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Emerging contaminants in groundwater

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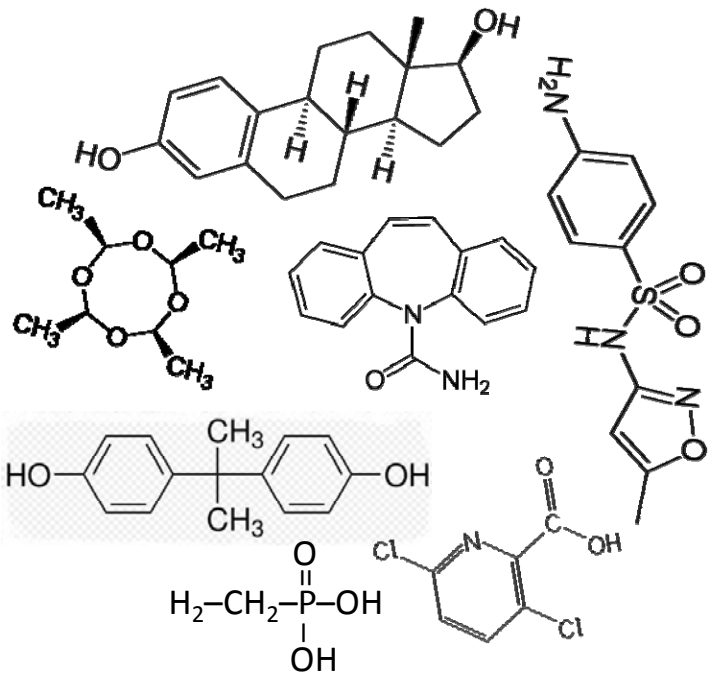

BRITISH GEOLOGICAL SURVEY

GROUNDWATER SCIENCE PROGRAMME

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Structures of selected polar organic micropollutants: bisphenol A, clopyralid, carbamazepine, estradiol, glyphosate metabolite AMPA, metaldehyde, sulfamethoxazole,

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Foreword

This report is the published product of a national capability study by the British Geological Survey (BGS) on emerging organic micropollutants. It was begun as a study of emerging pesticides in groundwater as part of project NEE 3344S, "Agrochemicals in aquifers". It has been extended to include other organic micropollutants under NEE 4059S, "Emerging pollutants".

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The authors are grateful to Fenella Brown of the Environment Agency for the provision monitoring data for organic micropollutants.

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Summary

The term ‘emerging contaminants’ is generally used to refer to compounds previously not considered or known to be significant to groundwater (in terms of distribution and/or concentration) which are now being more widely detected. As analytical techniques improve, previously undetected organic micropollutants are being observed in the aqueous environment. Many emerging contaminants remain unregulated, but the number of regulated contaminants will continue to grow slowly over the next several decades. There is a wide variety of sources and pathways for these compounds to enter the environment and these include agriculture and urban areas. Some of these contaminants can have human or ecological health effects and there is a need for better understanding of their fate in environmental systems.

This report provides a short review of the types of organic micropollutants which can be found in the aqueous environment. These include nanomaterials, pesticides, pharmaceuticals, industrial additives and by-products, personal care products and fragrances, water treatment by-products, flame/fire retardants and surfactants, as well as caffeine and nicotine metabolites and hormones. Many of the compounds are relatively small polar molecules which are not effectively removed by conventional drinking water treatment using activated carbon.

Pesticides and some industrial compounds are presently covered by the Water Framework Directive, the Groundwater Regulations and the Drinking Water Directive. Additional parameters, such as bisphenol A and nonyl-phenol are anticipated to be covered by revisions to the Drinking Water Directive. Others are currently unregulated.

In order to assess the hazards presented by such compounds, information on usage, persistence, leachability and a robust sensitive analytical method is required. The UK metaldehyde problem was not originally discovered due to lack of an analytical method and was exacerbated by recalcitrance in water treatment. For many pesticides these requirements are fulfilled and an assessment of risk of leaching to groundwater can be made. However, for pesticide metabolites this information can be sparse and for compounds such as pharmaceuticals it can be lacking.

A simple hazard assessment for currently approved pesticides was made from information on UK usage, persistence, sorption to soil carbon and published leaching indices. The following compounds were assessed as having the greatest potential for leaching to water: 2,4-D, amidosulfuron, bentazone, clopyralid, dicamba, florasulam, fosthiazate, imazaquin, iodosulfuron-methyl-sodium, maleic hydrazide, MCPA, MCPP-P, metribuzin, metsulfuron-methyl, quinmerac, oxamyl, and triclopyr with a further 46 also having potential. Of these, 19 had an octanol/water partition coefficient (K_{ow}) less than that of metaldehyde and therefore are likely to be incompletely removed by water treatment.

A simple assessment for pesticide metabolites, based only on organic carbon/water partition coefficient (K_{oc}) and persistence data, in this study gave results which agreed in principle with other studies. The different approaches indicate that the metabolites of chlorothalonil, cyanazine, diflufenican, flufenacet, iodosulfuron-methyl, metaldehyde, metazachlor and metsulfuron-methyl are likely to pose the greatest risk to drinking water. In many cases these metabolites are derived from parents which have a lesser risk.

Other organic micropollutants, such as pharmaceuticals, cannot as yet be assessed in the same way due to a lack of persistence data since the majority of persistence studies have been directed at water treatment. A range of organic micropollutants from urban settings have been detected in ground and surface water. Commonly detected compounds include: bisphenol A,

carbamazepine, galaxolide, ibuprofen, iopamidol, phthalates, phenyl ethoxylates, and sulfamethoxazole. Case studies show that a small number of contaminants may be used to characterise the contaminant loading and also be used to assess the migration pathways in urban areas.

Data interpreted by BGS from the Environment Agency's monitoring programme for organic pollutants indicates that the 30 most frequently detected compounds comprise both established and emerging compounds and include a number of polyaromatic hydrocarbons, petroleum compounds, triazine herbicides, chlorinated solvents, degradation products and THMs, caffeine, DEET and industrial compounds such as bisphenol A and tributyl phosphate. Specific determinands include a range of currently licensed and phased out pesticides with a few metabolites, pharmaceuticals including carbamazepine and triclosan, caffeine, nicotine and food additives and alkyl phosphates. These data exhibit hot spots which may indicate possible research areas.

Future research should focus on a compound identified in the literature and detected by Environment Agency monitoring. Possible topics could be a study of migration through the unsaturated zone. In many cases the mechanism for migration of emerging contaminants from the surface to groundwater is very unclear.

1 Introduction

Increasingly sensitive analytical techniques have detected the presence of previously unregulated organic micropollutants in actual or potential sources of drinking water worldwide. The term ‘emerging contaminants’ is generally used to refer to such compounds often previously not considered or known to be significant to groundwater (in terms of distribution and/or concentration) but which are now being more widely detected.

This report provides a review of organic micropollutants which can be found in the aqueous environment, which are or could have the potential to become emerging contaminants. A source-pathway-receptor approach has been used to evaluate the possible important compounds, their persistence and the routes by which they enter groundwater. Sources could include newly identified compounds from well-studied issues, such as pesticide metabolites. Other compounds such as agricultural feed additives have been little studied in groundwater but travel by well-studied pathways. A significant pathway factor related to emerging contaminants is the degree to which they are removed by current drinking water treatments. The main receptor factors considered here are the hazards to humans if these contaminants enter drinking water supplies.

As well as pesticides, types of organic micropollutants can include pharmaceuticals, personal care products, hormones and a wide range of industrial chemicals and intermediates. These types are discussed in Chapter 3. Some of these contaminants can have human or ecological health effects and there is a need for better understanding of their fate in environmental systems.

Pesticides and their metabolites are probably the most studied group of emerging contaminants. The mechanisms of pesticide transport to groundwater are discussed in Chapter 4. The properties of most pesticides and their metabolites currently licensed in the UK have been assessed to identify other potential problems. Our approach highlights those compounds most likely to persist in the aqueous environment, and those which may evade current water treatment practices.

Persistence of other pollutants, particularly pharmaceuticals, is less-well characterised and these are assessed using literature case studies to indicate the compounds which have been identified in groundwater and possible concentrations. These are grouped into those compounds which are derived primarily from urban and industrial sources (Chapter 5) and veterinary medicines (Chapter 6).

Published data for emerging contaminants in groundwater of the UK are sparse. We have processed and summarised a large set of analyses collected by the EA on organic micropollutants in groundwater from England and Wales. The results of this work are reported in Chapter 7.

The UK regulatory setting for organic micropollutants in aquifers and drinking water is summarised. It is likely that regulation will be extended over the coming decades to cover more of the emerging contaminants.

2 Overview of source-pathway-receptor concepts related to emerging contaminants

Significant risks to human health may result from exposure to non-pathogenic, toxic contaminants that are often ubiquitous in waters from which drinking water is derived. The transport of contaminants in the aqueous environment can be described by a source-pathway-receptor model, which considers:

- the source of the contaminant, e.g. sewage sludge spread on to agricultural land
- the pathway by which it travels from the source, e.g. fracture flow through an aquifer
- the receptor, e.g. a consumer drinking tap water

This chapter provides an overview to these concepts as they relate to emerging contaminants.

2.1 SOURCES

Sources of contaminants to surface waters, groundwater, sediments, and drinking water are varied and include pesticide applications to agricultural land, horticulture, parks, gardens, golf courses, urban infrastructure, and the transport network, discharges or leaks of domestic, hospital or industrial wastewater containing pharmaceutical or personal care compounds, sewage sludge application to land, pharmaceutical and pesticides used to treat animals and solid waste disposal.

Sources can be divided into two types: (1) point-source pollution and (2) non-point-source pollution. Point-source pollution originates from discrete sources whose inputs into aquatic systems can often be defined in a spatially explicit manner. Examples of point-source pollution include industrial effluents (pulp and paper mills, steel plants, food processing plants), municipal sewage treatment plants and combined sewage-storm-water overflows, resource extraction (mining), and land disposal sites (landfill sites, industrial impoundments).

Non-point-source pollution, in contrast, originates from poorly defined, diffuse sources that typically occur over broad geographical scales. Examples of non-point-source pollution include agricultural runoff (pesticides, pathogens, and fertilizers), storm-water and urban runoff, and atmospheric deposition (wet and dry deposition of persistent organic pollutants such as polychlorinated biphenyls "PCBs" and mercury) (Bedding et al., 1982; Ritter et al., 2002).

2.2 PATHWAYS

For many emerging contaminants the pathway from the source to the receptor is very unclear, since there is a paucity of information for most such novel contaminants. The pathway taken by a contaminant through the environment will depend upon its physicochemical properties, such as its solubility in water. An overview of the different types of emerging contaminant and their typical properties are given in Chapter 3.

Contaminants applied to the soil surface will migrate through the soil zone, the unsaturated zone and the saturated zone in the well-established way. This may be the route for agricultural pesticides and components of sewage sludge. Another important pathway is groundwater-surface water interaction. In many instances treated effluent from industrial premises and sewage works is discharged to surface water. This may then infiltrate to groundwater from losing reaches of rivers.

A feature of some emerging contaminants is their recalcitrance to sewage treatment or drinking water treatment which allows them to pass through into the treated water. Filtration using granulated activated carbon (GAC) has been used widely to remove organic micropollutants from drinking water. However, small and/or very polar molecules can be difficult to remove by this method. Stackelberg et al. (2007) showed that there was substantial but not complete degradation or removal of 113 organic micropollutants by conventional DWT. Gibs et al. (2007) showed that 50 out of 98 such contaminants did not substantially degrade in the presence of chlorine during typical residence times in drinking water distribution systems.

The octanol/water partition coefficient (K_{ow}) has been used to provide an analogue of removal recalcitrance, with polar compounds having a low or negative log (K_{ow}). Figure 2.1 shows the time taken for breakthrough of selected pesticides using GAC annotated with the K_{ow} value. A number of widely used compounds are poorly removed. Johnson et al. (2007b) demonstrate that removal of some oestrogens can be as low as 30%.

Other treatment options can be:

- use of powdered active carbon (PAC) which has a higher surface area
- ozonation
- nano-filtration. Verliefde et al. (2007) assess nano-filtration as a solution using a priority list of micropollutants

However it has been questioned whether advanced treatment to remove endocrine disrupting compounds and pharmaceuticals from wastewater is cost-effective due to the increased energy consumption and associated economic costs and CO_2 emissions (Jones et al., 2007; 2005).

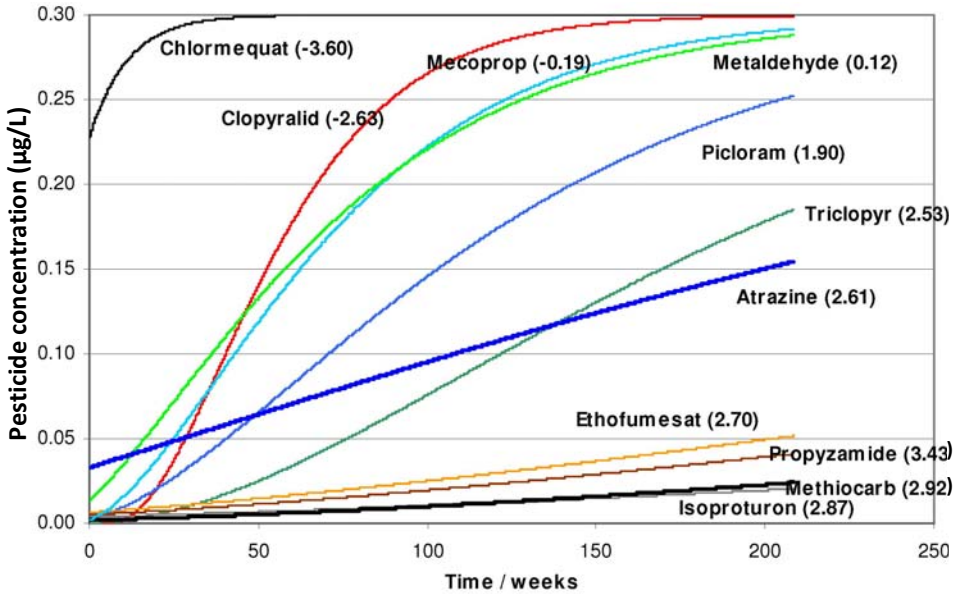

Figure 2.1 Concentration versus GAC performance annotated with log K_{ow} for selected pesticides (after Hall, 2010)

2.3 'RECEPTOR' CONCEPTS: HAZARDS

Receptors can be humans drinking tap water, other living creatures such as invertebrates and fish, or the environment more widely. Risks to the receptor depend upon the hazards related to the contaminant in question and the frequency and concentration of exposure to that substance. Here we give an overview of two hazards, toxicity and endocrine disruption,

which relate to living organisms. The hazards associated with specific types of contaminants are discussed in Chapter 3. In Box 1 we review toxicological approaches to prioritising emerging contaminants.

2.3.1 Toxicity

The harmful effects of chemicals can be evaluated in a number of ways. The acute toxicity of a chemical refers to its ability to do harm as a result of a single short exposure. This is likely to be relevant to accidents and spillages where the impact on health is rapid. Chronic toxicity refers to the ability of a chemical to do damage as a result of repeated or prolonged exposure, for example in an industrial environment or through food or drinking water.

The chronic effects of a substance can be classified into various types, such as: toxicity (ability to cause unspecified harm); carcinogenicity (ability to produce tumours); mutagenicity (ability to cause alteration of genetic material) and teratogenicity (effects on the foetus). Genotoxic carcinogens, which are considered to pose the greatest risk to humans, cause cancer by interfering with genetic information in the affected cells. Other potential effects are allergies and disruption of the immune and nervous systems. The toxic effects can be used to prioritise pollutant monitoring (Box 1).

2.3.2 Endocrine disruption

Substances which may not be directly toxic may have the ability to interfere with natural hormone actions and are known as endocrine disruptors. Endocrine substances which may be disrupted include:

- oestrogens – provide the stimulus for growth, development and function of the female reproductive tract. The principal oestrogen in vertebrates is 17β-oestrodiol
- androgens – produce masculine characteristics, the development of skeletal muscle and bone and the development of the male reproductive organs
- thyroid hormones – regulate almost all vital organs and functions, controlling development and metabolic activity
- neurohormones – released from the hypothalamus and maintain the functioning of the endocrine system

Oestrogenic endocrine disrupting substances include: alkylphenol polyethoxylates, (APEs) alkyl phenols, phthalates, and bisphenolic compounds. Pesticides may also have androgenic and hypothalmic activity.

Box 1 Toxicological approaches to prioritising emerging contaminants

In their editorial to the special issue of Water Research 'Emerging contaminants in water' Ternes and von Gunten (2010) state that to elucidate the relevance of micropollutants in aquatic systems their (eco)toxicological potential must be addressed.

Schriks et al. (2010) assessed a range of emerging contaminants detected in groundwater and surface water in the Rhine and Meuse basins. Only relatively polar compounds were considered (K_{ow}<3) as these were less likely to be removed in drinking water treatment. Data sources included water utility monitoring data from both Germany and the Netherlands and literature values. Provisional drinking water guideline values were attributed, either using existing values from USEPA or WHO (USEPA, 2006; WHO, 2010) or derived values based on toxicological data.

The highest observed concentrations were for EDTA and DTPA, (metal sequestors in textile and paper, descaler), p,p'-sulfonyldiphenol, and urotropine (resin precursors), 1,4-dioxane (solvent stabiliser) and AMPA (pesticide-glyphosate metabolite) whereas for groundwater the highest concentrations were for methyl tertiary-butyl ether, MTBE (fuel oxygenate).

The majority of compounds presented no appreciable risk using this approach. The compounds with the highest concentration to guideline ratio were 1,4-dioxane (solvent), carbamazepine (psychiatric drug) and perfluorooctane sulfonate, PFOS (fire fighting foam). The fuel oxygenates ethyl tertiary-butyl ether and MTBE were also high relative to an odour threshold.

Poynton and Vulpe (2009) applied an ecotoxicogenomics approach to assess the potential effects of a range of pharmaceuticals, endocrine disruptors, polybrominated flame retardants, perfluorinated compounds and nanomaterials. DNA-microarrays can be used to understand the effects of single compounds and mixtures, to suggest potential modes of action and predict exposure to pollutants in the environment.

Thomas et al. (2001) used the toxicological impact of a storm event in an agricultural catchment near Tunbridge Wells to determine that significant components not being measured were present, and used this to identify the surfactant nonylphenol as well as the pesticides diuron, simazine endosulphan sulphate and pendimethalin.

3 Types of organic micropollutants

The following types of organic micropollutants may be emerging contaminants. An overview of their sources, physical and chemical characteristics, mobility/behaviour in the aqueous environment and associated hazards is provided below. Some types have been more intensively studied than others, for example, much is known about pesticides, but other compounds, such as pharmaceuticals are much more poorly characterised. The hazards to human health of some compounds are well documented, but their ability to travel through the aqueous environment is only just being investigated, and persistence is unknown for many compounds.

3.1 NANOMATERIALS

Nanomaterials are materials with morphological features smaller than a one tenth of a micrometre in at least one dimension, or any material having a structure that has been designed at the nanoscale, or a sub micron particle sized material. Engineered nanoparticles are used in personal care products, ranging from cosmetics to sunscreen and also in hip replacement materials (Colvin, 2003). The facile movement and direct health impacts of the use of these substances is discussed by Colvin (2003). These particles may provide a vector for other pollutants to move through the water or soil. They may also be taken up by cells or organisms potentially leading to various types of toxic cell injury with higher level consequences for damage to animal health and ecological risk (Moore, 2006).

3.2 PESTICIDES

Pesticides have been detected at trace concentrations in UK groundwater for a considerable period. As those compounds which pose the greatest threat to the environment are gradually withdrawn, e.g. atrazine in 1993, the compounds which are substituted can in turn lead to problems e.g. diuron.

A number of compounds are currently causing concern. Metaldehyde is a selective pesticide used to control slugs. UK water companies have recently started monitoring for metaldehyde in drinking water supply catchments and in some sources have found levels close to and above the 0.1 microgram/Litre EU drinking water limit for pesticides (Bristol Water, 30/1/2009; Environment Agency, Jan 2010; Water UK, 2009). Attention has now also turned to pesticide metabolites, also termed degradates and reaction products (Kolpin et al., 1998).

By their nature these compounds are biologically active and many may be toxic. Such data forms part of the pesticide registration process.

Greater detail on pesticides and pesticide metabolites as emerging contaminants is provided in Chapter 4.

3.3 PHARMACEUTICALS

The primary route for pharmaceuticals into the environment is through human excretion, disposal of unused products or through agricultural usage (Poynton and Vulpe, 2009). A wide range of pharmaceutical products have been detected in surface water and groundwater, associated with wastewater disposal (Barnes et al., 2008; Miller and Meek, 2006; Nikolaou et al., 2007; Ternes and Hirsch, 2000; Watkinson et al., 2009). These have included:

- veterinary and human antibiotics: e.g. ciprofloxacin, erythromycin, sulfamethoxazole, tetracycline

- other prescription drugs: codeine, salbutamol, carbamazepine
- non prescription drugs: acetaminophen (paracetamol), ibuprofen
- iodinated X-ray contrast media: iopromide, iopamidol

Other potential threats to surface water which have been identified are tamiflu and chemotherapy drugs, such as 5-fluorourcil or cyclophosphamide (Buerge et al., 2006; Johnson et al., 2008a; Moldovan, 2006; Singer et al., 2007)and illicit drugs: such as cocaine and amphetamines (Kasprzyk-Hordern et al., 2008; Zuccato et al., 2008).

By their nature these compounds are biologically active. Toxicity and other hazard data forms part of the registration process.

