0.43	4.81	0.52	0.63	0.96
49	0.14	0.08	0.76	0.17	0.27	0.01	0.06	0.68	0.21	0.14	0.31	1.75	1.90	1.04	0.40	0.57	1.74	0.55	1.73	2.13	0.73	0.78	3.79	0.59	0.31	1.25	0.39	0.22	0.37	0.75	0.13	2.29	0.27	0.25	0.56
52	1.56	1.22	9.52	1.56	7.18	0.10	2.17	8.57	3.19	4.12	2.18	11.1	10.4	9.09	5.34	8.43	17.0	2.19	15.7	14.6	10.4	8.79	13.4	3.83	3.16	6.43	3.41	4.81	3.14	6.33	3.29	14.9	3.25	3.58	5.24
54	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
56/ 60	0.14	0.06	0.47	0.18	0.24	0.02	0.18	1.06	0.28	0.17	0.23	0.33	0.39	0.47	0.17	0.19	1.23	0.16	0.84	0.57	0.39	0.21	1.12	0.19	0.20	0.36	0.23	0.26	0.20	0.24	0.17	1.07	0.10	0.15	0.16
70	0.04	0.02	0.28	0.09	0.10	0.01	0.05	0.26	0.08	0.07	0.15	0.09	0.10	0.10	0.03	0.04	0.28	0.03	0.16	0.08	0.08	0.06	0.15	0.04	0.03	0.09	0.05	0.04	0.07	0.05	0.02	0.56	0.01	0.02	0.04
74	0.50	0.21	2.10	0.59	1.05	0.05	0.75	4.24	0.94	0.73	0.91	1.74	1.91	1.72	0.70	0.97	3.50	0.52	2.70	2.04	1.55	0.94	4.12	0.76	0.71	1.07	0.68	0.92	0.77	0.90	0.49	2.52	0.37	0.58	0.67
87	0.40	0.24	1.01	0.37	1.37	0.02	0.54	2.47	0.52	0.77	0.62	2.84	2.66	2.01	0.77	1.03	2.70	0.89	1.56	4.32	2.63	1.86	4.83	1.60	0.78	2.21	1.00	1.48	1.10	1.60	0.72	1.84	1.12	0.96	1.29
95	0.27	0.38	1.68	0.36	1.22	0.02	0.49	1.76	0.47	0.70	0.43	7.95	6.03	4.18	1.75	3.07	4.98	1.92	4.00	7.85	4.95	3.73	3.17	2.50	1.32	4.98	1.20	2.87	1.59	2.82	1.25	2.62	1.71	1.65	2.96
99	1.06	0.79	3.04	0.67	2.88	0.11	1.74	5.45	1.05	1.59	1.05	7.82	6.62	4.58	1.84	3.47	5.96	3.15	3.40	7.86	7.31	3.73	10.4	2.88	2.69	4.95	2.47	5.28	2.89	4.19	1.98	1.98	1.86	2.04	3.43
90/101	1.46	1.01	2.82	0.83	3.13	0.17	1.25	4.15	1.71	2.68	2.05	10.8	10.0	6.16	2.87	2.88	8.67	2.36	4.08	11.4	5.53	7.41	17.1	3.67	2.84	7.18	3.51	4.72	2.83	3.63	2.40	4.47	2.63	2.61	3.99
104	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
105	1.51	1.12	3.27	2.62	3.90	0.22	1.90	6.18	1.52	2.13	1.40	2.64	3.06	2.93	1.21	1.80	5.31	1.34	2.48	4.09	3.49	3.72	7.08	1.78	1.90	2.55	1.76	2.61	1.63	2.05	1.34	2.60	1.19	1.27	1.55
110	2.49	1.71	8.55	3.43	8.43	0.30	4.40	13.7	3.08	5.24	3.43	14.2	14.4	12.5	4.63	6.63	18.3	4.65	8.15	15	14	9.84	14.8	6.46	4.30	8.51	4.78	9.36	4.84	7.76	4.39	7.93	4.33	4.54	6.32
114	0.07	0.05	0.17	0.04	0.18	0.01	0.11	0.34	0.08	0.09	0.07	0.14	0.15	0.15	0.06	0.12	0.19	0.07	0.14	0.19	0.17	0.15	0.29	0.07	0.10	0.12	0.05	0.08	0.07	0.10	0.06	0.08	0.07	0.07	0.09
118	4.35	3.05	8.72	5.61	11.7	0.63	6.06	15.9	4.20	6.24	4.30	9.62	10.4	10.2	3.61	6.16	13.9	4.16	7.55	11.8	11.0	9.54	20.2	5.09	5.86	8.05	4.92	7.45	4.94	6.48	3.79	5.62	4.06	3.97	5.06
123	0.10	0.09	0.11	0.03	0.05	0.01	0.05	0.12	0.09	0.15	0.10	0.34	0.19	0.11	0.08	0.07	0.22	0.11	0.23	0.22	0.19	0.10	0.43	0.13	0.07	0.11	0.09	0.14	0.11	0.13	0.08	0.12	0.08	0.10	0.13
138	7.77	6.75	13.8	12.2	18.7	1.53	10.2	25.6	6.61	11.6	7.42	22.4	25.9	20.2	8.64	18.9	24.0	13.3	17.5	25.4	28.2	17.8	36.4	12.8	15.2	18.4	11.5	21.4	13.6	16.1	10.5	14.0	9.82	10.4	13.8
141	0.79	0.67	1.23	1.07	2.05	0.14	1.08	3.83	0.65	1.29	0.82	3.56	3.16	2.70	0.95	2.30	1.88	0.97	1.66	4.35	3.31	1.90	4.88	1.09	1.26	2.00	1.11	1.34	1.39	1.81	0.78	1.82	1.38	1.13	1.60
149	1.65	1.85	4.07	1.76	4.00	0.29	1.84	7.16	1.74	3.03	2.03	15.7	11.6	7.63	2.66	4.99	13.1	4.09	4.81	14.0	9.61	5.91	7.19	5.11	2.73	7.01	2.64	7.06	3.90	5.65	3.03	4.50	3.35	3.09	5.29
151	0.08	0.14	0.50	0.15	0.69	0.01	0.38	1.30	0.23	0.34	0.26	3.02	2.44	1.49	0.73	1.93	2.04	0.88	1.01	3.57	2.11	1.20	1.07	0.86	0.81	2.03	0.48	1.20	0.74	1.01	0.68	0.80	0.90	0.76	1.07
132/ 153	3.39	3.03	6.11	5.56	9.37	0.84	4.78	12.4	2.89	4.79	3.26	13.3	12.9	9.79	3.89	8.57	9.08	7.40	6.90	12.5	13.7	7.53	17.9	6.44	7.06	8.91	5.46	11.2	7.47	7.91	4.88	5.49	4.98	4.98	6.40
155	0.02	0.01	0.15	0.04	0.08	0.00	0.04	0.12	0.02	0.04	0.03	0.07	0.06	0.07	0.01	0.02	0.01	0.02	0.02	0.06	0.07	0.02	0.08	0.04	0.02	0.04	0.02	0.05	0.03	0.04	0.02	0.01	0.04	0.02	0.03
156	0.61	0.47	1.12	0.67	1.90	0.16	0.79	2.77	0.57	0.81	0.57	1.63	1.90	1.58	0.82	1.96	0.97	0.69	1.80	2.00	1.82	1.51	2.85	0.63	1.25	1.29	0.77	1.19	0.77	1.10	0.67	1.19	0.71	0.74	1.02
157	0.18	0.12	0.28	0.34	0.38	0.03	0.20	0.61	0.15	0.25	0.17	0.45	0.51	0.36	0.17	0.41	0.38	0.18	0.48	0.57	0.54	0.44	0.77	0.21	0.33	0.37	0.22	0.35	0.24	0.32	0.20	0.31	0.18	0.22	0.29
158	0.53	0.49	1.01	0.96	1.30	0.11	0.75	2.09	0.39	0.71	0.42	2.11	1.88	1.60	0.50	0.87	1.26	0.96	0.83	1.99	2.18	1.27	3.21	1.01	0.93	1.14	0.89	1.73	1.02	1.15	0.70	0.77	0.73	0.67	0.89
167	0.35	0.28	0.49	0.64	0.93	0.08	0.46	1.52	0.24	0.49	0.30	0.97	1.24	0.72	0.40	1.12	0.63	0.44	1.16	1.30	1.20	1.01	1.72	0.50	0.86	0.83	0.48	0.82	0.56	0.78	0.46	0.62	0.44	0.55	0.72
170	1.12	0.88	1.52	1.36	2.68	0.29	1.27	4.46	0.23	1.35	0.80	3.27	3.88	2.31	1.23	3.96	1.61	1.56	3.25	3.22	3.94	2.66	5.98	1.51	3.06	2.46	1.43	3.08	1.78	2.28	1.48	2.28	1.36	1.48	2.29
174	0.34	0.31	0.75	0.39	0.85	0.04	0.49	1.81	0.24	0.65	0.39	3.24	2.10	1.64	0.50	1.47	1.42	0.74	0.98	3.13	2.13	0.93	0.93	0.79	0.49	1.51	0.46	0.84	0.93	1.21	0.45	0.91	0.86	0.57	1.13
180	3.15	2.41	4.31	3.92	7.12	0.88	3.46	11.3	1.61	4.02	2.73	12.6	13.3	7.80	3.96	12.9	4.02	5.54	9.77	14.3	12.4	7.10	17.2	4.66	9.36	7.65	4.14	9.69	5.62	7.20	4.32	5.86	4.29	4.98	7.32
183	0.62	0.54	1.11	1.03	1.65	0.16	0.83	2.41	0.42	1.00	0.58	4.07	3.82	2.17	0.78	2.33	1.27	1.84	1.60	3.44	3.46	1.55	3.57	1.61	1.70	1.96	1.07	3.21	1.71	1.95	1.18	0.80	1.16	1.29	1.71
187	1.89	4.24	3.60	2.66	3.60	0.56	2.33	9.03	1.33	2.93	2.20	9.61	9.46	5.92	2.46	7.48	9.60	4.31	5.40	9.57	9.65	4.85	10.6	3.72	5.84	6.03	3.22	7.01	4.51	5.77	3.20	2.05	3.47	3.88	5.25
188	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.01	0.01	n/a	n/a	n/a	n/a	n/a	n/a	0.01	0.01	n/a	n/a	n/a	n/a	n/a	n/a	0.01	n/a	n/a	n/a	n/a	n/a	n/a	n/a
189	0.05	0.04	0.06	0.10	0.13	0.01	0.05	0.20	0.04	0.07	0.04	0.11	0.15	0.09	0.05	0.16	0.08	0.06	0.14	0.17	0.14	0.10	0.24	0.05	0.12	0.09	0.05	0.10	0.07	0.08	0.05	0.09	0.05	0.06	0.08
194	0.54	0.34	0.67	0.90	1.33	0.18	0.55	2.15	0.31	0.77	0.48	1.44	1.67	0.94	0.52	1.74	0.75	0.63	1.29	1.86	1.48	0.92	2.36	0.56	1.19	0.91	0.53	1.15	0.74	0.87	0.53	0.91	0.55	0.61	0.85
199	0.01	0.00	0.01	0.01	0.01	0.00	0.01	0.05	0.00	0.01	0.01	0.11	0.06	0.03	0.01	0.03	0.04	0.02	0.02	0.12	0.05	0.02	0.01	0.03	0.01	0.05	0.01	0.01	0.02	0.03	0.01	0.02	0.03	0.01	0.03
203	0.63	0.40	0.85	0.96	1.58	0.20	0.71	2.55	0.20	0.95	0.64	2.73	2.61	1.36	0.58	1.88	1.04	1.20	1.15	2.05	2.18	1.04	2.48	0.97	1.32	1.20	0.67	2.06	1.02	1.21	0.74	0.60	0.77	0.87	1.15

Table 8.1-4 Non-dioxin-like indicator PCBs (sum of ICES6 congeners: 28, 52, 101, 138, 153, 180) and ICES7 indicator PCBs (ICES6+PCB 118) [µg/kg fresh weight]

	Eel Sunbury, non-tidal												Woolwich, tidal																											
sum	E201	E202	E203	E205	E206	E207	E208	E209	E210	E211	E212	E213	E214	E215	E216	E217	E218	E219	E220	E221	E222	E223	E224	E225	E226	E227	E228	E229	E230	E231	E232	E233	E234	E235	E236
ICES6	17.4	14.5	37.4	24.3	45.7	3.53	22.0	62.8	16.2	27.4	17.9	70.9	73.3	53.7	24.9	51.9	64.1	31.0	55.0	78.9	71.0	49.1	104.0	31.7	37.8	49.2	28.3	52.1	33.0	41.5	25.5	46.1	25.1	26.7	37.1
ICES7	21.8	17.5	46.1	29.9	57.4	4.17	28.0	78.7	20.4	33.7	22.2	80.5	83.7	63.9	28.5	58.1	78.0	35.2	62.6	90.7	82.0	58.7	124.2	36.8	43.6	57.2	33.3	59.5	37.9	48.0	29.3	51.7	29.1	30.7	42.1

Table 8.1-5 Toxic equivalency concentrations based on WHO-TEF for PCBs 105, 114, 118, 123, 156, 157, 167, 189 [ng TCDD-TEQ/kg fresh weight] (Van den Berg *et al.* 2006)

	Eel Sunbury, non-tidal												Woolwich, tidal																											
TEQ	E201	E202	E203	E205	E206	E207	E208	E209	E210	E211	E212	E213	E214	E215	E216	E217	E218	E219	E220	E221	E222	E223	E224	E225	E226	E227	E228	E229	E230	E231	E232	E233	E234	E235	E236
WHO 1998 mammal	1.04	0.76	2.00	1.36	2.82	0.19	1.36	4.11	0.99	1.44	0.99	2.39	2.68	2.38	1.02	2.08	2.72	1.04	2.26	3.02	2.76	2.41	4.77	1.16	1.64	1.97	1.20	1.85	1.22	1.64	1.00	1.64	1.02	1.06	1.39
WHO 1998 bird	0.29	0.21	0.58	0.43	0.76	0.05	0.37	1.17	0.28	0.40	0.27	0.60	0.68	0.61	0.27	0.50	0.83	0.28	0.58	0.82	0.73	0.69	1.32	0.33	0.43	0.52	0.33	0.51	0.33	0.43	0.27	0.48	0.26	0.28	0.35
WHO 2005	0.22	0.16	0.43	0.30	0.58	0.03	0.29	0.83	0.21	0.31	0.21	0.48	0.53	0.48	0.19	0.35	0.65	0.21	0.42	0.61	0.56	0.50	1.01	0.25	0.31	0.40	0.25	0.38	0.25	0.33	0.20	0.32	0.20	0.21	0.27

Table 8.1-6 Organochlorine pesticides in individual eel carcasses [µg/kg fresh weight]

	Eel Sunbury, non-tidal											Woolwich, tidal																									
pest.	E201	E202	E203	E205	E206	E207	E208	E209	E210	E211	E212	E213	E214	E215	E216	E217	E218	E219	E220	E221	E222	E223	E224	E225	E226	E227	E228	E229	E230	E231	E232	E233	E234	E235	E236
pp' DDT	1.02	4.42	1.62	1.74	2.09	0.24	1.83	5.15	1.28	3.49	1.11	1.80	1.61	4.10	0.83	1.05	4.94	0.82	1.33	3.10	2.24	0.61	0.90	0.95	0.57	1.17	0.64	1.42	1.12	1.38	0.97	0.67	1.70	0.76	0.74
op' DDT	0.01	0.02	0.04	0.02	0.08	0.00	0.04	0.14	0.03	0.11	0.02	0.12	0.10	0.06	0.01	0.02	0.23	0.04	0.04	0.08	0.11	0.03	0.02	0.04	0.01	0.11	0.02	0.08	0.04	0.07	0.05	0.02	0.02	0.03	0.04
pp' DDE	6.58	4.55	15.5	11.7	13.5	1.30	9.34	22.0	5.11	13.5	6.90	15.2	15.1	13.5	4.76	8.61	21.0	7.81	9.49	15.5	17.2	7.18	24.8	8.53	7.33	11.5	7.69	15.1	8.22	9.78	7.33	4.44	7.23	6.57	7.53
op' DDE	n/a	n/a	0.01	n/a	0.01	n/a	n/a	0.01	n/a	n/a	n/a	0.02	0.02	0.01	n/a	0.01	0.02	n/a	0.02	0.03	0.02	0.01	0.01	0.01	0.01	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02
pp' DDD	1.96	1.74	4.99	3.58	4.12	0.15	2.90	10.2	1.73	4.11	2.16	8.30	9.13	6.52	2.87	5.47	8.54	3.37	7.49	8.25	9.57	3.66	4.96	4.48	3.06	5.67	3.06	7.18	3.57	5.04	3.32	6.50	2.54	3.33	4.44
op' DDD	0.01	0.00	0.08	0.01	0.06	n/a	0.01	0.10	0.03	0.03	0.03	0.79	0.77	0.33	0.15	0.30	0.25	0.11	0.46	0.68	0.53	0.35	0.29	0.26	0.15	0.81	0.11	0.19	0.14	0.41	0.11	0.42	0.08	0.25	0.38
α-chlordane	0.17	0.13	0.51	0.52	0.63	0.03	0.30	1.21	0.43	0.40	0.30	1.26	1.14	1.17	0.33	0.47	2.01	0.29	0.33	0.56	0.65	0.16	0.15	0.26	0.13	0.37	0.10	0.27	0.21	0.34	0.08	0.10	0.21	0.22	0.32
γ-chlordane	0.05	0.02	0.17	0.14	0.20	0.00	0.06	0.43	0.12	0.10	0.13	0.73	0.55	0.47	0.13	0.30	0.45	0.11	0.70	1.35	1.29	0.34	0.35	0.55	0.32	0.87	0.30	0.80	0.47	0.76	0.30	0.34	0.44	0.47	0.58
HCB	1.12	0.26	2.29	1.83	2.32	0.05	1.02	6.39	1.84	1.54	1.88	3.55	2.72	3.58	1.56	2.35	6.42	0.82	6.03	4.38	3.13	1.91	4.05	1.22	1.04	2.39	1.05	1.92	1.07	1.63	0.93	3.79	1.02	1.39	1.69
α-HCH	0.01	0.01	0.07	0.02	0.04	0.00	0.01	0.12	0.04	0.02	0.04	0.30	0.20	0.35	0.06	0.15	0.20	0.05	0.27	0.22	0.19	0.14	0.17	0.05	0.06	0.16	0.05	0.08	0.05	0.06	0.03	0.17	0.05	0.07	0.12
β-HCH	0.02	0.02	0.15	0.01	0.05	0.01	0.01	0.25	0.03	0.03	0.06	0.55	0.37	0.36	0.13	0.35	0.53	0.08	0.64	0.59	0.39	0.28	0.32	0.09	0.12	0.30	0.07	0.12	0.13	0.11	0.04	0.51	0.10	0.14	0.21
γ-HCH	0.25	0.14	1.19	0.42	0.58	0.05	0.25	1.91	0.54	0.36	0.65	2.10	1.49	1.33	0.50	1.23	2.40	0.38	2.82	2.01	1.49	1.07	1.32	0.41	0.53	1.31	0.44	0.65	0.50	0.52	0.27	1.61	0.42	0.55	0.89
α-endo-sulfan	0.01	n/a	n/a	0.01	0.01	n/a	n/a	n/a	n/a	0.01	n/a	n/a	n/a	n/a	0.01	n/a	n/a	n/a	n/a	0.01	0.01	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
β-endo-sulfan	0.02	n/a	0.10	0.05	0.06	0.02	0.03	0.23	0.05	0.09	0.04	0.37	0.38	0.25	0.10	0.19	0.31	0.10	0.26	0.50	0.34	0.17	0.15	0.15	0.09	0.34	0.10	0.23	0.12	0.21	0.11	0.29	0.10	0.13	0.19

8.1.3 Roach and bleak

Table 8.1-7 Details of the roach samples analysed.

Region	River	site	date	ID	fork length (mm)	weight [g]	dry matter	lipid content	condition factor[a]	age [y]
Anglian	Glen	Pinchbeck West	06/04/2009	GL09-0008	196	144	24%	3.6%	1.91	
				GL09-0009	185	115	23%	2.7%	1.82	
				GL09-0015	197	139	21%	1.4%	1.82	
				GL09-0016	195	154	27%	1.9%	2.08	
				GL09-0017	181	114	29%	2.2%	1.92	
	Nen	Cogenhoe	01/07/2008	NE08-0011	131	33	25%	4.7%	1.47	
				NE08-0012	148	53	25%	3.8%	1.65	
				NE08-0013	99	15	24%	3.4%	1.50	
				NE08-0014	101	14	23%	2.8%	1.40	
				NE08-0015	89	10	21%	1.6%	1.43	
				NE08-0017	73	5.9	20%		1.52	
				NE08-0018	72	5.1	19%		1.37	
				NE08-0019	71	4.9	20%		1.37	
				NE08-0020	71	4.6	19%		1.29	
		Thrapston	27/06/2008	NE08-0001	161	75	24%	7.9%	1.80	
				NE08-0002	117	25	26%	6.3%	1.56	
				NE08-0003	132	38	25%	4.9%	1.65	
				NE08-0004	115	23	28%	7.0%	1.51	
				NE08-0005	122	28	26%	6.5%	1.54	
				NE08-0006	98	16	23%	5.0%	1.70	
				NE08-0007	109	21	23%	4.6%	1.62	
				NE08-0008	100	14	29%	5.9%	1.40	
				NE08-0009	92	12	24%	5.6%	1.54	
				NE08-0010	95	13	43%	4.4%	1.52	
		Oundle	03/07/2008	NE08-0021	131	35	35%	4.3%	1.57	
				NE08-0023	153	55	40%	7.0%	1.54	
				NE08-0024	122	28	41%	3.5%	1.56	
				NE08-0025	122	30	27%	6.0%	1.65	
				NE08-0026	135	40	25%	4.7%	1.62	
				NE08-0027	134	38	25%	5.0%	1.57	
				NE08-0028	127	32	25%	6.1%	1.56	
				NE08-0029	130	32	24%	3.2%	1.47	
				NE08-0030	126	30	25%	3.1%	1.50	
ThamesTributaries	Kennet	Newbury: Northcroft-Westmills	04/11/2011	KE11-0001	200	135	27%	5.5%	1.69	7+
				KE11-0002	180	99	26%	5.4%	1.70	6+
				KE11-0003	170	76	27%	5.0%	1.54	6+
				KE11-0004	175	86	24%	3.7%	1.61	6+
				KE11-0005	140	43	27%	7.2%	1.56	5+
				KE11-0006	170	79	26%	4.4%	1.60	6+
				KE11-0007	160	62	27%	5.5%	1.50	6+
				KE11-0008	160	65	25%	3.8%	1.60	6+
				KE11-0009	140	43	27%	5.6%	1.58	5+
	Lee or Lea	Wheathamp-stead	16/08/2011	LE11-0001	209	172	33%	13.6%	1.89	8+
				LE11-0002	206	158	32%	11.5%	1.80	7+
				LE11-0003	196	141	31%	11.4%	1.87	6+
				LE11-0004	178	97	33%	12.7%	1.72	6+
				LE11-0005	186	116	31%	8.8%	1.80	6+
				LE11-0006	186	115	32%	11.3%	1.78	6+
				LE11-0007	202	143	32%	11.8%	1.73	7+
				LE11-0008	193	139	33%	12.4%	1.94	6+
				LE11-0009	175	92	31%	10.8%	1.71	6+
				LE11-0010	169	81	29%	11.4%	1.68	6+

Region	River	site	date	ID	fork length (mm)	weight [g]	dry matter	lipid content	condition factor[a]	age [y]
Thames Tributaries	Stort	Tednambury Mill	17/08/2011	ST11-0001	142	44	20%	5.6%	1.54	5+
			17/08/2011	ST11-0002	157	65	28%	5.3%	1.67	6+
			17/08/2011	ST11-0003	147	50	26%	4.9%	1.59	4+
			17/08/2011	ST11-0004	152	56	26%	4.8%	1.59	5+
			17/08/2011	ST11-0005	101	14	25%	5.1%	1.34	3+
			17/08/2011	ST11-0006	134	38	25%	4.5%	1.59	4+
			17/08/2011	ST11-0007	124	30	25%	5.0%	1.56	4+
			17/08/2011	ST11-0008	101	15	23%	3.9%	1.44	3+
			17/08/2011	ST11-0009	102	16	26%	5.0%	1.54	3+
			17/08/2011	ST11-0010	86	9	25%	5.1%	1.41	2+
Thames	**non-tidal Thames**	Castle Eaton	13/10/2011	TH11-0145	212	160	31%	4.9%	1.68	6+
			13/10/2011	TH11-0146	205	169	27%	4.8%	1.96	6+
			13/10/2011	TH11-0147	165	76	27%	5.7%	1.69	4+
			13/10/2011	TH11-0148	115	22	25%	3.6%	1.44	2+
			13/10/2011	TH11-0149	122	27	25%	3.7%	1.46	2+
			13/10/2011	TH11-0150	123	29	25%	3.8%	1.54	2+
			13/10/2011	TH11-0151	114	24	25%	5.3%	1.64	2+
			13/10/2011	TH11-0152	118	25	26%	4.5%	1.52	2+
			13/10/2011	TH11-0153	119	23	24%	3.9%	1.34	2+
			13/10/2011	TH11-0154	127	28	28%	4.9%	1.37	2+
		Caversham-Sonning	23/07/2008	TH08-0001	111	23	25%		1.67	
			23/07/2008	TH08-0002	145	58	28%	6.4%	1.89	
			23/07/2008	TH08-0003	129	38	26%		1.77	
			23/07/2008	TH08-0004	130	38	26%	7.3%	1.74	
			23/07/2008	TH08-0005	135	43	28%		1.74	
			23/07/2008	TH08-0006	134	40	27%		1.68	
			23/07/2008	TH08-0007	111	23	25%		1.70	
			23/07/2008	TH08-0008	124	31	28%		1.63	
			23/07/2008	TH08-0009	112	22	24%		1.59	
			23/07/2008	TH08-0010	116	25	24%		1.61	
			21/07/2010	TH10-0022	132	41		6.9%	1.76	
			30/07/2012	TH12-0011	142	43		7.9%	1.50	
			30/07/2012	TH12-0014	200	146		5.1%	1.83	
			30/07/2012	TH12-0017	199	141		4.7%	1.79	
			30/07/2012	TH12-0018	160	67		5.6%	1.63	
			30/07/2012	TH12-0020	169	75		4.6%	1.56	
		Temple-Marlow	03/09/2007	TH07-0103	195	124	27%	4.6%	1.67	
			03/09/2007	TH07-0104	170	78	26%	2.4%	1.59	
			03/09/2007	TH07-0105	159	67	26%	2.1%	1.66	
			03/09/2007	TH07-0106	150	56	28%	3.2%	1.67	
			03/09/2007	TH07-0107	136	42	24%		1.67	
		Bray-Boveney	03/09/2008	TH08-0068	129	35	24%		1.61	
			03/09/2008	TH08-0069	121	27	25%		1.54	
			03/09/2008	TH08-0070	125	31	25%		1.57	
			08/09/2009	TH09-0050	177	101	30%		1.83	
			08/09/2009	TH09-0052	148	48	25%		1.48	
			08/09/2009	TH09-0053	163	76	28%		1.74	
			08/09/2009	TH09-0056	159	66	27%		1.65	
			08/09/2009	TH09-0058	162	65	25%		1.52	
			04/09/2012	TH12-0064	132	37		4.4%	1.59	
			04/09/2012	TH12-0070	168	76		2.8%	1.59	
		Old Windsor-Bell	07/09/2007	TH07-0187	184	93	28%	3.8%	1.50	
			07/09/2007	TH07-0188	165	68	27%	4.6%	1.51	
			07/09/2007	TH07-0189	145	46	29%	4.9%	1.52	
			07/09/2007	TH07-0190	129	31	27%	5.2%	1.43	
			07/09/2007	TH07-0191	180	82	29%		1.41	
		Sunbury-Molesey	11/09/2012	TH12-0152	134	37		5.3%	1.55	
			11/09/2012	TH12-0156	155	59		7.0%	1.58	
			11/09/2012	TH12-0157	155	65		2.9%	1.75	
			11/09/2012	TH12-0158	144	48		7.9%	1.61	

Region	River	site	date	ID	fork length (mm)	weight [g]	dry matter	lipid content	condition factor[a]	age [y]
Thames	non-tidal Thames	Molesey-Kingston	16/09/2009	TH09-0097	124	27	24%		1.43	
			16/09/2009	TH09-0098	109	21	22%		1.64	
			16/09/2009	TH09-0112	114	21	27%		1.44	
			16/09/2009	TH09-0113	103	16	25%		1.48	
			16/09/2009	TH09-0114	144	49	27%		1.63	
			16/09/2009	TH09-0115	123	27	26%		1.45	
			16/09/2009	TH09-0116	114	23	24%		1.53	
			16/09/2009	TH09-0117	116	22	24%		1.38	
			16/09/2009	TH09-0118	119	28	29%		1.66	
			16/09/2009	TH09-0119	120	25	25%		1.42	

[a] Fulton's condition factor: K= weight/length^3 x 100 [g/cm^3]

Table 8.1-8 Details of the bleak samples analysed.