3.4 "LIFE-STYLE COMPOUNDS"

These include caffeine and nicotine. The primary route into the environment is through wastewater discharge. Caffeine's effect on the environment is not well understood, but does not appear to give cause for concern to freshwater organisms at currently detected concentrations (Moore et al., 2008). Extracts of tobacco have long been used against sucking insects and the toxicology of nicotine is well established (Feurt et al., 1958). Technical nicotine is still listed as an insecticide and neonicotinoid pesticides, such as imidacloprid, are widely used. Nicotine has a high toxicity to humans, compared to other alkaloids. Caffeine and nicotine, and the nicotine metabolite cotinine, are widely detected in groundwater impacted by sewage effluent (Godfrey et al., 2007; Seiler et al., 1999).

Van Stempvoort et al. (2011) found high concentrations of the artificial sweeteners acesulfame, saccharine, cyclamate and sucralose in groundwater impacted by sewage infiltration ponds.

3.5 PERSONAL CARE

Personal care compounds are commonly transmitted to the aqueous environment through wastewater treatment plants. These have included:

- DEET – N,N-diethyl-meta-toluamide, the most common active ingredient in insect repellents
- parabens – alkyl esters of p-hydroxybenzoic acid, used since the 1930s as bacteriostatic and fungistatic agents in drugs, cosmetics, and foods
- triclosan – bacteriocide and antifungal agent widely used in household products, such as toothpaste and soap
- polycyclic musks – tonalide and galaxolide are used as fragrances in a wide range of washing and cleaning agents and personal care products
- UV filters/sunscreen – organic filters include the benzophenones and methoxycinnamates

All of these compounds have toxic or oestrogenic effects. DEET has been found to inhibit the activity of a central nervous system enzyme, acetylcholinesterase, in both insects and mammals (Corbel et al., 2009). The parabens exert a weak oestrogenic activity (Oishi, 2002; Soni et al., 2002) and are capable of producing immunologically mediated, immediate systemic hypersensitivity reactions (Nagel et al., 1977). Some data on their environmental toxicity is now available (Bazin et al., 2010). Lindström et al. (2002) detected triclosan and its metabolite methyl triclosan in surface water in Switzerland and considered the metabolite to be persistent. It is degraded to dioxins and is toxic to aquatic bacteria at levels found in the environment (Ricart et al., 2010). Tonalide (AHTN), galaxolide (HHCB) and HHCB-lactone

have been detected in WWT effluents (Horii et al., 2007). These compounds have been used as markers for wastewater in surface water (Buerge et al., 2003; Fromme et al., 2001). Work on toxicity for these compounds has mainly assumed a dermal exposure pathway (Ford et al., 2000). They are degraded to more polar metabolites during treatment and in sediments and the soil. The majority of compounds used as sun screens are lipophilic, conjugated aromatic compounds, but are detected in the aqueous environment (Jeon et al., 2006).

3.6 INDUSTRIAL ADDITIVES AND BY-PRODUCTS

There are a wide range of industrial compounds which can be released to the environment. Many of these have led to well-established problems, such as the chlorinated solvents tetrachloroethene (PCE), trichloroethene (TCE) and 1,1,1-trichloroethane (1,1,1-TCA), petroleum hydrocarbons, including the polyaromatic hydrocarbons (PAH) and the fuel oxygenate methyl tertiary-butyl ether (MTBE) (Moran et al., 2005, 2006). The use of MTBE increased dramatically in the 1990s as an octane enhancer in lead-free petrol. It has very high water solubility and presents a serious groundwater threat near defective underground storage facilities (Garrett et al., 1986; Verliefde et al., 2007). Most of these industrial compounds now have drinking water limits.

However, some breakdown products may be regarded as emerging contaminants. The degradation pathway of PCE and TCE to cis 1,2-dichloroethene (cis 1,2 DCE) and vinyl chloride is well-known and has been the subject of much research (Vogel and McCarty, 1985). 1,4-dioxane a breakdown product of 1,1,1,-TCA, is highly soluble in groundwater, does not readily bind to soils, and readily leaches to groundwater (Abe, 1999). It is also resistant to naturally occurring biodegradation processes. Due to these properties, a 1,4-dioxane plume is often much larger (and further downgradient) than the associated solvent plume. In 2008, testing, sponsored by an independent consumers organization, found 1,4-dioxane in almost half of tested personal-care products. 1,4-dioxane is a carcinogen, affecting the liver, and possibly the nasal cavity and may be a weak genotoxin (Stickney et al., 2003).

Bisphenol A and F are used as a monomer for the production of polycarbonate and epoxy resins, polyester styrene resins and flame retardants (Fromme et al., 2002). The products are used in can coatings, powder paints, thermal paper, and dental fillings and as an antioxidant in plastics. They can be leached into the environment during the manufacturing process and by leaching from final products. The potential for human exposure is mainly via cans and polycarbonate bottles rather than the direct aqueous route. The health impacts are well established (Staples et al., 1998).

The polymer plasticiser n-butylbenzenesulfonamide (NBBS) has been detected in environmental samples including estuaries (Oros et al., 2003), runoff from agricultural fields (Pedersen et al., 2005), and effluent from waste water treatment plants(Gross et al., 2004). Additionally, most water treatment processes did not effectively remove NBBS (Soliman et al., 2007) and NBBS was not found to be readily biodegradable (Proviron Fine Chemicals, 2003). Reproductive and neural toxicity has been demonstrated (Nerurkar et al., 1993; Strong et al., 1991).

Phthalates have been in use for more than 40 years in the manufacture of PVC and in other resins for building materials, home furnishings, food packaging and insect repellents. They can be leached into the environment during the manufacturing process and by leaching from final products since they are not bonded to the polymeric matrix. Volatilisation to the atmosphere is an important mechanism for redistribution and phthalates mainly enter water by wet deposition. The health threats have been long recognised (Autian, 1973).

Benzotriazole is a complexing agent and as such is a useful a corrosion inhibitor, e.g. for silver protection in dishwashing detergents and an anti-fog agent in photographic development. Aircraft de-icer and anti-icer fluid contain benzotriazole. Benzotriazole derivatives are found in pharmaceuticals such as antifungal, antibacterial, and antihelmintic drugs. Benzotriazoles are persistent in the aqueous environment (Giger et al., 2006; Voutsa et al., 2006).

Dioxin is the term used to describe a family of toxic chlorinated organic compounds that can travel long distances and bioaccumulate in humans and wildlife due to their fat solubility. The most notorious of those is 2,3,7,8-tetrachlorodibenzo-p-dioxin, often abbreviated as TCDD. Dioxins are produced when organic material is burned in the presence of chlorine, whether the chlorine is present as chloride ions, or as organochlorine compounds, so they are widely produced in many contexts such as municipal and clinical waste incinerators and from metal industries. In the environment, these compounds can be produced as a consequence of degradation of other micropollutants e.g. from the antimicrobial additive triclosan (ENDS, 2010b; Mezcua et al., 2004).

Polycyclic musks in the aqueous environment are derived from wastewater treatment plants. These are used as fragrances in a wide range of washing and cleaning agents and personal care products. Tonalide (AHTN), galaxolide (HHCB) and HHCB-lactone have been detected in WWT effluents (Horii et al., 2007). These compounds have been used as markers for wastewater in surface water (Buerge et al., 2003; Fromme et al., 2001). Work on toxicity for these compounds has mainly assumed a dermal exposure pathway (Ford et al., 2000).

3.7 FOOD ADDITIVES

Triethyl citrate is used as a food additive to stabilise foams, e.g. egg white, and is also used in pharmaceutical coatings and as a plasticiser. Butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) are used to prevent fat spoilage in foods. Other food additives include camphor, 1,8-cineole (eucalyptol), citral, citronellal, cis-3-hexenol, heliotropin, hexanoic acid, menthol, phenylethyl alcohol, triacetin, and terpineol. Some of these may be implicated as oxidants or endocrine disruptors.

3.8 WATER TREATMENT BY-PRODUCTS

Chlorine reacts with natural organic compounds in the water to form potentially harmful chemical by-products such as trihalomethanes (THMs) and haloacetic acids (HAAs) (Boorman, 1999). Studies have linked these by-products with colon, rectal, bladder and breast cancer (Cantor et al., 1998; Cantor et al., 1999; Hildesheim et al., 1998), an increased frequency of stillbirths ((King et al., 2000; King et al., 2005) and birth defects of the brain and spinal cord (Klotz and Pyrch, 1999).

N-Nitrosodimethylamine (NDMA) is a member of a family of extremely potent carcinogens, the N-nitrosamines. Until recently, concerns about NDMA mainly focused on the presence of NDMA in food, consumer products, and polluted air. However, concern has also been focused on NDMA as a drinking water contaminant resulting from reactions occurring during chlorination or via direct industrial contamination. Because of the relatively high concentrations of NDMA formed during wastewater chlorination, the intentional and unintentional reuse of municipal wastewater is a particularly important area of concern (Mitch et al., 2003).

Acrylamide is used as a coagulant in drinking water treatment. Epichlorohydrin is generally used to make glycerine and as an ingredient in plastics and other polymers, some of which are

used as flocculating resins or pipe coatings in water supply systems. Both of these compounds affect the central nervous system and are carcinogenic (Smith and Oehme, 1991).

Richardson (2003) found that the change from disinfection with chlorine to ozone and chloramines can increase levels of other potentially toxic by-products, e.g. bromo- and iodo-THMs and brominated MX (3-chloro-4-dichloromethyl)-5-hydroxy-2(5H)-furanone).

3.9 FLAME/FIRE RETARDANTS

Flame retardants are used in plastics, textiles and furnishing foam to reduce their fire hazard by interfering with polymer combustion. Halogenated compounds act by interfering with gas phase reaction by removal of OH and H radicals by halogen. Brominated compounds tend to decompose at considerably lower temperatures than the host polymer and are therefore effective. Polybrominated diphenyl ether (PBDE) flame retardants have been found to bioaccumulate and have potential endocrine disrupting properties (Meerts et al., 2001; Rahman et al., 2001).

Phosphate-based retardants appear to work by forming an non-flammable barrier (Weil et al., 1996).One example is tris-(2-chloroethyl) phosphate (TRCP) which is used in industrial and consumer products and has been linked to brain damage (Matthews et al., 1993).

3.10 SURFACTANTS

Perfluorinated sulfonates and carboxylic acids including perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) have been used for over 50 years in food packaging and cookware coatings, in paints and in surfactants. They are found in sewage treatment works (STW) effluents and surface water and are very persistent in the environment (Ahrens et al., 2009; Poynton and Vulpe, 2009). There is relatively little information on toxicity (Hekster et al., 2003). As a surfactant, PFOS is used in a variety of applications that include lubricants, paints, cosmetics and fire-fighting foams. It has been detected in surface water (Harada et al., 2003; Saito et al., 2003) in Japan.

Octyl- and nonyl-phenol (OP and NP) are used in the production of alkyl phenol ethoxylates (APEs) which are used in the manufacture of surfactants. Their branched chain structure makes them resistant to biodegradation and both the parent ethoxylates and their metabolites, alkyl phenols and carboxylic degradation products, persist in the aquatic environment (Montgomery-Brown and Reinhard, 2003; Soares et al., 2008). These compounds have been long established as endocrine disruptors in fish (Petrovic et al., 2004; White et al., 1994).

The APEs can also be used as pesticide adjuvants. These can therefore be found in groundwater at significant concentrations as a result of agricultural activity (Lacorte et al., 2002; Latorre et al., 2003).

3.11 HORMONES AND STEROLS

This group includes sex hormones, phytoestrogens, and faecal indicator and plant sterols. Sex hormones include androgens, such as androstenedione and testosterone, and oestrogens (also spelled estrogens), such as oestrone, oestriol, 17 β-oestrodiol, 17 α-oestrodiol and progesterone. There are also synthetic androgens such as oxandrolone, nandrolone and more importantly synthetic oestrogens (xenoestrogens) such as 17 α-ethinyl oestrodiol and diethylstilbestrol, used as contraceptives. Some of these compounds are commonly present in wastewater and sewage treatment effluent (Johnson et al., 2000; Standley et al., 2008). Many of these compounds are regarded as endocrine disruptors.

A related group of compounds are cholesterol and its metabolite 5β-coprostanol, and the plant sterols stigmastanol, stigmasterol and β-sitosterol.

3.12 IONIC LIQUIDS

Ionic liquids are salts with low melting point which are being considered as replacements for industrial volatile compounds (Thuy Pham et al., 2010). These compounds include nitrocyclic rings (e.g. pyridinium, pyrrolidinium, morpholinium moieties) and quaternary ammonium salts. These compounds have significant water solubility.

4 Pesticides and pesticide metabolites in depth

4.1 PESTICIDE SOURCE TERMS

Pesticides are used for controlling or destroying pests. They can be synthetic chemical or natural substances. Pesticides vary in their use, properties and potential impact on the environment.

There are currently around 350 ingredients approved for use in agricultural pesticide products in the UK. Pesticides are used to control weeds, pests and diseases in crops (including grassland). Agriculture and horticulture use nearly 80 per cent of all plant protection pesticides in England and Wales. Over recent years there has been some reduction in the quantity of pesticides used in agriculture and the area that they are applied over. It is normal practice for several different pesticides to be applied to a single crop in any given growing season. There has been a trend towards more frequent treatments using complex tank mixes but using less persistent compounds and at an overall lower rate of application.

Pesticides are also used to control weeds and pests in gardens and weeds on pavements and along railway lines. The textile industry uses pesticides to stop insects attacking carpets or clothing, and timber is treated with pesticides to help it last longer.

Once released to the environment, pesticides may be degraded by abiotic and biotic processes. While parent compounds are assessed in detail in many regulatory schemes, the requirements for the assessment of transformation products are less well developed. The potential issue of pesticide metabolites was first highlighted by Kolpin et al. (2004) who found atrazine and metalochlor metabolite concentrations present in groundwaters at concentrations higher than the parent compounds. Pesticide metabolites can be more toxic than the parent compound and an initial assessment suggested that as many as 30% may be more toxic (Sinclair and Boxall, 2003). Their small molecular size and polar nature can make them difficult to determine.

In a catchment in France, Baran et al. (2010) studied the distribution of atrazine and metalochlor and their metabolites. Atrazine has been banned in France since 1993 and metalochlor restricted to the active S isomer. Metabolites for both compounds were detected at higher concentrations than the parents.

Pesticide usage data for the UK up to and including 2008 is available on the FERA website (FERA, 2010). Compounds currently licensed for use in the UK were confirmed using the 2010 Pesticide Guide (BCPC and CABI, 2010). The most widely applied compounds are shown in Figure 4.1.

4.2 PREDICTING RISK FROM PESTICIDES AND METABOLITES

4.2.1 Pathways

In order for pesticides to impact on receptors, there must be a pathway. If sufficiently mobile and persistent, pesticides can leach from the soil zone to groundwater through the unsaturated zone (Figure 4.2). They can then be present in abstracted water. If this is successfully treated before distribution then there is no pathway to the consumer. However, if water is not treated for pesticides, or treatment is not effective, then a pathway to the consumer may exist. Pesticides in wastewater could then pass into the environment and potentially into surface water and groundwater.

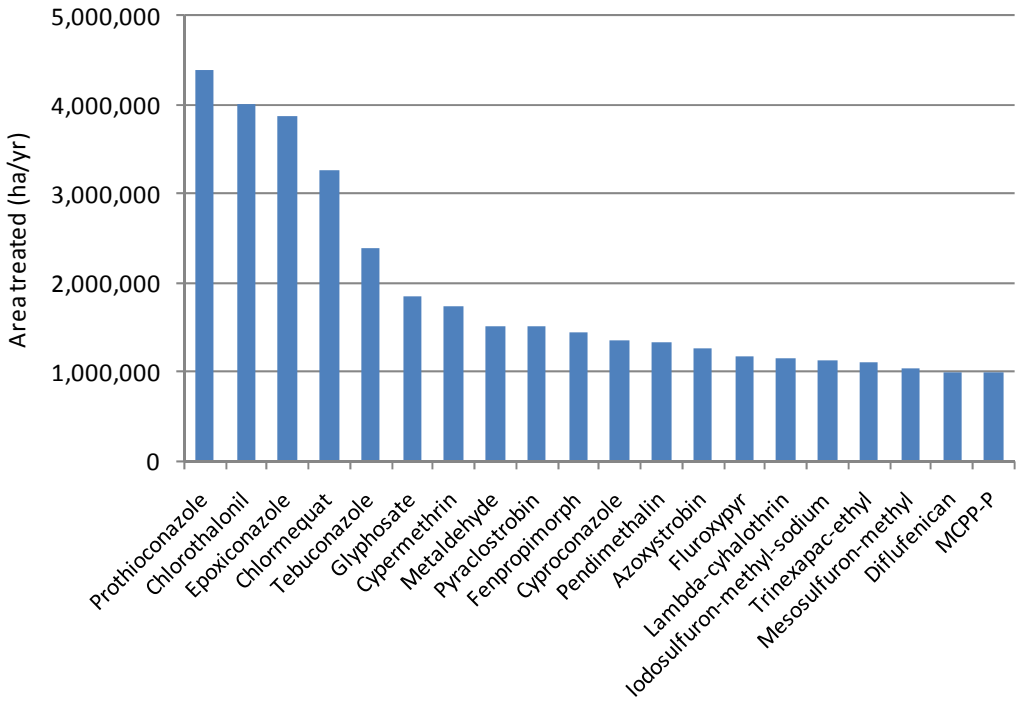

Figure 4.1 Top 20 most widely applied pesticides in the UK in 2008 (from FERA, 2010)

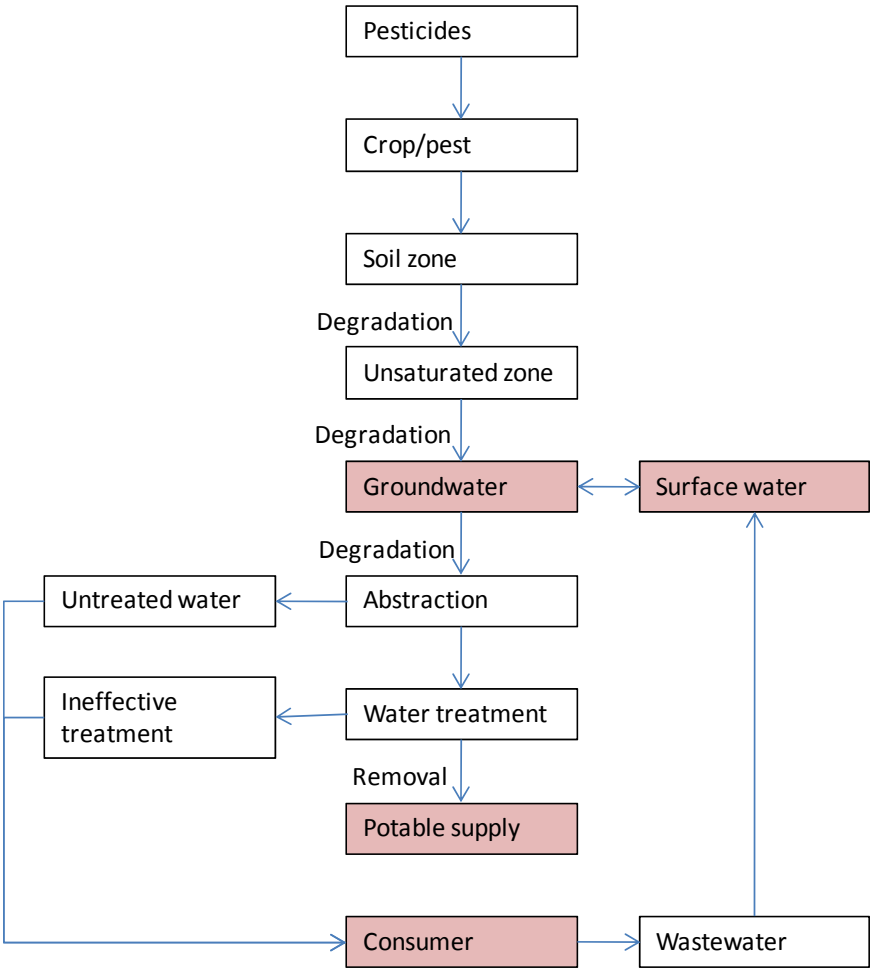

Figure 4.2 Pathways for pesticides to reach various receptors (shown in pink)

Table 4.1 Processes controlling pesticide mobility and persistence

Mechanism	Details	Property
Method of application	Vegetation or surface applied	-
Leaching from the soil zone	Sorption	Solubility and K_{ow} /K_{oc}
Degradation in groundwater	Microbiological processes	Soil, water and sediment half lives (DT_{50})
Water treatment	Removal by GAC	Solubility and K_{ow}

The processes controlling pesticide behaviour in soils and the subsurface are reasonably well understood (Table 4.1) and estimates of pesticide physical properties and soil and water persistence are available (see following sections).

The following factors may be important in hazard assessment for pesticides:

- widespread usage
- persistence in soil and/or water
- high leachability indicated by high solubility or low sorption to organic material

The recent interest in metaldehyde (Box 2) highlights the difficulties of understanding hazards posed by pesticides; the lack of a suitable analytical method allowed metaldehyde in drinking water to go undetected. Recalcitrance to water treatment may also be important. Other future problems may arise with pesticide metabolites.

4.2.2 Physicochemical properties

PERSISTENCE

DT50 is the time required for the pesticide concentration under defined conditions to decline to 50% of the amount at application. In many cases pesticides show "half-life" behaviour, in which concentrations decline exponentially; subsequent concentrations continue to decline by 50% in the same amount of time. A number of different estimates of persistence are available from the Footprint website (AERU, 2010). In this assessment the "Aqueous hydrolysis DT50 (days) at 20^{o}C and pH 7" and the "Water-sediment & water phase only DT50" were used. Data is given for the system as a whole and for the water phase only.

As well as the persistence of the parent, these calculations can tell us about the formation rate of degradates/breakdown products.

LEACHABILITY

Physical properties and leachability data are readily available from the Footprint website (AERU, 2010). Solubility and the partition coefficient between octanol and water (K_{ow}) can both give an indication of a compound's mobility and likely sorption in water treatment. K_{ow} is commonly expressed as log P, the logarithm (base-10) of the partition coefficient. It is used in environmental fate studies and large values (+4 or higher) are regarded as an indicator that a substance may tend to bioaccumulate. Conversely, low values indicate environmental mobility. Estimates of leachability include the Groundwater Ubiquity Score (GUS) and SCI-GROW Index. Both of these methods use a combination of the half-life in soil (DT_{50}) and partition coefficient between soil organic carbon and water (K_{oc}) (Gustafson, 1989; USEPA, 2007).Worrall et al. (2000) also proposed using a probability for predicting groundwater contamination risk also using soil K_{oc} and DT_{50}.

Box 2 Metaldehyde

Metaldehyde is the active ingredient in most slug pellets. It acts by causing molluscs to secret excessive slime and destroying their mucus cells. Death is due to desiccation. The pellet formulation is designed to deliver a large dose to the target. It was first introduced in 1940 has been widely used in all sectors (agriculture, horticulture, recreational land and gardens) since the 1970s. The most recent estimates of usage in the UK suggest that 278,819 kg were applied to 758,125 ha in 2006 (FERA, 2010).

Until 2007 there was not a satisfactory method for determining metaldehyde in treated water. The development of a new methodology by Bristol Water was able to demonstrate that metaldehyde was detectable in processed water. It has subsequently been shown to be widely disseminated and detected in groundwater and surface water. This would have been difficult to predict using leaching and persistence criteria.

Metaldehyde is a relatively simple compound correctly referred to as *r*-2,*c*-4,*c*-6,*c*-8-tetramethyl-1,3,5,7-tetroxocane or 2,4,6,8-tetramethyl-1,3,5,7-tetraoxacyclo-octane, more loosely as acetaldehyde tetramer (Figure 4.3).

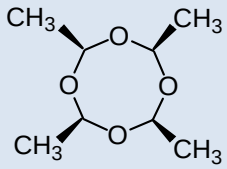

Figure 4.3 Metaldehyde structure

Metaldehyde is moderately soluble in water (188 mg/L) and has a low K_{ow}; the most recent estimates put this as 0.12. It has a moderate GUS leachability index and the SCI-Grow index is 0.00354 (AERU, 2010). It is not very toxic to non-target organisms; it is not a skin irritant or skin sensitiser and it appears to be non-mutagenic and non-teratogenic (BCPC, 2003).

The key to the problem is that metaldehyde is poorly removed by drinking water treatment methods, such as sorption by granulated activated carbon (GAC), apparently due to its relatively low K_{ow} (Hall, 2010).

Best practice methods for its use are being promoted to minimise possible migration to water courses by the Metaldehyde Stewardship Group (Get Pelletwise), the Environment Agency and a variety of other groups, such as Natural England, Farming Wildlife Advisory Group and the Voluntary Initiative.

During 2009 pesticide failures accounted for one third (387) of the total of 1,103 failures of drinking water standards, predominantly due to metaldehyde in central eastern and southern regions of England (DWI, 2010; ENDS, 2010a). However, water utilities reported that concentrations in raw water were falling during 2009 and additionally slug pellet sales were lower.

ANALYTICAL METHOD

In order to achieve drinking water objectives, concentrations of 0.1 µg/L must be measured with confidence, probably requiring a detection limit of 0.01 µg/L. Good limits of detection have been achieved for many compounds over the last two decades; methods have appeared

relatively recently for more difficult compounds such as glyphosate (Börjesson and Torstensson, 2000; Chang and Liao, 2002; Hidalgo et al., 2004).

There is also the issue of metabolites, which may have different properties from the parent compound, and for which analytical improvements have not been driven by legislative requirements.

MOLECULAR TOPOLOGY

A molecular topology is an area in chemistry that involves different mechanically-interlocked molecular architectures. The molecular topology approach to evaluating pesticide leaching was proposed by Worrall (2001). His model based on molecular descriptors showed leaching was related to the branching of molecules and worked well for linear and cyclic molecules, although not for nitro groups.

This approach was extended by Worrall and Thomsen (2004) where two groups of factors were used:

- quantum chemical descriptors calculated molecular geometry – 18 factors including dipole moment (μ), enthalpy of formation (ΔH_f), hydration energy (ΔH_{hyd}), octanol/water partition coefficient (K_{ow}), molecular refractivity (molref), polarisability (π), surface accessible volume (V_{sav}), solvent accessible volume (A_{sas}) van der Waals volume and surface area, various molecular orbital energies
- empirical descriptors – molecular descriptivity e.g. connectivity

The non-empirical descriptors $\Delta H_{hyd,}$ π, and μ and the volume and surface area descriptors are expected to reflect the affinity for leaching. For hydrophobic molecules ΔH_{hyd} (V_{sav}), solvent accessible volumes (A_{sas}) are normally inversely related to the aqueous solubility and π, and μ are normally proportional to it. For each compound in the study 31 connectivity parameters were calculated related to valence and vertices.

4.3 A SIMPLE HAZARD ASSESSMENT FOR PESTICIDES

A simple first pass hazard assessment was made for this study using pesticide physical properties, persistence and UK usage. The assessment was restricted to arable, horticultural, garden and amenity pesticides; microbial, seed dressing, fumigants and rodent control pesticides were excluded from the assessment.

4.3.1 Using pesticide properties

A series of simple tests were made using physicochemical properties, as shown in Table 4.2, in order to identify very soluble, poorly sorbed and persistent compounds.

Table 4.2 Leaching hazard tests using pesticide properties

Test	Criterion	No. of compounds
1	Solubility > 5000 µg/L	33
2	Log K_{oc} < 2	49
3	DT_{50} (aqueous) = stable and/or DT_{50} (water/sediment) > 100 days	127
4	Point shown in red on plot in Fig 5.3	91
5	GUS score >2 and/or SCI-Grow score >0.1	77

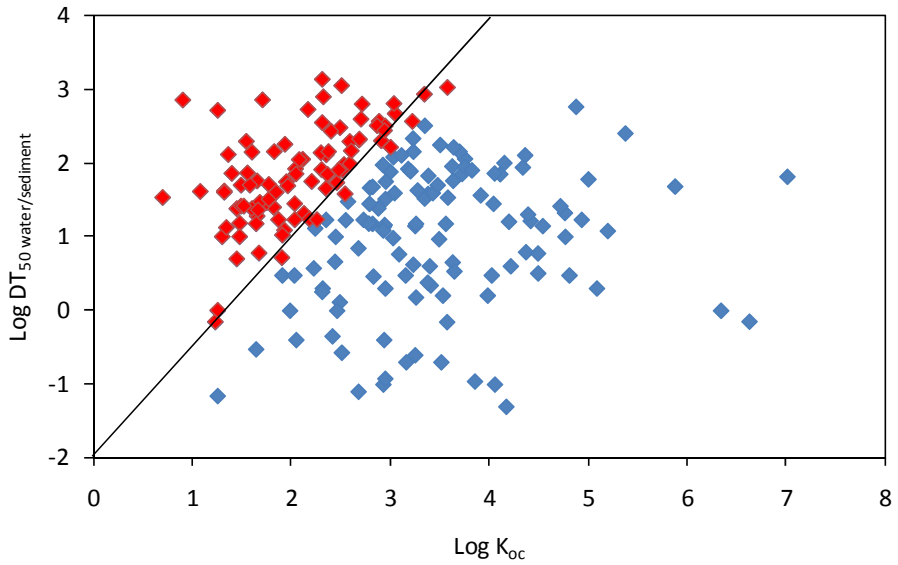

Figure 4.4 Classification of leaching probability of all compounds using K_{oc} and DT_{50} (after Worrall et al, 2000). Compounds in red assessed as leachers

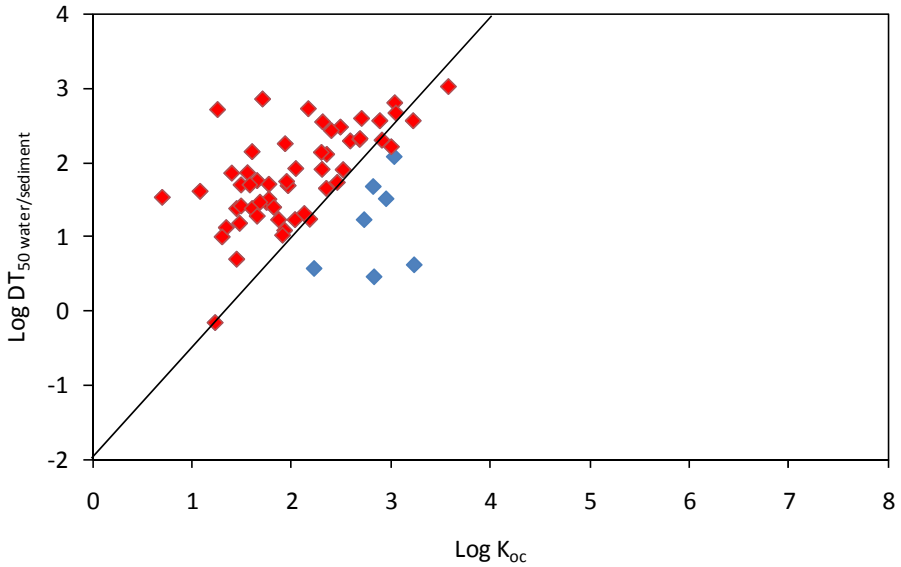

Figure 4.5 Classification of leaching probability of final list compounds using K_{oc} and DT_{50} (after Worrall et al, 2000)

A classification similar to that proposed by Worrall et al. (2000) was applied, as shown in Figure 4.4, where points along a diagonal line have a similar estimated leaching probability. The line shown is a cut-off between leachers and non-leachers. This was used as Test 4 (see Table 4.2). Values close to the line have been assessed as leachers. Compounds were assessed as non-leachers where Log K_{oc} > 4, Log DT_{50} <0.5 or where one of these values was missing.

4.3.2 Taking pesticide usage into account

The assessment was then restricted to widely used compounds by applying a usage criterion for 2008 of "Area applied >100,000 ha and/or Weight applied >20,000 kg". This left the 65 compounds shown in Figure 4.5 and listed in Table 4.3. Compounds meeting all five criteria assessed as having the highest leaching hazard.

Table 4.3 Results of leaching hazard tests using the criteria shown in Table 4.2. Compounds denoted with * are shown on the database as having a high affinity to particles. Compounds denoted in bold have K_{ow} less than or equal to that of metaldehyde (0.12).

Leaching hazard Highest → Lowest			
Score 5	**Score 4**	**Score 3**	**Score 2**
2,4-D	**Amidosulfuron**	Azoxystrobin	Carbendazim
Clopyralid	**Bentazone**	Boscalid	**Chlormequat Cl**
Dicamba	Fosthiazate	Carbetamide	Cycloxydim
Florasulam	**Maleic hydrazide**	Chloridazon	Difenoconazole*
Imazaquin	**MCPP-P**	Chloropicrin	**Diquat***
Iodosulfuron-me-Na	Metribuzin	Chlorotoluron	Epoxiconazole*
MCPA	**Metsulfuron-methyl**	Clomazone	Flusilazole*
Quinmerac	**Oxamyl**	Clothiandin	**Fosetyl-aluminium**
	Picloram	Cyproconazole	**Glyphosate**
	Triclopyr	Dimoxystrobin	MCPB
		Ethofumesate	**Mepiquat chloride**
		Ethoprophos	Metalaxyl-M
		Flufenacet	Metazachlor
		Fluopicolide	Metconazole*
		Fluoxastrobin*	Tebuconazole
		Flupyrsulfuron-methyl	**Thifensulfuron-methyl**
		Fluroxypyr	Triazoxide
		Flurtamone	Triflusulfuron-me
		Imidacloprid	
		Mesosulfuron-methyl	
		Metaldehyde	
		Metamitron	
		Pirimicarb	
		Propamocarb HCl	
		Propiconazole*	
		Silthiofam	
		Tepraloxydim	
		Tribenuron-methyl	
		Triticonazole	

Of these 65 compounds, only 6 have been introduced from 2000 onwards and for 2 the date is not recorded. There are 3 other compounds with a high leaching hazard for which there are no usage data up to 2008 (Table 4.4). Aminopyralid usage was suspended for a period in UK due to possible persistence in manure and subsequent impact on crops (HSE, 2009).

For compounds which have non-agricultural applications, such as application to urban hard standing areas, there will be routes to groundwater which would not be identified by this simple assessment.

Table 4.4 Compounds with a possible risk but no usage data up to 2006

Compound	Year	Leaching hazard score
Pyrosulam	2007	4
Aminopyralid	2005	4
Flazasulphuron	1989	3

4.3.3 Corroborating evidence for assessment

Worrall et al. (2000) used a list of 43 pesticides which had been reported in UK groundwater up to 1993 to assess which were likely to be leachers. Of these, 12 appear in Table 4.3: bentazone, chlorpyrifos, clopyralid, dicamba, ethofumasate, linuron, oxamyl, pendimethalin, phenmedipham, propyzamide, triallate and triclopyr. Many other compounds in this survey are no longer used in the UK, e.g. atrazine.

Gooddy et al. (2005) detected 23 pesticides in groundwater in south Yorkshire. Of these, 11 compounds appear in Table 4.3 and 9 compounds are no longer licensed. Three of the remainder were assessed as leachers by this method, but excluded due to insufficient national usage. Methiocarb was assessed as a non-leacher.

4.4 PESTICIDE METABOLITES

A separate assessment of pesticide metabolites needs to be made, as the physicochemical properties, persistence and toxicity of these compounds may be very different from those of their parent compounds. They may also be present at concentrations similar to or even exceeding the parent compound (Box 3).

4.4.1 Existing UK assessments

Sinclair et al. (2010) reported measured concentrations in groundwater of the UK from the Environment Agency and water companies for a range of compounds. The metabolites detected were all from compounds no longer licensed in the UK (DDT and heptachlor) and included op-DDE, pp-DDE, deethylatrazine, deisopropylatrazine, cis-heptachlor epoxide, trans-heptachlor epoxide, op-TDE and pp-TDE.

Sinclair et al. (2010) then selected 53 pesticide metabolites from a total of 485 from UK pesticides with available information for a desk study of metabolite impact on UK drinking water based on their potential to contaminate water (Table A1.1, Appendix 1). This assessment incorporated parent compound usage, formation rates in soil, persistence and mobility and estimated toxicity and/or potential to exhibit pesticidal activity. The study included compounds currently licensed and those which have recently lost approval, e.g. aldicarb, atrazine and isoproturon. About half of the compounds had been identified during environmental degradation as well as in mammalian toxicity testing of the parent. The study included the estimated efficiency of removal during drinking water treatment as well as during environmental degradation. The maximum predicted concentration in finished water was for metazachlor sulfonic acid which is not considered to have pesticidal properties.

For five of the metabolites significant concentrations in drinking water were predicted by their model. These were aldicarb sulphone (aldicarb metabolite), 3-carbamyl-1,2,4,5-tetrachlorobenzoic acid (chlorothalonil metabolite), cyanazine chloroacid (cyanazine metabolite), desisopropyl atrazine and methomyl (thiodicarb metabolite and also parent compound).

Box 3 Diuron metabolites

Diuron is a systemic herbicide, absorbed principally by the roots, with translocation in the xylem. It was used for total control of weeds and mosses on non-crop area and selective control of germinating grass and broad-leaved weeds in many crops, including fruit and perennial grass-seed crop. It was also used for long-term pre-emergence weed control in non-crop areas such as railway lines. Usage in the UK has declined from the mid 90s (in 1996 23122 kg were applied to 11569 ha declining ro to 5378 kg on 8024 ha in 2006 (FERA)). Approval for use in the UK was revoked on 13 December 2007 (HSE, 2007).

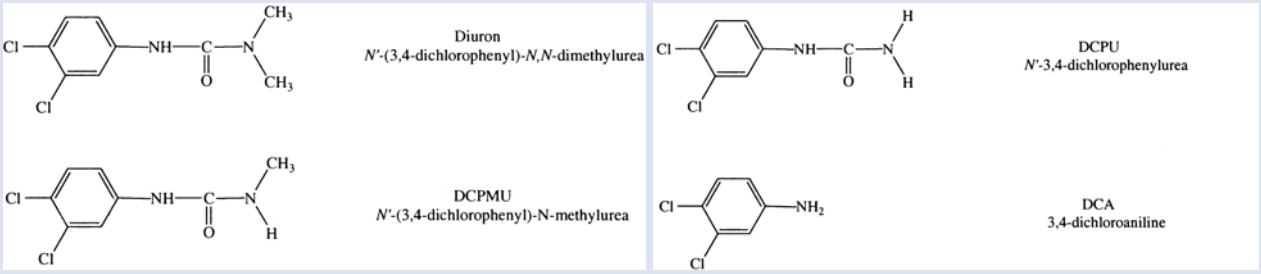

Figure 4.6 Diuron and its metabolites

Diuron forms a series of metabolites (Figure 4.6). These can be formed in the top few centimetres of the soil and migrate through the soil profile sorbing and desorbing from the soil matrix (Gooddy et al., 2002). There is also evidence of the continued formation of metabolites as the parent continues to leach. In a field study, after 50 days, 10% of the total pesticide found in the soil porewater and 20% in the soil matrix consisted of degradation products (Gooddy et al., 2002).

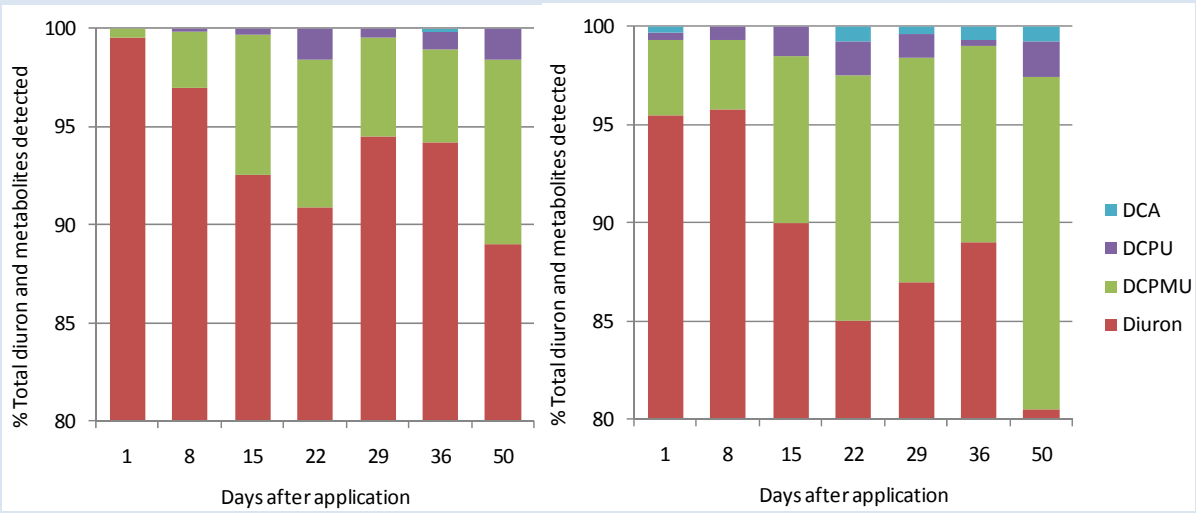

Figure 4.7 Relative proportions of diuron and metabolites in a) soil porewater and b) soil solid phase with time from (Gooddy et al., 2002)

In a regional study of the semi-confined Chalk of south east England, (Lapworth and Gooddy, 2006) found that diuron was detected in 90% of water analysed and in 60% of samples metabolites were at higher concentrations than the parent. Pesticide concentrations in groundwater samples showed a correlation with high water levels and with the pesticide content of recent recharge.

Parsons et al. (2008) carried out an assessment of risk from pesticide metabolites for both the US and the UK. For the UK, 54 pesticides were identified as representing 90% of all pesticide use. The three highest use pesticides without relevant metabolites data were stated to be chlormequat, MCPP and tri-allate.

A risk index (RI) was used derived from an exposure index, E and the acceptable daily intake in mg kg^{-1} body weight day^{-1} (ADI):

$$E = A \times F \times P$$

where A = amount index (derived from usage and fraction of metabolite formed), F = fraction of metabolite in the aqueous phase (derived from K_d) and P = persistence index (derived from DT_{50})

and

$$RI = E/ADI$$

Table A1.2, Appendix 1, shows metabolites assessed as having a risk index of >0.5. Metabolites with insufficient data were assigned a conservative default. Compounds with the highest risk index were metabolites of cyanazine, followed by those of isoproturon, flufenacet, tebuconazole and dicamba.

4.4.2 Simple hazard assessment for pesticide metabolites

A simple hazard assessment was made as part of this study. Significant metabolites were identified from the Footprint website. Key metabolites for pesticides with usage of >50,000 ha are listed in Table A1.3, Appendix 1. Some properties are also available for metabolites but these are much less comprehensive than for the parent compounds. The leaching probability for those metabolites for which data are available is plotted in Figure 4.8 as a possible first pass approach. Here DT_{50} for soil has been used as this is the most commonly available parameter for metabolites. Metabolites assessed as vulnerable to leaching are shown in red in Figure 4.8 and listed in Table 4.5. This approach takes no account of the activity or toxicity of these metabolites and some of the metabolites may be trivial.