Region	River	site	date	ID	fork length (mm)	weight [g]	dry matter	lipid content	condition factor[a]	age
Thames	non-tidal Thames	Caversham-Sonning	23/07/2008	TH08-0011	106	14	26%		1.13	
				TH08-0012	130	24	22%	1.9%	1.10	
				TH08-0013	113	17	26%		1.19	
				TH08-0014	132	26	30%		1.12	
				TH08-0015	111	18	25%		1.29	
				TH08-0016	125	24	26%		1.25	
				TH08-0017	120	21	26%		1.20	
				TH08-0018	102	12	22%		1.12	
				TH08-0019	119	20	27%		1.17	
				TH08-0020	110	15	24%	6.1%	1.16	
				TH08-0021	111	17	27%	11.0%	1.21	
				TH08-0022	109	14	26%		1.05	
				TH08-0023	105	12	23%		1.04	
		Temple-Marlow	03/09/2007	TH07-0108	90	7	25%	5.1%	0.95	
				TH07-0109	94	8	26%	5.4%	1.00	
				TH07-0110	82	5	25%	5.3%	0.95	
				TH07-0111	83	5	24%	3.8%	0.84	
				TH07-0112	82	6	23%	3.6%	1.01	
		Bray-Boveney	03/09/2008	TH08-0071	123	21	30%		1.15	
		OldWindsor-Bell	07/09/2007	TH07-0182	125	15	28%	5.89%	0.74	
				TH07-0183	124	17	27%	6.86%	0.91	
				TH07-0184	120	17	28%	5.85%	0.98	
				TH07-0185	116	14	25%	3.38%	0.89	
				TH07-0186	112	15	21%	6.58%	1.09	
		Sunbury-Molesey	13/09/2007	TH07-0078	121	18	30%	9.59%	1.03	
				TH07-0079	100	9.1	28%	6.0%	0.91	
				TH07-0080	101	9.2	27%	7.7%	0.89	
				TH07-0081	102	8.9	28%	6.6%	0.84	
				TH07-0082	105	11	29%	9.1%	0.92	
				TH07-0083	129	21	28%	7.5%	0.98	
				TH07-0084	103	11	29%	8.1%	0.98	
				TH07-0085	119	17	30%	8.8%	1.02	
				TH07-0086	111	9.1	30%	11.3%	0.67	
				TH07-0087	101	9.2	29%	7.1%	0.89	

[a] Fulton's condition factor: K= weight/length^3 x 100 [g/cm^3]

Table 8.1-9 Metals in roach [mg/kg wet weight]

	Glen					Nene																													
	Pinchbeck West					Cogenhoe									Thrapston										Oundle									Kennet	Newbury	
	2009					2008									2008										2008									2011		
Metal	GL09-0008	GL09-0009	GL09-0015	GL09-0016	GL09-0017	NE08-0011	NE08-0012	NE08-0013	NE08-0014	NE08-0015	NE08-0017	NE08-0018	NE08-0019	NE08-0020	NE08-0001	NE08-0002	NE08-0003	NE08-0004	NE08-0005	NE08-0006	NE08-0007	NE08-0008	NE08-0009	NE08-0010	NE08-0021	NE08-0023	NE08-0024	NE08-0025	NE08-0026	NE08-0027	NE08-0028	NE08-0029	NE08-0030	KE11-0001	KE11-0002
Al	17.05	18.75	7.06	39.56	51.76	6.643	1.301	27.18	4.524	68.95	10.74	52.14	18.25	17.80	2.441	38.81	24.50	32.54	3.078	5.71	66.71	86.29	49.26	109.1	38.97	19.32	42.77	14.60	21.74	34.46	13.57	11.64	25.12	16.09	5.733
As	0.140	0.116	0.156	0.199	0.194	0.351	0.327	0.268	0.243	0.208	0.089	0.220	0.102	0.102	0.347	0.269	0.244	0.246	0.272	0.232	0.257	0.352	0.197	0.489	0.347	0.408	0.347	0.244	0.259	0.228	0.234	0.216	0.174	0.187	0.173
Cd	0.001	0.002	0.001	0.001	0.019	0.003	0.001	0.004	0.001	0.003	0.001	0.005	0.005	0.002	0.002	0.010	0.006	0.002	0.005	0.007	0.008	0.013	0.003	0.012	0.011	0.010	0.005	0.002	0.005	0.004	0.008	0.003	0.004	0.006	0.003
Co	0.027	0.025	0.017	0.036	0.057	0.013	0.008	0.021	0.008	0.035	0.008	0.054	0.019	0.016	0.009	0.035	0.024	0.021	0.009	0.018	0.048	0.049	0.038	0.102	0.039	0.025	0.051	0.017	0.026	0.026	0.030	0.023	0.027	0.031	0.012
Cr	0.109	0.106	0.521	0.370	0.645	0.154	0.177	0.732	0.860	1.712	1.572	9.188	5.896	1.793	1.117	1.181	0.577	0.420	0.388	1.299	1.077	1.838	2.137	4.863	0.421	0.227	0.477	0.266	0.493	0.335	0.270	0.310	0.486	0.672	0.706
Cu	1.156	1.168	0.935	2.120	1.604	0.843	0.857	2.288	0.811	0.757	0.578	1.004	1.687	0.598	0.786	0.955	0.765	0.609	0.580	0.726	0.693	1.047	0.713	2.055	0.810	0.989	0.805	0.737	0.668	0.687	0.587	0.479	0.529	0.786	0.676
Fe	36.29	41.99	26.80	73.10	109.6	15.68	8.846	48.75	16.06	113.2	28.58	184.1	61.69	46.13	16.33	78.09	57.51	57.01	12.98	27.64	137.3	158.4	114.1	390.9	73.58	55.18	93.54	29.99	54.77	49.23	33.78	38.07	48.63	41.02	24.16
Hg	0.031	0.040	0.043	0.035	0.052	0.024	0.026	0.025	0.027	0.024	0.006	0.013	0.017	0.015	0.024	0.041	0.041	0.015	0.028	0.017	0.025	0.019	0.015	0.045	0.047	0.053	0.044	0.068	0.042	0.022	0.028	0.046	0.038	0.018	0.023
Mn	4.553	3.767	2.650	3.247	8.936	2.296	2.105	5.344	1.745	6.635	1.361	8.981	3.282	1.904	2.529	5.673	4.668	4.181	1.758	1.653	9.204	7.736	5.019	18.05	10.81	4.099	24.29	6.271	6.652	10.44	8.776	8.242	12.20	2.093	1.361
Mo	0.023	0.022	0.039	0.029	0.047	0.029	0.026	0.054	0.058	0.077	0.131	0.337	0.270	0.092	0.069	0.085	0.034	0.046	0.039	0.079	0.069	0.087	0.110	0.214	0.066	0.050	0.053	0.032	0.041	0.044	0.036	0.037	0.037	0.039	0.034
Ni	0.134	0.175	0.152	2.093	0.416	0.019		0.210		0.057	0.047	0.301	0.189	0.118		0.181	0.149			0.150	0.192	0.053	0.159	0.114				0.105	0.075		0.070	0.031	0.026	0.117	0.073
Pb	0.021	0.019	0.015	0.035	0.101	0.033	0.013	0.058	0.024	0.143	0.044	0.147	0.055	0.058	0.027	0.085	0.058	0.083	0.020	0.030	0.154	0.161	0.134	0.311	0.097	0.074	0.136	0.049	0.053	0.072	0.051	0.048	0.070	0.108	0.079
Sb					0.002	0.001	0.000	0.001	0.000	0.003	0.002	0.003	0.002	0.003	0.000	0.003	0.002	0.001	0.000	0.001	0.004	0.003	0.002	0.003	0.004	0.001	0.003	0.001	0.002		0.002	0.002	0.001	0.001	0.000
Se	0.815	0.753	0.853	0.964	1.006	0.553	0.595	0.592	0.463	0.411	0.135	0.281	0.279	0.216	0.459	0.462	0.348	0.393	0.559	0.348	0.392	0.489	0.249	0.891	0.800	0.545	0.689	0.485	0.421	0.441	0.415	0.319	0.342	0.668	0.899
Sr	16.58	11.65	15.69	18.81	27.72	12.62	13.38	12.36	11.39	10.54	6.080	7.995	6.447	7.624	18.06	13.62	15.97	11.41	12.36	11.73	8.547	15.47	7.362	23.22	25.82	21.10	25.67	17.23	14.83	22.17	15.49	14.23	10.60	10.21	11.63
V	0.031	0.031	0.011	0.064	0.239	0.021		0.073	0.009	0.175		0.218	0.051	0.039	0.057	0.137	0.107	0.104	0.014	0.051	0.226	0.190	0.131	0.339	0.101	0.054	0.122	0.088	0.112	0.101	0.069	0.051	0.071	0.051	0.020
Zn	27.89	40.58	39.52	43.33	47.63	51.79	43.60	56.89	43.15	45.98	22.06	52.68	53.87	42.89	26.35	50.67	45.69	47.35	47.50	45.89	42.98	53.97	44.75	89.91	69.42	56.11	77.82	51.73	32.63	47.46	47.74	37.38	51.60	39.27	38.53

Table 8.1-9 continued Metals in roach [mg/kg wet weight]

	Kennet							Lee (or Lea)										Stort										Thames							
	Newbury: Northcroft - Westmills							Wheathampstead										Tednambury Mill										Castle Eaton							
	2011							2011										2011										2011							
Metal	KE11-0003R	KE11-0004R	KE11-0005R	KE11-0006R	KE11-0007	KE11-0008	KE11-0009	LE11-0001	LE11-0002	LE11-0003	LE11-0004	LE11-0005	LE11-0006	LE11-0007	LE11-0008	LE11-0009	LE11-0010	ST11-0001	ST11-0002	ST11-0003	ST11-0004	ST11-0005	ST11-0006	ST11-0007	ST11-0008	ST11-0009	ST11-0010	TH11-0145	TH11-0146	TH11-0147	TH11-0148	TH11-0149	TH11-0150	TH11-0151	TH11-0152
Al	0.896	0.289	5.228	1.138	4.816	46.44	8.864	1.787	5.350	4.268	4.869	2.700	3.453	6.326	7.323	4.549	4.850	2.000	1.487	5.758	2.941	2.714	7.024	10.59	3.087	35.86	11.79	28.83	20.65	25.24	34.44	52.38	44.37	67.78	34.40
As	0.192	0.176	0.155	0.237	0.171	0.125	0.108	0.302	0.397	0.192	0.144	0.204	0.271	0.202	0.299	0.212	0.118	0.103	0.093	0.087	0.112	0.061	0.078	0.070	0.082	0.092	0.069	0.118	0.087	0.102	0.076	0.091	0.119	0.096	0.090
Cd	0.002	0.003	0.003	0.002	0.002	0.004	0.012	0.004	0.008	0.005	0.005	0.006	0.005	0.005	0.007	0.007	0.007	0.002	0.004	0.010	0.004	0.003	0.004	0.004	0.010	0.005	0.004	0.022	0.023	0.019	0.020	0.018	0.027	0.027	0.018
Co	0.007	0.008	0.009	0.008	0.012	0.038	0.027	0.016	0.038	0.029	0.027	0.024	0.030	0.033	0.057	0.057	0.046	0.017	0.016	0.018	0.027	0.013	0.020	0.020	0.017	0.034	0.024	0.036	0.024	0.023	0.040	0.039	0.036	0.052	0.031
Cr	0.202	0.778	0.475	0.800	0.430	0.522	1.869	0.235	0.278	0.401	0.450	0.509	0.217	0.362	0.337	0.198	0.346	0.156	0.108	0.083	0.156	0.660	0.373	0.240	0.164	1.061	1.274	0.298	0.183	0.117	0.409	0.361	0.447	0.251	0.166
Cu	0.510	0.399	0.445	0.651	0.679	0.592	0.681	0.939	1.771	1.343	1.583	1.513	1.374	1.162	2.253	2.270	1.987	0.282	0.592	0.917	2.407	0.470	0.742	0.464	1.347	1.186	0.632	0.579	0.561	0.597	0.426	0.580	0.624	0.708	0.550
Fe	17.94	17.82	23.81	25.44	24.44	54.00	66.75	16.43	29.84	27.35	30.33	24.86	24.95	37.86	65.06	38.41	36.65	20.14	27.66	31.73	38.43	30.03	35.91	37.53	32.00	66.85	50.17	30.69	22.57	25.50	39.54	46.74	135.9	86.01	48.95
Hg	0.015	0.031	0.014	0.027	0.016	0.016	0.025	0.029	0.033	0.024	0.015	0.024	0.033	0.044	0.025	0.027	0.013	0.016	0.021	0.024	0.022	0.013	0.015	0.023	0.019	0.024	0.011	0.029	0.022	0.018	0.016	0.018	0.014	0.012	0.015
Mn	1.623	1.486	0.930	0.908	0.953	1.836	1.635	1.956	4.550	3.213	4.003	2.305	3.503	3.876	5.311	6.424	3.802	3.472	4.085	4.196	5.213	2.920	5.515	5.271	2.452	5.938	5.429	7.049	8.081	4.644	5.583	8.213	5.276	7.527	5.546
Mo	0.030	0.045	0.034	0.048	0.039	0.043	0.078	0.026	0.035	0.032	0.044	0.036	0.025	0.028	0.033	0.033	0.036	0.022	0.026	0.025	0.027	0.038	0.040	0.028	0.030	0.055	0.061	0.031	0.025	0.028	0.035	0.045	0.034	0.029	0.026
Ni	0.031	0.026	0.052	0.053	0.036	0.049	0.031	0.045	0.114	0.113	0.106	0.135	0.100	0.145	0.217	0.222	0.221	0.282	0.122	0.112	0.160	0.112	0.126	0.112	0.101	0.119	0.156				0.113	0.015	0.088	0.074	0.014
Pb	0.044	0.087	0.057	0.060	0.082	0.310	0.089	0.044	0.072	0.075	0.073	0.118	0.072	0.096	0.096	0.274	0.210	0.056	0.035	0.041	0.047	0.034	0.046	0.062	0.042	0.136	0.066	0.079	0.058	0.058	0.070	0.087	0.086	0.116	0.065
Sb		0.000			0.000	0.003	0.002	0.001	0.003	0.002	0.001	0.001	0.001	0.002	0.002	0.014	0.002	0.001	0.001	0.001	0.001	0.001	0.002	0.001	0.000	0.003	0.002	0.002	0.001	0.001	0.002	0.004	0.002	0.002	0.002
Se	1.044	0.656	0.474	0.750	0.796	0.682	0.727	0.315	0.716	0.521	0.644	0.459	0.542	0.415	0.664	0.447	0.667	0.614	0.912	0.875	0.684	0.817	0.795	0.843	0.807	1.250	0.880	0.552	0.697	0.540	0.436	0.595	0.607	0.428	0.529
Sr	10.28	14.72	9.73	15.88	10.64	14.04	12.32	9.821	13.92	10.28	12.68	10.33	12.11	12.12	12.02	14.41	14.64	18.95	23.23	20.20	18.82	11.41	15.86	16.27	14.57	13.56	11.90	11.15	14.26	14.38	17.10	14.10	12.49	13.17	15.52
V	0.014	0.031	0.026	0.018	0.028	0.090	0.030	0.190			0.019	0.011	0.061	0.117	0.187	0.206	0.220	0.190	0.030		0.047	0.057	0.079	0.083	0.086	0.102	0.063	0.059	0.059	0.124	0.099	0.131			
Zn	32.82	31.32	39.65	34.31	39.79	37.95	44.09	36.51	29.96	30.39	42.18	31.91	32.16	26.84	40.57	36.47	32.26	31.21	32.02	49.89	33.60	67.08	39.81	47.97	38.42	37.71	43.63	31.78	26.70	26.89	43.67	38.96	37.61	30.41	37.63

Table 8.1-9 continued Metals in roach [mg/kg wet weight]

	Thames																													
	Castle Eaton		Caversham-Sonning										Temple-Marlow					Bray-Boveney								Old Windsor-Bell				
	2011		2008										2007					2008			2009					2007				
Metal	TH11-0153	TH11-0154	TH08-0001	TH08-0002	TH08-0003	TH08-0004	TH08-0005	TH08-0006	TH08-0007	TH08-0008	TH08-0009	TH08-0010	TH07-0103	TH07-0104	TH07-0105	TH07-0106	TH07-0107	TH08-0068	TH08-0069	TH08-0070	TH09-0050	TH09-0052	TH09-0053	TH09-0056	TH09-0058	TH07-0187	TH07-0188	TH07-0189	TH07-0190	TH07-0191
Al	28.32	22.17	66.12	65.54	40.06	56.65	65.46	53.44	22.59	0.656	6.140	0.471	0.327	0.507	1.258	0.722	0.855	0.789	6.461	4.277	16.35	5.100	0.100	6.866	23.45	0.726	0.599	0.832	48.65	0.683
As	0.080	0.104	0.239	0.316	0.287	0.318	0.337	0.297	0.275	0.188	0.262	0.230	0.267	0.370	0.318	0.391	0.355	0.116	0.121	0.141	0.525	0.276	0.362	0.351	0.345	0.346	0.339	0.386	0.295	0.329
Cd	0.009	0.025	0.006	0.007	0.006	0.006	0.007	0.005	0.006	0.003	0.003	0.009	0.003	0.007	0.012	0.011	0.006	0.004	0.007	0.006	0.005	0.003	0.002	0.005	0.008	0.005	0.006	0.007	0.007	0.008
Co	0.026	0.031	0.040	0.048	0.026	0.041	0.038	0.033	0.016	0.005	0.010	0.005	0.003	0.003	0.008	0.003	0.005	0.007	0.013	0.012	0.025	0.012	0.007	0.021	0.037	0.005	0.001	0.009	0.031	0.002
Cr	0.377	0.883	0.380	0.322	0.252	0.447	0.420	0.251	0.407	0.726	0.256	0.889	0.174	0.289	0.396	0.705	0.624	0.311	1.029	0.498	0.362	0.554	0.247	0.104	0.453	0.457	0.351	0.560	0.948	0.428
Cu	0.481	1.077	0.826	0.683	0.947	0.763	0.756	0.641	0.692	0.671	0.556	0.634	0.442	0.376	0.627	1.034	0.456	0.737	0.936	0.847	0.593	0.538	0.726	1.325	0.708	0.597	0.413	0.980	0.566	0.602
Fe	34.21	38.42	99.69	109.9	78.12	107.0	95.67	75.65	35.11	16.09	22.04	21.30	5.206		6.607	8.097		16.58	29.47	23.81	38.98	22.55	15.68	29.46	55.06	8.175	4.010	4.101	71.40	6.231
Hg	0.011	0.014	0.033	0.024	0.030	0.038	0.046	0.027	0.028	0.032	0.025	0.029	0.033	0.038	0.042	0.044	0.039	0.030	0.022	0.022	0.030	0.023	0.023	0.027	0.032	0.028	0.042	0.041	0.016	0.048
Mn	5.717	4.354	5.831	7.767	4.674	4.788	5.738	5.673	3.242	1.001	2.660	1.849	3.851	3.148	3.266	1.362	1.576	1.168	1.511	2.002	4.052	1.669	1.040	2.015	4.674	3.009	2.078	1.852	4.260	1.591
Mo	0.029	0.058	0.030	0.053	0.042	0.039	0.046	0.040	0.039	0.059	0.047	0.057	0.023	0.017	0.029	0.036	0.026	0.026	0.068	0.036	0.028	0.031	0.028	0.031	0.037	0.033	0.023	0.033	0.053	0.027
Ni	0.026	0.065	0.347	0.037	0.063	0.065	0.089	0.082	0.038	0.018	0.016	0.031	0.024	0.026	0.020	0.027	0.107	0.129	0.760	0.095	0.090	0.047	0.027	0.071	0.125	0.016	0.018	0.045	0.099	0.031
Pb	0.066	0.070	0.286	0.281	0.145	0.202	0.257	0.171	0.121	0.095	0.037	0.041	0.025	0.028	0.029	0.028	0.028	0.040	0.051	0.042	0.097	0.044	0.024	0.054	0.146	0.043	0.026	0.032	0.162	0.037
Sb	0.002	0.002	0.003	0.004	0.003	0.003	0.005	0.003	0.002	0.002	0.001	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.001	0.001	0.001		0.001	0.004			0.001	0.003	0.000
Se	0.411	0.766	0.524	0.654	0.748	0.688	0.730	0.662	0.643	0.737	0.646	0.655	0.531	0.762	0.610	0.679	1.230	0.549	0.511	0.621	0.375	0.375	0.439	0.446	0.442	0.592	0.661	0.675	0.430	0.757
Sr	13.68	19.34	10.29	16.72	12.44	12.01	14.28	13.25	12.77	11.91	10.81	15.33	14.84	21.55	20.01	15.34	13.70	8.94	11.94	13.12	10.13	10.36	9.92	12.90	12.76	20.29	11.91	14.99	12.15	17.76
V			0.147	0.177	0.123	0.193	0.182	0.133	0.061	0.032	0.038	0.022	0.016	0.032	0.014	0.009	0.014	0.125	0.106	0.129	0.041	0.030		0.033	0.105	0.026	0.018	0.017	0.120	0.023
Zn	34.26	38.15	27.37	30.43	37.98	46.59	32.39	34.13	40.16	41.46	45.29	41.87	42.67	36.72	40.77	54.57	31.99	35.71	33.71	37.31	42.95	54.81	40.54	47.34	41.95	38.58	40.94	39.50	40.80	41.79

Table 8.1-10 Metals in bleak [mg/kg wet weight]