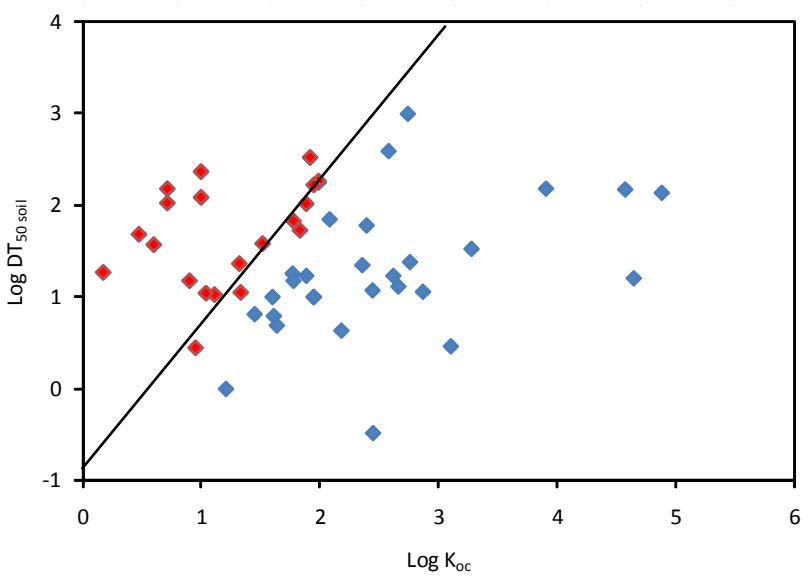

Figure 4.8 Leaching classification for key metabolites (red are leachers)

Table 4.5 Key metabolites assessed as having leaching potential from Figure 4.8

Parent compound	**Key metabolite**	**DT_{50}**	**K_{oc}**
Chlorothalonil	2-amido-3,5,6-trichlo-4-cyanobenzenesulphonic acid	121	10
	3-carbamyl-2,4,5-trichlorobenzoic acid	103	77
Cymoxanil	2-cyano-2-methoxyiminoacetic acid	2.8	9
	3-ethyl-4-(methoxyamino)-2,5-dioxoimidazolidine-4-carboxamide	11.2	21.6
Cyproconazole	1H-1,2,4-triazol-1-ylacetic acid	15	8
Diflufenican	2-(3-trifluoromethylphenoxy)nicotinic acid	10.6	13
Florasulam	5-(aminosulfonyl)-1H-1,2,4-triazole-3-carboxylic acid	328	83
	N-(2,6-difluorophenyl)-8-fluoro-5-hydroxy[1,2,4]triazolo[1,5-c]pyrimidine-2-sulfonamide	23	21
Flufenacet	FOE oxalate	11	11
	FOE sulphonic acid	230	10
Fluoxastrobin	HEC-5725-des-chlorophenyl	67	60
Fluroxypyr	4-amino-3,5-dichloro-6-fluoro-2-pyridinol	37	4
Iodosulfuron-methyl- Na	2-amino-4-methoxy-6-methyl-1,3,5-triazine	181	97.7
Mesosulfuron-methyl	4,6-dimethoxypyrimidine-2-yl-urea	48	3
	Mesosulfuron	53	68
Metaldehyde	Acetaldehyde	18.5	1.5
Metsulfuron-methyl	Saccharin	150	5.2
Thiram	N,N dimethyl carbamosulfonic acid	38	33
Tribenuron-methyl	N-methyl triazine amine	165	89
	Saccharin	105	5.2

Some of the parent compounds listed in Table 4.5 are not themselves assessed as being vulnerable to leaching: these are chlorothalonil, cymoxil, diflufenican, linuron and thiram. For example, the primary metabolite of chlorothalonil (4-hydroxy- 2,5,6 trichloroisophthalonitrile) has been found in soil, plants and animals during the breakdown of chlorothalonil (Caux et al., 1996). It is about 30 times more acutely toxic than chlorothalonil itself and is more persistent and mobile in soil.

Metabolites from the pesticides identified above could present a particular problem as the parent may have been excluded from monitoring on the basis of low perceived risk to groundwater.

We compared the metabolites identified as prone to leaching by our methodology with those identified by Sinclair (2010). The results are given in full in Table 4.6. This comparison shows that only a few metabolites are common to both assessments. A further five parent compounds are in common but the metabolites are different.

Table 4.6 Common metabolites identified by this study and by Sinclair (2010)

Compound	This study	Sinclair
Chlorothalonil	2-amido-3,5,6-trichlo-4-cyanobenzenesulphonic acid	2-amido-3,5,6-trichloro-4-cyanobenzenesulphonic acid (R417888)
	3-carbamyl-2,4,5-trichlorobenzoic acid	3-carbamyl-2,4,5-trichlorobenzoic acid (3-carboxy, 2,5,6-trichlorobenzamide) (R611965, SDS46851)
Diflufenican	2-(3-trifluoromethylphenoxy) nicotinic acid (AE B107137)	2-(3-trifluoromethylphenoxy) nicotinamide (AE 0542291)
Florasulam	5-(aminosulfonyl)-1H-1,2,4-triazole-3-carboxylic acid	5-hydroxy-XDE-570 (5-hydroxyflorasulam)
	N-(2,6-difluorophenyl)-8-fluoro-5-hydroxy[1,2,4]triazolo[1,5-c] pyrimidine-2-sulfonamide	
Flufenacet	FOE oxalate	FOE oxalate
	FOE sulphonic acid	thiadone
Iodosulfuron-methyl-sodium	2-amino-4-methoxy-6-methyl-1,3,5-triazine	AE F145740
		metsulfuron-methyl
Metaldehyde	Acetaldehyde	acetaldehyde
Metsulfuron-methyl	Saccharin	2-(aminosulfonyl) benzoic acid (IN-D5119)
		methyl 2-(aminosulfonyl) benzoate (IN-D5803)

4.4.3 Corroborating evidence for assessment

There have been some studies of pesticide metabolites in groundwater, these have tended to be in areas where the suite of applications differs from that currently used in the UK (Chang and Liao, 2002; Fava et al., 2005; Giacomazzi and Cochet, 2004; Hildebrandt et al., 2007; Kolpin et al., 2004).

Glyphosate is now the most widely used herbicide in the world, with dramatic increases in agricultural use since the introduction of glyphosate resistant crops. Microbial degradation produces aminomethyl phosphonic acid (AMPA) (Kolpin et al., 2000) and it has been anticipated that AMPA may be problematic. The high water solubility of both the parent and the metabolite has meant that their analysis has been difficult. Although AMPA has a DT_{50} of about 151 days and is therefore persistent it also has a relatively high K_{oc} of 8087 and would not be classified as vulnerable to leaching by the simple method described above.

Similarly for parent compounds which have non-agricultural applications, there will be routes to groundwater which would not be identified, such as routes which do not pass through the soil zone. Kolpin (2006) showed AMPA to be detected in wastewater-impacted surface waters about four times as frequently as the parent.

4.5 CASE STUDIES: PESTICIDES AND METABOLITES DETECTED IN GROUNDWATERS

This section summarises the results from a review of selected literature describing observations of pesticides and pesticide metabolites. This was focussed on Europe as agricultural practice in the USA differs considerably from the UK, and where the majority of studies have focussed on maize. A study from Norway was also included although agricultural practices may not be directly comparable with the UK.

4.5.1 Monitoring groundwater for pesticides and metabolites in England and Wales

The Environment Agency measures pesticides in groundwaters in England and Wales from their national monitoring network. Figure 4.9 shows the most recently published data for the compounds most frequently detected. Of these compounds, atrazine, simazine, diuron, isoproturon and dieldrin are now not used in the UK.

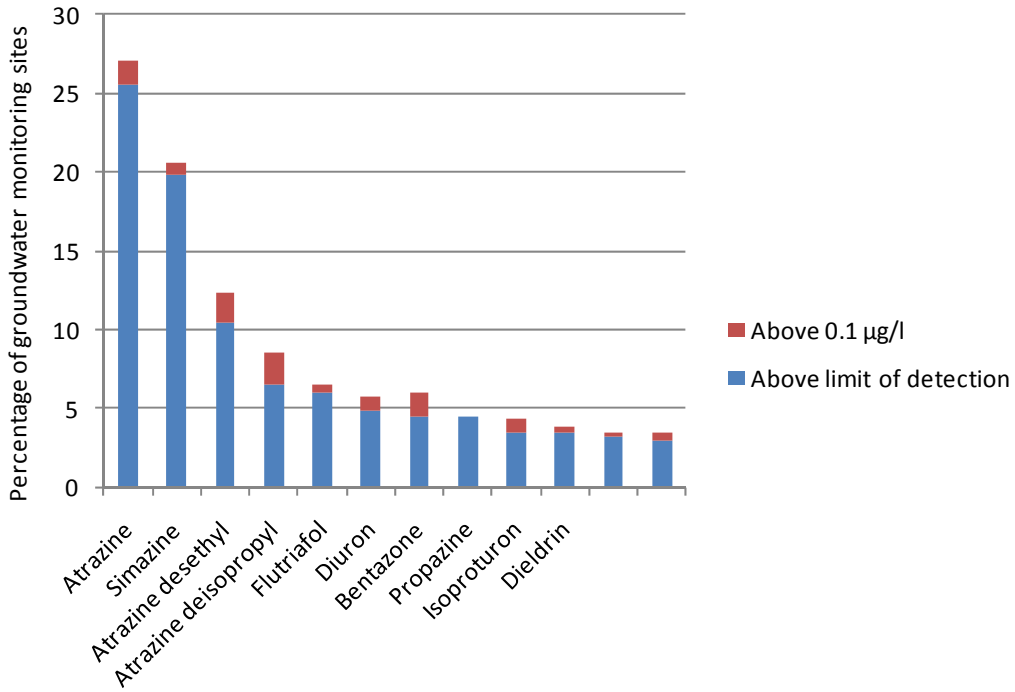

Figure 4.9 Pesticide detections in groundwater in England and Wales in 2007 (Environment Agency, 2008b)

In Chapter 7 we describe the results of our new analysis of organic micropollutant data of the Environment Agency's groundwater monitoring network.

4.5.2 Denmark

A summary of pesticide monitoring from the national monitoring system and from all groundwater monitoring programmes in Denmark identified the ten most frequently detected pesticides and metabolites in groundwater (Jacobsen et al., 2005). These are shown in Table 4.7. The most frequently detected compound was 2,6-dichlorobenzamide, a metabolite of dichlobenil. There were also a number of metabolites of atrazine and also ethylenethiurea, a metabolite of dithiocarbamate fungicides such as mancozeb. The authors also highlight increasing detection of the desamino-diketo- and diketo- metabolites of metribuzin.

Table 4.7 Most frequently detected pesticides and metabolites in Denmark (Jacobsen et al., 2005)

	National programme	All data
1	2,6-dichlorobenzamide	2,6-dichlorobenzamide
2	Deethylatrazine	Deethyldeisopropylatrazine
3	Deisopropylatrazine	Deethylatrazine
4	Atrazine	Deisopropylatrazine
5	Bentazone	Bentazone
6	MCPP	Atrazine
7	Dichlorprop	Simazine
8	MCPA	Dichlorprop
9	Simazine	Ethylenethiurea
10	Hydroxyatrazine	MCPP

4.5.3 Norway

Ten years of pesticide monitoring in groundwater in Norway (Haarstad and Ludvigsen, 2007) detected DDT, dimethoate, azoxystrobin, cyproconazole, fenpropimorph, fluazinam, metalaxyl, prochloraz, propiconazole, thiabendazole, kresoxim, atrazine, dichlorprop, glyphosate, isoproturon, clopyralid, linuron, MCPA, MCPP, metamitron, bentazone, metribuzin, propachlor and terbuthylazine. Metabolites detected were desethyl atrazine, 2,6-dichlorobenzamide and AMPA.

4.5.4 Other studies

Other studies which have looked at pesticide metabolites in groundwaters are summarised in Table 4.8.

Table 4.8 Summaries of selected studies finding pesticide metabolites in groundwater

Area	Pesticides detected	Metabolites detected	Process	Ref
Hesse, Germany	chloridazon	desphenyl-chloridazon	Parent and metabolite in STW effluent, surface water and groundwater	Buttiglieri et al. (2009)
Rome province, Italy	bentazone, MCPA, 2,4-D	8-hydroxybentazone	Survey	Laganà et al. (2002)
Lincolnshire, UK	MCPP (chiral mixture)	4-chloro-2-methylphenol	Change in enantiomeric ratio during degradation	Williams et al. (2003)

4.6 CONCLUSIONS FOR PESTICIDES AND PESTICIDE METABOLITES

The following conclusions are drawn:

- some parent compounds and many metabolites are probably present but undetected in groundwater due to a lack of analysis or a suitably sensitive analytical method
- data required to make an assessment of the risk of pesticides and metabolites entering the aquatic environment are: usage, soil sorption and persistence in soil or groundwater
- pesticides may also pose a risk to drinking water and thus to the environment due to incomplete removal by water treatment
- a simple risk assessment using usage, sorption and persistence suggests that 2,4-D, clopyralid, dicamba, florasulam, imazaquin, iodosulfuron-methyl-sodium, MCPA, and quinmerac pose the greatest risk followed by amidosulfuron, bentazone, fosthiazate, maleic hydrazide, MCPP-P, metribuzin, metsulfuron-methyl, oxamyl and triclopyr
- a similar assessment can be made for metabolites although the required data can be sparse. A number of different approaches indicate that the metabolites of chlorothalonil, cyanazine, diflufenican, flufenacet, iodosulfuron-methyl-sodium, metaldehyde, metazachlor and metsulfuron-methyl are likely to pose the greatest risk to drinking water. In many cases these metabolites are derived from parents which have a lesser risk
- metabolites from parent compounds with low perceived risk can be persistent, mobile and toxic
- few of the compounds assessed as posing risk to groundwater were new and would therefore not be considered as emerging contaminants, although for some compounds there were insufficient data available to make an assessment

5 Urban and industrial organic micropollutants in depth

5.1 POTENTIAL URBAN AND INDUSTRIAL SOURCE TERMS

Potential source terms include wastewater, derived from domestic, industrial or hospital premises and waste disposal sites (Stangroom et al., 1998). The presence of persistent organic pollutants in wastewater has been long established (BGS et al., 1998). The pollutants comprise polyaromatic hydrocarbons, polychlorinated biphenyls, dioxins and furans, chlorinated solvents and benzene derivatives. To these could be added plasticisers and detergent breakdown products. Landfill leachates contain short- and long-chain fatty acids, and can also contain caffeine, nicotine, phenols, sterols, PAH, chlorinated solvents and phthalates (Stuart and Klinck, 1998).

See Chapter 3 for more information on types of urban and industrial emerging contaminants.

5.1.1 Pharmaceuticals

The primary sources of pharmaceuticals in the environment are human excretion and disposal of unused products. Verlicchi et al. (2010) surveyed hospital wastewater and found a wide range of organic micropollutants, including disinfectants and musks, as well as trace metals, and iodised contrast media (Table 5.1). Watkinson et al. (2009) also provide a list of antibiotics found in hospital effluents.

Table 5.1 Main classes of organic micropollutants used in hospitals

Class	Examples
Antibiotics	cefazolin, chlortetracycline, ciprofloxacin, coprofloxacin, doxycycline, erythromycin, lincomycin, norfloxacin, ofloxacin, oxytetracycline, penicillin, sulfamethoxazole, tetracycline, trimethoprim
Analgesics and anti-inflammatories	codeine, diclofenac, dipyrone, ibuprofen, indomethacin, ketoprofen, efenamic acid, naproxen, paracetamol, propyphenazone, salicylic acid
Cytostatics	5-fluorouracil, ifosfamide
Anaesthetics	propofol
Disinfectants	glutaraldehyde, triclosan
Psychiatric drugs	carbamazepine, gabapentin, phenytoin, valproic acid
Antihistamines	cimetidine, ranitidine
Antihypertensives	diltiazem
Antidiabetics	glibenclamide
β-blockers	atenolol, metroprolol, propanolol, solatolol
Hormones	17 β-oestradiol, oestriol, oestrone, ethinyloestradiol
Diuretics	furosemide, hydrochlorotiazide
Lipid regulators	atorvastatina, bezafibrate, clofibric acid, gemfibrozil, pravastatin
Stimulants	Caffeine
Musks and fragrances	galaxolide, tonalide

Jones et al. (2002) made an environmental assessment for the 25 most-used prescription pharmaceuticals in the UK using estimated removal in treatment works, based on sorption and dilution (Table 5.2). Degradation was modelled due to lack of data and was predicted to be very limited for most compounds.

Use of prescribed drugs for contraception in England has remained overall broadly constant with a drop from 1.44 million doses of combined formulations in 2005 to 1.25 million doses in 2010 balanced by an equivalent increase in progesterone only formulations (PCT, 2010).

Table 5.2 Assessment of usage, K_{ow}, and predicted degradation in sewage treatment works for the top 25 prescription drugs used in the UK in 2000 compared to environmental detections (tick in Det.UK column if detected in UK environment) (from Jones et al., 2002)

Compound	**Use**	**Amount (kg)**	**K_{ow}**	**% removal in STW**	**Det. UK**
Paracetamol	Analgesic	390954	0.46	1.8	✓
Metformin hydrochloride	Antihyperglycaemic	205795	-2.64	1.9	
Ibuprofen	Analgesic	162209	3.50	28.7	✓
Amoxicillin	Antibiotic	71466	0.87	1.9	
Sodium valproate	Anti-epileptic	47479	-0.85	2.0	
Sulphasalazine	Anti-rheumatic	46430	3.81	22.2	
Mesalazine	Ulcerative colitis treatment	40421	0.98	1.9	
Carbamazepine	Anti-epileptic	40348	2.25	3.0	✓
Ferrous sulphate	Iron supplement	37538	-0.37	1.9	
Ranitidine hydrochloride	Anti-ulcer drug	36319	-	-	
Cimetidine	H_2 receptor antagonist	35654	0.40	1.9	
Naproxen	Anti-inflammatory	35065	3.18	7.6	✓
Atenolol	β-blocker	28976	0.16	1.9	
Oxytetracycline	Antibiotic	27195	-0.90	1.9	✓
Erthyromycin	Antibiotic	26483	3.06	6.2	✓
Diclofenac sodium	Anti-inflammatory & analgesic	26120	0.70	1.9	✓
Flucloxacillin sodium	Antibiotic	23381	-	-	
Phenoxymethyl penicillin	Antibiotic	2227	3.09	2.3	
Allopurinol	Anti gout drug	22095	-0.55	1.9	
Diltiazem hydrochloride	Calcium antagonist	21791	2.70	3.8	
Gliclazide	Antihyperglycaemic	18783	2.12	2.4	
Aspirin	Analgesic	18105	1.19	1.9	✓
Quinine sulphate	Muscle relaxant	16731	5.40	86.9	
Mebeverine hydrochloride	Antispasmodic	15497	3.82	22.6	
Mefanamic acid	Anti-inflammatory	14522	5.12	81.0	

5.1.2 Perfluorinated hydrocarbons (including PFOS and PFOA)

Perfluorinated hydrocarbons have been used for over 50 years for a range of industrial applications (Sections 3.4 and 3.7). The main compounds of interest are PFOS and PFOA, both of which have been widely detected in the environment and human and animal tissues (Environment Agency, 2008a). PFOS is persistent, bio-accumulative and toxic (OECD, 2002).

The potential for these contaminants to occur in groundwater was highlighted in the aftermath of the Buncefield incident. An explosion at the Buncefield oil depot in Hertfordshire in 2005 led to major fires: 750 000 litres of foam concentrate and 55 million litres of water were used to extinguish them (BMIIB, 2006). Some of the foam contained PFOS and this was detected in groundwaters in the vicinity following the incident. The Buncefield Investigation report points out that no sampling for PFOS was done prior to the incident so the possibility that it originated prior to the incident cannot be ruled out.

The manufacture and use of PFOS is being phased out due to concerns about its persistence in the environment. The Environment Agency reviewed the available data on the physicochemical properties of perfluorinated hydrocarbons in a 2008 report: data reported included solubility and K_{ow}. They also undertook laboratory experiments to determine partition coefficients (K_d) between some perfluorinated compounds and aquifer materials from England and Wales (Environment Agency, 2008). Partition coefficients were shown to vary significantly between different aquifer materials and with differing concentrations of the compound. For example, a 10 μg/L solution of PFOA exhibited a K_d of 0.97 with Mercia Mudstone, while the K_d between the same solution and Lower Oxford Clay was 13 8, an order of magnitude larger. The availability of more-accurate property values enables better environmental assessments of the fate and behaviour of these compounds. Replacements for PFOS and PFOA include perfluorobutane sulfonate (PBFS) (Environment Agency, 2008).

5.1.3 Other source terms

Other types of compounds anticipated to require treatment in urban wastes and waters are set out in Gibs et al. (2007) and Stackelberg et al. (2007) (Table 5.3). These include detergent degradates, flame retardants and plasticisers, and fragrances and flavourings. Gibs et al. (2007) and Stackelberg et al. (2007) also considered a wide range of pharmaceuticals and a small set of pesticides which are not being considered in this section.

Table 5.3 Urban organic micropollutants excluding pharmaceuticals from Gibs et al. (2007) and Stackelberg et al. (2007).

Class	Examples
Detergent degradates	4-nonyl-phenol, diethoxynonylphenol, diethoxyoctyl-phenol, ethoxyoctyl-phenol
Flame retardants and plasticisers	bisphenol a, diethyl hexylphthalate, diethylphthalate , tetrabromodiphenyl ether, tri(2-butoxyethyl) phosphate, tributyl phosphate, triphenyl phosphate
Polyaromatic hydrocarbons	anthracene, benzo[α]pyrene, fluoranthene, naphthalene, pyrene
Fragrances and flavourings	acetophenone, camphor, galaxolide, isoborneol, menthol, skatol, tonalide
Plant and animal steroids	b-sitosterol, b-stigmasterol, cholesterol
Repellents	DEET
Misc	1,4-dichlorobenzene, 4-cresol, anthraquinone, benzophenone, isophorone, tetrachloroethene, triclosan., triethyl citrate

5.2 PREDICTING RISK FROM URBAN AND INDUSTRIAL MICROPOLLUTANTS

An important issue is to establish which of these compounds would be considered to be emerging contaminants. For example, some compounds, such as the fuel-oxygenate MTBE were considered to be emerging contaminants in the 1990s (Hyet, 1994) due to their mobility in the aqueous environment and apparent persistence. However, MTBE has been shown to be slowly naturally attenuated and appears to now be rather less topical (Chisala et al., 2007; Wealthall et al., 2001). This example illustrates that risk assessments utilising physicochemical properties of compounds need to be verified by field observations.

5.2.1 Pathways

Pathways for pharmaceuticals, urban and industrial contaminants to reach groundwater include leaking sewers, effluents from sewage treatment works (discharged to surface water which then infiltrates), landfill leachate, leaking storage tanks and direct discharge to the ground (Figure 5.1). For Coventry, Birmingham and Madras the main sources of urban groundwater pollution were considered to be industry and inadequate sewerage (1992).

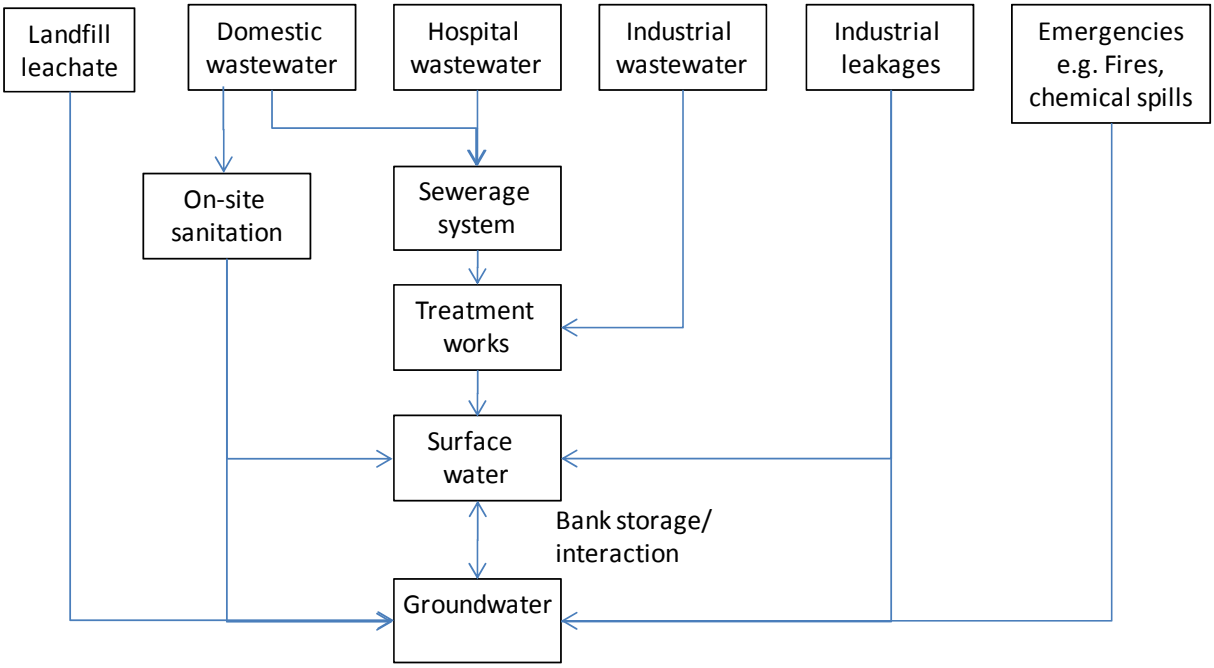

Figure 5.1 Pathways for contaminants to reach groundwater in the urban environment

PHARMACEUTICALS

Bound and Voulvoulis (2005) set out the pathways for domestic pharmaceuticals to reach the aqueous environment (Figure 5.2). There are two main routes: via effluent from STW after excretion from the body and from the disposal of out-of-date or unwanted medicines via the wastewater system or in household waste to landfill. Those entering STWs in wastewater may either pass into the effluent due to incomplete removal or possibly be retained in biosolids. Only a small proportion of unused dispensed medicines are returned to the pharmacy. Bound and Voulvoulis (2005) estimated that for metaprolol, where 27% of the total dispensed was discarded almost 18% of this total may enter the aqueous environment through landfills, whereas almost 90% of dispensed ibuprofen was used rather than discarded.

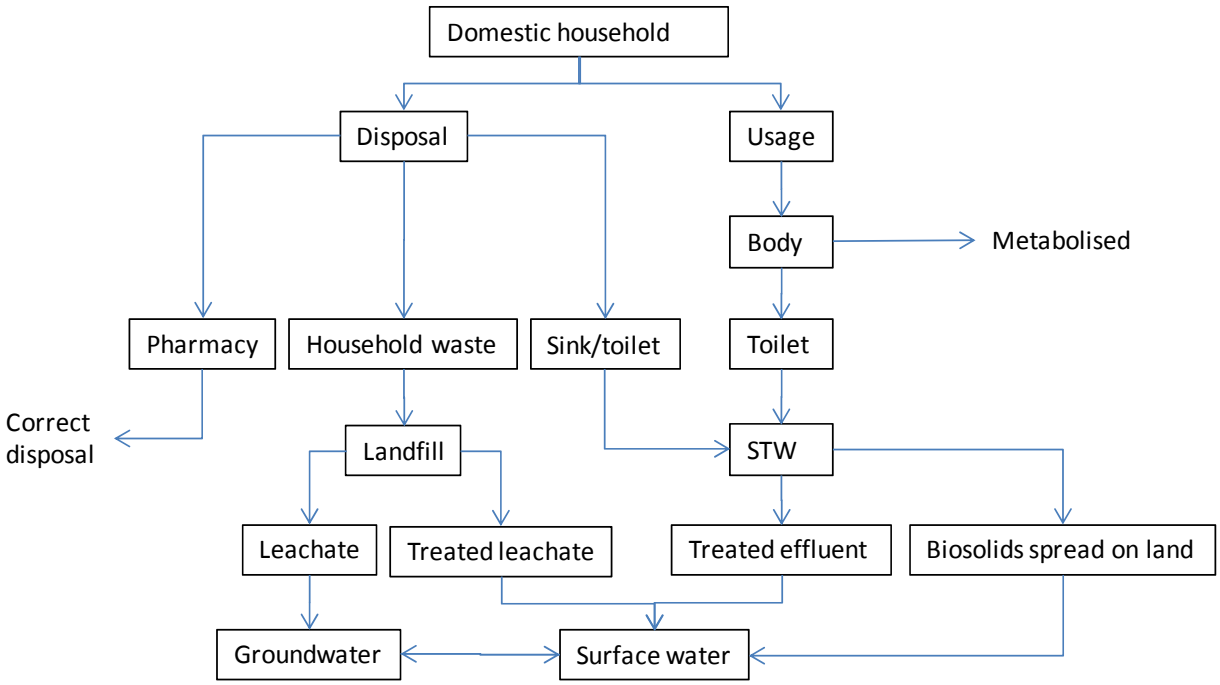

Figure 5.2 Pathways for domestic pharmaceuticals to reach the aqueous environment (adapted from Bound and Voulvoulis, 2005)

Jones et al. (2005) assessed the potential for pharmaceuticals to enter the aqueous environment, reviewed the levels reported in drinking water world-wide and assessed the implications. Johnson et al. (2007a) applied an existing GIS model to predict the concentrations of 2 pharmaceuticals, diclofenac and propanalol, in surface water catchments. The model input parameters included consumption, excretion and fate. Concentrations predicted throughout the catchments were 1 ng/L under low flow except for downstream of small STW where concentrations of up to 25 ng/L were predicted.

OTHERS

Plant sterols (phyto-oestrogens) are ingested in edible plants and excreted to wastewater. Wastewater may therefore be the largest source of these compounds in the environment (Liu et al., 2010).

Synthetic musks are widely employed in the perfume and cosmetics industries as well as for cleaning, polishing and washing (Fromme et al., 2001). Rimkus (1999) estimated a world-wide production of about 6000 tonnes in 1999. The main route into the environment for these compounds is also via the sewerage system. They are degraded to more polar metabolites during treatment and in sediments and soil.

Bisphenol A is used in can coatings, powder paints, additives in thermal paper and as an antioxidant in plastics (Fromme et al., 2002). Routes to the environment are from manufacturing and leaching from the final product. Phthalates are similar, being used mainly in the manufacture of PVC and a plasticisers for building materials, home furnishings, food packaging and insect repellents (Fromme et al., 2002). Routes to the environment are also from manufacturing and leaching from the final product.

Polybrominated diphenyl ether flame retardants are extensively used in resins for household and industrial use (Rahman et al., 2001). They may enter the environment via waste disposal to landfill and incineration. Water runoff from dumps and landfill leachate may be a pathway. PFOS was used in fire-fighting foams and entry to the environment was by run-off from sites

of major fires (e.g. Buncefield). Harada et al. (2003) showed it to be present in sewage effluent in Japan.

Ionic liquids are not yet widely used but current formulations are likely to be toxic and poorly degradable (Thuy Pham et al., 2010).

5.2.2 Removal during sewage treatment

There have been a number of studies evaluating the efficacy of sewage treatment to remove pharmaceuticals. Rosal et al. (2010) report a survey of over 70 individual pollutants in a sewage treatment plant using biological treatment followed by ozonation. They found caffeine, paraxanthine (caffeine metabolite) and acetaminophen were the main individual contaminants usually found at concentrations over 20 µg/L. Several important groups of pharmaceuticals had typical removal efficiencies of <20%. These included: the β-blockers atenolol, metoprolol and propanolol; the lipid regulators bezafibrate and fenofibric acid; the antibiotics erythromycin, sulfamethoxazole and trimethoprim; the anti-inflammatories diclofenac, indomethacin, ketoprofen and mefenamic acid; the antiepileptic carbamazepine; and the antiacid omeprazole. Ashton et al. (2004) suggested that most STWs in England and Wales are likely to be routinely discharging small quantities of pharmaceuticals.

The oestrogenic effects of STW effluent ascribed to ethinyl oestradiol and alkyl phenols have been recognised for two decades (Montagnani et al., 1996; Purdom et al., 1994). An assessment of oestrogen removal efficiency for STW (Johnson et al., 2007b), showed simple biological plants to be poor with only about 30% removal. Johnson and Williams (2004) were able to estimate the amount likely to be discharged using predictions of excretion fate and behaviour in the sewage treatment system.

Horii et al. (2007) showed that removal efficiencies for synthetic musks by STWs ranged from 72% to 98% but concentrations of the galaxolide metabolite HHCB-lactone increased during treatment.

Degradation of APEs in wastewater treatment plants or in the environment generates more persistent shorter-chain APEs and alkyl phenols such as NP, OP and alkylphenol mono- to tri-ethoxylates (Ying et al., 2002). There is concern that APE metabolites can mimic natural hormones and that the levels present in the environment may be sufficient to disrupt endocrine function in wildlife and humans. The physicochemical properties of the APE metabolites, in particular the high K_{ow} values, indicate that they will partition effectively into sediments following discharge from STWs. The aqueous solubility data for the APE metabolites indicate that the concentration in water combined with the high partition coefficients will provide a significant reservoir (load) in various environmental compartments. APE removal can be enhanced by GAC filtration, UV treatment or ozonolysis but these techniques do not resolve accumulation in sludge (Soares et al., 2008).

Flame retardants may be present in effluent from STWs accepting landfill leachate (Rahman et al., 2001). This may also be a route for other industrial compounds.

The potential for organic contaminants present in sewage sludge to leach following application to agricultural land was highlighted by Wilson et al. (1996), although in this study no problems were found using a screening exercise.

Table 5.4 Examples of organic micropollutants with K_{ow} <1

Class	Compound
Analgesic/antipyretic	acetaminophen (paracetamol)
Antiasthmatic	salbuterol
Antibiotics	ciprofloxacin, doxycycline, lincomycin norfloxaxin, ofloxacin, sulfamethoxazole, sulfathiazole,
Anticonvulsants	primadone
Antimicrobial	sulfapyridine, trimethoprim
Cosmetic ingredient	triethyl citrate
Psychoactive	meprobamate
Stimulants and metabolites	caffeine, 1,7-dimethylxanthine (caffeine metabolite), cotinine (nicotine metabolite)
X-ray contrast medium	iopromide
Vasodilator	pentoxifylline

5.2.3 Physicochemical properties of organic micropollutants

Physicochemical properties such as K_{ow} are available for the majority of urban and industrial organic micropollutants from the SRC database (SRC, 2010). As a first pass estimate of recalcitrance to water treatment, of the compounds listed by Gibs et al. (2007), Stackelberg et al. (2007) and Glassmeyer et al. (2008), only 19 had a K_{ow} of <1. Examples are shown in Table 5.4.

5.2.4 Aqueous persistence

Many of these compounds are considered to be persistent in the aqueous environment. Zweiner (2007) describes the processes which reduce the concentrations of pharmaceuticals in treated sewage effluent which reaches the aqueous environment as biodegradation, sorption, photolysis and oxidation successively in surface water, bank filtration and drinking water treatment.

However there are few data on persistence in the environment available. For a group of 8 pharmaceuticals (acetaminophen, atorvastatina, caffeine, carbamazepine, levofloxacin, sertraline, sulfamethoxazole, and trimethoprim) Lam et al. (2004) showed that photolysis was much more significant than hydrolysis.

Löffler et al. (2005) studied four ^{14}C-labelled pharmaceuticals (diazepam, ibuprofen, iopromide, and acetaminophen) as well as six non-labelled compounds (carbamazepine, clofibric acid, 10,11-dihydroxycarbamazepine, 2-hydroxyibuprofen, ivermectin, and oxazepam). Ibuprofen, 2-hydroxyibuprofen, and paracetamol displayed a low persistence with DT_{50} values in the water/sediment system less <20 d. The sediment played a key role in the elimination of acetaminophen due to the rapid and extensive formation of bound residues. A moderate persistence was found for ivermectin and oxazepam with DT_{50} values of 15 and 54 d, respectively. Iopromide also exhibited a moderate persistence and was transformed into at least four transformation products. For diazepam, carbamazepine, 10,11-dihydroxycarbamazepine, and clofibric acid, system DT_{90} values of >365 days were found, which exhibit their high persistence in the water/sediment system. An elevated level of sorption onto the sediment was observed for ivermectin, diazepam, oxazepam, and carbamazepine.

Jürgens et al. (2002) measured the degradation of oestrodiol and ethinyl oestrodiol in English rivers and estimated a half-life of 10 days or less. Lai et al. (2000) showed that synthetic oestrogens were more readily removed from the aqueous phase than natural compounds due to their higher K_{ow}. Sorption was to both organic carbon and iron oxides in sediments.

Synthetic musks are assessed as being non-degradable. Sorption and sedimentation appear to be minor processes. Tonalide can be removed from surface water by direct photolysis but galaxolide shows negligible photochemical degradation (Buerge et al., 2003).

APE surfactants appear to be attenuated during infiltration of river water to groundwater (Ahel et al., 1996).

Instead of attempting to assess persistence directly, a number of case studies are summarised in Section 5.3. These show that persistence is likely to be more important than sorption in controlling behaviour.

5.2.5 Drinking water treatment

The efficacy of drinking water treatment for pharmaceuticals was evaluated for adsorption on activated carbon, oxidation and membrane filtration by Zweiner (2007). A good correlation was found between the percentage removal by activated carbon and K_{ow} for many compounds with $K_{ow}>3$. Exceptions to this were N-heterocyclic compounds, such as pentoxifylline and trimethoprim, which were more efficiently removed than predicted, and compounds with carboxyl groups, such as clofibric acid, ibuprofen and diclofenac, which are at least partially dissociated and negatively charged and removed less efficiently.

High rates of removal by ozonation are usually observed for compounds with double bonds, aromatic structure or heteroatoms (such as N or S), and this was the case for diclofenac, carbamazepine and sulfamethoxazole (Zwiener, 2007). Lower rates were observed for clofibric acid and ibuprofen which do not have reactive sites. These types of compounds are more readily degraded by advanced oxidation using, for example, the OH radical. Nanofiltration was effective for negatively charged compounds. Chlorine and chlorine dioxide were shown to be ineffective and also produced undesirable by-products (Zwiener, 2007).

In a study of 98 organic micro-compounds, Gibs et al. (2007) showed that 50% were not substantially degraded by combined and free chlorine. In an overall assessment for 113 organic micro-compounds Stackelburg et al. (2007), 15% of the loading was removed by clarification. 32% by hypochlorite disinfection and 53% by GAC filtration. Compounds most frequently detected in finished water were carbamazepine, DEET, cotinine, tonalide, caffeine and camphor.

5.2.6 Detections

Chlorinated alkyl phosphates, the plasticiser NBBS, DEET, pharmaceuticals such as ibuprofen and naproxen, and polycylic musks were reported in Norwegian landfill leachate (2010). They also found perfluorinated compounds, such as PFOS. Buszka et al. (2009) detected a wide range of organic micropollutants in groundwater downgradient of a landfill, including acetaminophen, fluoxetine and ibuprofen, as well as caffeine and cotinine. Drewes and Shore (2001) show that pharmaceuticals could be a particular problem where waste water is reused, for example for irrigation or recharge, as well as in animal waste.

Rudel et al. (1998) identified alkyl phenols in wastewater and found NP at concentrations of >1000 µg/L in 5 septage (waste from septic tanks) samples analysed. Groundwater downgradient of an infiltration bed for secondary effluent also contained alkyl phenols. Zoller

et al. (1990) also found alkyl phenols in groundwater in areas where surface water was impacted by sewage. They can also be used as pesticide adjuvants and reach the environment in a similar way (Lacorte et al., 2002).

Johnson et al. (2008b) showed that water quality model predictions compare well with measured values for polar organic micropollutants from a point source, but both approaches have their advantages and drawbacks.

5.2.7 Risk assessments for pharmaceuticals

There have been recent attempts to predict environmental risk from human pharmaceuticals, which utilise different data about the usage and physicochemical properties of the compounds studied. Some of the approaches used are simplistic, but provide a useful means of assessing which compounds should be prioritised for more detailed study.

Stuer-Lauridsen et al. (2000) and Webb (2000), quoted in Ayscough et al. (2000), made risk assessments of pharmaceuticals in the aquatic environment using the comparison of predicted environmental concentration (PEC) and predicted no-effect concentration (PNEC). Stuer-Lauridsen et al. (2000) calculated PEC using the amount of compound used divided into the amount of wastewater generated both per capita diluted into the environment using a default value of 10, and estimating K_{ow} and DT_{50} from literature values. They found limited ecotoxicity data to be available for calculation of PNEC and showed for the six compounds possible, PEC/PNEC>1 for ibuprofen, paracetamol and acetyl-salicylic acid. Webb (2000) made a similar assessment for drugs used in the UK in 1995 (Table 5.5). Of the 67 compounds assessed only 7 had PEC/PNEC>1 and only 11 had PEC/PNEC>0.1.

The process for registration of new drugs at the European level requires a risk assessment of the PEC (EMEA, 2005). The EMEA (2005) assessment utilises data on the volume of drug prescribed and the amount of dilution in the wastewater stream, this being the predominant pathway for pharmaceuticals to enter the aquatic environment. The method assumes “no biodegradation or retention of the drug substance in the sewage treatment plant” and is therefore conservative. This approach can also be used to assess existing compounds. Bound and Voulvoulis (2006) used the proportion of the population being treated, the dosage, the amount of wastewater generated per day and an estimate of dilution to identify candidate compounds for a study of pharmaceuticals in UK rivers.

Table 5.5 Aquatic risk assessment for selected pharmaceuticals in the UK (after Webb, 2000)

Compound	**Use in 1997 (t/a)**	**PEC/PNEC**
Paracetamol	2000	39.92
Dextroproxyphene	42.5	2.06
Oxytetracycline	33.7	26.8
Propanalol	11.8	1.16
Amitiptyline	5.5	1.29
Thioridazine	3.8	2.59
Fluoxetine	2	14.2
Aspirin	770	1.00
Quinine	29.7	0.54
Metronidazole	15.5	0.23
Verapamil	9.9	0.31

Cooper et al. (2008) ranked drugs by their potential environmental exposure and risk using annual prescriptions dispensed, surface water concentrations, effluent concentration, environmental half life, biological half life, mammal, fish and crustacean toxicity, K_{ow}, solubility and ECOSAR (software used to estimate the aquatic toxicity of industrial chemicals. These were compiled into the PEIAR (Pharmaceuticals in the Environment, Information for Assessing Risk) database (CHBR, 2009). A preliminary assessment indicated that anti-infective, cardiovascular and central nervous system (analgesic, anti-inflammatory and psychotherapeutic) pharmaceuticals had the highest risks.

Kostich and Lazorchak (2008) used a simpler approach, prioritising pharmaceuticals using marketing data and predicted concentrations of likely activity in wastewater to evaluate the risk to aquatic organisms using a PEC. This approach was extended by comparison with regulatory data (Kostich et al., 2010). A study of 12 compounds used local sales data and wastewater production rates to give local PECs which could be up to 10 times higher than the national average PECs. Predicted concentrations were also compared to published measured concentrations.

5.3 RECENT SURVEYS OF URBAN AND INDUSTRIAL CONTAMINANTS IN THE AQUEOUS ENVIRONMENT

5.3.1 Leipzig and Halle, Germany

The anthropogenic impacts on the urban surface water and groundwater in large cities, was first demonstrated for Halle/Saale and Leipzig, Germany by Strauch et al. (2008). Indicator substances were selected related to human activities in urban areas: these were the pharmaceutical carbamazepine, the polycylic musk compounds galaxolide and tonalide, the lifestyle product caffeine, and industrial chemicals such as bisphenol A and NP.