	Thames																																
	Caversham-Sonning													Temple-Marlow					Old Windsor-Bell					Br-Bov	Sunbury-Molesey								
	2008													2007					2007					2008	2007								
Metal	TH08-0011	TH08-0012	TH08-0013	TH08-0014	TH08-0015	TH08-0016	TH08-0017	TH08-0018	TH08-0019	TH08-0020	TH08-0021	TH08-0022	TH08-0023	TH07-0108	TH07-0109	TH07-0110	TH07-0111	TH07-0112	TH07-0182	TH07-0183	TH07-0184	TH07-0185	TH07-0186	TH08-0071	TH07-0078	TH07-0079	TH07-0080	TH07-0081	TH07-0082	TH07-0083	TH07-0084	TH07-0085	TH07-0086	TH07-0087
Al	1.926	0.756	1.840	1.649	2.296	1.714	1.883	2.286	2.777	1.365	0.953	1.137	1.004	14.57	2.525	9.213	3.847	2.667	1.958	9.946	1.380	1.755	41.71	2.469	1.217	1.782	4.708	0.589	1.398	2.030	1.634	0.466	1.247	1.995
As	0.108	0.115	0.090	0.126	0.072	0.072	0.070	0.071	0.113	0.178	0.132	0.081	0.071	0.195	0.230	0.189	0.240	0.178	0.239	0.166	0.213	0.180	0.173	0.089	0.283	0.192	0.311	0.353	0.329	0.212	0.260	0.298	0.213	0.289
Cd	0.009	0.009	0.007	0.011	0.007	0.009	0.016	0.009	0.009	0.008	0.010	0.007	0.006	0.005	0.004	0.009	0.008	0.005	0.002	0.007	0.003	0.008	0.014	0.012	0.010	0.008	0.002	0.003	0.002	0.012	0.008	0.004	0.001	0.002
Co	0.003	0.001	0.002	0.005	0.003	0.002		0.002	0.002	0.004	0.003	0.002	0.002	0.017	0.006	0.020	0.058	0.005	0.000	0.004			0.085	0.004	0.004	0.004	0.004	0.005	0.003	0.005	0.004	0.002	0.011	0.026
Cr	0.254	0.188	0.202	0.092	0.126	0.222	0.227	0.373	0.078	0.269	0.220	0.507	0.250	7.545	3.996	7.399	22.35	3.709	0.432	2.180	0.406	1.410	12.86	0.463	0.771	0.946	0.771	1.139	0.660	2.870	0.951	1.016	4.629	9.553
Cu	0.936	0.819	0.914	0.946	0.870	1.101	0.899	0.978	0.971	0.714	0.822	0.935	0.755	0.815	0.589	1.012	1.161	0.584	0.695	0.738	0.492	0.590	6.607	3.930	0.966	0.348	0.638	0.591	0.644	0.799	0.575	0.511	0.526	0.644
Fe	22.69	16.46	21.43	22.23	18.04	17.43	19.74	20.48	18.62	16.02	14.36	19.99	17.99	49.41	21.41	56.21	146.3	23.73	6.997	16.60	3.770	12.15	116.4	19.17	7.161	8.904	3.951	6.557	3.274	22.65	9.19	10.01	30.72	61.84
Hg	0.040	0.056	0.029	0.031	0.037	0.066	0.051	0.042	0.042	0.038	0.029	0.049	0.054	0.029	0.035	0.020	0.037	0.029	0.049	0.043	0.047	0.067	0.041	0.035	0.034	0.010	0.021	0.030	0.017	0.041	0.030	0.051	0.029	0.029
Mn	1.610	2.402	1.919	2.693	3.002	2.841	3.117	3.344	2.375	2.263	1.608	1.416	2.824	4.306	3.606	4.002	4.112	2.670	4.012	2.611	3.593	2.697	3.957	3.636	2.003	1.699	3.291	3.237	2.770	3.633	2.213	2.918	1.376	2.359
Mo	0.020	0.024	0.028	0.021	0.021	0.025	0.026	0.029	0.023	0.025	0.022	0.030	0.027	0.232	0.116	0.233	0.710	0.089	0.024	0.082	0.014	0.047	0.357	0.024	0.033	0.036	0.028	0.034	0.026	0.110	0.037	0.044	0.161	0.327
Ni	0.013	0.075	0.017	0.041	0.007	0.022	0.014	0.020	0.003	0.030	0.022	0.076	0.012	0.448	0.157	0.238	0.793	0.116	0.069	0.109	0.047	0.074	5.478	0.028	41.07	0.605	0.098	0.121	0.121	0.128	0.071	0.059	0.173	0.317
Pb	0.013	0.014	0.014	0.015	0.014	0.046	0.021	0.022	0.017	0.012	0.009	0.013	0.016	0.053	0.008	0.030	0.019	0.040	0.021	0.020	0.017	0.017	0.314	0.015	0.013	0.008	0.008	0.012	0.012	0.022	0.012	0.008	0.008	0.014
Sb	0.001	0.001	0.001	0.001	0.002	0.001	0.001	0.001	0.000	0.002	0.000	0.000	0.001	0.002	0.000	0.001	0.003	0.001	0.001	0.002	0.001	0.000	0.031	0.000	0.000	0.000	0.001	0.000	0.001	0.001	0.000	0.001	0.001	0.002
Se	1.275	1.200	1.262	2.007	1.719	1.211	1.530	1.561	1.439	0.752	0.995	2.164	1.447	0.978	1.275	0.800	0.869	1.158	1.377	0.931	1.063	1.795	1.000	1.204	0.717	0.499	0.633	0.675	0.541	1.331	0.642	1.528	1.001	0.642
Sr	7.21	10.40	6.129	7.460	6.355	7.372	7.255	7.241	6.604	8.413	6.030	6.735	8.321	7.465	9.840	7.953	9.211	7.687	10.94	7.944	10.23	9.706	7.251	9.210	7.619	5.386	9.821	9.071	9.943	7.776	7.261	8.816	6.229	8.176
V	0.002	0.031	0.003	0.061	0.011	0.012	0.009	0.017	0.007	0.034	0.012	0.016	0.059	0.068	0.030	0.083	0.217	0.032	0.018	0.018	0.009	0.010	0.078	0.136	0.016	0.023	0.012	0.019	0.014	0.033	0.022	0.007	0.033	0.036
Zn	29.07	27.45	22.56	24.10	23.44	25.52	25.03	30.04	26.53	25.18	21.79	30.66	27.37	35.84	38.04	40.19	39.82	37.89	29.67	24.51	29.42	32.91	95.53	23.91	22.78	22.00	30.97	35.92	30.48	26.65	27.67	28.04	24.95	27.17

Table 8.1-11 PCBs in roach [µg/kg wet weight]

	Glen				Nene					Nene					Nene					Kennet										Lee (or Lea)						
	Pinchbeck West				Cogenhoe					Thrapston					Oundle					Newbury: Northcroft - Westmills										Wheathampstead						
	2009				2008					2008					2008					2011										2011						
PCB	GL09-0008	GL09-0009	GL09-0015	GL09-0016	NE08-0011	NE08-0012	NE08-0013	NE08-0014	NE08-0015	NE08-0001	NE08-0004	NE08-0005	NE08-0008	NE08-0010	NE08-0026	NE08-0027	NE08-0028	NE08-0029	NE08-0030	KE11-0001	KE11-0002	KE11-0003	KE11-0004	KE11-0005	KE11-0006	KE11-0007	KE11-0008	KE11-0009	LE11-0001	LE11-0002	LE11-0003	LE11-0004	LE11-0005	LE11-0006	LE11-0007
18	0.08	0.14	0.08	0.09	0.24	0.18	0.16	0.15	0.08	0.30	0.26	0.22	0.18	0.12	n/a	n/a	0.21	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.91	n/a	0.79	0.38	n/a	0.43	0.70
22	0.13	0.11	0.15	0.08	0.12	0.12	0.14	0.08	0.04	0.20	0.24	0.12	0.10	0.09	n/a	n/a	n/a	n/a	n/a	n/a	0.05	0.09	0.05	n/a	0.10	0.12	n/a	0.05	0.43	0.19	0.34	0.26	0.16	0.40	0.11
28/ 31	0.77	0.61	0.89	0.57	0.91	0.82	0.76	0.69	0.29	1.18	1.43	0.98	0.83	0.60	0.31	0.17	0.39	0.19	0.17	0.09	0.16	0.12	0.10	0.09	0.09	0.12	0.09	0.11	1.27	0.57	1.00	0.84	0.44	1.35	1.46
41/ 64	0.26	0.22	0.35	0.17	0.35	0.33	0.44	0.39	0.21	0.73	0.48	0.61	0.47	0.36	0.16	0.06	0.27	0.10	0.11	0.03	0.05	0.04	0.09	0.04	0.05	0.04	0.04	0.05	0.47	0.22	0.35	0.27	0.14	0.43	n/a
44	0.33	0.23	0.38	0.18	0.48	0.41	0.53	0.39	0.18	0.80	0.64	0.57	0.45	0.36	0.31	0.24	0.40	0.21	0.16	0.07	0.06	0.10	0.12	0.08	0.10	0.10	0.11	0.09	1.29	0.68	0.94	0.81	0.43	1.27	n/a
49	0.29	0.23	0.37	0.19	0.45	0.40	0.54	0.36	0.21	0.81	0.68	0.59	0.45	0.42	0.27	0.11	0.40	0.19	0.16	0.08	0.09	0.12	0.17	0.08	0.11	0.11	0.12	0.10	1.09	0.57	0.85	0.78	0.38	1.13	0.26
52	0.44	0.35	0.52	0.27	1.13	1.05	1.08	0.97	0.46	1.33	1.09	0.99	0.82	0.65	0.59	0.23	0.87	0.38	0.36	0.15	0.20	0.24	0.27	0.17	0.24	0.25	0.26	0.21	2.83	1.56	2.26	1.96	1.01	3.13	1.74
54	n/a	n/a	n/a	n/a	0.00	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
56/ 60	0.26	0.23	0.39	0.18	0.27	0.25	0.21	0.27	0.12	0.58	0.54	0.40	0.31	0.28	0.14	0.05	0.20	0.10	0.09	0.05	0.06	0.09	0.08	n/a	0.04	0.04	0.04	0.04	0.42	0.23	0.29	0.23	0.12	0.38	0.02
70	0.49	0.39	0.69	0.30	0.62	0.50	0.58	0.56	0.24	0.98	0.79	0.72	0.48	0.46	0.33	0.10	0.59	0.19	0.22	0.07	0.12	0.24	0.09	0.10	0.13	0.17	0.19	0.12	1.24	0.96	1.23	1.18	0.53	1.85	n/a
74	0.35	0.29	0.46	0.25	0.47	0.44	0.43	0.40	0.24	0.64	0.63	0.61	0.45	0.37	0.32	0.13	0.40	0.25	0.23	0.11	0.14	0.15	0.26	0.06	0.16	0.16	0.16	0.16	1.04	0.60	0.79	0.71	0.34	1.11	0.27
87	0.21	0.19	0.26	0.13	0.81	0.78	1.42	0.85	0.65	0.68	0.38	0.60	0.40	0.34	0.37	0.16	0.48	0.29	0.29	0.15	0.20	0.22	0.25	0.12	0.27	0.23	0.27	0.18	1.48	0.99	1.17	1.12	0.59	1.70	0.24
95	0.26	0.22	0.27	0.15	1.10	0.98	2.79	0.99	0.59	0.96	0.54	0.76	0.56	0.43	0.45	0.21	0.67	0.32	0.27	0.19	0.24	0.28	0.27	0.34	0.33	0.29	0.36	0.25	2.40	1.60	1.92	1.88	0.91	2.73	2.59
99	0.20	0.19	0.24	0.13	0.80	0.73	1.62	0.82	0.81	0.68	0.38	0.73	0.46	0.41	0.58	0.26	0.69	0.44	0.56	0.25	0.32	0.38	0.44	0.14	0.41	0.35	0.34	0.28	1.61	1.10	1.25	1.20	0.63	1.88	0.33
90/ 101	0.42	0.38	0.50	0.26	1.94	1.88	4.31	2.15	1.82	1.87	0.89	1.54	1.10	0.94	0.59	0.27	0.77	0.44	0.50	0.25	0.31	0.36	0.41	0.18	0.40	0.34	0.40	0.26	1.96	1.31	1.61	1.54	0.80	2.41	1.14
104	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.00	0.00	0.00	n/a	0.00	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.01	n/a	n/a	n/a	n/a	n/a	n/a
105	0.18	0.18	0.23	0.12	0.64	0.61	1.03	0.66	0.59	0.34	0.21	0.51	0.31	0.25	0.35	0.16	0.34	0.26	0.33	0.20	0.26	0.30	0.38	0.09	0.30	0.25	0.25	0.22	1.36	0.96	1.01	1.06	0.52	1.53	1.21
110	0.52	0.43	0.63	0.31	1.99	1.92	3.47	2.12	1.41	1.89	0.84	1.70	1.08	0.91	1.11	0.45	1.38	0.79	0.81	0.39	0.52	0.57	0.67	0.53	0.71	0.56	0.76	0.48	4.18	2.89	3.39	3.18	1.71	5.15	4.35
114	0.02	0.01	0.02	0.01	0.04	0.04	0.06	0.04	0.04	n/a	0.02	0.04	0.02	0.02	0.12	0.14	0.06	0.10	0.08	0.02	0.02	0.02	0.04	0.01	0.02	0.02	0.02	0.02	0.07	0.05	0.05	0.05	0.03	0.08	n/a
118	0.42	0.42	0.56	0.28	1.50	1.39	2.52	1.82	1.69	1.39	0.77	1.63	0.93	0.88	0.84	0.36	0.90	0.64	0.85	0.68	0.84	0.97	1.27	0.33	1.07	0.84	0.90	0.64	4.10	2.82	3.16	3.12	1.61	4.75	4.89
123	0.03	0.03	0.03	0.02	0.06	0.07	0.07	0.06	0.07	0.13	0.06	0.14	0.07	0.07	0.18	0.07	0.20	0.12	0.11	0.05	0.06	0.06	0.07	0.07	0.08	0.06	0.07	0.05	0.29	0.19	0.25	0.21	0.12	0.38	0.24
138	0.52	0.58	0.61	0.38	2.50	2.17	4.02	2.81	3.07	2.40	1.31	3.06	1.61	1.63	2.57	1.28	2.75	1.78	2.78	1.35	1.65	1.70	2.37	1.19	1.92	1.73	1.82	1.32	9.08	5.15	5.39	5.03	2.89	7.17	0.38
141	0.06	0.07	0.07	0.04	0.32	0.28	0.51	0.36	0.34	0.43	0.19	0.35	0.23	0.21	0.27	0.14	0.33	0.18	0.25	0.12	0.17	0.17	0.21	0.15	0.21	0.18	0.22	0.13	1.03	0.60	0.69	0.62	0.34	0.88	0.58
149	0.27	0.32	0.30	0.20	1.37	1.19	1.98	1.29	1.01	1.63	0.68	1.47	0.82	0.77	1.01	0.54	1.28	0.69	0.82	0.44	0.64	0.60	0.75	0.64	0.78	0.67	0.77	0.53	4.21	2.40	2.85	2.38	1.39	3.57	2.62
151	n/a	n/a	0.01	0.11	0.31	0.26	0.40	0.26	0.19	0.26	0.27	0.22	0.47	n/a	0.24	0.15	0.36	0.15	0.17	0.13	0.18	0.18	0.19	0.18	0.24	0.22	0.23	0.14	1.11	0.64	0.76	0.61	0.33	0.88	0.34
132/ 153	0.51	0.58	0.61	0.37	2.66	4.49	3.04	3.20	3.42	3.42	1.71	3.60	2.03	1.97	1.32	0.71	1.48	0.96	1.51	0.92	1.02	1.02	1.60	0.62	1.26	1.13	1.04	0.79	4.84	2.64	2.93	2.57	1.53	3.86	4.20
155	0.00	0.00	0.00	0.00	0.02	0.02	0.01	0.01	0.00	0.01	0.13	0.01	0.04	0.02	0.02	0.01	0.03	0.01	0.01	n/a	n/a	n/a	0.01	n/a	0.01	0.01	0.01	n/a	0.03	0.01	0.02	0.02	0.01	0.02	n/a
156	0.04	0.06	0.05	0.03	0.24	0.22	0.28	0.29	0.26	0.22	0.09	0.25	0.11	0.14	0.18	0.08	0.20	0.13	0.21	0.08	0.08	0.09	0.14	0.05	0.12	0.12	0.10	0.06	0.42	0.23	0.27	0.23	0.13	0.32	1.18
157	0.03	0.01	0.04	0.07	0.06	0.06	0.04	0.07	0.06	0.11	0.10	0.08	0.05	0.08	0.15	0.25	0.06	0.10	0.07	0.03	0.03	0.04	0.05	0.03	0.05	0.03	0.04	0.03	0.17	0.08	0.10	0.08	0.05	0.13	n/a
158	0.05	0.06	0.06	0.04	0.24	0.23	0.41	0.28	0.26	0.16	0.12	0.25	0.15	0.14	0.15	0.08	0.17	0.11	0.18	0.06	0.07	0.09	0.10	0.06	0.08	0.08	0.10	0.06	0.45	0.25	0.27	0.29	0.15	0.36	1.02
167	0.02	0.02	0.02	0.02	0.12	0.11	0.16	0.16	0.15	0.06	0.05	0.14	0.08	0.07	0.12	0.06	0.12	0.07	0.12	0.06	0.06	0.06	0.10	0.04	0.07	0.07	0.07	0.05	0.26	0.14	0.18	0.15	0.08	0.20	0.04
170	0.07	0.08	0.08	0.04	0.35	0.27	n/a	0.46	0.36	0.50	0.28	0.61	0.34	0.34	0.41	0.23	0.41	0.32	0.53	0.25	0.16	0.28	0.45	0.23	0.32	0.32	0.37	0.21	1.54	0.86	0.89	0.89	0.50	1.10	n/a
174	0.04	0.06	0.05	0.04	0.22	0.19	0.25	0.22	0.17	0.39	0.16	0.32	0.19	0.19	0.27	0.14	0.30	0.16	0.22	0.16	0.16	0.18	0.24	0.17	0.20	0.21	0.26	0.15	1.12	0.69	0.81	0.75	0.42	1.01	0.02
180	0.13	0.17	0.15	0.09	0.28	0.21	0.66	0.34	0.67	0.69	0.27	0.67	0.38	0.46	1.00	0.55	1.02	0.69	1.31	0.58	0.51	0.63	0.96	0.51	0.60	0.63	0.73	0.45	3.35	2.02	2.21	2.11	1.25	2.86	0.89
183	0.03	0.04	0.03	0.03	0.20	0.17	0.19	0.22	0.19	0.32	0.14	0.30	0.16	0.16	0.23	0.13	0.26	0.17	0.28	0.15	0.14	0.17	0.23	0.13	0.16	0.16	0.19	0.14	0.91	0.52	0.58	0.54	0.31	0.75	n/a
187	0.10	0.14	0.12	0.08	0.49	0.39	0.43	0.58	0.40	0.99	0.34	0.99	0.51	0.43	0.66	0.35	0.83	0.42	0.72	0.46	0.48	0.48	0.70	0.39	0.57	0.51	0.56	0.41	2.55	1.43	1.66	1.55	0.87	2.06	2.26
188	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.01	n/a	n/a	n/a	n/a	n/a	n/a
189	n/a	n/a	n/a	n/a	0.01	0.01	n/a	0.01	0.01	n/a	n/a	0.02	0.01	n/a	0.01	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.02	0.01	0.02	0.02	0.04	0.02	0.03	0.02	0.02	0.03	n/a
194	n/a	0.02	0.01	0.02	0.11	0.09	0.07	0.15	0.11	n/a	0.04	0.22	0.13	0.02	0.17	0.11	0.19	0.15	0.26	0.11	0.09	0.11	0.18	0.09	0.10	0.12	0.16	0.08	0.65	0.39	0.42	0.44	0.28	0.56	0.25
199	0.00	0.00	0.00	0.00	0.02	0.02	0.02	0.02	0.01	0.03	0.01	0.03	0.02	0.02	0.02	0.01	0.03	0.01	0.02	0.01	0.01	0.02	0.02	0.01	0.01	0.02	0.02	0.01	0.08	0.05	0.06	0.05	0.03	0.07	0.01
203	0.03	0.04	0.04	0.03	0.17	0.13	0.35	0.22	0.15	0.27	0.14	0.31	0.17	0.17	0.25	0.15	0.29	0.20	0.34	0.17	0.15	0.17	0.25	0.12	0.14	0.17	0.24	0.13	0.89	0.50	0.60	0.58	0.33	0.74	n/a

Table 8.1-11 continued PCBs in roach [µg/kg wet weight]

PCB	Lee (or Lea)			Stort									Thames										Thames						Thames			
	Wheathampstead			Tednambury Mill									Castle Eaton										Caversham-Sonning						Temple-Marlow			
	2011			2011									2011										2008		2010	2012			2007			
	LE11-0008	LE11-0009	LE11-0010	ST11-0001	ST11-0002	ST11-0003	ST11-0004	ST11-0005	ST11-0006	ST11-0007	ST11-0008	ST11-0009	ST11-0010	TH11-0145	TH11-0146	TH11-0147	TH11-0148	TH11-0149	TH11-0150	TH11-0151	TH11-0152	TH11-0153	TH11-0154	TH08-0002	TH08-0004	TH10-0022	TH12-0011	TH12-0014	TH12-0017	TH12-0018	TH12-0020	TH07-0103	TH07-0104	TH07-0105	TH07-0106
18	n/a	0.53	0.54	n/a	n/a	0.20	0.23	n/a	0.18	n/a	0.19	0.27	0.42	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	1.02	0.96	1.55	0.27	0.33	0.35	0.53	0.35	0.66	0.11	0.16	0.07
22	0.07	0.35	0.38	0.19	0.11	0.15	0.18	0.19	0.09	0.08	0.12	n/a	0.18	n/a	n/a	0.04	0.20	0.14	0.09	0.11	0.09	0.10	0.05	0.38	0.48	0.87	0.16	0.21	0.17	0.39	0.26	0.31	0.13	0.09	0.19
28/ 31	0.23	1.15	1.05	0.13	0.43	0.41	0.41	0.64	0.42	0.36	0.36	0.49	0.56	0.21	0.10	0.25	0.32	0.22	0.18	0.30	0.24	0.20	0.14	2.34	3.37	2.55	0.54	0.84	0.71	1.50	1.12	0.10	0.04	0.03	0.08
41/ 64	0.12	0.39	0.42	n/a	0.22	0.20	0.23	0.32	0.23	0.21	0.19	0.19	0.24	0.16	0.08	0.16	0.13	0.15	0.11	0.16	0.17	0.12	0.10	0.93	1.37	1.49	0.34	0.68	0.49	1.21	0.73	0.96	0.40	0.44	0.86
44	0.33	1.20	0.72	0.03	0.61	0.56	0.59	0.86	0.62	0.53	0.50	0.44	0.68	0.30	0.19	0.37	0.29	0.31	0.27	0.35	0.36	0.25	0.21	0.97	1.46	2.75	0.61	1.18	0.83	2.17	1.34	1.11	0.16	0.44	0.72
49	0.28	0.98	0.80	0.15	0.70	0.63	0.73	1.00	0.68	0.61	0.56	0.59	0.78	0.30	0.17	0.34	0.32	0.30	0.25	0.35	0.35	0.25	0.20	0.98	1.68	2.60	0.64	1.31	0.96	2.42	1.52	1.32	0.56	0.54	1.01
52	0.68	2.77	2.18	0.22	1.55	1.37	1.55	2.20	1.60	1.45	1.22	1.14	1.77	0.71	0.40	0.77	0.63	0.70	0.60	0.80	0.82	0.61	0.48	1.36	2.18	3.26	1.00	1.80	1.33	3.19	2.11	2.06	0.85	0.83	1.55
54	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.00	0.00	0.00	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
56/ 60	0.15	0.28	0.23	n/a	0.19	0.19	0.19	0.35	0.19	0.19	0.19	0.12	0.15	0.13	0.08	0.16	0.15	0.11	0.09	0.14	0.13	0.10	0.07	0.48	0.69	1.03	0.19	0.43	0.30	0.65	0.41	n/a	n/a	n/a	n/a
70	0.62	0.88	0.59	0.03	0.81	0.72	0.82	1.41	0.97	0.82	0.77	0.45	0.79	0.43	0.29	0.50	0.51	0.47	0.34	0.56	0.54	0.42	0.31	0.88	1.63	4.14	1.14	1.90	1.56	3.05	2.30	1.59	0.59	0.64	0.88
74	0.39	0.92	0.45	0.02	0.57	0.50	0.53	0.97	0.60	0.63	0.51	0.48	0.47	0.26	0.17	0.34	0.43	0.30	0.29	0.31	0.29	0.20	0.20	0.78	1.30	2.02	0.58	1.23	0.75	2.17	1.52	1.10	0.37	0.45	0.74
87	0.81	1.31	0.48	0.04	1.37	1.13	1.56	2.14	1.51	1.53	1.10	0.45	1.07	0.57	0.39	0.63	0.52	0.53	0.46	0.57	0.60	0.47	0.32	0.71	1.21	1.42	0.56	1.24	0.86	1.73	1.07	3.01	0.33	0.74	2.02
95	0.99	2.34	2.13	0.28	1.97	1.71	2.04	2.60	2.04	1.83	1.50	1.41	2.08	1.44	0.91	1.57	0.73	1.47	1.21	1.57	1.60	1.38	1.05	1.11	2.04	1.77	0.71	1.35	1.07	1.98	1.31	1.58	0.61	0.67	1.54
99	0.83	1.41	0.54	0.08	1.56	1.30	1.80	2.37	1.68	1.90	1.27	1.08	1.37	0.64	0.44	0.71	0.84	0.64	0.57	0.68	0.68	0.54	0.43	0.91	1.69	1.38	0.61	1.34	0.95	1.95	1.35	1.69	0.66	0.75	1.30
90/ 101	1.02	1.75	1.38	0.07	1.85	1.55	2.13	2.76	2.03	2.16	1.53	1.38	1.75	0.82	0.56	0.93	0.79	0.78	0.68	0.83	0.86	0.68	0.51	2.04	3.73	1.80	0.77	1.57	1.12	2.38	1.57	4.40	1.50	1.67	3.40
104	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.01	0.01	n/a	n/a	n/a	n/a	n/a	0.00	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
105	0.81	1.13	0.95	0.32	1.20	1.08	1.46	2.23	1.34	1.57	1.07	0.61	0.65	0.46	0.30	0.60	0.65	0.36	0.38	0.44	0.48	0.34	0.24	0.53	0.91	1.00	0.51	1.01	0.55	1.38	0.86	1.07	0.51	0.56	1.03
110	2.39	3.81	3.57	1.20	4.42	3.56	5.35	6.76	4.72	4.89	3.56	3.19	3.41	2.45	1.68	2.58	1.49	2.21	1.88	2.18	2.43	2.06	1.53	1.83	2.98	3.66	1.74	3.55	2.75	5.14	3.06	4.02	1.49	1.67	3.11
114	0.04	0.06	0.01	n/a	0.06	0.05	0.08	0.11	0.07	0.09	0.06	n/a	0.06	0.04	0.04	0.05	0.05	0.04	0.03	0.04	0.04	0.03	0.03	0.03	0.06	0.05	0.03	0.06	0.04	0.08	0.04	0.07	n/a	0.04	n/a
118	2.51	3.51	2.90	0.73	3.99	3.46	5.01	6.99	4.64	5.03	3.62	2.84	2.94	1.86	1.26	2.25	2.27	1.41	1.31	1.46	1.70	1.29	0.90	1.47	2.56	2.39	1.22	2.50	1.58	3.41	2.34	3.79	1.37	1.73	2.77
123	0.17	0.27	0.29	0.05	0.21	0.16	0.28	0.31	0.22	0.27	0.19	0.06	0.16	0.27	0.17	0.26	0.18	0.24	0.19	0.20	0.24	0.21	0.13	0.08	0.12	0.20	0.12	0.31	0.19	0.38	0.21	n/a	n/a	n/a	n/a
138	4.40	5.88	0.27	0.25	5.68	5.49	8.09	11.18	7.90	8.35	5.87	6.46	5.47	4.78	3.64	6.24	4.02	4.14	4.04	5.06	5.15	3.91	2.77	2.51	4.75	3.09	2.17	4.10	3.48	5.43	4.14	5.75	2.41	2.60	4.60
141	0.53	0.64	0.34	0.68	0.55	0.50	0.80	1.02	0.74	0.78	0.57	0.55	0.53	0.60	0.45	0.70	0.40	0.55	0.52	0.61	0.59	0.48	0.37	0.36	0.60	0.36	0.25	0.48	0.49	0.63	0.47	0.75	0.27	0.32	0.58
149	2.02	2.88	2.48	0.73	2.30	2.15	3.28	3.60	2.86	2.83	2.09	2.07	2.05	2.46	1.79	2.78	1.57	2.40	2.13	2.53	2.48	2.13	1.57	1.32	2.30	1.62	1.07	2.22	2.06	2.77	2.06	3.19	1.19	1.32	2.52
151	0.47	0.73	0.50	0.01	0.41	0.39	0.51	0.66	0.45	0.51	0.38	0.36	0.40	0.59	0.47	0.67	0.50	0.62	0.56	0.68	0.67	0.61	0.43	0.28	0.53	0.38	0.24	0.49	0.52	0.65	0.46	0.70	0.29	0.30	0.62
132/ 153	2.23	3.20	3.12	1.14	2.38	2.38	3.56	4.75	3.36	3.74	2.68	2.42	2.31	2.74	2.02	3.39	2.62	2.09	2.06	2.54	2.42	1.88	1.42	5.55	5.65	1.55	1.05	2.01	1.82	2.61	2.16	7.08	3.20	3.06	5.48
155	0.01	0.02	0.01	n/a	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.07	0.01	0.01	0.01	0.01	0.01	0.01	0.04	0.15	0.23	0.04	0.12	0.08	0.14	0.17	0.09	0.04	0.05	0.09
156	0.20	0.25	0.46	0.77	0.38	0.37	0.51	0.76	0.54	0.53	0.30	n/a	0.24	0.21	0.15	0.30	0.21	0.15	0.17	0.20	0.19	0.13	0.11	0.24	0.34	0.25	0.17	0.42	0.31	0.43	0.38	0.60	n/a	0.27	n/a
157	0.08	0.09	n/a	n/a	0.11	0.11	0.16	0.22	0.18	0.16	0.09	0.09	0.09	0.09	0.06	0.11	0.09	0.06	0.06	0.08	0.08	0.06	0.05	0.06	0.09	0.05	0.04	0.08	0.07	0.09	0.07	0.18	n/a	0.06	n/a
158	0.24	0.28	2.27	1.07	0.36	0.37	0.52	0.65	0.45	0.49	0.29	0.09	0.22	0.24	0.18	0.32	0.17	0.21	0.22	0.29	0.29	0.21	0.11	0.26	0.40	0.16	0.10	0.21	0.15	0.31	0.21	n/a	n/a	0.17	n/a
167	0.13	0.16	0.03	n/a	0.19	0.22	0.30	0.39	0.26	0.28	0.17	0.29	0.27	0.18	0.13	0.26	0.14	0.13	0.15	0.15	0.15	0.10	0.08	0.17	0.23	0.14	0.11	0.18	0.15	0.21	0.17	0.28	n/a	0.15	n/a
170	0.71	0.99	n/a	n/a	0.56	0.54	0.82	1.18	0.81	0.90	n/a	n/a	0.53	0.95	0.73	1.30	0.89	0.78	0.70	0.94	0.97	0.73	0.54	0.37	0.54	0.37	0.37	0.72	0.64	0.86	0.67	n/a	n/a	0.45	n/a
174	0.67	0.79	0.04	n/a	0.33	0.34	0.49	0.55	0.44	0.45	0.32	0.23	0.29	0.73	0.53	0.83	0.58	0.65	0.56	0.68	0.68	0.62	0.45	0.26	0.43	0.27	0.27	0.55	0.57	0.65	0.46	0.75	0.28	0.29	0.47
180	1.91	2.24	1.15	0.13	0.96	0.96	1.50	1.93	1.34	1.46	1.32	0.64	0.69	2.48	1.82	3.40	1.91	1.90	1.73	2.19	2.04	1.47	1.19	0.84	1.05	0.76	0.72	1.42	1.36	1.65	1.36	2.48	n/a	1.14	n/a
183	0.49	0.57	0.28	0.04	0.25	0.25	0.37	0.43	0.29	0.34	0.25	0.19	0.22	0.59	0.43	0.78	0.53	0.44	0.43	0.57	0.51	0.41	0.34	0.25	0.35	0.18	0.17	0.32	0.31	0.42	0.20	0.55	0.22	0.26	0.31
187	1.29	1.77	0.78	0.15	0.69	0.73	1.21	1.29	0.95	0.95	0.82	0.50	0.53	1.68	1.35	2.27	1.57	1.28	1.18	1.44	1.44	1.17	0.88	0.55	0.94	0.47	0.45	1.00	1.05	1.15	0.91	1.64	0.87	0.70	1.17
188	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.00	0.00	0.00	0.00	0.00	0.00	n/a	n/a	n/a	n/a
189	0.02	0.03	n/a	n/a	0.03	0.02	0.03	0.04	0.03	0.02	n/a	n/a	0.02	0.03	0.02	0.04	0.04	0.02	0.02	0.03	0.03	0.02	0.02	0.01	0.01	0.02	0.01	0.03	0.01	0.03	0.03	n/a	n/a	0.02	n/a
194	0.37	0.40	0.17	0.01	0.16	0.15	0.23	0.30	0.20	0.23	0.21	0.04	0.12	0.41	0.31	0.54	0.30	0.29	0.29	0.36	0.37	0.27	0.23	0.15	0.31	0.12	0.12	0.27	0.25	0.25	0.22	n/a	n/a	0.17	n/a
199	0.05	0.05	0.01	n/a	0.02	0.02	0.03	0.03	0.02	0.03	0.02	0.01	0.02	0.05	0.04	0.05	0.05	0.04	0.03	0.04	0.04	0.04	0.03	0.02	0.03	0.02	0.02	0.04	0.04	0.04	0.03	0.05	0.02	0.02	0.03
203	0.50	0.60	n/a	n/a	0.24	0.25	0.36	0.46	0.33	0.35	0.11	n/a	0.18	0.58	0.41	0.78	0.54	0.41	0.43	0.56	0.53	0.42	0.34	0.21	0.25	0.15	0.16	0.31	0.30	0.36	0.28	0.29	0.16	0.25	n/a

Table 8.1-11 continued PCBs in roach [µg/kg wet weight]

PCB	Thames Bray-Boveney 2012		Thames Old Windsor-Bell 2007					Thames Sunbury-Molesey 2012			
	TH12-0064	TH12-0070	TH07-0187	TH07-0188	TH07-0189	TH07-0190	TH07-0191	TH12-0152	TH12-0156	TH12-0157	TH12-0158
18	0.11	0.20	0.24	n/a	0.45	0.54	0.29	0.32	0.65	0.31	0.44
22	0.06	0.08	0.11	0.02	0.17	0.20	0.17	0.12	0.19	0.11	0.19
28/ 31	0.27	0.40	0.01	0.00	0.03	0.05	0.02	0.61	0.94	0.55	0.81
41/ 64	0.16	0.39	0.49	0.08	0.77	0.77	0.98	0.51	0.62	0.45	0.73
44	0.33	0.55	0.43	0.06	0.65	0.64	0.80	0.83	1.11	0.70	1.10
49	0.35	0.70	0.37	0.10	0.74	0.60	0.85	0.99	1.20	0.94	1.09
52	0.67	1.16	0.69	0.13	1.23	1.07	1.24	1.51	1.97	1.29	2.03
54	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
56/ 60	0.08	0.29	0.30	0.05	0.50	0.48	0.67	0.22	0.37	0.29	0.43
70	0.61	0.86	0.51	0.09	0.83	0.83	1.18	1.24	1.22	0.98	1.52
74	0.36	0.58	0.32	0.06	0.55	0.54	0.77	0.79	0.79	0.65	0.87
87	0.54	0.90	0.43	0.29	1.10	1.02	0.88	1.04	0.95	0.81	1.11
95	0.63	1.24	0.56	n/a	1.67	1.42	1.02	1.30	1.56	1.18	1.79
99	0.60	1.35	0.35	0.34	1.26	1.28	0.97	1.25	1.18	1.05	1.19
90/ 101	0.79	1.57	1.01	0.86	3.05	2.87	2.23	1.46	1.38	1.24	1.55
104	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
105	0.44	0.92	0.32	0.19	0.75	0.77	0.63	0.92	0.68	0.58	0.97
110	1.45	3.24	1.13	0.89	3.22	2.77	2.66	3.02	2.87	2.73	3.46
114	0.02	0.04	0.02	n/a	0.08	0.08	0.06	0.05	0.04	0.04	0.06
118	1.18	2.42	1.00	0.76	2.76	2.90	2.28	2.21	2.09	1.93	2.63
123	0.12	0.14	0.11	0.13	0.35	0.33	0.26	0.22	0.19	0.12	0.18
138	2.28	4.63	1.54	1.20	4.44	4.25	3.17	4.13	4.15	4.01	4.34
141	0.26	0.48	0.21	0.15	0.56	0.50	0.36	0.50	0.52	0.45	0.56
149	1.06	2.09	0.80	0.71	2.68	2.25	1.70	1.92	1.88	2.00	2.05
151	0.22	0.41	0.17	0.15	0.56	0.42	0.33	0.48	0.47	0.44	0.51
132/ 153	1.21	2.57	1.58	1.31	4.68	4.54	3.16	2.19	2.08	1.97	2.27
155	0.02	0.05	0.01	0.01	0.05	0.03	0.04	0.03	0.03	0.03	0.02
156	0.18	0.47	0.16	0.09	0.43	0.36	0.32	0.34	0.24	0.34	0.40
157	0.04	0.12	0.04	0.02	0.11	0.10	0.09	0.07	0.07	0.08	0.08
158	0.11	0.26	0.13	0.13	0.40	0.39	0.31	0.22	0.18	0.10	0.17
167	0.10	0.20	0.09	0.05	0.25	0.19	0.17	0.17	0.15	0.11	0.15
170	0.34	0.58	0.29	0.06	0.74	0.75	0.47	0.67	0.60	0.41	0.65
174	0.23	0.40	0.17	0.14	0.52	0.40	0.32	0.45	0.44	0.41	0.41
180	0.78	1.40	0.61	0.41	1.60	1.45	0.97	1.40	1.50	1.33	1.48
183	0.16	0.37	0.10	0.12	0.40	0.38	0.23	0.34	0.35	0.37	0.24
187	0.47	0.88	0.29	0.44	1.40	1.03	0.75	0.99	0.88	0.93	0.75
188	0.00	0.00	n/a	n/a	n/a	n/a	n/a	0.00	0.00	0.00	0.00
189	0.01	0.02	0.01	n/a	0.02	0.03	0.02	0.02	0.02	0.01	0.02
194	0.13	0.21	0.12	n/a	0.29	0.25	0.18	0.22	0.24	0.26	0.24
199	0.01	0.02	n/a	n/a	0.03	n/a	0.02	0.03	0.04	0.04	0.03
203	0.16	0.26	n/a	n/a	n/a	n/a	n/a	0.29	0.33	0.35	0.24

Table 8.1-12 PCBs in bleak [µg/kg wet weight]

	Thames Caversham-Sonning 2008			Thames Temple-Marlow 2007					Thames Sunbury-Molesey 2007								
PCB	TH08-0012	TH08-0020	TH08-0021	TH07-0108	TH07-0109	TH07-0110	TH07-0111	TH07-0112	TH07-0079	TH07-0080	TH07-0081	TH07-0082	TH07-0083	TH07-0084	TH07-0085	TH07-0086	TH07-0087
18	0.73	2.26	1.83	n/a	n/a	n/a	n/a	n/a	1.65	1.42	2.07	2.29	1.17	1.06	1.42	2.89	1.84
22	0.47	0.87	0.83	0.30	0.35	0.31	n/a	0.30	0.49	0.37	0.53	0.46	0.36	0.29	0.51	0.75	0.46
28/ 31	3.34	6.37	5.97	1.20	1.37	1.35	0.08	1.28	0.24	0.15	0.17	0.11	0.07	0.11	0.11	0.09	0.14
41/ 64	1.04	2.15	1.98	0.95	1.23	1.06	n/a	1.26	1.88	1.69	2.44	2.00	2.02	1.16	2.07	2.64	2.54
44	1.11	2.34	2.05	0.88	1.13	0.98	0.20	1.09	1.82	1.74	2.40	1.87	1.69	0.99	1.79	2.70	2.38
49	1.34	2.54	2.20	0.94	1.33	1.04	0.27	1.32	2.24	2.06	2.91	2.37	2.10	1.30	2.43	3.35	2.86
52	1.73	3.75	3.19	1.51	2.00	1.69	0.41	1.91	3.43	3.23	5.13	3.60	3.42	2.01	3.66	5.25	4.65
54	0.00	0.01	0.00	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.00	0.01	n/a
56/ 60	1.25	1.26	1.26	0.71	0.96	0.78	0.31	1.11	1.27	1.30	0.83	1.43	1.45	1.01	2.04	2.58	1.99
70	2.30	2.93	2.60	1.32	1.81	1.35	0.58	1.86	2.09	2.38	3.22	2.64	2.41	1.44	3.13	4.25	2.88
74	1.79	1.91	1.84	0.86	1.22	0.86	0.70	1.28	1.55	1.56	1.96	1.57	2.06	1.14	2.15	2.77	1.97
87	1.17	2.12	1.71	0.67	0.95	0.66	0.76	0.94	1.17	1.36	2.20	1.68	1.89	1.66	2.79	2.76	3.11
95	0.86	2.88	2.35	0.75	1.00	0.77	0.78	0.88	1.63	1.89	2.72	2.19	2.04	1.94	3.24	3.42	4.38
99	1.71	3.02	2.57	0.93	1.31	0.81	0.99	1.34	1.58	1.88	2.65	2.18	2.96	2.85	3.99	3.86	4.04
90/ 101	3.17	6.32	5.00	1.92	2.70	1.75	2.07	2.71	3.78	4.33	6.09	4.81	5.96	4.52	8.31	8.04	8.92
104	n/a	0.00	n/a	n/a	n/a	0.13	0.20	0.28	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
105	1.28	2.05	1.63	0.71	1.02	0.57	0.71	1.03	0.84	1.09	1.31	1.13	1.80	1.50	2.36	2.55	2.22
110	2.29	5.19	4.27	1.68	2.23	1.57	1.86	2.26	3.09	3.70	5.08	4.31	4.37	3.89	7.33	6.14	8.42
114	0.08	0.11	0.08	0.03	0.06	0.03	0.05	0.06	0.08	0.08	0.11	0.10	0.15	0.14	0.16	0.19	0.14
118	3.58	5.54	4.33	2.06	3.16	1.75	2.31	3.33	3.13	4.14	4.66	4.21	6.83	6.23	8.25	9.16	7.24
123	0.10	0.18	0.15	0.15	n/a	0.12	n/a	0.22	0.65	0.39	0.49	0.37	0.53	0.43	0.77	0.70	1.00
138	5.07	7.75	6.85	3.04	4.25	2.24	3.18	4.38	6.45	5.82	7.25	6.26	8.24	9.21	11.51	9.95	11.54
141	0.52	0.96	0.71	0.35	0.48	0.28	0.37	0.46	0.95	0.67	0.90	0.68	0.88	0.74	1.31	1.14	1.48
149	1.60	3.53	2.66	1.10	1.53	0.90	1.21	1.43	3.72	2.60	3.67	2.83	3.47	2.75	5.19	4.43	6.24
151	0.33	0.81	0.64	0.30	0.36	0.23	0.27	0.32	1.10	0.55	0.83	0.60	0.68	0.72	1.03	0.99	1.52
132/	8.92	7.92	n/a	3.56	5.11	2.67	3.94	5.18	8.05	6.31	8.57	6.52	10.17	11.10	13.11	11.67	12.95
155	0.10	0.17	0.14	0.03	0.06	0.03	0.04	0.05	n/a	n/a	0.06	0.02	0.04	0.06	0.06	0.05	0.15
156	0.61	0.83	0.53	0.33	0.50	0.22	0.33	0.50	0.40	0.55	0.57	0.56	1.08	1.00	1.13	1.14	0.73
157	0.13	0.20	0.13	0.08	0.12	0.05	0.07	0.11	n/a	0.11	0.16	0.13	0.22	0.23	0.29	0.26	0.24
158	0.46	0.74	0.60	0.29	0.39	0.19	0.28	0.32	0.54	0.49	0.62	0.51	0.77	0.74	1.08	0.91	1.05
167	0.38	0.51	0.37	n/a	0.28	0.13	0.20	0.30	0.27	0.32	0.40	0.32	0.57	0.59	0.69	0.67	0.49
170	0.91	1.00	0.31	n/a	n/a	n/a	n/a	n/a	1.50	1.00	1.00	1.00	1.46	1.84	1.67	1.51	1.00
174	0.27	0.56	0.36	0.23	0.30	0.16	0.23	0.26	1.27	0.52	0.58	0.53	0.54	0.46	0.80	0.60	1.06
180	1.72	1.81	1.41	1.21	1.80	0.86	1.29	1.73	4.29	2.23	2.45	2.16	3.30	3.05	3.75	3.25	3.50
183	0.44	0.55	0.49	0.26	0.39	0.19	0.29	0.37	1.09	0.47	0.68	0.44	0.72	0.83	0.91	0.73	1.01
187	0.89	1.27	1.08	0.71	0.87	0.46	0.65	0.82	3.00	1.21	1.67	1.23	1.82	2.99	2.17	1.71	2.51
188	n/a	0.00	0.00	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.00	n/a	n/a	n/a	n/a
189	0.04	0.03	0.00	n/a	n/a	0.02	0.03	0.04	n/a	n/a	n/a	n/a	0.06	0.09	0.06	0.06	n/a
194	0.39	0.31	0.08	n/a	n/a	0.13	0.20	0.28	0.60	0.36	0.33	0.38	0.57	0.77	0.55	0.45	0.48
199	0.02	0.04	0.02	0.02	0.02	n/a	0.02	0.02	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
203	0.39	0.47	n/a	0.17	0.31	0.14	0.22	0.30	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a

Table 8.1-13 PBDEs in roach [µg/kg wet weight]

	Glen					Nene															Kennet									Lee (or Lea)					
	Pinchbeck West					Cogenhoe					Thrapston					Oundle					Northcroft-Westmills									Wheathampstead					
	2009					2008					2008					2008					2011									2011					
PBDE	GL09-0008	GL09-0009	GL09-0015	GL09-0016	GL09-0017	NE08-0011	NE08-0012	NE08-0013	NE08-0014	NE08-0015	NE08-0001R	NE08-0004	NE08-0005	NE08-0008	NE08-0010	NE08-0026	NE08-0027	NE08-0028	NE08-0029	NE08-0030	KE11-0001	KE11-0002	KE11-0003	KE11-0004	KE11-0005	KE11-0006	KE11-0007	KE11-0008	KE11-0009	LE11-0001	LE11-0002	LE11-0003	LE11-0004	LE11-0005	LE11-0006
28	0.286	0.203	0.399	0.164	0.234	0.723	0.786	0.264	0.692	0.154	0.978	0.811	0.741	0.640	0.392	0.431	0.185	0.416	0.275	0.422	0.086	0.095	0.127	0.101	0.206	0.123	0.103	0.106	0.087	1.644	0.873	1.115	1.021	0.539	1.476
47	2.213	2.116	3.334	1.478	2.198	28.47	29.75	7.125	22.80	4.191	21.99	31.40	24.31	22.07	14.36	11.83	4.842	11.90	7.605	9.248	1.752	2.923	2.612	3.133	3.213	3.249	2.943	2.632	1.905	32.17	16.09	22.32	20.39	10.96	29.77
99		0.005	0.008	0.001	0.005		0.173			0.015	0.009	2.191	0.015	0.018	0.028	0.018	0.009	0.572	0.055	0.018	0.009	0.023	0.009		0.011	0.013	0.024	0.019	0.029	0.040	0.381	0.028	0.025	0.024	0.396
100	0.272	0.261	0.515	0.224	0.219	3.074	3.159	0.594	3.205	0.607	4.337	6.155	4.135	3.301	2.923	2.340	1.186	2.708	1.893	2.100	0.334	0.415	0.386	0.469	0.450	0.439	0.420	0.442	0.304	3.767	1.952	2.577	2.456	1.228	3.367
153	0.017	0.018	0.162	0.014	0.002	0.255	2.058	0.038	0.238	0.042	0.353	1.944	0.298	0.242	0.156	0.232	0.057	2.556	1.563	0.192	0.018	0.111	0.024	0.014	0.169	0.014	0.126	0.041	0.026	0.232	0.648	0.105	0.122	0.085	1.188
154	0.104	0.105	0.185	0.088	0.051	1.229	1.607	0.119	2.133	0.276	1.323	1.479	1.006	1.208	0.835	1.023	0.595	1.264	1.011	1.070	0.098	0.110	0.100	0.156	1.566	0.104	0.132	0.218	0.091	0.875	0.581	0.646	0.805	0.462	1.042
17	0.015	0.026	0.013	0.011	0.011	0.239	0.321	0.033	0.070	0.013	0.395	0.203	0.215	0.182	0.143	0.084	0.049	0.129	0.033	0.099	0.017	0.013	0.015	0.014	0.014	0.014	0.017	0.021		0.854	0.169	0.634	0.222	0.101	0.157
32	0.004	0.002	0.004	0.003	0.001	0.010	0.008	0.008	0.007		0.010	0.032	0.006	0.013	0.007	0.006	0.004	0.006	0.003	0.001	0.004		0.005		0.017				0.005	0.014	0.007	0.007	0.006	0.004	0.008
35	0.009	0.005	0.006	0.007	0.003			0.007			0.042	0.041	0.070	0.033	0.030	0.009	0.016	0.006	0.009	0.006	0.028	0.029	0.028	0.029	0.020	0.030	0.033	0.031	0.027	0.174	0.115	0.124	0.090	0.062	0.156
37	0.005	0.005	0.007	0.005	0.006	0.009	0.012				0.004	0.023	0.009	0.006	0.006		0.020	0.016	0.012	0.009										0.029	0.035	0.027	0.021	0.022	0.039
49	0.272	0.176	0.377	0.198	0.193	0.479	0.418	0.114	0.323	0.080	0.909	0.700	0.736	0.474	0.344	0.633	0.192	0.994	0.184	0.343	0.055	0.142	0.248	0.047	1.003	0.088	0.183	0.185	0.142	0.929	0.686	0.773	0.695	0.269	1.022
51																0.339	0.307	0.345	0.324	0.343	0.400	0.406	0.407	0.394	0.496	0.407	0.456	0.354	0.393	0.413	0.301	0.416	0.247	0.343	0.375
66	0.003	0.003			0.002						0.002	0.188	0.019	0.003	0.009	0.010	0.014	0.071	0.012	0.016		0.022					0.015			0.037	0.062	0.021			0.084
71				0.000	0.001		0.024	0.118			0.009	0.026		0.002	0.001						0.012		0.013	0.015		0.013	0.017	0.019		0.025	0.036	0.018	0.019	0.013	0.038
75	0.005	0.005	0.003	0.003	0.004	0.025	0.025	0.013	0.027	0.005		0.037	0.026	0.022	0.010	0.018	0.014	0.023	0.013	0.022	0.008	0.009	0.011	0.008		0.010	0.009	0.010	0.008	0.036	0.023	0.023	0.026	0.016	0.034
77							0.006									0.006	0.004	0.011	0.014	0.005					0.013										
85	0.000										0.004					0.023	0.024	0.018	0.019	0.033										0.014	0.009	0.010	0.010		0.010
118			0.004	0.003	0.004							0.111	0.006			0.001	0.001	0.020	0.006	0.002					0.010					0.005	0.014	0.006	0.004		0.017
119	0.009	0.002	0.015		0.005		0.038		0.036		0.022	0.044	0.039	0.032	0.023	0.040	0.016	0.065	0.038	0.041	0.009	0.014	0.011	0.007	0.269	0.007	0.009	0.012	0.010	0.057	0.019	0.024	0.027	0.015	0.039
126	0.003	0.002	0.003	0.003	0.002						0.013	0.020	0.004	0.008	0.009	0.002	0.003	0.002	0.002	0.003	0.009	0.010	0.010	0.012	0.026	0.009	0.011	0.012	0.009	0.016	0.015	0.015	0.014	0.013	0.021
138						0.020	0.025	0.012	0.028	0.020						0.012	0.016	0.010	0.002	0.014						0.026	0.024								
166					0.004	0.026	0.037	0.018	0.048	0.033			0.002																						
183	0.000		0.007	0.007	0.003	0.007	0.019	0.009	0.007	0.005	0.004	0.028						0.047	0.030		0.017		0.020	0.020	0.030		0.019	0.028	0.021	0.022	0.039			0.022	0.038
196						1.329	1.076	0.876	0.941	0.358															0.063			0.056							
197																0.022			0.016												0.018				0.049