River water was sampled along the flow path of the rivers Saale and Weisse Elster through the city of Halle/Saale, the rivers Luppe and Weisse Elster, and through the city of Leipzig. Samples were also collected from the effluent of the local waste water treatment plants. Groundwater samples from Quaternary plain aquifers along the rivers and from different urban locations were collected at the same time. The indicators were analysed and assessed according to their sources, concentration and distribution patterns.

LEIPZIG

The behaviour of organic micropollutants was studied in an area in the western part of Leipzig (Musolff et al., 2009). The urban area is drained by a combined wastewater and storm water sewer system which takes water to the municipal treatment plant and discharges to a river outside of the study area. Other STWs discharge to the Weisse Elster River in the south of the study area. The city is underlain by a Quaternary shallow sand and gravel aquifer.

Micropollutants were present in almost all samples (Figure 5.3) with only the polycyclic musks being correlated with each other. The loading of micropollutants in surface water varied with temperature with removal of caffeine and polycyclic musks in warmer summer months and an increase in caffeine, and 4-NP during cooler, wetter months. In groundwater the patterns were complex both spatially and temporally.

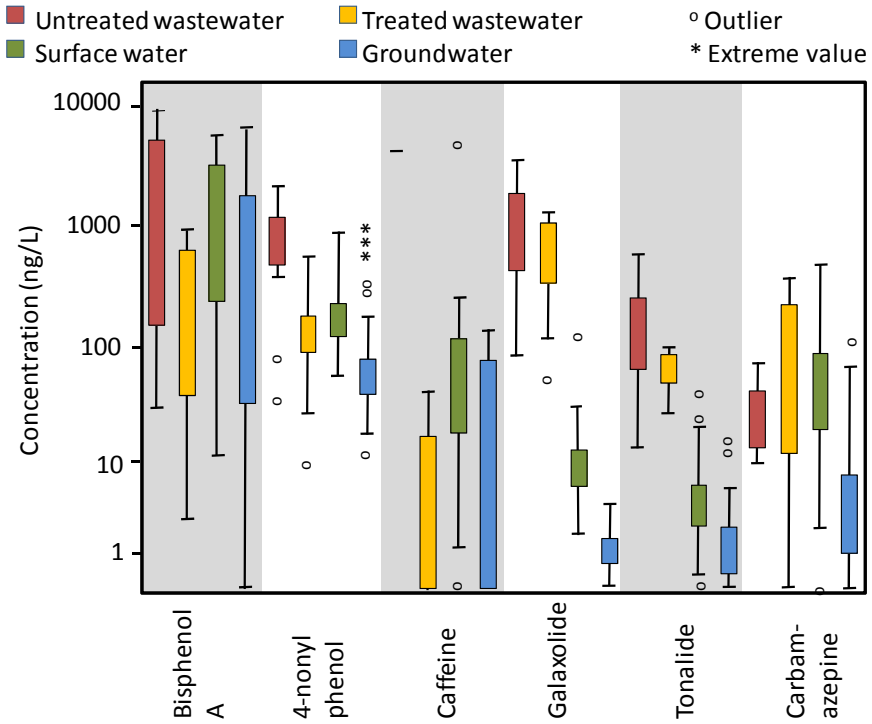

Figure 5.3 Box plots of micropollutant concentrations in water samples from Leipzig (from Musolff et al., 2009).

HALLE

A similar study was conducted beneath the city of Halle (Osenbrück et al., 2007). The city is underlain by a series of Quaternary shallow sand and gravel aquifers in the Saale River floodplain. The confluence of the Weisse Elster river (35 km below Leipzig) and the Saale River is south of the city.

High concentrations of pollutants enter groundwater when hydraulic conditions allow the infiltration of river water. Sewer exfiltration and storm water runoff are also sources. Carbamazepine and galaxolide were shown to be sorbed around sewer exfiltration points due to higher organic loading. Carbamazepine was affected by attenuation processes and galaxolide was found to be a much better marker of urban groundwater (Table 5.6).

Reinstorf et al. (2009) modelled the flux of micropollutants from surface water to groundwater during surface water flooding events and were able to simulate the pulse. Concentrations of bisphenol A were the most attenuated. The attenuation of carbamazepine could be modelled. Mass balances showed increases of all micropollutants in surface water below the city compared to above in the order of 100 kg/year, except for bisphenol A (11 kg/year) and galaxolide (272 kg/year).

Table 5.6 Concentration in µg/L for organic micropollutants in Halle (from Osenbrück et al., 2007)

	STW effluent	**Surface water**	**Quaternary aquifers**
Carbamazepine	0.210	0.096	<0.002 – 0.051
Galaxolide	1.81	0.040	0.003-0.019
Bisphenol A	0.129	0.089	<0.001 – 1.136

5.3.2 Berlin, Germany

A series of studies in Berlin are summarised by Heberer (2002). The shallow, slow-moving Spree and Havel Rivers cross the urban area where there are six STWs discharging to surface water. In the winter all of the effluent is discharge to the rivers, but during the summer, when the rivers are used for leisure activities, some effluent is discharged into the Teltowkanal which crosses the city. Concentrations of pharmaceutical residues measured in this canal are shown in Figure 5.4.

Concern has also been reported about water derived from bank filtration which is used for drinking water supply. A number of pharmaceuticals and pharmaceutical metabolites were found at concentrations up to the µg/L-level in groundwater samples taken from supplied water from a drinking water treatment plant (Heberer et al., 1997). These included clofibric acid, diclofenac, fenofibrate, genistic acid, gemfibrozil, ibuprofen, ketoprofen, phenazone, primidone, propyphenazone and salicylic acid. Additionally, two metabolites were detected: N-methylphenacetin probably originating from phenacetin; and a derivative of clofibric acid.

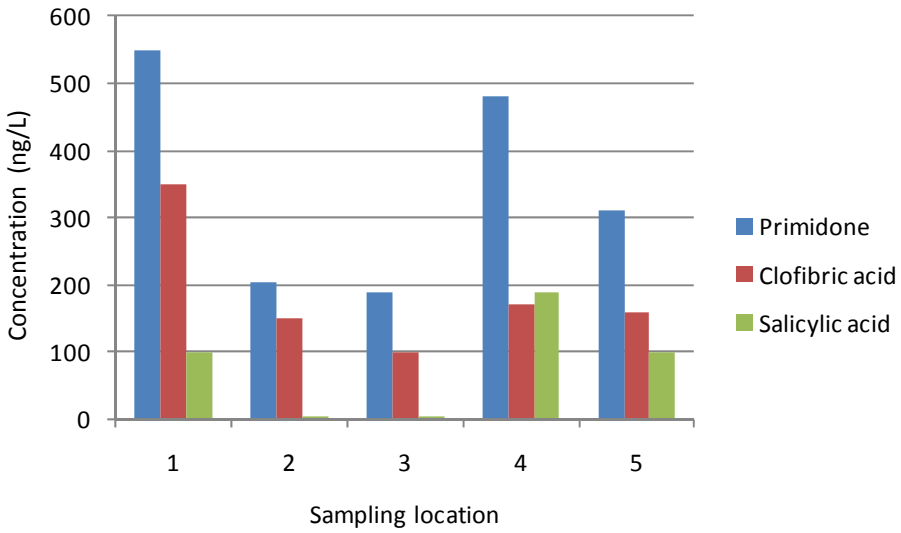

Figure 5.4 Pharmaceuticals in the Teltowkanal, Berlin in 1999 (from Heberer, 2002)

5.3.3 Flanders and the Netherlands

A suite of organic micropollutants was targeted in a study of waters in Flanders and the Netherlands, based on human health risk, possible occurrence of high concentrations of the pollutant in drinking water due to high usage or persistence, customer risk perception or low removal efficiency in water treatment (Verliefde et al., 2007). Results for drinking water in the Netherlands showed the main contaminants to be industrial chemicals such as phthalates and alkyl phenols (Figure 5.5); for these chemicals concentrations were generally orders of magnitude less than surface waters. Pharmaceuticals were less attenuated.

The effectiveness of nanofiltration to remove these compounds from drinking water was related to their K_{ow}, molecular size and molecular charge, suggesting that small hydrophobic molecules, such as NP, atrazine and simazine from the examples in Figure 5.4,, would be the least effectively removed.

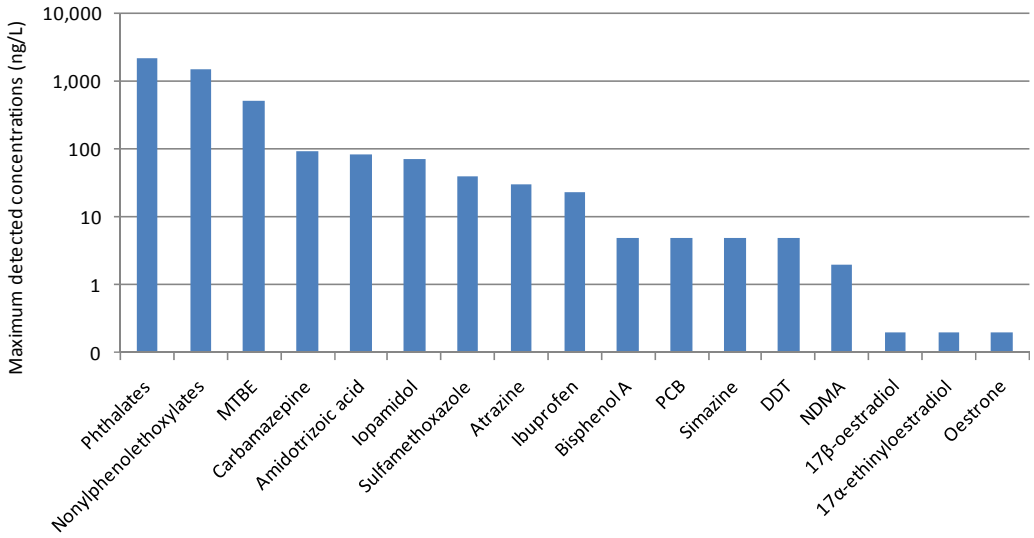

Figure 5.5 Organic micropollutants in drinking water in the Netherlands. Note log scale and plotting of below detection limit values as 0.5 of the detection limit for MTBE, Bisphenol A, PCB, DDT, simazine, hormones (from Verliefde et al., 2007)

5.3.4 Somes River, Romania

Samples collected from site downstream of sewage treatment works serving Cluj-Napoca and Gherla on the Somes River in Romania (Moldovan, 2006) showed a range of pharmaceutical and industrial organic micropollutants, classed as neutral and moderately acidic (Figure 5.6). Caffeine was detected at the highest concentrations, but two metabolites of the anti-inflammatory metamizole (4-acetyl aminophenazone and 4-formamyl aminophenazone) were also prominent. The compounds p-chlorophenyl sulfone and N,N-bis (3,3-dimethyl-2-oxetanyl)-3,3-dimethyl-2-oxetanamine are industrial precursors.

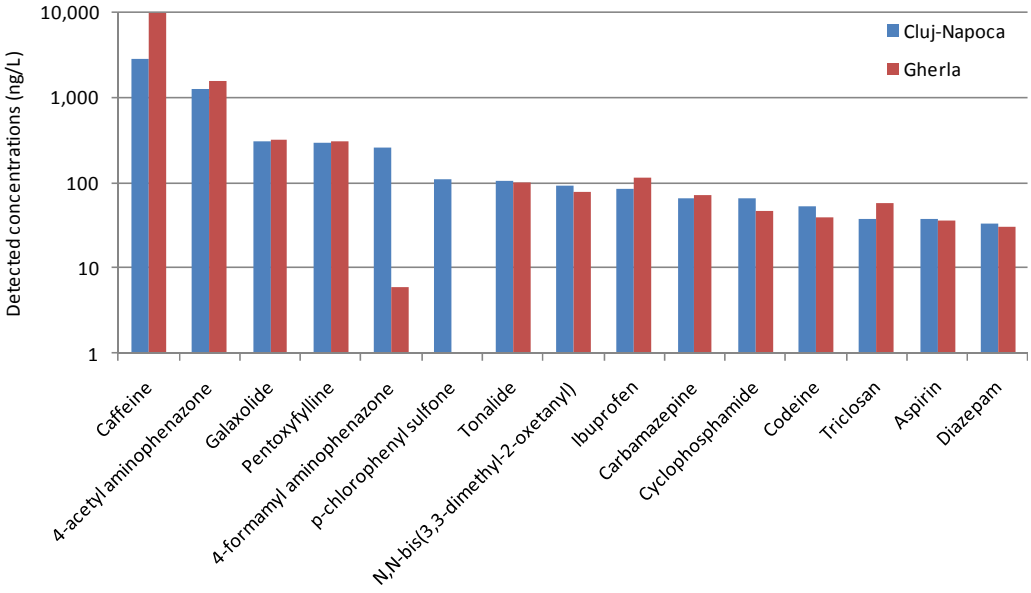

Figure 5.6 Organic micropollutants in the Somes River, Romania. Note log scale (from Moldovan, 2006)

5.3.5 US national survey for organic wastewater contaminants

Groundwater samples were collected and analysed from a network of 47 sites (Barnes et al., 2008). Site selection focussed on areas suspected to be susceptible to contamination from animal or human waste. Sixty-five compounds were targeted, including 19 antibiotics, 16 other drugs and selected metabolites and hormones.

Contaminants were detected at 81% of sites with 35 of the 65 compounds being detected at least once. The most frequently detected compounds were DEET, bisphenol A (plasticiser), tri(2-chloroethyl) phosphate (fire retardant), sulfamethoxazole (antibiotic) and 4-octyl-phenol monoethoxylate (detergent metabolite) (Figure 5.7). DEET and 4-nonylphenoldiethoxylate were detected at above 5 µg/L with a further 14 compounds being detected at above 0.5 µg/L.

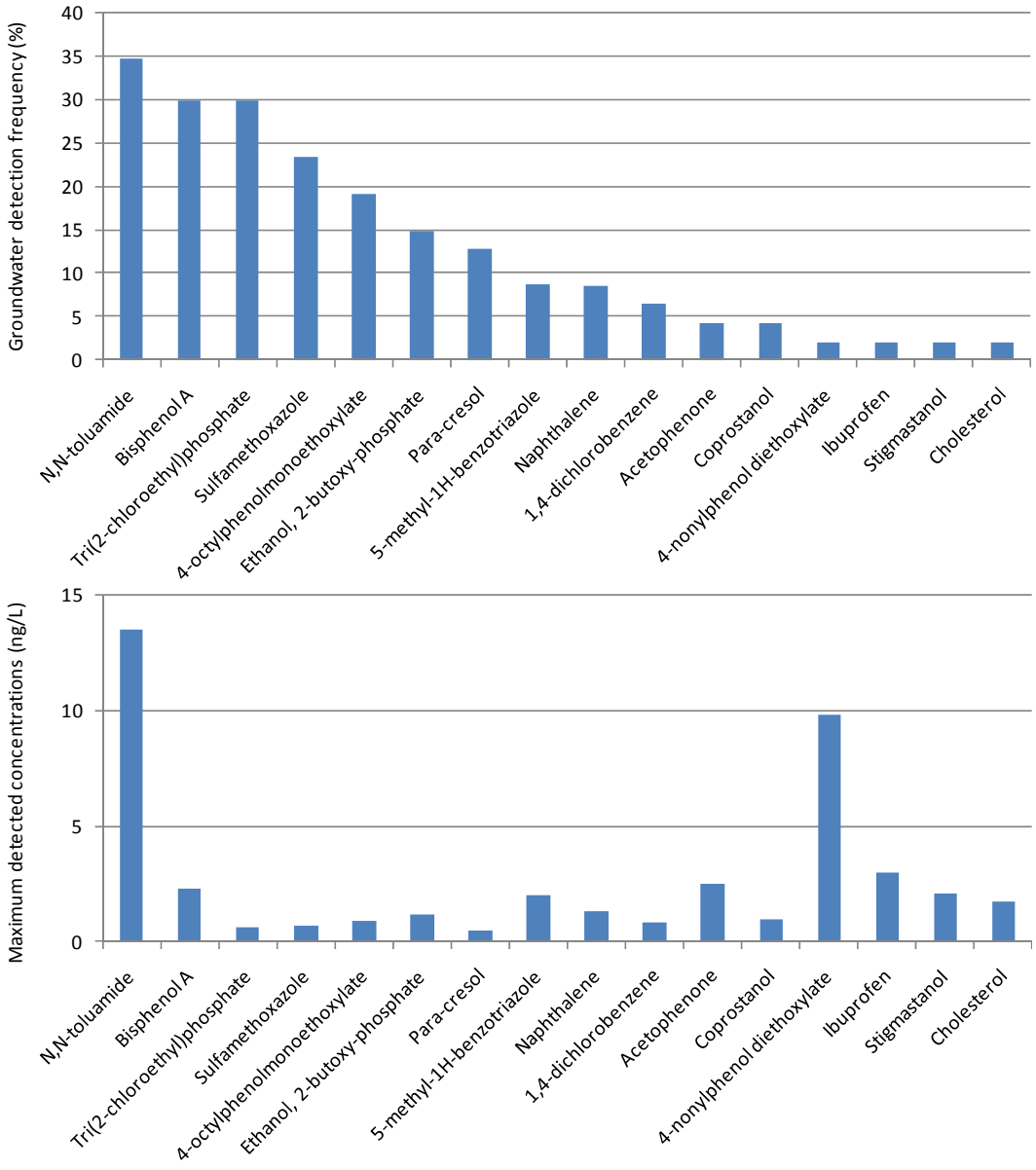

Figure 5.7 Detection frequencies and maximum concentrations for organic pollutants in groundwater in a USA national survey where detected at >0.5 µg/L (from Barnes et al., 2008).

5.3.6 US drinking water surveys for pharmaceuticals and endocrine disrupting compounds

Drinking water was screened for a diverse group of pharmaceuticals, potential endocrine disrupting compounds (EDCs) and other unregulated organic contaminants (Benotti et al., 2008). Source water, finished drinking water and distribution system water from 19 US water utilities, supplying more than 28 million people, was analysed for 51 compounds between 2006 and 2007. The 11 most frequently detected compounds were atenolol, atrazine, carbamazepine, oestrone, gemfibrozil, meprobamate, naproxen, phenytoin, sulfamethoxazole, TCEP and trimethoprim. Median concentrations of these compounds were less than 10 ng/L, except for sulfamethoxazole in source water (12 ng/L), TCEP in source water (120 ng/L), and atrazine in source, finished, and distribution system water (32, 49, and 49 ng/L). Atrazine was detected in source waters far removed from agricultural application where wastewater was the only known source of organic contaminants.

The occurrence of compounds in finished drinking water was controlled by the type of chemical oxidation (ozone or chlorine) used at each plant. Atenolol, atrazine, DEET, oestrone, meprobamate, and trimethoprim can serve as indicator compounds representing potential contamination from other pharmaceuticals and EDCs and can gauge the efficacy of treatment processes.

Guo and Krasner (2009) assessed the wastewater impact on US drinking water sources using three compounds – primidone, carbamazepine, and caffeine – as indicators, and determination of precursor concentrations for the disinfection by-product *N*-nitrosodimethylamine (NDMA) using a formation potential (NDMAFP) test. Samples were collected from rivers impacted by wastewater treatment plant discharges, at drinking water treatment plant intakes upstream or downstream from these discharges, and from STW effluents. The levels [10th percentile − maximum (median)] of primidone, carbamazepine, caffeine, and NDMAFP were 2-95 (7) ng/L, 2-207 (18) ng/L, 7-687 (78) ng/L, and 12-321 (35) ng/L, respectively. The highest concentrations of primidone, carbamazepine, and NDMA precursors were from one of the waste water treatment plant effluents, whereas the highest concentration of caffeine was detected in a river heavily impacted by treated wastewater discharges. The lowest concentrations of the three PPCPs (Pharmaceuticals and Personal Care Products as Pollutants) were from a drinking water treatment plant influent upstream of a metropolitan urban area with minimum wastewater impact. The results show that measurement of the two pharmaceuticals and NDMAFP tests can be used to evaluate wastewater impact in different watersheds, whereas caffeine results were more variable.

5.3.7 Llobregat river basin, Barcelona, Spain

The Llobregat River drains a densely-inhabited area in the northeast of Catalonia. It receives urban wastewater, industrial wastewater and runoff from agricultural areas. The river is used for drinking water supply. Wastewater, surface water and drinking water were analysed for several suites of compounds: pharmaceuticals, oestrogens, progestogens and pesticides (Kuster et al., 2008). Temporal and spatial distributions were very variable and average concentrations are shown in Figure 5.8.

All pharmaceuticals analysed (acetyl-salicylic acid, atenolol, clofibric acid, diclofenac, ibuprofen and triclosan) were detected at least once, apart from atenolol. The highest concentrations were found in sewage effluent, with surface water at lower concentrations and none detected in drinking water. Target oestrogens included both natural and synthetic compounds. Only three were detected with oestriol only detected once (in a drinking water sample). Progestone concentrations were very low.