Table 8.1-13 continued PBDEs in roach [µg/kg wet weight]

	Lee (or Lea)				Stort										Thames										Cavers								Temple-Marlow		
	Wheathampstead				TednamburyMill										CastleEaton																					
	2011				2011										2011										2008		2010	2012					2007		
PBDE	LE11-0007	LE11-0008	LE11-0009	LE11-0010	ST11-0001	ST11-0002	ST11-0003	ST11-0004	ST11-0005	ST11-0006	ST11-0007	ST11-0008	ST11-0009	ST11-0010	TH11-0145	TH11-0146	TH11-0147	TH11-0148	TH11-0149	TH11-0150	TH11-0151	TH11-0152	TH11-0153	TH11-0154	TH08-0002	TH08-0004	TH10-0022	TH12-0011	TH12-0014	TH12-0017	TH12-0018	TH12-0020	TH07-0103	TH07-0104	TH07-0105
28	0.941	0.812	1.102	0.768	0.217	0.536	0.405	0.582	0.687	0.489	0.440	0.372	0.579	0.466	0.570	0.467	0.734	0.259	0.637	0.591	0.818	1.024	0.739	0.440	0.155	0.288	0.227	0.141	0.252	0.222	0.332	0.290	0.546	0.217	0.264
47	17.85	16.41	22.71	14.99	3.887	14.20	10.63	16.60	20.82	16.29	18.59	11.70	6.737	16.62	8.336	7.352	9.590	5.844	9.013	7.480	10.14	9.941	8.942	6.649	2.875	5.628	4.682	3.266	6.132	5.751	7.727	5.434	11.02	4.022	6.552
99	0.045	0.365	0.041	0.352	0.019	0.013	0.102	0.011	0.197	0.012	0.014	0.121	0.050	0.026	0.009	0.060	0.117	0.028	0.144	0.014	0.014	0.070	0.015	0.020	0.008	0.009	0.162	0.006	0.009	0.008	0.139	0.009			
100	2.207	2.108	2.491	2.196	0.612	1.807	1.309	2.294	2.951	2.197	2.153	1.772	1.853	1.718	1.596	1.452	2.134	0.957	1.621	1.115	1.484	1.938	1.555	1.207	0.405	0.948	0.702	0.420	0.700	0.651	1.026	0.660			0.966
153	0.248	0.806	0.227	0.952	0.014	0.073	0.523	0.056	0.634	0.133	0.188	0.372	0.095	0.126	0.245	2.553	4.271	0.085	2.806	0.520	0.529	3.048	0.466	0.409	0.039	0.068	0.486	0.100	0.321	0.337	0.865	0.187	0.176	0.087	0.061
154	0.638	0.701	0.697	0.731	0.125	0.330	0.498	0.482	0.534	0.483	0.631	0.295	0.296	0.383	6.962	5.032	7.623	0.323	4.511	3.143	4.578	4.825	4.507	3.256	0.274	0.324	0.586	0.436	1.052	0.953	1.063	0.688	1.192	0.740	0.905
17	0.100	0.158	0.233	0.118		0.031	0.045	0.113	0.035	0.048	0.064	0.045	0.092	0.131	0.052	0.019	0.034	0.055	0.060	0.015	0.033	0.049	0.019	0.025	0.038	0.054	0.046	0.023	0.048	0.038	0.039	0.023	0.071	0.033	0.014
32		0.008	0.009			0.005	0.008	0.010	0.011	0.006	0.008	0.009	0.010	0.010	0.034	0.027	0.045		0.062	0.020	0.084	0.061	0.045	0.030	0.007	0.009					0.001	0.001	0.013		
35		0.080	0.134	0.049		0.058	0.044	0.048	0.058	0.052	0.051	0.041	0.038	0.056	0.038	0.035	0.041	0.076	0.038	0.030	0.046	0.037	0.036	0.040		0.011	0.006	0.005	0.004		0.006	0.005	0.022	0.012	0.014
37		0.032	0.024	0.027		0.018	0.020		0.026		0.019	0.021		0.025	0.018	0.029	0.040		0.047	0.020	0.018	0.041		0.026		0.009	0.007	0.001	0.001		0.006	0.006	0.011		
49		0.623	0.603			0.520	0.471	0.548	0.881	0.662	0.678	0.532	0.192	0.800	3.796	1.492	2.183	0.364	2.292	2.409	5.410	2.459	4.130	2.145	0.142	0.342	0.642	0.351	0.557	0.500	0.657	0.548	0.766		0.416
51	0.299	0.266	0.441	0.382	0.271	0.377	0.411	0.423	0.424	0.435	0.392	0.338	0.375	0.616	0.968	0.571	0.757	1.139	0.750	0.795	1.167	0.872	1.059	0.975										0.024	0.066
66		0.068	0.028				0.033		0.051					0.023		0.155	0.219		0.277	0.026	0.018	0.213	0.018	0.022			0.051	0.003	0.018	0.009	0.053	0.012			
71		0.029				0.014	0.018	0.021	0.015	0.013				0.022	0.156	0.020	0.031	0.046	0.083	0.027	0.088	0.143	0.033	0.058			0.008	0.005	0.014	0.016	0.006	0.003			
75		0.022	0.026			0.021	0.018	0.022	0.032	0.026	0.021	0.016		0.025	0.014	0.020	0.021	0.028	0.016	0.014	0.017	0.021	0.022	0.025	0.005	0.010	0.009	0.005	0.006	0.007	0.010	0.008	0.240		0.005
77							0.008		0.010							0.029	0.046		0.062	0.009	0.006	0.059					0.010			0.004	0.007				
85		0.010																									0.006	0.004	0.004	0.005	0.004	0.005			
118		0.014			0.010		0.008		0.013			0.009			0.012	0.158	0.229		0.300	0.025	0.028	0.216	0.023	0.034			0.018	0.005	0.011	0.009	0.025	0.006			
119	0.038	0.022	0.028	0.035	0.008	0.027	0.020	0.029	0.051	0.027	0.017	0.035	0.045	0.022	0.528	1.613	2.781	0.024	2.195	1.169	1.011	2.094	0.886	1.049	0.013		0.085	0.035	0.147	0.170	0.099	0.057	0.917	0.438	0.043
126	0.010	0.016	0.015	0.010		0.011	0.011	0.012	0.011	0.010	0.014	0.010	0.009	0.017	0.063	0.067	0.081	0.025	0.056	0.027	0.037	0.056	0.045	0.030			0.004	0.003	0.005	0.005	0.005	0.004			
138			0.023													0.208	0.321		0.340	0.035	0.030	0.233	0.028		0.018	0.014	0.030	0.013	0.017	0.013	0.040	0.015		0.004	
166																									0.017	0.012	0.005		0.008	0.004	0.004	0.004			
183	0.022	0.027		0.035	0.034		0.031	0.018	0.022			0.021	0.022	0.028	0.029	0.175	0.229		0.323	0.039	0.054	0.213	0.045	0.049	0.008	0.009	0.067	0.024	0.027	0.048	0.114	0.086		0.022	0.014
196			0.039						0.047						0.038	0.083	0.084		0.136	0.054	0.062	0.092	0.031	0.040	1.451	1.067									
197																0.074	0.088		0.110			0.050													

Table 8.1-13 continued PBDEs in roach [µg/kg wet weight]

PBDE	Thames Templ 2007 TH07-0106	Bray-Boveney 2012 TH12-0064	TH12-0070	Old Windsor-Bell 2007 TH07-0187	TH07-0188	TH07-0189	TH07-0190	TH07-0191	Sunbury-Molesey 2012 TH12-0152	TH12-0156	TH12-0157	TH12-0158
28	0.443	0.365	0.395	0.190	0.138	0.209	0.169	0.278	0.331	0.303	0.263	0.392
47	9.226	14.88	6.634	3.937	3.545	4.669	4.548	5.965	8.458	6.107	5.682	9.009
99		0.035	0.005	0.004		0.020	0.068	0.005	0.007	0.086	0.006	0.010
100		2.123	1.113	0.931	0.730	0.960	0.978	1.113	1.192	1.113	1.057	1.412
153	0.228	1.367	0.093	0.078	0.098	0.197	0.444	0.093	0.175	0.816	0.067	0.244
154	0.720	1.317	0.700	0.439	0.348	0.540	0.470	0.555	0.895	0.937	1.064	0.844
17	0.026	0.006	0.039	0.028	0.014	0.045	0.039	0.043	0.015	0.036	0.017	0.019
32			0.020			0.002		0.003	0.001			
35	0.020	0.004	0.026	0.049	0.044	0.068	0.055	0.066	0.005	0.052	0.036	0.063
37				0.002		0.006	0.010	0.004	0.001			
49	0.298	0.364	0.373	0.191	0.169	0.228		0.367	0.376	0.303	0.316	0.486
51												
66		0.011				0.009	0.033	0.009	0.006	0.028	0.003	
71		0.001	0.015	0.005		0.007	0.005	0.006		0.016	0.011	
75	0.173	0.011	0.020	0.005	0.004	0.006	0.008	0.008	0.009	0.018	0.008	0.017
77									0.003			
85		0.003							0.004	0.016		
118		0.008	0.002						0.004	0.013	0.003	0.005
119	0.850	0.066	0.030	0.033	0.041	0.058	0.048	0.038	0.029	0.033	0.033	0.037
126		0.012	0.005						0.004	0.010	0.003	0.008
138		0.010							0.010			
166		0.007							0.005			
183		0.083		0.008	0.012	0.011	0.029	0.007	0.051	0.042	0.029	
196											0.012	0.018
197			0.010							0.026	0.010	0.020

Table 8.1-14 PBDEs in bleak [µg/kg wet weight]

PBDE	Thames											
	Caversham-Sonning			Sunbury-Molesey								
	2008			2007								
	TH08-0020	TH08-0021	TH08-0012	TH07-0079	TH07-0080	TH07-0081	TH07-0082	TH07-0083	TH07-0084	TH07-0085	TH07-0086	TH07-0087
28	0.151	0.332	0.116	0.292	0.353	0.325	0.656	0.441	0.447	0.691	0.650	0.426
47	4.353	5.619	2.795	6.564	8.356	9.053	12.84	9.452	9.051	11.83	14.44	8.802
99	0.227	0.189	0.089	0.274	0.369	0.282	0.469	0.205	0.280	0.182	0.536	0.312
100	0.708	0.292	0.621	1.461	1.950	2.483	2.371	1.845	1.624	1.811	2.404	1.904
153	0.820	0.397	0.768	0.745	1.151	1.240	1.215	1.707	0.944	1.370	1.838	1.130
154	0.749	0.343	0.697	0.657	0.823	1.059	0.882	1.157	0.683	0.950	1.152	0.789
17	0.018	0.050	0.010	0.052	0.106	0.058	0.201	0.050	0.085	0.075	0.075	0.083
32	0.011	0.012					0.005				0.004	
35				0.118	0.104	0.152	0.120	0.150	0.125	0.119	0.167	0.174
37	0.020	0.029	0.009	0.029	0.030	0.026	0.039	0.021	0.027	0.019	0.050	0.025
49	0.359	0.501	0.232					0.302		0.511	0.782	
51												
66				0.099	0.087	0.085	0.126	0.100	0.108	0.075	0.192	0.075
71					0.024	0.037	0.025	0.010	0.019	0.011	0.025	
75	0.009	0.013	0.006	0.019	0.024	0.032	0.030	0.016	0.019	0.021	0.029	0.022
77	0.015		0.005									
85												
118												
119	0.065	0.038	0.057	0.054	0.080	0.107	0.092	0.110	0.071	0.097	0.113	0.096
126												
138	0.035	0.028	0.019									
166	0.042	0.033	0.048									
183	0.028	0.021	0.012	0.081	0.066	0.095	0.069	0.053	0.070	0.050	0.123	0.076
196	1.271	4.532	0.781					0.031				0.063
197												

Table 8.1-15 Organochlorine pesticides in individual roach [µg/kg fresh weight]

	Glen				Nene													Kennet									Lee (or Lea)						
l	Pinchbeck West				Cogenhoe					Thrapston					Oundle					Northcroft-Westmills								Wheathampstead						
	2009				2008					2008					2008					2011								2011						
pest.	GL09-0008	GL09-0009	GL09-0015	GL09-0016	NE08-0011	NE08-0012	NE08-0013	NE08-0014	NE08-0015	NE08-0001	NE08-0004	NE08-0005	NE08-0008	NE08-0010	NE08-0026	NE08-0027	NE08-0028	NE08-0029	NE08-0030	KE11-0001	KE11-0002	KE11-0003	KE11-0004	KE11-0005	KE11-0006	KE11-0007	KE11-0008	KE11-0009	LE11-0001	LE11-0002	LE11-0003	LE11-0004	LE11-0005	LE11-0006	LE11-0007
pp' DDT	0.066	0.039	0.008	0.047	0.068	0.054	0.047	0.032	0.017	0.050	0.051	0.094	0.065	0.071	0.040	0.010	0.071	0.008	0.013	0.012	0.023	0.012	0.011	0.149	0.022	0.008	0.012	0.018	0.791	1.114	1.377	7.215	0.493	1.467	6.631
op' DDT	0.130	0.127	0.104	0.090	0.054	0.058	0.029	0.042	0.017	0.190	0.163	0.111	0.123	0.081	0.044	0.046	0.054	0.026	0.041	0.014	0.009	0.020	0.018	0.004	0.015	0.009	0.007	0.008	2.954	2.019	3.197	8.933	2.761	3.420	11.57
pp' DDE	11.16	12.08	10.25	8.234	4.700	4.642	3.950	4.367	2.589	7.926	4.585	8.401	5.487	4.813	2.898	1.550	4.081	2.486	2.986	1.156	1.669	1.642	1.960	0.320	1.958	1.678	1.340	1.298	62.24	31.53	48.84	50.46	32.99	44.88	79.38
op' DDE	0.093	0.057	0.231	0.239	0.088	0.108	0.228	0.068	0.143	0.147	0.186	0.039	0.046	0.140	0.011	0.005	0.020	0.009	0.009	0.004	0.003	0.006	0.006	0.002	0.006	0.008	0.010	0.006	0.432	0.145	0.287	0.191	0.136	0.154	0.183
pp' DDD	1.633	1.793	1.271	1.208	0.971	0.840	0.871	0.779	0.456	1.461	0.836	1.074	0.967	0.786	0.815	0.352	1.509	0.574	0.645	0.222	0.269	0.242	0.258	0.135	0.290	0.280	0.268	0.249	7.723	5.750	6.166	4.150	2.504	4.940	6.821
op' DDD	0.180	0.178	0.144	0.146	0.477	0.821	0.156	0.320	0.045	0.542	0.263	0.274	0.217	0.191	0.090	0.037	0.171	0.059	0.065	0.050	0.050	0.050	0.040	0.029	0.061	0.072	0.065	0.064	1.331	0.947	1.172	1.014	0.388	0.792	0.909
α-chlordane	0.061	0.048	0.046	0.042	0.171	0.138	0.230	0.127	0.053	0.311	0.203	0.397	0.213	0.151	0.103	0.044	0.158	0.077	0.065	0.026	0.029	0.030	0.024	0.022	0.036	0.037	0.040	0.036	0.546	0.441	0.404	0.392	0.158	0.505	0.418
γ-chlordane	0.028	0.018	0.017	0.017	0.097	0.075	0.151	0.063	0.026	0.192	0.126	0.215	0.123	0.078	0.054	0.021	0.085	0.037	0.028	0.013	0.013	0.014	0.011	0.011	0.015	0.018	0.020	0.020	0.333	0.233	0.229	0.246	0.092	0.293	0.300
HCB	0.234	0.223	0.182	0.206	1.329	1.076	0.876	0.941	0.358	1.081	1.043	0.946	0.835	0.650	0.191	0.064	0.330	0.304	0.140	0.161	0.196	0.201	0.171	0.264	0.244	0.299	0.255	0.364	0.485	0.107	0.450	0.298	0.193	0.551	0.694
α-HCH					0.008		0.004	0.006	0.002						0.423	0.065	1.264	0.410	0.173				0.060		0.072	0.061		0.091	0.053	0.136	0.041	0.822	0.240		0.072
β-HCH					0.056	0.048	0.029	0.038	0.012						1.074	0.254	2.274	0.903	0.504	0.094	1.018	0.556	0.512	0.197	0.659	0.923	0.392	0.575	1.985	0.402	1.672	1.873	0.399	1.259	2.071
γ-HCH					0.271	0.294	0.161	0.180	0.096								1.703	1.230					1.310		3.329	2.922	2.544	1.213	9.853	4.578	10.21	6.552	4.694	9.908	13.72
δ-HCH					0.012	0.016		0.001																											
α-endo-sulfan																																			
β-endo-sulfan							0.001																						0.711	0.640	0.513	0.594	0.269	0.560	

Table 8.1-15 continued Organochlorine pesticides in individual roach [µg/kg fresh weight]

	Lee (or Lea)			Stort										Thames										Caversham-Sonning								Temple-Marlow			
l	Wheathampstead			Tednambury Mill										Castle Eaton																					
	2011			2011	2011	2011	2011	2011	2011	2011	2011	2011	2011	2011										2008		2010	2012					2007			
pest.	LE11-0008	LE11-0009	LE11-0010	ST11-0001	ST11-0002	ST11-0003	ST11-0004	ST11-0005	ST11-0006	ST11-0007	ST11-0008	ST11-0009	ST11-0010	TH11-0145	TH11-0146	TH11-0147	TH11-0148	TH11-0149	TH11-0150	TH11-0151	TH11-0152	TH11-0153	TH11-0154	TH08-0002	TH08-0004	TH10-0022	TH12-0011	TH12-0014	TH12-0017	TH12-0018	TH12-0020	TH07-0103	TH07-0104	TH07-0105	TH07-0106
pp' DDT	0.613	53.78	6.696		0.048	0.032	0.213	0.194	0.039	0.019			0.030				0.030		0.023	0.013	0.011	0.026	0.076	0.126	0.131	0.032	0.015	0.020	0.023	0.031	0.022			0.032	
op' DDT	1.940	30.11	17.03		0.065	0.054	0.059	0.106	0.070	0.023	0.014	0.009	0.031	0.013	0.005	0.014	0.035	0.017	0.019	0.011	0.009	0.020	0.037	0.037	0.059	0.019	0.021	0.030	0.023	0.055	0.028			0.087	
pp' DDE	27.01	173.5	84.95	1.383	4.638	3.684	5.255	7.111	4.864	5.246	3.624	3.151	3.584	1.687	1.196	2.012	3.890	1.380	1.191	1.496	1.490	2.099	1.054	1.971	3.901	2.126	1.136	1.918	1.874	3.179	2.083	9.206	3.244	4.137	6.917
op' DDE	0.100	0.770	0.352	0.014	0.014	0.042	0.092	0.026	0.025	0.017	0.014	0.019	0.024	0.011	0.003	0.008	0.012	0.008	0.005	0.007	0.009	0.010	0.012	0.168	0.150	0.015	0.007	0.022	0.018	0.022	0.015		0.145	0.047	0.131
pp' DDD	4.283	9.645	13.28		1.516	1.480	1.481	1.913	1.659	1.278	1.020	1.053	1.484	0.443	0.314	0.485	0.666	0.459	0.433	0.556	0.536	0.500	0.523	0.742	1.186	0.898	0.247	0.362	0.281	0.685	0.439	1.819	0.804	0.819	1.496
op' DDD	0.681	1.914			0.261	0.267	0.322	0.259	0.265	0.230	0.195	0.080	0.359	0.134	0.067	0.122	0.155	0.136	0.077	0.127	0.143	0.110	0.094	0.234	0.376	0.322	0.163	0.300	0.264	0.372	0.233	0.530	0.229	0.173	0.379
α-chlordane	0.217	0.618	0.304		0.136	0.121	0.116	0.136	0.123	0.092	0.082	0.081	0.107	0.122	0.080	0.112	0.085	0.120	0.081	0.118	0.113	0.114	0.081	0.271	0.520	0.212	0.057	0.074	0.062	0.127	0.089				
γ-chlordane	0.119	0.392	0.226		0.067	0.068	0.064	0.081	0.070	0.050	0.045	0.045	0.051	0.067	0.046	0.062	0.045	0.068	0.043	0.063	0.045	0.068	0.045	0.175	0.369	0.117	0.033	0.041	0.042	0.077	0.049				
HCB	0.030	0.541	0.413	0.042	0.247	0.337	0.325	0.578	0.278	0.166	0.301	0.429	0.449	1.018	0.277	1.396	0.839	1.087	0.949	1.480	1.304	0.484	0.915	1.451	1.067	0.447	0.176	0.219	0.175	0.322	0.274				
α-HCH				0.044			0.233	0.239	0.155			0.052	0.153		0.039		0.497	0.228			0.096	0.057		0.007	0.011										
β-HCH		1.920	4.127	0.325	0.333	0.705	1.187	1.366	0.978	0.655	1.034	2.329	0.267	0.469	0.129	0.591	1.982	0.776	0.185	0.138	0.186	0.286	0.444	0.032	0.046										
γ-HCH	1.828	9.522	10.21	3.392	1.318	2.475	1.060	1.227	1.021	1.174	1.487	6.809	2.224					0.979						0.262	0.290										
δ-HCH																								0.001	0.014										
α-endo-sulfan																																			
β-endo-sulfan		0.969				0.558	0.517					0.514											0.834												

Table 8.1-15 continued Organochlorine pesticides in individual roach [µg/kg fresh weight]

	Thames										
l	Bray-Boveney		OldWindsor-Bell					Sunbury-Molesey			
	2012		2007					2012			
pest.	TH12-0064	TH12-0070	TH07-0187	TH07-0188	TH07-0189	TH07-0190	TH07-0191	TH12-0152	TH12-0156	TH12-0157	TH12-0158
pp' DDT	0.010	0.022	0.018	0.049	0.115	0.132	0.093	0.023	0.029		0.036
op' DDT	0.019	0.145	0.049	0.042	0.178	0.139	0.136	0.052	0.054	0.011	0.035
pp' DDE	2.042	4.638	1.667	2.220	5.576	5.479	4.597	2.808	2.479	1.852	2.316
op' DDE	0.005	0.013	0.008	0.019	0.111	0.030	0.019	0.016	0.030	0.011	0.010
pp' DDD	0.235	0.493	0.842	0.476	1.785	1.654	1.298	0.522	0.666	0.585	0.761
op' DDD	0.060	0.160	0.464	0.368	0.958	1.014	0.816	0.245	0.397	0.213	0.376
α-chlordane	0.042	0.063	0.285	0.303	0.882	0.810	0.657	0.101	0.149	0.087	0.153
γ-chlordane	0.022	0.036	0.158	0.214	0.595	0.487	0.485	0.051	0.079	0.039	0.072
HCB	0.113	0.158	0.253	0.060	0.565	0.446	0.332	0.242	0.456	0.168	0.330
α-HCH			0.005	0.014	0.008	0.012	0.006				
β-HCH							0.019				
γ-HCH			0.154	0.448	0.217	0.299	0.160				
δ-HCH											
α-endo-sulfan											
β-endo-sulfan											

Table 8.1-16 Organochlorine pesticides in individual bleak [µg/kg fresh weight]

pest.	Thames																
	Caversham-Sonning			Temple-Marlow					Sunbury-Molesey								
	2008			2007					2007								
	TH08-0012	TH08-0020	TH08-0021	TH07-0108	TH07-0109	TH07-0110	TH07-0111	TH07-0112	TH07-0079	TH07-0080	TH07-0081	TH07-0082	TH07-0083	TH07-0084	TH07-0085	TH07-0086	TH07-0087
pp' DDT	0.028	0.062	0.170	0.080	0.084	0.176	0.069	0.050	0.087	0.147	0.090	0.119	0.073	0.200	0.140	0.321	0.133
op' DDT	0.034	0.112	0.147	0.090	0.112	0.368	0.101	0.091	0.211	0.253	0.363	0.228	0.185	0.173	0.244	0.280	0.271
pp' DDE	3.178	6.177	7.301	3.986	5.897	5.038	4.260	6.237	7.682	9.548	9.968	9.585	10.72	15.36	12.92	15.56	14.55
op' DDE	0.043	0.137	0.149	0.069	0.068	0.056	0.057	0.029		0.115	0.066	0.053	0.094	0.250	0.242	0.072	0.106
pp' DDD	0.414	2.232	2.648	0.611	0.883	0.962	0.638	0.845	1.637	2.600	2.594	2.710	1.804	5.751	2.362	4.449	4.359
op' DDD	0.097	0.519	0.475	0.151		2.366			0.509	0.775	0.631	0.955	0.418	1.173	0.529	1.160	1.291
α-chlordane	0.082	0.424	0.401	0.538	0.517	0.648	0.415	0.616	0.598	0.803	0.744	0.937	0.730	1.007	0.663	1.072	1.028
γ-chlordane	0.054	0.331	0.336	0.694	0.652	0.759	0.476	0.686	0.438	0.461	0.510	0.603	0.371	0.608	0.411	0.684	0.713
HCB	0.781	1.271	4.532						1.051	0.484	1.232	1.108	0.884	0.700	1.273	1.725	0.917
α-HCH		0.011	0.010				0.133		0.031	0.028			0.018	0.026	0.024	0.037	0.022
β-HCH	0.014	0.038	0.047				0.538										
γ-HCH	0.128	0.237	0.286			1.235		0.894	0.792	0.900		0.958	0.459	0.706	0.667	0.890	0.558
δ-HCH	0.010		0.005														
α-endo-sulfan																	
β-endo-sulfan																	

8.2 PCB and PBDE congener numbers

Table 8.2-1 PCB congener numbers (from Wikipedia: http://en.wikipedia.org/wiki/PCB_congener_list), PBDE congeners are numbered in the same way – replacing "biphenyl" with "diphenylether" and "chloro with bromo"

BZ Congener Number	IUPAC Name	CASRN	Descriptors
0	Biphenyl	92-52-4	
1	2-Chlorobiphenyl	2051-60-7	CP1
2	3-Chlorobiphenyl	2051-61-8	CP0
3	4-Chlorobiphenyl	2051-62-9	CP0
4	2,2'-Dichlorobiphenyl	13029-08-8	
5	2,3-Dichlorobiphenyl	16605-91-7	CP1
6	2,3'-Dichlorobiphenyl	25569-80-6	CP1
7	2,4-Dichlorobiphenyl	33284-50-3	CP1
8	2,4'-Dichlorobiphenyl	34883-43-7	CP1
9	2,5-Dichlorobiphenyl	34883-39-1	CP1
10	2,6-Dichlorobiphenyl	33146-45-1	
11	3,3'-Dichlorobiphenyl	2050-67-1	CP0, 2M
12	3,4-Dichlorobiphenyl	2974-92-7	CP0
13	3,4'-Dichlorobiphenyl	2974-90-5	CP0
14	3,5-Dichlorobiphenyl	34883-41-5	CP0, 2M
15	4,4'-Dichlorobiphenyl	2050-68-2	CP0, PP
16	2,2',3-Trichlorobiphenyl	38444-78-9	
17	2,2',4-Trichlorobiphenyl	37680-66-3	
18	2,2',5-Trichlorobiphenyl	37680-65-2	
19	2,2',6-Trichlorobiphenyl	38444-73-4	
20	2,3,3'-Trichlorobiphenyl	38444-84-7	CP1, 2M
21	2,3,4-Trichlorobiphenyl	55702-46-0	CP1
22	2,3,4'-Trichlorobiphenyl	38444-85-8	CP1
23	2,3,5-Trichlorobiphenyl	55720-44-0	CP1, 2M
24	2,3,6-Trichlorobiphenyl	55702-45-9	
25	2,3',4-Trichlorobiphenyl	55712-37-3	CP1
26	2,3',5-Trichlorobiphenyl	38444-81-4	CP1, 2M
27	2,3',6-Trichlorobiphenyl	38444-76-7	
28	2,4,4'-Trichlorobiphenyl	7012-37-5	CP1, PP
29	2,4,5-Trichlorobiphenyl	15862-07-4	CP1
30	2,4,6-Trichlorobiphenyl	35693-92-6	
31	2,4',5-Trichlorobiphenyl	16606-02-3	CP1
32	2,4',6-Trichlorobiphenyl	38444-77-8	
33	2,3',4'-Trichlorobiphenyl	38444-86-9	CP1
34	2,3',5'-Trichlorobiphenyl	37680-68-5	CP1, 2M
35	3,3',4-Trichlorobiphenyl	37680-69-6	CP0, 2M
36	3,3',5-Trichlorobiphenyl	38444-87-0	CP0, 2M
37	3,4,4'-Trichlorobiphenyl	38444-90-5	CP0, PP
38	3,4,5-Tricholobiphenyl	53555-66-1	CP0, 2M
39	3,4',5-Trichlorobiphenyl	38444-88-1	CP0, 2M

BZ Congener Number	IUPAC Name	CASRN	Descriptors
40	2,2',3,3'-Tetrachlorobiphenyl	38444-93-8	4CL, 2M
41	2,2',3,4-Tetrachlorobiphenyl	52663-59-9	4CL
42	2,2',3,4'-Tetrachlorobiphenyl	36559-22-5	4CL
43	2,2',3,5-Tetrachlorobiphenyl	70362-46-8	4CL, 2M
44	2,2',3,5'-Tetrachlorobiphenyl	41464-39-5	4CL, 2M
45	2,2',3,6-Tetrachlorobiphenyl	70362-45-7	4CL
46	2,2',3,6'-Tetrachlorobiphenyl	41464-47-5	4CL
47	2,2',4,4'-Tetrachlorobiphenyl	2437-79-8	4CL, PP
48	2,2',4,5-Tetrachlorobiphenyl	70362-47-9	4CL
49	2,2',4,5'-Tetrachlorobiphenyl	41464-40-8	4CL
50	2,2',4,6-Tetrachlorobiphenyl	62796-65-0	4CL
51	2,2',4,6'-Tetrachlorobiphenyl	68194-04-7	4CL
52	2,2',5,5'-Tetrachlorobiphenyl	35693-99-3	4CL, 2M
53	2,2',5,6'-Tetrachlorobiphenyl	41464-41-9	4CL
54	2,2',6,6'-Tetrachlorobiphenyl	15968-05-5	4CL
55	2,3,3',4-Tetrachlorobiphenyl	74338-24-2	CP1, 4CL, 2M
56	2,3,3',4'-Tetrachlorobiphenyl	41464-43-1	CP1, 4CL, 2M
57	2,3,3',5-Tetrachlorobiphenyl	70424-67-8	CP1, 4CL, 2M
58	2,3,3',5'-Tetrachlorobiphenyl	41464-49-7	CP1, 4CL, 2M
59	2,3,3',6-Tetrachlorobiphenyl	74472-33-6	4CL, 2M
60	2,3,4,4'-Tetrachlorobiphenyl	33025-41-1	CP1, 4CL, PP
61	2,3,4,5-Tetrachlorobiphenyl	33284-53-6	CP1, 4CL, 2M
62	2,3,4,6-Tetrachlorobiphenyl	54230-22-7	4CL
63	2,3,4',5-Tetrachlorobiphenyl	74472-34-7	CP1, 4CL, 2M
64	2,3,4',6-Tetrachlorobiphenyl	52663-58-8	4CL
65	2,3,5,6-Tetrachlorobiphenyl	33284-54-7	4CL, 2M
66	2,3',4,4'-Tetrachlorobiphenyl	32598-10-0	CP1, 4CL, PP
67	2,3',4,5-Tetrachlorobiphenyl	73575-53-8	CP1, 4CL, 2M
68	2,3',4,5'-Tetrachlorobiphenyl	73575-52-7	CP1, 4CL, 2M
69	2,3',4,6-Tetrachlorobiphenyl	60233-24-1	4CL
70	2,3',4',5-Tetrachlorobiphenyl	32598-11-1	CP1, 4CL, 2M
71	2,3',4',6-Tetrachlorobiphenyl	41464-46-4	4CL
72	2,3',5,5'-Tetrachlorobiphenyl	41464-42-0	CP1, 4CL, 2M
73	2,3',5',6-Tetrachlorobiphenyl	74338-23-1	4CL, 2M
74	2,4,4',5-Tetrachlorobiphenyl	32690-93-0	CP1, 4CL, PP
75	2,4,4',6-Tetrachlorobiphenyl	32598-12-2	4CL, PP
76	2,3',4',5'-Tetrachlorobiphenyl	70362-48-0	CP1, 4CL, 2M
77	3,3',4,4'-Tetrachlorobiphenyl	32598-13-3	CP0, 4CL, PP, 2M
78	3,3',4,5-Tetrachlorobiphenyl	70362-49-1	CP0, 4CL, 2M
79	3,3',4,5'-Tetrachlorobiphenyl	41464-48-6	CP0, 4CL, 2M
80	3,3',5,5'-Tetrachlorobiphenyl	33284-52-5	CP0, 4CL, 2M
81	3,4,4',5-Tetrachlorobiphenyl	70362-50-4	CP0, 4CL, PP, 2M
82	2,2',3,3',4-Pentachlorobiphenyl	52663-62-4	4CL, 2M
83	2,2',3,3',5-Pentachlorobiphenyl	60145-20-2	4CL, 2M
84	2,2',3,3',6-Pentachlorobiphenyl	52663-60-2	4CL, 2M
85	2,2',3,4,4'-Pentachlorobiphenyl	65510-45-4	4CL, PP
86	2,2',3,4,5-Pentachlorobiphenyl	55312-69-1	4CL, 2M
87	2,2',3,4,5'-Pentachlorobiphenyl	38380-02-8	4CL, 2M

BZ Congener Number	IUPAC Name	CASRN	Descriptors
88	2,2',3,4,6-Pentachlorobiphenyl	55215-17-3	4CL
89	2,2',3,4,6'-Pentachlorobiphenyl	73575-57-2	4CL
90	2,2',3,4',5-Pentachlorobiphenyl	68194-07-0	4CL, 2M
91	2,2',3,4',6-Pentachlorobiphenyl	68194-05-8	4CL
92	2,2',3,5,5'-Pentachlorobiphenyl	52663-61-3	4CL, 2M
93	2,2',3,5,6-Pentachlorobiphenyl	73575-56-1	4CL, 2M
94	2,2',3,5,6'-Pentachlorobiphenyl	73575-55-0	4CL, 2M
95	2,2',3,5',6-Pentachlorobiphenyl	38379-99-6	4CL, 2M
96	2,2',3,6,6'-Pentachlorobiphenyl	73575-54-9	4CL
97	2,2',3,4',5'-Pentachlorobiphenyl	41464-51-1	4CL, 2M
98	2,2',3,4',6'-Pentachlorobiphenyl	60233-25-2	4CL
99	2,2',4,4',5-Pentachlorobiphenyl	38380-01-7	4CL, PP
100	2,2',4,4',6-Pentachlorobiphenyl	39485-83-1	4CL, PP
101	2,2',4,5,5'-Pentachlorobiphenyl	37680-73-2	4CL, 2M
102	2,2',4,5,6'-Pentachlorobiphenyl	68194-06-9	4CL
103	2,2',4,5',6-Pentachlorobiphenyl	60145-21-3	4CL
104	2,2',4,6,6'-Pentachlorobiphenyl	56558-16-8	4CL
105	2,3,3',4,4'-Pentachlorobiphenyl	32598-14-4	CP1, 4CL, PP, 2M
106	2,3,3',4,5-Pentachlorobiphenyl	70424-69-0	CP1, 4CL, 2M
107	2,3,3',4',5-Pentachlorobiphenyl	70424-68-9	CP1, 4CL, 2M
108	2,3,3',4,5'-Pentachlorobiphenyl	70362-41-3	CP1, 4CL, 2M
109	2,3,3',4,6-Pentachlorobiphenyl	74472-35-8	4CL, 2M
110	2,3,3',4',6-Pentachlorobiphenyl	38380-03-9	4CL, 2M
111	2,3,3',5,5'-Pentachlorobiphenyl	39635-32-0	CP1, 4CL, 2M
112	2,3,3',5,6-Pentachlorobiphenyl	74472-36-9	4CL, 2M
113	2,3,3',5',6-Pentachlorobiphenyl	68194-10-5	4CL, 2M
114	2,3,4,4',5-Pentachlorobiphenyl	74472-37-0	CP1, 4CL, PP, 2M
115	2,3,4,4',6-Pentachlorobiphenyl	74472-38-1	4CL, PP
116	2,3,4,5,6-Pentachlorobiphenyl	18259-05-7	4CL, 2M
117	2,3,4',5,6-Pentachlorobiphenyl	68194-11-6	4CL, 2M
118	2,3',4,4',5-Pentachlorobiphenyl	31508-00-6	CP1, 4CL, PP, 2M
119	2,3',4,4',6-Pentachlorobiphenyl	56558-17-9	4CL, PP
120	2,3',4,5,5'-Pentachlorobiphenyl	68194-12-7	CP1, 4CL, 2M
121	2,3',4,5',6-Pentachlorobiphenyl	56558-18-0	4CL, 2M
122	2,3,3',4',5'-Pentachlorobiphenyl	76842-07-4	CP1, 4CL, 2M
123	2,3',4,4',5'-Pentachlorobiphenyl	65510-44-3	CP1, 4CL, PP, 2M
124	2,3',4',5,5'-Pentachlorobiphenyl	70424-70-3	CP1, 4CL, 2M
125	2,3',4',5',6-Pentachlorobiphenyl	74472-39-2	4CL, 2M
126	3,3',4,4',5-Pentachlorobiphenyl	57465-28-8	CP0, 4CL, PP, 2M
127	3,3',4,5,5'-Pentachlorobiphenyl	39635-33-1	CP0, 4CL, 2M
128	2,2',3,3',4,4'-Hexachlorobiphenyl	38380-07-3	4CL, PP, 2M
129	2,2',3,3',4,5-Hexachlorobiphenyl	55215-18-4	4CL, 2M
130	2,2',3,3',4,5'-Hexachlorobiphenyl	52663-66-8	4CL, 2M
131	2,2',3,3',4,6-Hexachlorobiphenyl	61798-70-7	4CL, 2M
132	2,2',3,3',4,6'-Hexachlorobiphenyl	38380-05-1	4CL, 2M
133	2,2',3,3',5,5'-Hexachlorobiphenyl	35694-04-3	4CL, 2M
134	2,2',3,3',5,6-Hexachlorobiphenyl	52704-70-8	4CL, 2M
135	2,2',3,3',5,6'-Hexachlorobiphenyl	52744-13-5	4CL, 2M

BZ Congener Number	IUPAC Name	CASRN	Descriptors
136	2,2',3,3',6,6'-Hexachlorobiphenyl	38411-22-2	4CL, 2M
137	2,2',3,4,4',5-Hexachlorobiphenyl	35694-06-5	4CL, PP, 2M
138	2,2',3,4,4',5'-Hexachlorobiphenyl	35065-28-2	4CL, PP, 2M
139	2,2',3,4,4',6-Hexachlorobiphenyl	56030-56-9	4CL, PP
140	2,2',3,4,4',6'-Hexachlorobiphenyl	59291-64-4	4CL, PP
141	2,2',3,4,5,5'-Hexachlorobiphenyl	52712-04-6	4CL, 2M
142	2,2',3,4,5,6-Hexachlorobiphenyl	41411-61-4	4CL, 2M
143	2,2',3,4,5,6'-Hexachlorobiphenyl	68194-15-0	4CL, 2M
144	2,2',3,4,5',6-Hexachlorobiphenyl	68194-14-9	4CL, 2M
145	2,2',3,4,6,6'-Hexachlorobiphenyl	74472-40-5	4CL
146	2,2',3,4',5,5'-Hexachlorobiphenyl	51908-16-8	4CL, 2M
147	2,2',3,4',5,6-Hexachlorobiphenyl	68194-13-8	4CL, 2M
148	2,2',3,4',5,6'-Hexachlorobiphenyl	74472-41-6	4CL, 2M
149	2,2',3,4',5',6-Hexachlorobiphenyl	38380-04-0	4CL, 2M
150	2,2',3,4',6,6'-Hexachlorobiphenyl	68194-08-1	4CL
151	2,2',3,5,5',6-Hexachlorobiphenyl	52663-63-5	4CL, 2M
152	2,2',3,5,6,6'-Hexachlorobiphenyl	68194-09-2	4CL, 2M
153	2,2',4,4',5,5'-Hexachlorobiphenyl	35065-27-1	4CL, PP, 2M
154	2,2',4,4',5,6'-Hexachlorobiphenyl	60145-22-4	4CL, PP
155	2,2',4,4',6,6'-Hexachlorobiphenyl	33979-03-2	4CL, PP
156	2,3,3',4,4',5-Hexachlorobiphenyl	38380-08-4	CP1, 4CL, PP, 2M
157	2,3,3',4,4',5'-Hexachlorobiphenyl	69782-90-7	CP1, 4CL, PP, 2M
158	2,3,3',4,4',6-Hexachlorobiphenyl	74472-42-7	4CL, PP, 2M
159	2,3,3',4,5,5'-Hexachlorobiphenyl	39635-35-3	CP1, 4CL, 2M
160	2,3,3',4,5,6-Hexachlorobiphenyl	41411-62-5	4CL, 2M
161	2,3,3',4,5',6-Hexachlorobiphenyl	74472-43-8	4CL, 2M
162	2,3,3',4',5,5'-Hexachlorobiphenyl	39635-34-2	CP1, 4CL, 2M
163	2,3,3',4',5,6-Hexachlorobiphenyl	74472-44-9	4CL, 2M
164	2,3,3',4',5',6-Hexachlorobiphenyl	74472-45-0	4CL, 2M
165	2,3,3',5,5',6-Hexachlorobiphenyl	74472-46-1	4CL, 2M
166	2,3,4,4',5,6-Hexachlorobiphenyl	41411-63-6	4CL, PP, 2M
167	2,3',4,4',5,5'-Hexachlorobiphenyl	52663-72-6	CP1, 4CL, PP, 2M
168	2,3',4,4',5',6-Hexachlorobiphenyl	59291-65-5	4CL, PP, 2M
169	3,3',4,4',5,5'-Hexachlorobiphenyl	32774-16-6	CP0, 4CL, PP, 2M
170	2,2',3,3',4,4',5-Heptachlorobiphenyl	35065-30-6	4CL, PP, 2M
171	2,2',3,3',4,4',6-Heptachlorobiphenyl	52663-71-5	4CL, PP, 2M
172	2,2',3,3',4,5,5'-Heptachlorobiphenyl	52663-74-8	4CL, 2M
173	2,2',3,3',4,5,6-Heptachlorobiphenyl	68194-16-1	4CL, 2M
174	2,2',3,3',4,5,6'-Heptachlorobiphenyl	38411-25-5	4CL, 2M
175	2,2',3,3',4,5',6-Heptachlorobiphenyl	40186-70-7	4CL, 2M
176	2,2',3,3',4,6,6'-Heptachlorobiphenyl	52663-65-7	4CL, 2M
177	2,2',3,3',4,5',6'-Heptachlorobiphenyl	52663-70-4	4CL, 2M
178	2,2',3,3',5,5',6-Heptachlorobiphenyl	52663-67-9	4CL, 2M
179	2,2',3,3',5,6,6'-Heptachlorobiphenyl	52663-64-6	4CL, 2M
180	2,2',3,4,4',5,5'-Heptachlorobiphenyl	35065-29-3	4CL, PP, 2M
181	2,2',3,4,4',5,6-Heptachlorobiphenyl	74472-47-2	4CL, PP, 2M
182	2,2',3,4,4',5,6'-Heptachlorobiphenyl	60145-23-5	4CL, PP, 2M
183	2,2',3,4,4',5',6-Heptachlorobiphenyl	52663-69-1	4CL, PP, 2M

BZ Congener Number	IUPAC Name	CASRN	Descriptors
184	2,2',3,4,4',6,6'-Heptachlorobiphenyl	74472-48-3	4CL, PP
185	2,2',3,4,5,5',6-Heptachlorobiphenyl	52712-05-7	4CL, 2M
186	2,2',3,4,5,6,6'-Heptachlorobiphenyl	74472-49-4	4CL, 2M
187	2,2',3,4',5,5',6-Heptachlorobiphenyl	52663-68-0	4CL, 2M
188	2,2',3,4',5,6,6'-Heptachlorobiphenyl	74487-85-7	4CL, 2M
189	2,3,3',4,4',5,5'-Heptachlorobiphenyl	39635-31-9	CP1, 4CL, PP, 2M
190	2,3,3',4,4',5,6-Heptachlorobiphenyl	41411-64-7	4CL, PP, 2M
191	2,3,3',4,4',5',6-Heptachlorobiphenyl	74472-50-7	4CL, PP, 2M
192	2,3,3',4,5,5',6-Heptachlorobiphenyl	74472-51-8	4CL, 2M
193	2,3,3',4',5,5',6-Heptachlorobiphenyl	69782-91-8	4CL, 2M
194	2,2',3,3',4,4',5,5'-Octachlorobiphenyl	35694-08-7	4CL, PP, 2M
195	2,2',3,3',4,4',5,6-Octachlorobiphenyl	52663-78-2	4CL, PP, 2M
196	2,2',3,3',4,4',5,6'-Octachlorobiphenyl	42740-50-1	4CL, PP, 2M
197	2,2',3,3',4,4',6,6'-Octachlorobiphenyl	33091-17-7	4CL, PP, 2M
198	2,2',3,3',4,5,5',6-Octachlorobiphenyl	68194-17-2	4CL, 2M
199	2,2',3,3',4,5,5',6'-Octachlorobiphenyl	52663-75-9	4CL, 2M
200	2,2',3,3',4,5,6,6'-Octachlorobiphenyl	52663-73-7	4CL, 2M
201	2,2',3,3',4,5',6,6'-Octachlorobiphenyl	40186-71-8	4CL, 2M
202	2,2',3,3',5,5',6,6'-Octachlorobiphenyl	2136-99-4	4CL, 2M
203	2,2',3,4,4',5,5',6-Octachlorobiphenyl	52663-76-0	4CL, PP, 2M
204	2,2',3,4,4',5,6,6'-Octachlorobiphenyl	74472-52-9	4CL, PP, 2M
205	2,3,3',4,4',5,5',6-Octachlorobiphenyl	74472-53-0	4CL, PP, 2M
206	2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl	40186-72-9	4CL, PP, 2M
207	2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl	52663-79-3	4CL, PP, 2M
208	2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl	52663-77-1	4CL, 2M
209	Decachlorobiphenyl	2051-24-3	4CL, PP, 2M

Explanation of PCB "Descriptors"

(from Wikipedia)

Congener descriptors give a shorthand notation for geometry and substituent positions. The twelve congeners that display all four of the descriptors are referred to as being "dioxin-like", referring both to their toxicity and structural features which make them similar to 2,3,7,8-tetrachlorodibenzo-p-dioxin.

CP0: This group of 20 congeners are coplanar with chlorine substitution at none of the ortho positions on the biphenyl backbone and are referred to as CP0 or non-ortho congeners.

CP1: This group of 48 congeners are also co-planar but have their chlorine substitution at only one of the ortho positions and are referred to as CP1 or mono-ortho congeners.

4CL: These 169 congeners have a total of four or more chlorine substituents, regardless of position.

PP: These 54 congeners have both para positions chlorinated.

2M: These 140 congeners have two or more of the meta positions chlorinated

9 Publications

Papers

Jürgens, M. D., Johnson, A. C., Jones, K. C., Hughes, D. and Lawlor, A. J. (2013). The presence of EU priority substances mercury, hexachlorobenzene, hexachlorobutadiene and PBDEs in wild fish from four English rivers. Science of the Total Environment **461–462**: 441-452. DOI: 10.1016/j.scitotenv.2013.05.007

This paper is open access and is reproduced on the following pages:

Jürgens, M. D., Chaemfa, C., Hughes, D., Johnson, A. C. and Jones, K. C. (2015). PCB and organochlorine pesticide burden in eels in the lower Thames river (UK) Chemosphere **118**: 103-111. DOI: 10.1016/j.chemosphere.2014.06.088

Posters

The posters are reproduced at the end of this section

A UK National Fish Tissue Archive (2009)
Monika Jürgens, Andrew Johnson, Kevin Jones, David Hughes, Chakra Chaemfa,

The UK Fish Tissue Archive and its application to EU priority substances (2011)
Monika Jürgens, Andrew Johnson, Alan Lawlor, Dave Hughes, Aşkın Birgül Athanasios Katsogiannis, Kevin Jones

Reports

The first two reports are not at the moment publicly available and are not included here. Please contact the authors or the commissioning organisations if you require a copy. The download link for the third one is given below.

Jürgens , M. D., Johnson, A. C., Chaemfa, C., Jones, K. C. and Hughes, D. (2009). The organic chemical contamination of eels in the lower Thames in 2007 - A Report by CEH for Darryl Clifton-Dey of the Environment Agency for England and Wales, Thames Region.