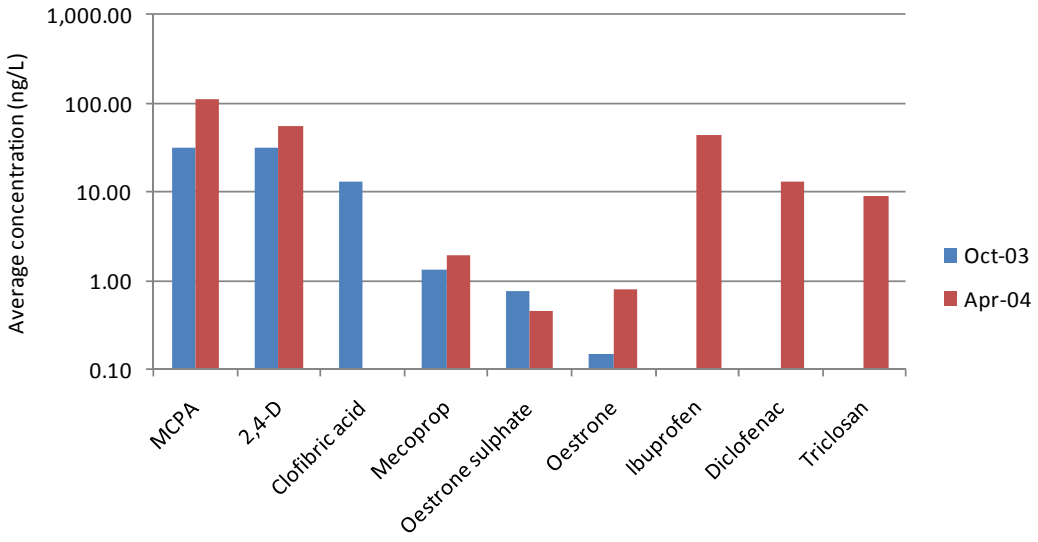

Figure 5.8 Average concentrations of organic micropollutants detected in surface water Llobregat river basin. Note log scale (from Kuster et al., 2008)

MCPA and 2,4-D were the most ubiquitous and abundant compounds with MCPP and propanol also detected. None were detected in drinking water at >0.1 µg/L.

5.3.8 Danish National Monitoring Programme

Juhler and Felding (2003) present results of analyses of 7671 groundwater samples collected in the period 1993 to 2001 for the Danish National Groundwater Monitoring Program. Data originate from monitoring areas and are supplemented with data from the waterworks' control of nearly 6000 water supply wells. In addition to pesticides, a series of other organic compounds are included. These are grouped according to chemical properties: aromatic hydrocarbons, chlorophenols, detergents, halogenated aliphatic hydrocarbons, ethers (MTBE), phenols, and phthalates. The most frequently found compounds were toluene (18.7%), phenol (14.6%), xylene (10.9), trichloromethane (9.5%), and benzene (in 8.8% of the screens monitored). The five compounds most frequently found at a concentration above the maximum residue limits (MRL) for drinking water were: dibuthylphthalate (28%), phenol (14%), 2,4-dichlorophenol (10%), trichloromethane (10%), pentachlorophenol (7% of findings exceeding the MRL for drinking water).

5.3.9 Helena valley, Montana

The city of Helena obtains its groundwater supply from a complex series of Tertiary and Quaternary valley fill deposits. Thirty eight wells were analysed for 28 organic micropollutants, of which 22 were detected (Miller and Meek, 2006). The most frequently detected compounds were sulfamethoxazole (antibiotic), atrazine (pesticide), and the pharmaceuticals carbamazepine, dilantin and diclofenac (Figure 5.9). Maximum concentrations over 400 ng/L were observed for sulfamethoxazole, bisphenol A and carbamazepine. Concentrations of atrazine were correlated with chloride and TDS and were ascribed to input of domestic wastewater, but other pollutants were not clearly related.

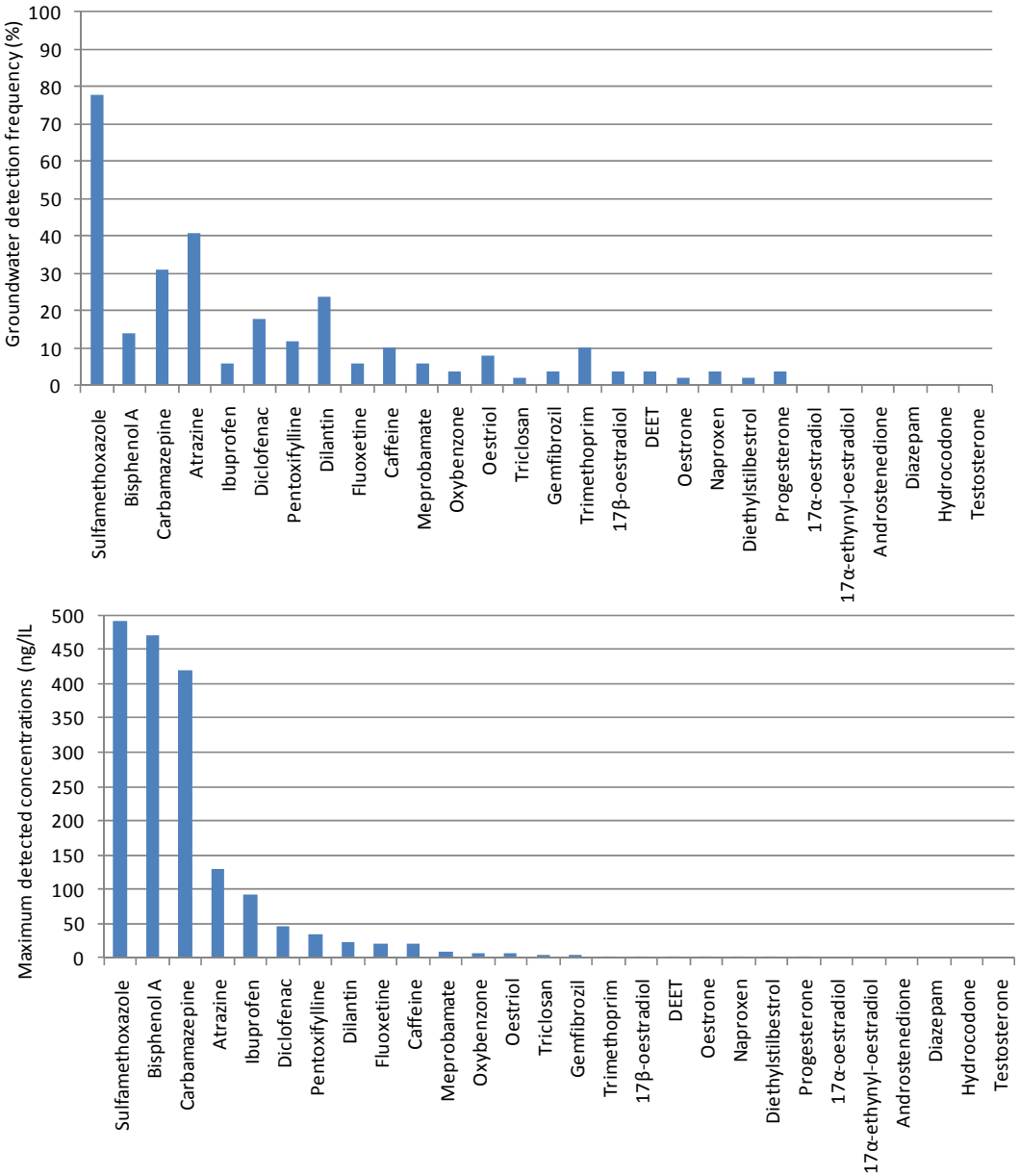

Figure 5.9 Detection frequencies and maximum concentrations for 28 organic pollutants in Helena Valley groundwater (from Miller and Meek, 2006).

5.3.10 European surface water study

Loos et al. (2009) report an EU-wide reconnaissance of the occurrence of polar organic persistent pollutants in European river waters. Samples from over 100 rivers from 27 European countries were analysed for 35 compounds, comprising pharmaceuticals, pesticides, PFOS, PFOA, benzotriazoles, hormones and endocrine disrupters. The compounds detected most frequently and at the highest concentrations were benzotriazole, caffeine, carbamazepine, tolyltriazole and nonyl-phenoxy acetic acid (NPE1C). Only about 10% of the river water samples analysed could be classified as "very clean" in terms of chemical pollution.

5.3.11 European groundwater study

Loos et al. (2010) report a pan-European reconnaissance for polar persistent organic pollutants. In total, 164 individual groundwater samples from 23 European countries (Figure 5.10) were collected and analysed (among others) for 59 selected organic compounds, comprising pharmaceuticals, antibiotics, pesticides (and their metabolites), perfluorinated acids (PFAs), benzotriazoles, hormones, alkylphenolics (endocrine disrupters), caffeine, DEET, and triclosan.

Figure 5.11 shows the frequency of detection for compounds present in 20% or more of samples and Figure 5.12 shows the maximum concentrations detected. The most relevant compounds in terms of both frequency of detection and maximum concentrations detected were DEET, caffeine, PFOA, atrazine, desethylatrazine, 1H-benzotriazole methylbenzotriazole, desethylterbuthylazine, PFOS, simazine, carbamazepine, nonyl-phenoxy acetic acid (NPE1C), bisphenol A, perfluorohexane sulfonate (PFHxS), terbuthylazine, bentazone, propazine, perfluoroheptanoic acid (PFHpA), 2,4-dinitrophenol, diuron and sulfamethoxazole.

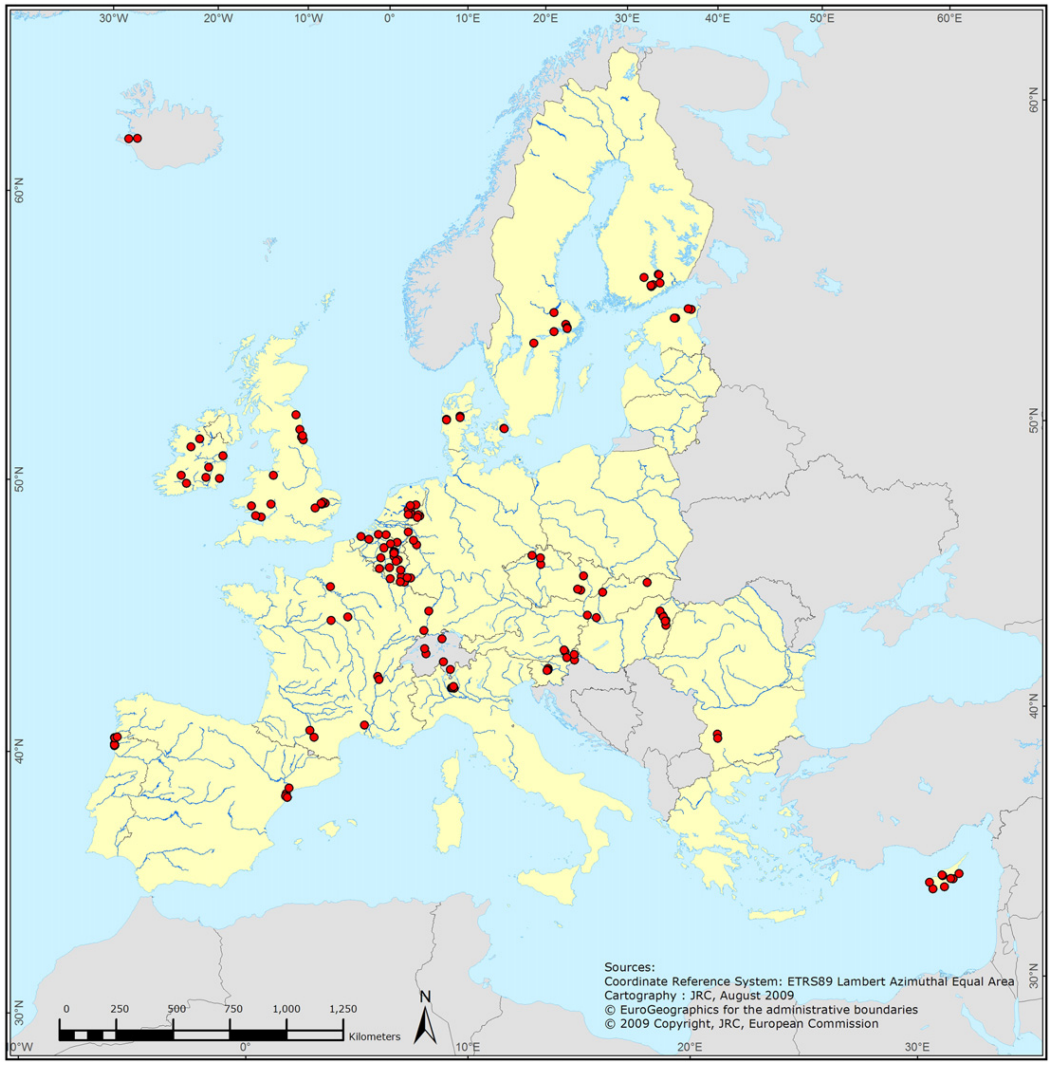

Figure 5.10 Map of European groundwater monitoring sites (from Loos et al., 2010)

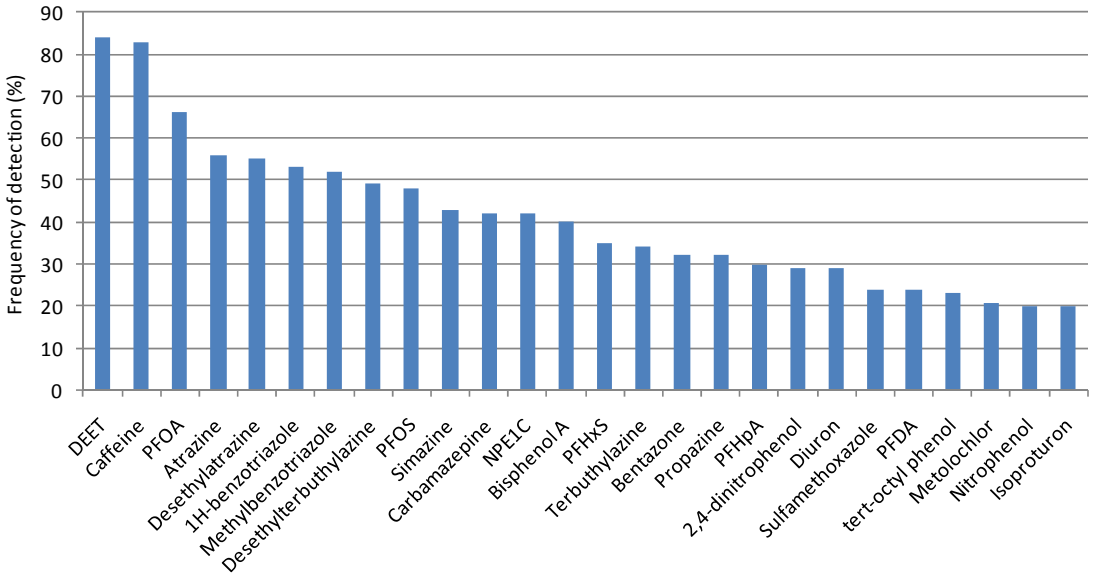

Figure 5.11 Frequency of detection of polar persistent pollutants in European groundwater (from Loos et al., 2010)

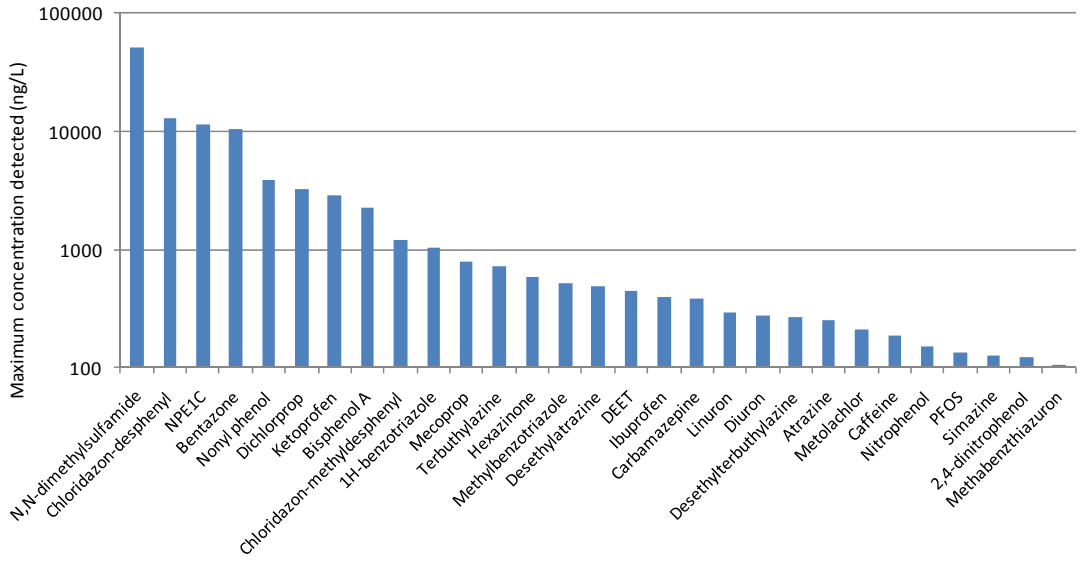

Figure 5.12 Maximum detected concentrations of polar persistent pollutants in European groundwater (from Loos et al., 2010)

The number of times compounds were detected above the European groundwater quality standard for pesticides of 0.1 mg/L is shown in Figure 5.13. However, only 1.7% of all single analytical measurements (in total 8000) were above this threshold value of 0.1 mg/L; 7.3% were > than 10 ng/L. The numbers of detections exceeding this lower limit are shown in Figure 5.14.

Other compounds detected were PFBS, PFNA, diazinon, MCPA, chlortoluron, diclofenac, alachlor, 2,4-D, 2,4,5-T, triclosan and oestrone. Not detected were naproxen, propanil, fenarimol, bezafibrate, gemfibrozil, PFHxA, PFUnA, metoxuron, carbaryl, and molinate.

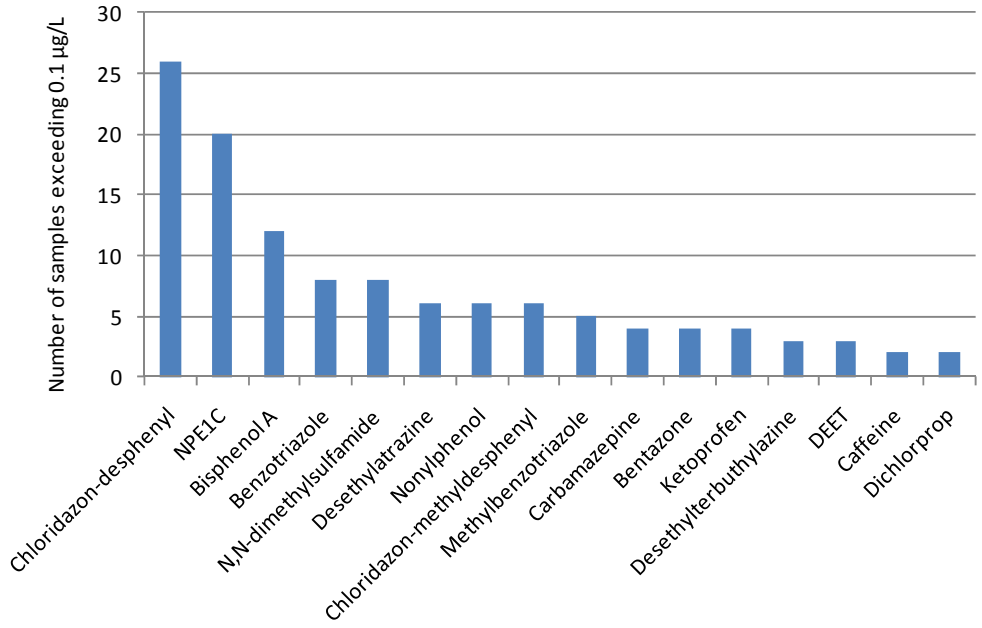

Figure 5.13 Numbers of detections of polar persistent pollutants in European groundwater exceeding the 0.1µg/L pesticide limit (from Loos et al. 2010)

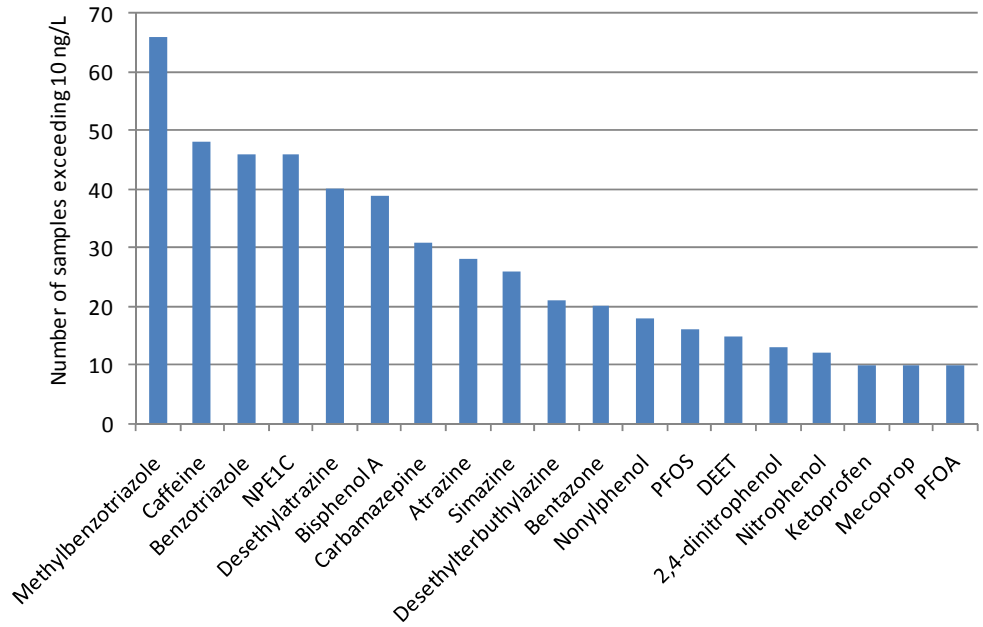

Figure 5.14 Numbers of detections of polar persistent pollutants in European groundwater exceeding a concentration of 10 ng/L (from Loos et al. 2010)

5.3.12 Perfluorinated hydrocarbons in groundwaters of England and Wales

The Environment Agency carried out an investigation into the occurrence of perfluorinated compounds in groundwaters of England and Wales in 2006 (Environment Agency, 2007). Perfluorinated compounds were detected in 26% (57 of 219) of groundwater monitoring sites, with detectable concentrations of PFOS found at about 14% of sites (Environment Agency, 2008a). The locations of the 219 sampling points and the maximum total of detected perfluorinated compounds (PFXmax) at each site are show in Figure 5.15. The distribution of perfluorinated compounds in different aquifers is tabulated in Table 5.7, which also gives summary data for total perfluorinated compounds in those different aquifers.