Hamilton, P. B., Jürgens, M. D., Tyler, C. R. and Johnson, A. C. (2014). Effects of complex chemical ‘cocktails’ on the genetic diversity of fish populations. Report for Defra

Asmund, G., Conrad, A., Dulio, V., Giurisato, M., Gawlik, B. M., Grotti, M., Jürgens, M., Koschorreck, J., Müller, J., Rüther, M., Schröter-Kermani, C., Slododnik, J. and Utriainen, J. (2010). Conference for European Environmental Specimen Banks. http://www.umweltprobenbank.de/upb_static/fck/download/Manuskript%20ESB%20Conf%20final.pdf

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PCB and organochlorine pesticide burden in eels in the lower Thames River (UK)

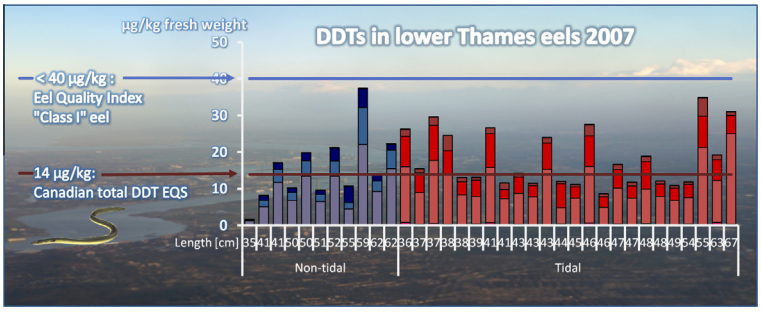
Monika D. Jürgens [a,*], Chakra Chaemfa [b,c], David Hughes [b], Andrew C. Johnson [a], Kevin C. Jones [b]

[a] CEH Wallingford, Benson Lane, OX10 8BB, United Kingdom
[b] Lancaster Environment Centre, Lancaster University, LA1 4YQ, United Kingdom
[c] Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, 511 Kehua Street, Wushan, Tianhe District, Guangzhou, GD 510640, China

HIGHLIGHTS

- 35 Eels, caught in the Thames near London in 2007, were analysed for some POPs.
- Pesticide and PCB contamination was relatively low compared to previous studies.
- No EU food or environmental standards (EQS) were exceeded.
- However, dioxin-like PCBs and total DDT exceeded a Canadian EQS.
- Tidal eels had more lipid and fewer *A. crassus* infections than upstream ones.

GRAPHICAL ABSTRACT



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ABSTRACT

Thirty-five European eels (*Anguilla anguilla*), caught in 2007 in the river Thames upstream and downstream of both London and the tidal limit, were analysed for PCBs and organochlorine pesticides. Most chemicals were detectable in every fish, although they have been banned or severely restricted for many years. In general, the tidal eels were more contaminated than upstream ones, which was related to their higher lipid contents.

The ICES7 indicator PCB concentrations ranged overall from 4.2 to 124 µg kg^{-1} fresh weight with averages of 33 and 56 µg kg^{-1} for the upstream and tidal eels; 3.5–104 µg kg^{-1}, average 26 and 48 µg kg^{-1} of that were ICES6 PCBs. Total DDT was on average 16 µg kg^{-1} (1.7–38 µg kg^{-1}) upstream and 18 µg kg^{-1} (8.6–35 µg kg^{-1}) downstream with about half of that provided by *pp'*DDE. Lindane (γ-HCH) was found at up to 2.8 µg kg^{-1} (averages 0.58 and 1.1 µg kg^{-1} upstream and downstream) and hexachlorobenzene (HCB) was on average 1.9 and 2.5 µg kg^{-1} in the two groups with a maximum of 6.4 µg kg^{-1} in each. Therefore all individuals passed the European Environmental Quality Standard (EQS) of 10 µg kg^{-1} for HCB. PCB contamination was fairly typical for recent UK eel data, whilst DDE and lindane concentrations were lower than most previous UK eel studies, perhaps reflecting a downward trend.

Although not as highly contaminated as some eels from previous UK and European studies, the presence of so many of these chemicals, with their known health effects may represent a stress for the fish or higher predators, such as birds.

Abbreviations: EQS, environmental quality standard; EQI, eel quality index; TEF, toxic equivalency factor; TEQ, toxic equivalent concentration TEQ = $TEF_1 * conc_1 + TEF_2 * conc_2 + \ldots$; NGR, National Grid Reference.

* Corresponding author. Tel.: +44 1491 838800.
E-mail address: mdj@ceh.ac.uk (M.D. Jürgens).

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1. Introduction

1.1. Concern over eel numbers

The European Eel (*Anguilla anguilla*) is an important species for commercial fisheries. There is, however, much concern over sharply declining numbers from about 1980 onwards (ICES, 2011). The European eel is now on the IUCN Red List classified as a "critically endangered species" (Freyhof and Kottelat, 2010). All European Union countries where eels occur, have to produce eel management plans, with the long term aim of ensuring silver (mature) eel escapement to the sea recovers to at least 40% of what it would be if there were no anthropogenic influences (European Union, 2007). Successful recovery plans are however hindered by a lack of certainty about the main cause(s) of the decline. Climate change leading to reduced ocean productivity (Bonhommeau et al., 2008), and to variations in ocean currents (Baltazar-Soares et al., 2014), overfishing and loss of habitat perhaps particularly in coastal areas relatively near to the Sargasso Sea (Kettle et al., 2011), infections-especially with the nematode *Anguillicola crassus* (Palstra et al., 2007), barriers to migration (Chadwick et al., 2007), and pollution (Robinet and Feunteun, 2002) have all been implicated.

1.2. The eels' life cycle in relation to pollution

Since eels are benthic carnivores with a high fat content and long life span, they tend to accumulate higher amounts of persistent chemicals from water, food, and sediment than other species (Belpaire and Goemans, 2007; Jürgens et al., 2013). In other fish species the females, and to a lesser extent males, offload lipids and with them part of their contaminant burden annually during spawning, but because eels only spawn once at the end of their lives they do not have that opportunity. These characteristics, along with the fact, that during their yellow (growth) phase most eels are highly sedentary, make them ideal for monitoring chemical pollution in the water systems where they reside. However, these features may also quite literally store up problems for their own future or present a problem to their predators. During the long spawning migration, sexual maturation occurs and they do not feed but rely instead entirely on their fat reserves. Thus chemicals that were incorporated into the fat can either be remobilized, causing potential problems to the eels during this important stage of sexual maturation, or are concentrated further in the remaining fat, much of which is later incorporated into the eggs. Palstra et al. (2006) claimed to have found a link between environmental dioxin-like contamination of eels and early death during the larval development of their offspring. Developmental failure in the offspring of contaminated females has been observed in other fish species: for example Burdick et al. (1964) reported the complete loss of lake trout fry at a particular stage in development due to DDT contamination passed on to the eggs. For a detailed review of effects of chemicals on eels see Geeraerts and Belpaire (2010).

1.3. Chemicals studied

PCBs were widely used in the 50s and 60s as cooling fluids in transformers and many other uses. Their release into the environment peaked in the 1960s before concerns over human and environmental health effects led to severe restrictions from the 1970s onwards (the dates chemicals were banned are given in Table 1). PCBs have been linked to thyroid hormone disruption (Brar et al., 2010) and reduced reproductive success (Daouk et al., 2011) in fish.

Organochlorine pesticides were hailed as part of the agricultural revolution after the war, but concerns about their bio-accumulating properties led to a ban or severe restriction for most of these compounds since about the 1980s. In this study the insecticides DDT, chlordane, lindane (γ-HCH) and endosulfan and the fungicide hexachlorobenzene (HCB) as well as some of their degradation- or by-products were selected for study. Apart from endosulfan, which could be used in EU agriculture until 2007 (European Commission, 2005a), they were all banned or very severely restricted from 1981.

DDT is probably the most widely studied pesticide. Its acute toxicity to fish at high concentrations was noted early on when fish kills were observed in sprayed areas (e.g., Surber, 1946). In the 50s it was observed that the offspring from DDT contaminated female lake trout did not survive past the stage where the yolk sac is absorbed, which was explained by maternal transfer of DDT to the eggs (Burdick et al., 1964) and by the 70s effects on osmoregulation of different fish species, including eels, became known (e.g., Janicki and Kinter, 1971). Technical DDT consists of about 85% *pp*′DDT, the active insecticidal ingredient, and 15% *op*′DDT with minor contributions of *pp*′ and *op*′ DDEs and DDDs (ATSDR, 2002).

The minor component *op*′DDT along with its degradation products *op*′DDE and *op*′DDD is estrogenic and *pp*′DDE, the compound most commonly found in the environment, is an anti-androgen. These effects were initially noticed in humans and mammals but have also been shown for fish both in vitro and in vivo (Baatrup and Junge, 2001; Bayley et al., 2002; Okoumassoun et al., 2002; Uchida et al., 2010). DDT was also related to effects on thyroid function in fish (Brar et al., 2010).

The other pesticides in this study, while less intensely studied than DDT, are also all known or suspected endocrine disruptors in fish. For example, chlordane was linked to thyroid problems in wild fish (Brar et al., 2010), Lindane (γ-HCH) caused reduction in sex steroid hormones along with other effects on the reproductive axis of both sexes of catfish (Singh and Canario, 2004), endosulfan was shown in vitro to stimulate medaka estrogen receptor α (Chakraborty et al., 2011) and HCB exposure increased estradiol in females and reduced 11-keto-testosterone in males of crucian carp (Zhan et al., 2000).

1.4. Study area and aims

The river Thames is the longest river entirely in England (about 255 km from the source to the tidal limit west of London). Eel fisheries in its lower reaches have been reported as far back as the Domesday Book of 1086, but eel recruitment all but disappeared due to heavy pollution around London from the industrial revolution of the 19th century until sewage treatment improved water quality from the 1960s (DEFRA, 2010). Today, there is a relatively small commercial eel fishery in the lower reaches of the Thames, which reported catches of 7 t of yellow eels and 0.5 t silver eel in 2007 (the year of this study). Slightly smaller numbers were removed more recently (3.8 t yellow and 0.3 t silver eels in 2013).

Apart from two individual eels caught in 1995 (Yamaguchi et al., 2003) and one composite sample from the estuary (Santillo et al., 2005), we are not aware of any previous studies of persistent organic pollutants in river Thames eels. The aims of this study were therefore to examine what recent level of contamination with PCBs and organochlorine pesticides occurred in eels from the lower Thames and to review this with respect to previous UK and European studies and environmental quality standards.

Recognizing the usefulness of eels for monitoring long-term water quality as well as the consideration, that spawner *quality* is likely to be as important as *quantity* for successful eel reproduction, an eel quality database has recently been set up (Belpaire

Table 1
Summary of the main determinants in this study. All values given as mean (standard deviation, range).

Determinand	Unit	Non-tidal Thames [fresh weight]	Thames estuary [fresh weight]	Sig. diff?[a]	Non-tidal Thames [lipid weight]	Thames estuary [lipid weight]	Sig. diff?[a]	Banned in UK[b]	EQS
Fishing date		13.9.2007	1.10.2007	–					
Number	–	11	24	–					
Length	cm	51 (9.0, 35–62)	46 (7.9, 36–67)	10%					
Weight	g	228 (133, 60–482)	186 (142, 75–667)	n.s.[c]					
Age[d]	y	12 (3, 7–18)	9 (2, 6–14)	5%					
Fulton's condition factor[e]	–	0.15 (0.03, 0.12–0.20)	0.18 (0.03, 0.12–0.26)	10%					
Lipid content	%	10.0 (9.1, 1.7–29)	16.5 (8.3, 5.1–36)	5%					
Number of *A. crassus*[f]	–	2.6(2.7, 0–10)	1.0 (1.7, 0–7)	10%					
PCBs (Sum 46)[g]	µg kg^{-1}	63 (43, 7.3–166)	113 (50, 56–232)	5%	877 (540, 303–1854)	746 (239, 408–1408)	n.s.	in stages from 1972[h]	
Sum ICES7 PCBs[i]	µg kg^{-1}	33 (21, 4.2–79)	56 (24, 28–124)	5%	472 (295, 166–1007)	375 (132, 200–753)	n.s.		
Sum ICES6 PCBs[j]	µg kg^{-1}	26 (17, 3.5–63)	48 (20, 25–104)	5%	380 (235, 132–789)	325 (112, 172–630)	n.s.		
Mono-ortho PCBs as partial WHO1998 TEQ (mammals)[k,l]	ng kg^{-1}	1.6 (1.1, 0.2–4.1)	1.9 (0.9, 1.0–4.8)	n.s.	22 (14, 8.0–49)	13 (5.1, 6.5–29)	10%		Canada:0.79[m]
mono-ortho PCBs as partial WHO2005 TEQ[k,n]	ng kg^{-1}	0.32 (0.22, 0.035–0.83)	0.39 (0.19, 0.19–1.0)	n.s.	4.6 (3.0, 1.7–10)	2.6 (1.1, 1.3–6.1)	10%		EU:6.5[o]
Total DDT[p]	µg kg^{-1}	15.7(9.6, 1.7–38)	18.2 (7.8, 8.6–35)	n.s.	236 (167, 66–528)	124 (48, 57–229)	10%	1981[q]	Canada:14[r]
op′DDT	µg kg^{-1}	0.047 (0.046, 0.001–0.14)	0.059 (0.050, 0.01–0.23)	n.s.	0.57 (0.49, 0.04–1.5)	0.37 (0.23, 0.09–0.91)	n.s.		
pp′DDT	µg kg^{-1}	2.2 (1.5, 0.24–5.2)	1.5 (1.1, 0.57–4.9)	n.s.	43 (60, 6.7–217)	10 (6.3, 2.9–27)	1%		
pp′DDE	µg kg^{-1}	10.0 (5.9, 1.3–22)	10.9 (5.2, 4.4–25)	n.s.	147 (95, 41–336)	76 (35, 30–150)	1%		
α-chlordane	µg kg^{-1}	0.42 (0.32, 0.03–1.2)	0.46 (0.47, 0.08–2.0)	n.s.	5.3 (3.2, 1.8–11)	2.7 (1.8, 0.65–7.8)	0.5%	1981[q]	
γ-chlordane	µg kg^{-1}	0.13 (0.12, 0.003–0.43)	0.54 (0.31, 0.11–1.3)	0.5%	1.4 (0.78, 0.16–3.0)	3.6 (1.9, 1.1–7.0)	0.01%	1981[q]	
γ-HCH (Lindane)	µg kg^{-1}	0.58 (0.54, 0.05–1.9)	1.1 (0.71, 0.27–2.8)	1%	6.0 (1.9, 3.2–8.9)	6.4 (2.3, 3.5–14)	n.s.	2002[s]	
β-endosulfan	µg kg^{-1}	0.06 (0.06,<0.02–0.23)	0.22 (0.11, 0.09–0.50)	0.05%	0.71 (0.29, 0.33–1.1)	1.4 (0.40, 0.82–2.2)	0.01%	2007[t]	
HCB	µg kg^{-1}	1.9 (1.7, 0.05–6.4)	2.5 (1.6, 0.82–6.4)	n.s.	21 (12, 2.8–38)	15 (5.9, 7.7–29)	n.s.	1981[q]	EU:10[o]

[a] Significance level in Student's *t*-tests (for equal or unequal variance as determined with *F*-test (5% level)), on log transformed data for the chemical analysis, and on untransformed data for the other parameters.
[b] Or severely restricted (de facto ban).
[c] n.s.: not significant at 10% level.
[d] Years continental age, determined from stained otolyths. In a few cases the age could not be accurately determined and was for statistical purposes instead estimated from the linear length/age relationship of these eels.
[e] Weight[g]/(length[cm])^3 * 100.
[f] Juveniles + adults, no larval stages were found.
[g] 46 PCBs (see Section 2.1).
[h] Open uses prohibited 1972, ban in all new systems 1986, most existing equipment with > 5 L 2000 (The UK Department of the Environment, 1997; DEFRA, 2002).
[i] Commonly found congeners 28,52,101,118,138,153, and 180.
[j] ICES7 without the dioxin-like congener 118.
[k] To calculate the complete TEQ, dioxins, furans, and non-ortho-substituted PCBs would also need to be measured.
[l] Van den Berg et al. (1998).
[m] Canadian Council of Ministers of the Environment (2001) for dioxin-like PCBs.
[n] Van den Berg et al. (2006).
[o] European Union (2013) for dioxins, furans and dioxin-like PCBs.
[p] sum of pp′DDT, op′DDT, pp′DDE, op′DDE, pp′DDD, op′DDD.
[q] EEC (1978).
[r] Canadian Council of Ministers of the Environment (1999).
[s] European Commission (2000), technical HCH, which is typically dominated by the α-congener was already banned 1981 EEC (1978).
[t] European Commission (2005a).

et al., 2011a). This study can help to address the relative lack of recent UK data in that database.

2. Material and methods

2.1. Sampling sites and eel collection

Eels were caught at two locations in the lower part of the river Thames in autumn 2007 (for numbers of fish and biometrical data refer to Table 1 or the supplementary information): Both sites are in the Greater London area about 55 river km apart (Fig. 1). The stretch between Sunbury and Molesey (about 12–17 km upstream of the tidal limit, NGR TQ105681 to TQ144692) lies upstream of central London and was chosen as a non-tidal reach that is low in the catchment and therefore likely to contain sufficient numbers of eels. Eels from that reach were caught by electrofishing with a boom boat. The tidal reach is in the Thames estuary near Woolwich, downstream of Central London, about 42 river km from the tidal limit and about 50 km from the sea (NGR TQ438796). This is an area of commercial eel fishing and the eels from this site were caught by commercial fishermen using fyke nets. All eels were returned to the laboratory alive and sacrificed 2 or 5 weeks later. They were assessed for parasite infections by dissection and microscopy in a commercial laboratory (Thames Valley Aquatic Services, 2007) and sections of eel were frozen in fluoro-ethylene-propylene bags and stored at −80 °C for 16 months until analysis. Silvering stage was not determined, but most of the individuals are likely to have been in the yellow eel stage, because migrating eels use preferentially the deeper middle part of the river which is unsuitable for fyke nets and also too deep for efficient electro fishing (personal communication from Darryl Clifton-Dey, Environment Agency).

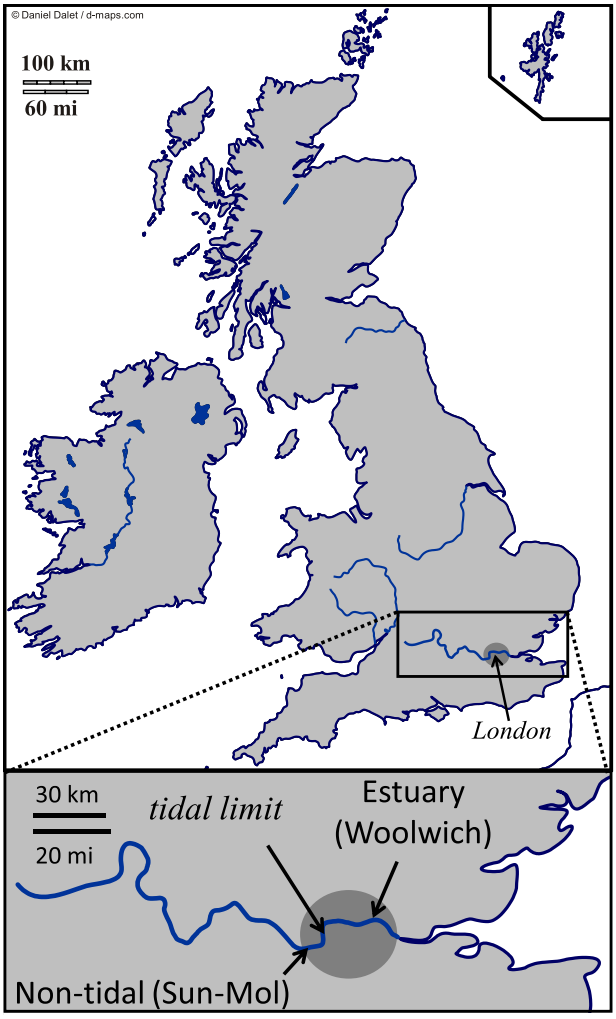

Fig. 1. Approximate locations of the eel sampling sites on the river Thames (outline © Daniel Dalet/d-maps.com).

Five of the upstream eels and 15 of the tidal ones have been analysed for otolith microchemistry (Walker et al. *in preparation*). This revealed that all had initially recruited to freshwater with those caught upstream never having returned to higher salinity. Three of the tidal eels analysed, also showed only a freshwater signal, suggesting that they had very recently arrived in the estuary from upstream, but only one of those also had the high (>20%) fat content typical of migrating silver eels. Two others had a "nomadic" signal of having moved between fresh and brackish water more than once and the rest had returned to the estuary after initially recruiting to freshwater.

2.2. Sample preparation and analysis

A portion from the central section of the eels (muscle, skin and bones) was homogenized with sodium sulphate to remove water, then $^{13}C_{12}$ –labelled ICES6 PCBs (#28, 52, 101, 138, 153, 180, Cambridge Isotope Laboratories, Andover, Massachusetts) were added as recovery standards and the sample was extracted for about 16 h with DCM in a soxhlet apparatus. Procedural blanks of sodium sulphate with internal standards were run with every batch. The DCM was solvent-exchanged to hexane which was added to a glass column with 11 g acidified silica (200 mL silica baked at 450 °C and acidified with 25 mL concentrated sulfuric acid) and eluted with hexane as a first clean up step, which removes the fats. The eluent was reduced by vacuum rotary evaporation and a subsequent cleanup was performed using gel permeation chromatography (GPC) employing a 25 mm internal diameter column containing 6 g Bio-Beads S-X3 (Bio-Rad Laboratories Ltd., Hemel Hempstead, Hertfordshire, UK) and eluting with a 1:1 v/v mixture of hexane and DCM to remove molecules outside the size range of interest. The final extract was solvent exchanged into 25 μL dodecane containing internal standards (PCB30, ^{13}C-PCB141, ^{13}C-PCB208, Wellington Laboratories Inc., Guelph, Ontario, Canada). The extracts were analysed by gas GCMS in negative chemical ionisation (NCI) mode (30 m, DB-5, 0.25 μm ID, 0.1 μm film, J&W Scientific) for HCH and endosulfan and electron impact (EI+) mode (50 m CPSil8, 0.25 mm ID, 0.12 μm film, Varian) for the other pesticides and PCBs. Target analytes were PCBs 18,22,28,31,30,41,44,49,52,54,56,60,64,70,74,87,90,101,95,99,104,105,110,114,118,123,132,138,141,149,151,154,155,156,157,158,167,170,174,180,183,187,188,189,194,199,203, *o,p′*-DDT, *p,p′*-DDT, *o,p′*-DDE, *p,p′*-DDE, *o,p′*-DDD, *p,p′*-DDD, α-endosulfan, β-endosulfan, endosulfan sulphate, α-chlordane, γ-chlordane, α-HCH, β-HCH, γ-HCH, δ-HCH and HCB (standards from Wellington Laboratoris Inc., Guelph Ontario, Canada).

Lipid content was determined by weighing the air-dried residue from a soxhlet extract of an adjacent body section to the one analysed for PCBs and pesticides.

3. Results and discussion

3.1. Parasites, condition factor, and lipid content

About half of the estuary eels and all but two of the 11 non-tidal ones were infected with adult or juvenile stages of the nematode *A. crassus*, no larval stages were found. The estuary eels tended to have a higher lipid content and a higher Fulton's condition factor (K = weight[g]/(length[cm])^3 ∗ 100) than their upstream

counterparts, which could not simply be explained by different size ranges (Table 1). These parasite and lipid results confirm findings of a German study (Marohn et al., 2013), which found higher fat content and lower *A. crassus* infections in eels from coastal or estuarine regions than in those from freshwater. Fat contents above about 20% of body weight appear to be necessary for successful migration and spawning (e.g., Belpaire et al., 2009). This makes the tidal Thames eels possibly better candidates for successful spawning, despite the fact that due to their higher lipid content they were slightly more contaminated. All chemicals measured were strongly related to lipid content of the individuals, while correlations to length or weight were much weaker. Both fresh weight and lipid-normalised data are given in Table 1 and the supplementary material available online, but we focus the discussion on fresh weight concentrations because regulatory values are framed that way.

3.2. PCBs

Most of the PCBs, including all seven indicator PCBs (ICES7), were detectable in every one of the eel samples from 2007, despite them having been banned from use in open systems in the UK since the early 70s and in closed systems since 1981. Total PCB levels (46 congeners) ranged from 7 to 232 μg kg^{-1}, fresh weight with the ICES7 indicator PCBs providing about half of that (Table 1). These values are towards the lower end of recent European measurements and fairly typical for recent UK data (see Table 2). Although the high PCB values reported in some UK sites in the 1990s (Table 2) were not repeated in this and other recent studies, there is insufficient data to show a clear trend over time for the UK. More extensive data exists for Belgium, where there is evidence that PCB contamination has decreased recently at a rate which would take about 14 years to reduce by an order of magnitude (Maes et al., 2008).

A number of PCBs have structural features that are similar to 2,3,7,8-tetra-chloro-dibenzo-dioxin (TCDD). These "dioxin-like" PCBs are the non-ortho and mono-ortho substituted PCBs and have been assigned toxicity equivalency factors (TEF) by the World Health Organization (Van den Berg et al., 1998,2006). There are indications that contamination with dioxin-like PCBs has adverse effects on eels: For example Sures and Knopf (2004) found that the most potent dioxin-like PCB126 (not analysed here) completely suppressed the immune response of eels experimentally infected with the nematode *A. crassus*, making them much more susceptible to this disease.

The European Union (European Union, 2013) recently agreed on a biota EQS to protect wildlife and humans from dioxin-like toxicity of 6.5 ng kg^{-1} for the sum of dioxins, furans and dioxin-like PCBs expressed as WHO 2005 TEQ, which is the same as the EU food standard for fish other than eel (European Commission, 2011). Of the dioxin-like substances only the mono-ortho PCBs were measured here and on their own contribute a maximum of 1 ng kg^{-1} (average 0.37) WHO 2005 TEQ. Canada has a more stringent tissue residue guideline of 0.79 ng kg^{-1} (WHO 1998 TEQ for mammals and humans) for the protection of wildlife consumers from PCBs in their prey (Canadian Council of Ministers of the Environment, 2001). This is based on studies with mink and includes a safety factor of 10 in case other mammalian predators are more sensitive. All but two of the eels analysed here (both from the non-tidal reach) exceeded this Canadian threshold even just for the mono-ortho substituted PCBs alone. The difference between passing the EU standards (at least for the measured part of the dioxin-like toxicity) and failing the Canadian ones is due both to the difference in EQS (6.5 ng kg^{-1} vs 0.79 ng kg^{-1}) and to the Canadian use of the older WHO 1998 assessment factors (Van den Berg et al., 1998), which assigned higher toxicity relative to 2,3,7,8 TCDD to the mono-ortho substituted PCBs, than the updated 2005 factors (Van den Berg et al., 2006). None of the lower Thames eels exceeded the food standards (European Commission, 2011) for eel for non-dioxin-like PCBs (300 μg kg^{-1}, sum of 6 ICES congeners) or dioxin-like toxicity (10 ng kg^{-1}, WHO 2005 TEQ), but as above, not all of the chemicals contributing to the TEQ were measured.

3.3. Organochlorine pesticides

All of the organochlorine pesticides and most of their by-products or degradation products were detected in the eel tissue despite having been banned or severely restricted decades ago (Table 1 and supporting information). The largest contribution to the pesticide burden is from the main DDT degradation product *pp′*DDE, which contributes on average 49% (SD 9%) to the total pesticides measured, with *pp′*DDD contributing a further 21% (SD 5%) (Table 1). The concentrations of *pp′*DDE ranged from 1.3 to 22 μg kg^{-1} fresh weight (average 10.0) in the upstream eels and from 4.4 to 25 μg kg^{-1} (average 10.9) in the tidal ones, with total DDT 1.7–38 (average 15.7) and 8.6–35 μg kg^{-1} (average 18.2) respectively. There is currently no EQS for DDT in the EU, but the Canadian tissue residue guidelines can give an idea as to whether contamination with that pesticide may be problematic to predators. The limit is 14 μg kg^{-1} for total DDT, which is based on the most sensitive endpoint (eggshell thinning in birds) with a safety factor of 10, to account for species differences, and the precautionary assumption that all members of the DDT family are as toxic as the most commonly studied *pp′*DDT (Canadian Council of Ministers of the Environment, 1999). At both sites more than half of the eels exceeded this value, suggesting that there may be some concern from the pesticide burden in particular to avian predators. It is however unclear, whether this level of pesticide contamination has an effect on the eels themselves.

The next-highest pesticide contribution was from HCB, which was on average 1.9 μg kg^{-1} fresh weight in the upstream eels and 2.5 μg kg^{-1} in the tidal ones (maximum 6.4 μg kg^{-1} for both groups). An EQS of 10 μg kg^{-1} fresh weight exists for HCB (European Union, 2013), which is not exceeded in any of the studied individuals. Lindane concentrations were on average 0.58 (0.05–1.9) and 1.1 (0.27–2.8) μg kg^{-1} in the two groups and α-Chlordane averaged 0.42 (0.03–1.2) μg kg^{-1} in the upstream eels and 0.46 (0.08–2.0) μg kg^{-1} in the tidal ones with γ-chlordane adding an average of 0.13 (0.003–0.43) and 0.54 (0.11–1.3) μg kg^{-1}. The β-endosulfan concentrations were never more than 0.5 μg kg^{-1}, with averages of 0.06 (<0.02–0.23) and 0.22 (0.09–0.50) μg kg^{-1} for the upstream and tidal groups. Of the pesticides measured, only the DDT family exceed the EU default limit for pesticide residues in food of 10 μg kg^{-1}, but for total DDT the much higher limit of 1000 μg kg^{-1} applies. The food limits for the other pesticides in this study are between 20 and 200 μg kg^{-1} (European Commission, 2005b).

The contamination of eels with DDE in this study was lower than much of the previously published UK and recent European eel data summarized in Table 2. Lindane was comparable to some studies from France and Italy but lower than in previous UK and recent studies from Germany and the Benelux countries. The lower values of those chemicals compared to older UK studies may reflect the expected declining trend following a ban. However, since the sites, sizes and methods vary between studies, such conclusions are only tentative. HCB was not measured in older UK studies and was in a similar range as most recent European studies that measured this chemical. Temporal downwards trends for some of these chemicals have been observed more clearly in other countries, for example in Belgium, where large numbers of eels were analysed over 11 years: Lindane concentrations fell by almost two orders of magnitude during that time, whereas the reduction

Table 2
Previous UK and recent European literature data for selected contaminants in yellow or silver eel (μg kg^{-1} fw) compared to the present study (in bold), median and range of site averages. Sorted by country and sampling date. Some data estimated from graphs or calculated from values given by lipid content or dry weight.

Year(s) of capture	Locations	Number of sites	Samples per site	DDE	γ-HCH (lindane)	HCB	ICES7 PCB	References
United Kingdom								
1983	Sheep dip impacted sites, SW England[a,b]	4	6–8	245 (77–298)	58 (30–79)	–	–	Hamilton (1985)
	Unimpacted sites, SW England[a]	3	7–8	54 (51–83)	48 (21–171)	–	–	
1984	Sheep dip impacted sites, SW England[a,b]	5	n.a.	<14 (<5–230)	–	–	–	
	Unimpacted sites, SW England[a]	3	n.a.	<15 (<5–<36)	–	–	–	
1985	Sheep dip impacted sites, SW England[a,b]	3	n.a.	<190 (<47–209)	–	–	–	
	Unimpacted sites, SW England[a]	1	n.a.	40	–	–	–	
1986	Urban sites in Scotland	8	1 Pooled	186 (43–557)	45 (25–63)	–	–	cited in Macgregor et al. (2010)
	Rural sites in Scotland	10	1 Pooled	322 (33–994)	33 (2.8–1413)	–	–	
	Mixed u/r sites in Scotland	2	1 Pooled	91 (61, 120)	56 (11 100)	–	–	
1991	Scottish Reed beds	11	1 Pooled	60 (<10–270)	–	–	Ca. 20 (ca. 3–ca. 250)[c]	Mason (1993)
1994/95	Contaminated sites Sussex, S England	18	5	79 (18–635)	16 (<0.1–60)	–	26 (6.8–383)[d]	Foster and Block (2006)
1995/96	Rivers Thames & Windrush SE England	2	2	–	3.3 (1.6, 4.9)	–	<13[e]	Yamaguchi et al. (2003)
1996	River Severn, W England/Wales	2	5 Pooled	–	–	–	100 (92 109)	Harrad and Smith (1999)
2004–08	Urban sites in Scotland	12	5	49 (<1–225)	<3.9 (<1–4.68)	ca. 1.5 (⩽1–ca. 2.5)	69 (7.1–1878)	Macgregor et al. (2010)
	Rural sites in Scotland	14	5	84 (<1.5–358)	<3.9 (<1–2.82)	ca. 1.5 (⩽1.1–ca. 2.5)	15 (5.9–54)	
	Mixed u/r sites in Scotland	3	5	33 (12–51)	<1 (<1–4.79)	<1 (<1–1.8)	22 (15–172)	
2005	Thames estuary, SE England	1	1 Pooled	–	–	–	136	Santillo et al. (2005)
2005/06	Contaminated sites Sussex, S England	21	5	43 (11–178)	<1.5 (<1–<25)	–	29 (7.5–89)	Foster and Block (2006)
2007	**Thames, near London SE England**	**2**	**11, 24**	**10 (10, 11)**	**0.84 (0.58, 1.1)**	**2.2 (1.9, 2.5)**	**44 (33, 56)**	**Current study**
Ireland								
2005/07	Lakes and rivers	5–7	1 Pooled	3.2 (1.6–7.1)	0.21 (<0.2–0.45)	<0.9 (<0.5–<2)	3.9 (1.9–18.1)	McHugh et al. (2010)
France								
2004/05	Gironde	4	13–58[a]	–	–	–	316 (278–345)	Tapie et al. (2011)
2005–07	Adour estuary	3	3–7	0.48 (0.43–0.57)	0.34 (0.33–1.49)	Total range <1–9.1[f]	98 (48–370)	Tabouret et al. (2011)
2008	3 Lagoons	3	12–22	32 (3.3–273)	–	–	3.7 (2.4–4.6)	Amilhat et al. (2014)
2008–10	All of France grouped into 6 major basins	6	16–160	–	–	2.3 (0.7–26)	587 (186–1276)	ONEMA (2012)
2009–11	Loire	3	11–16[a]	–	–	–	137 (80–193)	Blanchet-Letrouvé et al. (2014)
Italy								
2002	Tuscany	7	15	2.8 (1.3–6.1)	0.82 (0.21–45)	0.09 (0.06–0.16)	8.8 (5.7–14)[g]	Corsi et al. (2005)
2005/06	Garigiliano estuary	1 × 3[h]	10	28 (17–38)	–	2.0 (0.75–5.9)	239 (138–622)	Ferrante et al. (2010)
2007/08	River, lake, lagoon	3	15–23	98 (15–162)	0.20 (0.06–0.20)	1.2 (0.27–5.6)	32 (7.9–269)[g]	Quadroni et al. (2013)
2008/09	Campania region	7	1–2	–	–	–	22 (11–195)[e]	Pacini et al. (2012)
2009	Polluted R. Tiber + clean Lake Bolzena	2	30, 6	37 (29, 45)	–	5.7 (4.4, 7.0)	126 (38, 214)	Pujolar et al. (2012)
Belgium								
2000–07	Flanders	48	1 Pooled	–	–	–	226 (11–7753)	Belpaire et al. (2011b)
2001–05	Flanders	260[i]	1–21[j]	37 (3.0–232)	3.0 (<0.03–2076)	4.3 (0.11–62)	263 (7–5252)	Belpaire (2008)
The Netherlands								
2004	Lakes, rivers and canals	8	1 Pooled[k]	75 (25–96)	6.7 (3.5–11)	16 (4.5–30)	869 (308–1281)	de Boer et al. (2010)

Table 2 (*continued*)

Year(s) of capture	Locations	Number of sites	Samples per site	DDE	γ-HCH (lindane)	HCB	ICES7 PCB	References
Luxembourg								
2007	North Luxemburg	3	3–9	–	–	–	78 (53–346)	Boscher et al. (2010)
Germany								
1998/00	River Rhine	15–25	3–25	75 (11–180)[l]	9 (3–46)	110 (5–260)	480 (210–1330)[e]	Heinisch et al. (2004) and Heinisch et al. (2005a,b, 2006a,b, 2007)[m]
1996–03	Berlin area	10–11	3–20	750 (350–3300)	20 (4–40)	–	460 (90–1450)	
1999	River Elbe	7–8	3–20	190 (65–400)	–	–	290 (125–540)	
Europe-wide								
2005	10 European countries	20	1 Pooled	–	–	–	122 (<7–1512)	Santillo et al. (2005)

[a] Only eels >30 cm.
[b] Includes a site that was thought to be un-impacted, but showed high levels of dieldrin and DDE.
[c] Estimated using the conversion arochlor1260 = 3.6 * ICES7 PCB (Weatherley et al., 1997).
[d] Calculated from the individual PCB concentrations given in that report.
[e] Only 6 congeners.
[f] Site averages were not calculated due to non-detects.
[g] Includes additional congeners.
[h] One area three times.
[i] Only samples from 2001 onwards chosen: 260 sampling occasions from 219 sites.
[j] Typically 5.
[k] 6 Annual pooled samples from 2001 to 2006 chosen for PCBs, but only one of those (2004) supplied for the other chemicals.
[l] Sum of *op′* and *pp′* DDE.
[m] Only eels >10% lipid.

was slower for HCB, α-HCH and total DDT (estimated to take between 20 and 25 years to reduce by one order of magnitude, Maes et al., 2008).

In Belgium, an eel quality index (EQI) has been developed (Goemans et al., 2003; Belpaire and Goemans, 2007) in recognition that for successful reproduction, the quality of potential spawners is as important as their quantity. This is based on an original dataset of eels from 303 Belgian sites and is now also used in other countries (e.g., Amilhat et al., 2014). For each site the mean concentrations were calculated for a number of chemicals; for each compound these means were then ranked and the 5%ile defined as background or reference value (RV). Eels are classed depending on how much they deviate from that value with log(conc/RV)<0.4, classed as "I: not deviating" 0.4–0.8 "II: slightly deviating", 0.8–1.2 "III: deviating" and > 1.2 "IV: strongly deviating". An average classification can then also be derived across different chemicals. For example, the total DDT RV is: 16 μg kg^{-1}, therefore less than $16 * 10^{0.4} = 40$ μg kg^{-1} is class I, and therefore high quality. According to the EQI, the eels in the current study were all class I for total DDT, *pp′*DDE, and lindane, while for PCBs 91% of the upstream and 75% of the estuary eels were class I with the rest class II and for HCB the largest number (16) are in class II with 11 and 8 in classes I and III respectively. Although this is a purely statistical approach and does not state whether the observed concentrations are toxic, it helps to compare data from different studies and shows that the observed concentrations of most of the measured chemicals in the lower Thames eels are comparable to those from some of the less contaminated sites in Belgium.

3.4. Significance of pollutants in eels

In general the principle of assessing the risks of chemicals and setting appropriate standards is based on the most sensitive species and most sensitive endpoints observed, which should then (usually with some safety factor to account for a lack of data about the species or endpoints not analysed) be sufficient to protect any other species too. With regards to eels, there are however some difficulties with this approach. Until relatively recently, it was assumed that eels are fairly tolerant to pollution since they were observed in a very wide range of habitats including those with high organic loads and low oxygen content. However, very little is known about the critical life-stages of sexual maturation and spawning when, due to prolonged fasting, pollutants stored in the lipid can be re-mobilized and may affect either the eels themselves or their offspring via maternal transfer (Robinet and Feunteun, 2002). As it has so far neither been possible to observe most of the migration or the spawning or the early larval development at sea nor conduct entirely successful reproduction of European eels in captivity (for Japanese eels a full life-cycle in captivity was achieved for the first time as recently as 2010 (Ijiri et al., 2011)), we cannot yet know what the critical chemical thresholds are.

For the reasons mentioned in the introduction, eels are probably the best species for monitoring water quality, but that alone would not justify the use of a critically endangered species, as other organisms or methods are also suitable (see discussion in Jürgens et al., 2013). However, given that we still do not know for sure **why** their numbers are declining and therefore we do not know what, if anything, can be done to reverse the trend, it is necessary to learn as much as possible about eels. This includes their pollution status, especially with chemicals that may interfere with aspects of reproduction. For that reason the removal of a number of eels for analysis is justifiable and will give insights with regards to the state of the eels as well as the state of the watercourses from which they are taken.

While it is likely that the chemical pollution adds to the problems eels are facing, this alone does not seem to explain the phenomenon of the sharply declining eel numbers, given that the decline of eel recruitment corresponds to a period of generally *improving* water quality across Europe and reducing pollutant burdens in eels. However, as yet, chemicals cannot be completely ruled out, because due to the long generation times, effects on aspects of reproduction may only become apparent many years after an exposure. Climate change, water pollution, overfishing (including predation by fish eating birds), obstacles such as locks, and diseases or parasites may all be contributing factors to the decline (OSPAR Comission, 2010).

4. Conclusions

- The contamination of the 2007 Thames eels with PCBs and organochlorine pesticides appears to be relatively low compared to other UK and European studies.
- Eels from the estuary were slightly more contaminated than those from the non-tidal reach, but they also had higher lipid contents and condition factors and lower infection rates with *A. crassus*, making them possibly better spawning candidates overall.
- While none of the measured chemicals exceeded European food or environmental standards (although in the case of dioxin-like toxicity, only a small proportion of the contributing chemicals has been measured), over half the eels exceeded a Canadian tissue residue guideline to protect wildlife consumers from effects of total DDT and all but two individuals exceeded the equivalent Canadian guideline for dioxin-like PCBs, even though not all the congeners contributing to the standard were measured.
- Although not as highly contaminated with persistent organic pollutants as some of the eels from previous UK and European studies, the presence of so many of these harmful chemicals in the 2007 lower Thames eels may be a matter of concern for these fish, adding to other known or suspected problems eels face, such as fishing, infection with parasites, barriers impeding both upstream and downstream migration and climate change. Reducing the chemical burden alongside other measures should help towards the recovery of European eel populations.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2014.06.088.

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A UK National Fish Tissue Archive

Monika Jürgens*[1], Andrew Johnson[1], Kevin Jones[2], David Hughes[2], Chakra Chaemfa[2]

Why should we develop a National Fish Tissue Archive to assess chemical contamination in rivers?

- Our ability to assess what is happening in the environment is all too often hampered by our **ignorance** of the situation in the **past**
- Storing samples for the future allows to analyse **today's samples** both **with tomorrow's methods** and **for tomorrow's questions**
- This will allow us to determine temporal and spatial **trends**

Collecting

Recording

Why Rivers ?

- Lots of the chemicals we use on a daily basis are **discharged** into rivers (via sewage works)
- Our rivers are relatively small by international comparison and the population is dense – giving **little dilution** per head of population

Fish immediately frozen on site

Why Fish ?

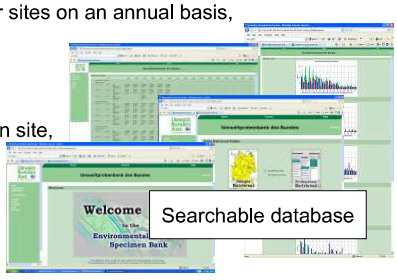
- **Fish integrate** what is present in the water/food web. This is potentially more revealing than occasional water samples
- **Uptake** is a prerequisite for potential effects on wildlife, therefore tissue concentration of a chemical is a more meaningful measure of exposure than water concentration
- The Environment Agency (EA) already catch fish to **monitor** their number, species, and size at many river sites on an annual basis, so it is sensible to work together

Dividing into homogenized sub-samples

Long term - 80°C Storage

How does it operate ?

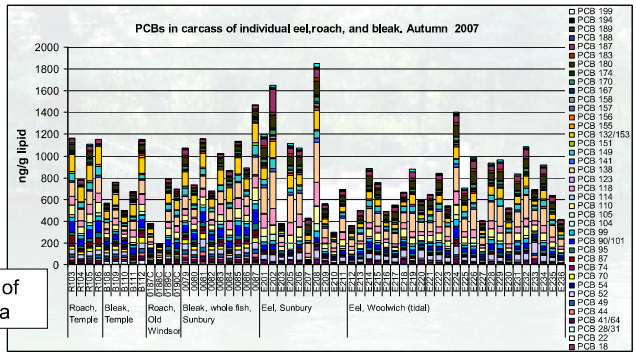
- Fish collected in the field by the EA are frozen on site, and while frozen homogenised and divided into **sub-samples** back in the laboratory
- Some sub-samples are analysed immediately, but most are stored long term at -80°C as a resource for **retrospective monitoring**
- The chemical results together with other relevant information are stored in a **database**, which will be made available through the internet



Searchable database

Examples of data retrieval from German Environmental Specimen Bank (fully operational since 1985).

Chemical analysis of some sub-samples



Some of the first results from individual fish show PCBs, banned in the UK in 1981, can still be found in three species of fish collected from the River Thames in 2007

Long term data storage

Interpretation of chemical data

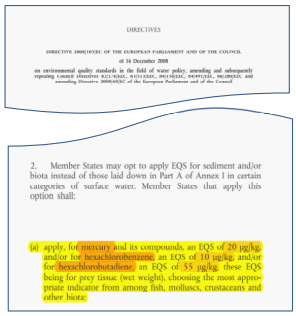
[1] CEH Wallingford, OX10 8BB,UK, * mdj@ceh.ac.uk, tel: +44 1491 692397
[2] Lancaster Environment Centre (LEC), Lancaster University, LA1 4YQ, UK

The UK Fish Tissue Archive and its application to EU priority substances

Monika Jürgens[1], Andrew Johnson[1], Alan Lawlor[2], Dave Hughes[3], Aşkın Birgül[3], Athanasios Katsogiannis[3], Kevin Jones[3]

The Fish Tissue Archive

In 2007 Scientists from CEH and the Environment Agency started to build fish tissue archive for the UK.
Roach and to a small extent bleak and eel were collected annually from a number of rivers in England. The samples were frozen on site and then stored long term at -80°C providing a resource for future retrospective monitoring for chemical contaminants.



DIRECTIVES

DIRECTIVE 2008/105/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL
of 16 December 2008
on environmental quality standards in the field of water policy, amending and subsequently repealing Council Directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC of the European Parliament and of the Council

2. Member States may opt to apply EQS for sediment and/or biota instead of those laid down in Part A of Annex I in certain categories of surface water. Member States that apply this option shall:

(a) apply, for mercury and its compounds, an EQS of 20 µg/kg, and/or for hexachlorobenzene, an EQS of 10 µg/kg, and/or for hexachlorobutadiene, an EQS of 55 µg/kg, these EQS being for prey tissue (wet weight), choosing the most appropriate indicator from among fish, molluscs, crustaceans and other biota;

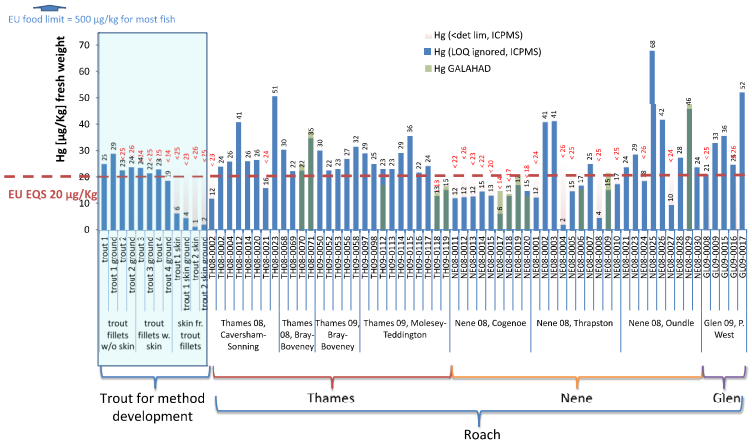
Priority Substances

The Priority Substances Directive of the EU (Directive 2008/105/EC) lists freshwater environmental quality standards (EQS) for over **30** substances, but only for **3** of these the legislation includes a standard for their concentration in biota. Measuring pollutants in biota is often preferable to water measurements, because fish and other biota accumulate many pollutants over their lifetime both from the water and the food chain. Therefore, compared to water, biota measurements are often less variable, more relevant to the potential threat to flora or fauna or easier to measure because the concentrations are higher.

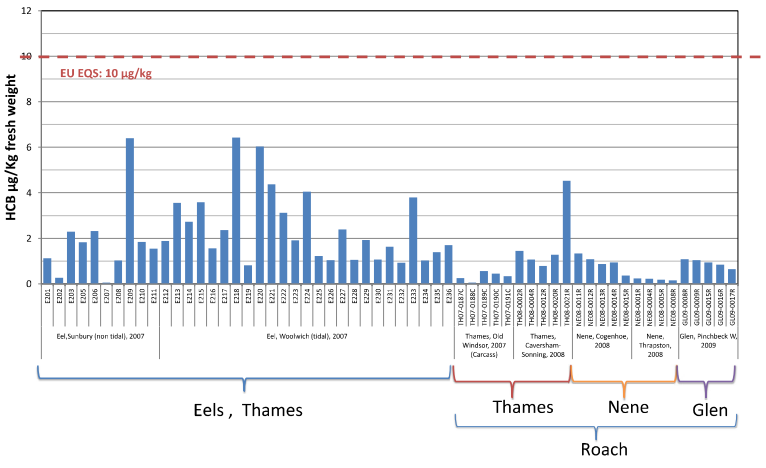
We analysed homogenized sub-samples of some of the fish from the UK Fish Tissue Archive for the three priority substances for which an EQS has been set.

Results

Mercury (Hg) is above the EQS of 20 µg/Kg fresh weight in around half the samples analysed. This includes some store bought trout fillets that were used for method development, though most samples were at least an order of magnitude lower than the limit for human consumption of 500 µg/Kg



Hexachlorobenzene (HCB), a fungicide which is no longer used in the EU, was well below the EQS of 10 µg/Kg fresh weight (max 6.4 µg/Kg), in all fish analysed so far.



Hexachlorobutadiene (HCBD) was in the past used as a solvent in the production of rubber and other polymers and also as a fungicide and seed dressing. Today the deliberate use has virtually ceased in Europe but it is still generated as a by-product of tetrachloroethylene and tetrachloromethane production.
In most of the analysed fish in this study HCBD was undetectable.

Conclusions

- The samples stored in the Fish Tissue Archive are well suited for monitoring of priority substances, especially those for which an EQS has already been set.
- Mercury levels are of some concern in many English rivers.
- As the Fish Archive grows it will become possible to determine temporal and spatial trends of these and other substances

[1] Centre for Ecology and Hydrology (CEH) Wallingford, OX10 8BB, UK
[2] CEH Lancaster, LA1 4AP, UK [3] Lancaster University, LA1 4YQ, UK

Environment Agency
LANCASTER UNIVERSITY
enquiries@ceh.ac.uk
www.ceh.ac.uk