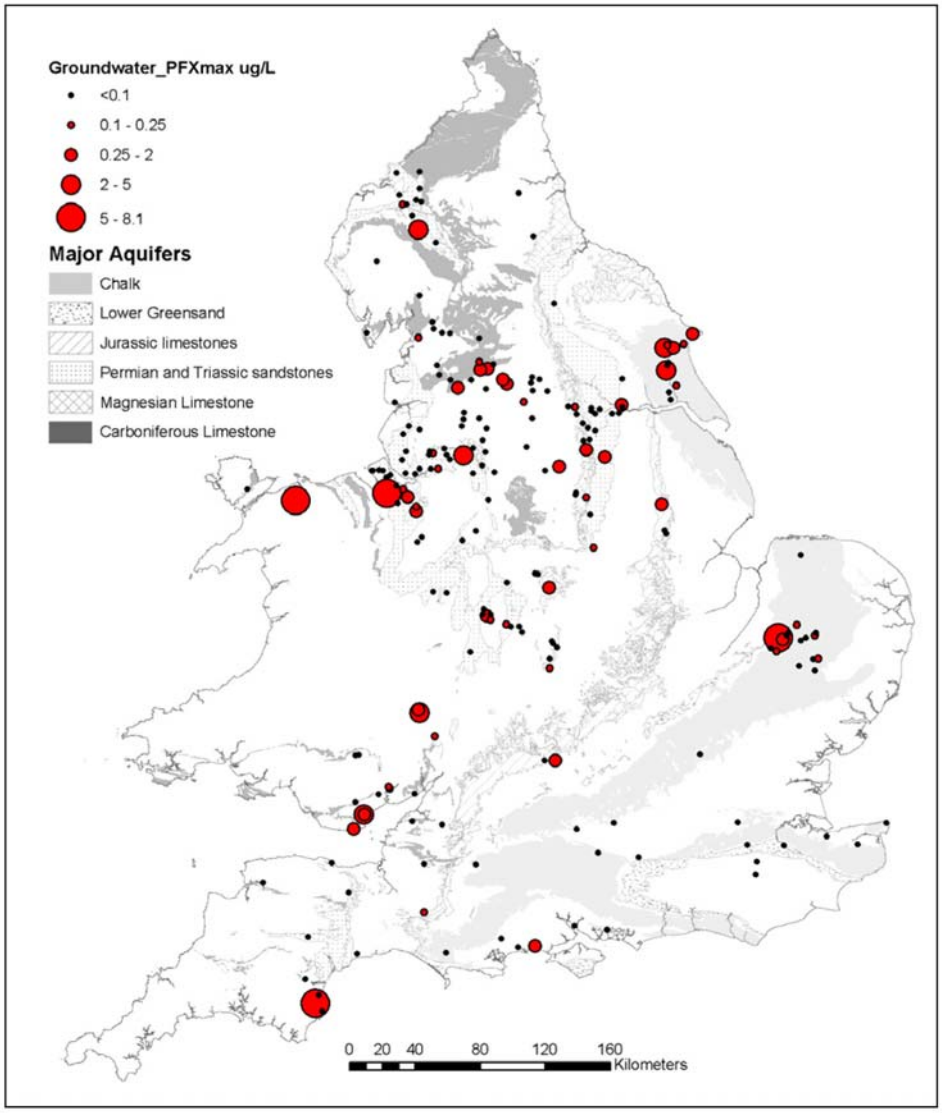

Figure 5.15 Distribution of groundwater monitoring for perfluorinated chemicals, showing maximum total of detected perfluorinated compounds (PFXmax) per site (Environment Agency, 2008a)

Table 5.7 Perfluorinated compounds in groundwater by aquifer type, PFX is total perfluorinated compounds (Environment Agency, 2008a)

Aquifer	Number of sites monitored	Sites with detected PFX		PFX concentration (µg/L) excluding non-detections			
		Number of sites	% of sites	Min	Mean	Median	Max
Drift	6	1	16.7	0.20	0.20	0.20	0.20
Minor	75	18	24.0	0.12	1.18	0.39	6.56
Chalk	36	13	36.1	0.10	1.35	0.22	8.10
Lower Greensand	3		0.0				
Jurassic limestone	3	2	66.7	0.22	1.04	1.04	1.85
Permo-Triassic	72	14	19.4	0.10	1.46	0.31	7.47

This work was extended in 2008 when the concentrations of perfluorinated hydrocarbons were compared to land use, groundwater vulnerability, distance to landfill, thickness of superficial deposits and concentrations of other pollutants in groundwater (Environment Agency, 2008a). The average maximum detected concentration of chlorinated solvents, petroleum and PAH compounds appeared to be higher at locations where perfluorochemical compounds were detected, but no reasons for this apparent correlation were reported. As would be expected, perfluorinated hydrocarbons were less commonly detected at sites where the superficial deposits were over 5 m thick. No clear relationship was identified between the presence of perfluorinated hydrocarbons and the other parameters considered.

5.3.13 Pharmaceuticals in UK urban groundwater from sewer exfiltration

As part of a study investigating the downstream dilution patterns of PPCPs in an urban stream with a STW outfall, Ellis (2006) reviewed the occurrence of PPCPs in UK urban groundwater. They found very few studies investigating pharmaceuticals. They describe the distribution below a main trench sewer in north east London. Previous studies had identified exfiltration (Ellis et al., 2002) to groundwater in river terrace gravels. They saw some evidence of contamination due to exfiltration adjacent to and below the sewer, peaking at a depth of about 0.5 m below the pipe (Figure 5.16).

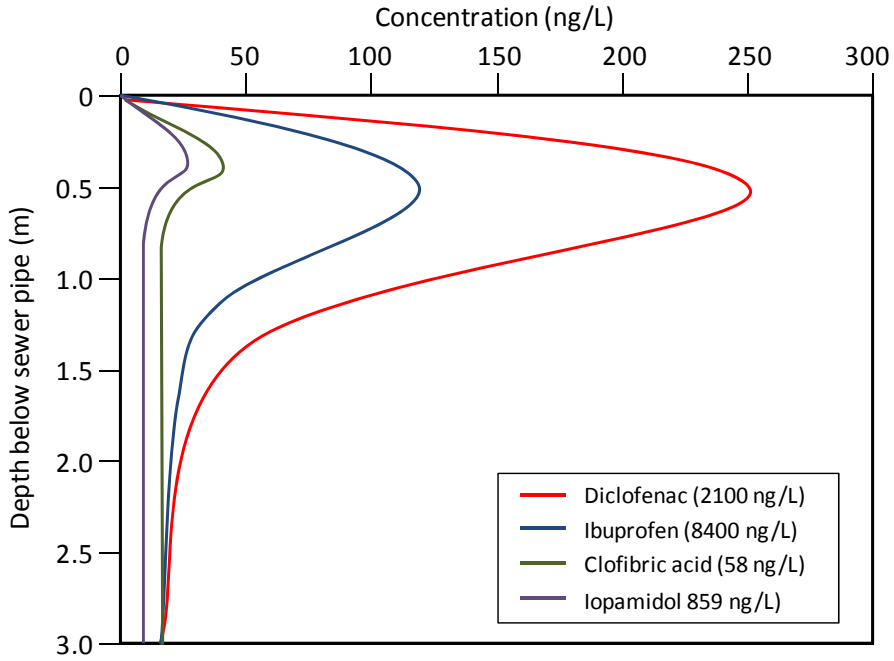

Figure 5.16 Distribution of pharmaceuticals in groundwater with depth below sewer. Concentrations given in the key are average values recorded in raw sewage effluent within the overlying trunk sewer (after Ellis et al., 2006)

5.3.14 England and Wales survey of pharmaceuticals

The Environment Agency carried out a screening exercise and targeted monitoring programme at five STW sites in eastern England in 2003 (Hilton et al., 2003). Ten compounds were detected in sewage works' final effluent samples, including the metabolite acetyl-sulfamethoxazole, and, except tamoxifen and sulfamethoxazole, in receiving waters (Table 5.8). Sulfamethoxazole was irregularly detected, and paracetamol and lofepramine were not detected in any of the samples collected.

Table 5.8 Pharmaceuticals detected in STW effluents and receiving waters in eastern England (Hilton et al., 2003).

	Effluent			Receiving water		
	Max (µg/L)	Mean (µg/L)	Freq (%)	Max (µg/L)	Mean (µg/L)	Freq (%)
Ibuprofen	27.2	4.2	84	5	1.1	69
Diclofenac	2.3	0.6	86	0.56	0.15	47
Propanolol	0.28	0.09	100	0.21	0.04	87
Mefenamic acid	1.44	0.27	81	0.37	0.09	60
Erythromycin	1.84	0.11	44	1.02	0.16	38
Dextropropoxyphene	0.68	0.15	53	0.58	0.20	74
Trimethoprim	1.29	0.13	65	0.042	0.012	38
Acetyl-sulfamethoxazole	2.23	0.16	33	0.24	0.70	33

5.3.15 England and Wales Water industry groundwater surveys

A 2002 study analysed samples from 21 utility borehole sites in the Chalk of the South Downs. No MTBE or BTEX compounds detected with a detection limit of 10 µg/L. Bromoform detected at up to 1.6 µg/L in 12 sites. Organophosphorus flame retardants have been reported in a few sources in this area (Jones and Robins, 1999).

5.3.16 Hormones and APEs in Cape Cod groundwater from residential septic systems

Swartz et al. (2006) found a range of oestrogenic hormones, NP and NP ethoxylates (NPEO) and caffeine and its paraxanthine metabolite, in a residential septic system and in downgradient groundwater (Figure 5.17). These were compared to traditional indicators of wastewater impact, namely the fluorescent whitening agents 4,4-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino]stilbene (DAS) and 4,4-bis(2-sulphostyryl)biphenyl (DSBP). These authors suggested that caffeine and paraxanthine could have utility as effective indicators of oestrogenic wastewater contamination.

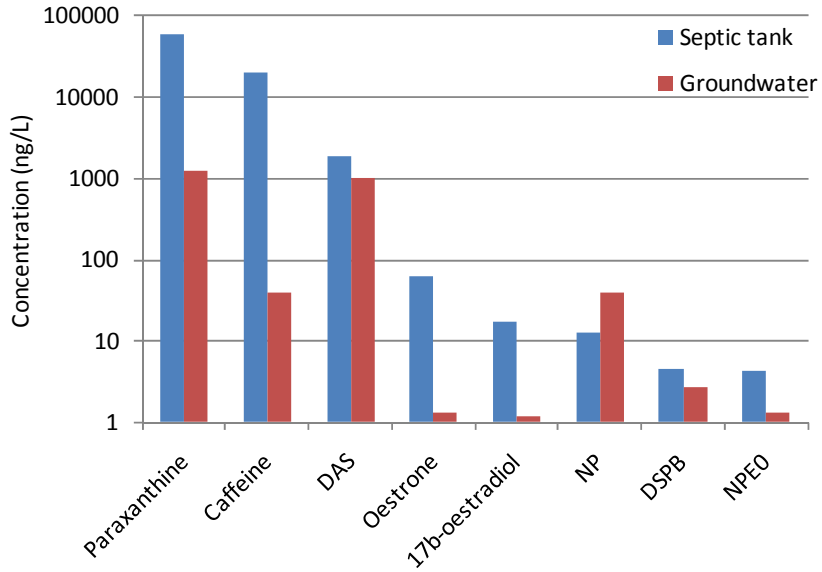

Figure 5.17 Microorganics in septage and groundwater, Cape Cod (Swartz et al. 2006)

5.3.17 Summary of other studies of organic contaminants in UK surface water

A possible indication of future groundwater contamination may be given by current surface water issues. A summary of published work related to detection of organic micropollutants in UK surface waters is shown in Table 5.9. This demonstrates that a wide range of pharmaceuticals as well as industrial compounds and pesticides have been detected. Most of these studies have been associated with the impact of STWs. It is well established that endocrine disruption in UK rivers is likely to be associated with sewage effluents, and due primarily to natural and synthetic oestrogens (Johnson et al., 2007b).

Mason et al. (1999) showed that point source contamination of surface water from pesticides was more significant than previously recognised.

It has long been recognised that the pollutant loading to surface waters is both temporally and spatially variable (Haith, 1985; Vega et al., 1998) although the risk and uncertainty can be modelled (Persson and Destouni, 2009).

5.3.18 Negative results

Watkinson et al. (2009) found no antibiotics above the detection limit in drinking water in a study in South-East Queensland, Australia, despite detecting them frequently in STW effluent and surface water. Liu et al. (2010) found no evidence of phyto-oestrogens in drinking water despite their detection in STW effluent and surface water. This can be explained by processes such as dilution and degradation, or removal by drinking water treatments.

5.4 CONCLUSIONS FOR URBAN AND INDUSTRIAL POLLUTANTS

The following conclusions can be drawn:

- a range of organic micropollutants from urban and industrial sources have been detected in groundwater and surface water
- the sorption behaviour of these compounds can be estimated or predicted from existing data but there is very limited information on persistence in the environment. The majority of studies have been directed at persistence in water treatment
- a range of organic micropollutants from urban and industrial settings have been detected in groundwater and surface water. Commonly detected compounds include: bisphenol A, carbamazepine (Box 4), galaxolide, ibuprofen, iopamidol, phthalates, phenyl ethoxylates, and sulfamethoxazole
- other significant detections have been for flame retardants, DEET, and MTBE.
- pesticides are considered separately in this report (Chapter 4) but many of these studies show the continued persistence of the triazine pesticides
- some studies found that commonly used compounds that are observed in STW effluent and/or surface waters were not present at detectable concentrations in drinking water
- the broadscan studies demonstrate that in any setting a small number of contaminants may be used to characterise the contaminant loading. The German studies show how a selected suite of compounds may be used to assess the migration pathways in urban areas.

Table 5.9 Organic micropollutants detected in UK surface water (LOD = limit of detection; STW = sewage treatment works)

Site	Source	Compounds detected	Reference
England and Wales	Contaminated & control sites	• polychlorinated dibenzo-p-dioxins and dibenzofurans detected in all sediments sampled	Rose et al. (1994)
Thames in south west London and rural river	STW	• ibuprofen, paracetamol and salbutamol quantified in all samples. • mefenamic acid (NSAID) in 70% of samples. • propanolol (β-blocker) <LOD	Bound and Voulvoulis (2006)
Tyne Estuary	STW	• clotrimazole, dextropropoxyphene, erythromycin, ibuprofen, propanalol, tamoxifen, trimethoprim quantified • clofibric acid, diclofenac, mefenamic acid, paracetamol <LOD	Roberts and Thomas (2006)
Tees, Mersey, Aire river and estuary	Industry?	• APEs detected above threshold	Blackburn et al. (1999)
Taff & Ely, South Wales	STW	• trimethoprim, erythromycin, amoxicillin, paracetamol, tramadol, codeine, naproxen, ibuprofen, diclofenac, carbamazepine, gabapentin most frequently detected • 41 others detected including illicit drugs	Kasprzyk-Hordern et al. (2008)
Inland streams	STW	• ibuprofen, mefamic acid, diclofenac, propanalol, dextropropoxyphene, erythromycin, trimethoprim, acetyl-sulfamethazole detected • paracetamol, lofepramine not detected	Ashton et al. (2004)
Ouse, west Sussex	STW	• bisphenol A, oestrone, 17β-estodiol consistently detected • propanalol, sulfamethoxazole, carbamazepine, indomethacine, diclofenac variably detected • mebeverine, thioridazine, tamoxifen, meclofenanic acid <LOD	Zhang et al. (2008)
UK		• diuron	Alvarez et al. (2004)
Stream, Tunbridge Wells	Storm event, Fruit growing	• simazine, diuron, NP, endosulfan sulphate, pendimethalin	Thomas et al. (2001)
Thames, 1988-1997		• atrazine, simazine, lindane	Power et al. (1999)

Box 4 Carbamazepine

Carbamazepine is an anticonvulsant and mood stabilizing drug used primarily in the treatment of epilepsy and bipolar disorder, as well as trigeminal neuralgia. It is also used off-label for a variety of indications, including attention-deficit hyperactivity disorder, schizophrenia, phantom limb syndrome, paroxysmal extreme pain disorder and post-traumatic stress disorder. It is metabolised in the liver initially to an epoxide derivative and about 2-3% of the dose is excreted unchanged in urine. It has a half life in the body of 25-65 hours .

Carbamazepine is a dibenzazepine, formally known as 5*H*-dibenzo[*b*,*f*]azepine-5-carboxamide (Figure 5.18). An impurity, 10,11-dihydrocarbamazepine, can be present at up to 1%.

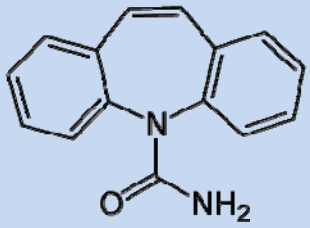

Figure 5.18 Structure of carbamazepine

Carbamazepine can enter groundwater by a number of routes including: direct discharge from wastewater treatment plants, exfiltration from sewers or septic systems, infiltration of storm run-off or river water, land spreading of human or animal waste, landfills and artificial recharge of treated wastewater (Environment Agency, 2010).

Carbamazepine is persistent in wastewater treatment and in the aquatic environment (Clara et al., 2004). It can be degraded by ozonation, possibly to anthranilic acid and to a series of C2 and C3 organic acids (Andreozzi et al., 2002).

In the study by Loos et al. (2010) carbamazepine was the pharmaceutical compound most frequently detected at 'elevated' concentations in groundwater: it was detected in 42% of the samples, with a maximum concentration of 390 ng/L. Its persistent character is well established, and it has also been proposed as a possible anthropogenic marker in the aquatic environment (Clara et al., 2004). Carbamazepine was one of the substances identified for consideration by the EU under the Water Framework Directive.

6 Veterinary medicines in depth

6.1 POTENTIAL VETERINARY MEDICINE SOURCE TERMS

A wide range of compounds are used as veterinary medicines in the UK (Boxall et al., 2002; Boxall et al., 2003) to treat disease and to protect the health of animals. Dietary enhancing feed additives (growth promoters) are also incorporated into the feed of animals reared for food in order to improve their growth rates. These products must be assessed for their quality, efficacy and safety (to both humans and the environment). Release occurs both directly, e.g. in fish farms, and indirectly via the application of animal manure to land.

Veterinary medicines include substances used to kill or control a range of infections due to microorganisms (antimicrobials), internal and external parasites (ectoparasitides and endectocides) and fungi (antifungals). Other substances used include hormones, anaesthetics, tranquilisers, euthanasia products and anti-inflammatories (Table 6.1). Many of these compounds are also used as pesticides (e.g. cypermethrin and diazinon) and as human medicines (e.g. oxytetracycline).

Table 6.1 Major usage veterinary medicines for the UK and the Netherlands (from Boxall, 2002; 2003a; 2003b). Priority 1in **bold**, possible priority 1 in *italics*

Type	**Applications**	**Examples**
Antimicrobial	Treatment of bacterial diseases	**amoxicillin**, apramycin, *baquiloprim*, *cefhalexin*, *clavulanic acid*, **chlortetracycline**, *clindamycin*, **dihydrostreptomycin**, *enrofloxacin*, *flavomycin*, *florfenicol*, *lincomycin*, *neomycin*, *oxolonic acid*, **oxytetracycline**, *procaine benzyl penicillin procaine penicillin*, **sarafloxacin**, **sulfadiazine**, **tetracycline**, *tiamulin*, *tilmicosin*, *trimethoprim*, **tylosin**.
Ectoparasitides & sheep dip	Control of ectoparasites	*amitraz*, *cypromazin*, **cypermethrin**, *deltamethrin*, **diazinon**, *emamectin benzoate*, *flumethrin*, *phosmet*, *piperonyl butoxide*
Endectocides	Control of endoparasites	*ivermectin*, *fenbendazole*, *levamisole*, *morantel*, *nitroxynil*, pyrantel, *triclabendazole*
Coccidiostats & antiprotozoals	Control of single cell parasites	*amprolium*, *clopidol*, *decoquinate*, *diclazuril*, dimetriazole, narasin, *lasalocid sodium*, *maduramicin*, *nicarbazin*, *robenidine hydrochloride*, *toltazuril*
Antifungals	Treatment of fungal and yeast infections	chlohexidine, griseofulvin, miconazole
Aquaculture	Treatment of sea lice and funrunculosis	*amoxicillin*, azamethiphos, *cypermethrin*, *ememectin benzoate*, florfenicol, hydrogen peroxide, oxolinic acid, *oxytetracycline*,
Hormones	Control of oestrus, progesterone therapy	altrenogest, oestrodiol benzoate, ethinyl oestrodiol, methyltestosterone, medroxyprogesterone, melatonin, progesterone
Growth promoters	Increase food digestion	*flavophospolipol*, *monensin*, *salinomycin sodium*
Anaesthetics		halothane, isoflurane, *lidicaine*, *lignocaine*, procaine
Euthanasia products		pentophenobarbitone
Tranquilizers		phenobarbitone
NSAIDS	Non-steroidal anti-inflammatories	phenylbutazone
Bloat preparations	Treatment of enteric bloat	*dimethicones*, *poloxalene*

6.2 PREDICTING RISK FROM VETERINARY MEDICINES

Veterinary medicines were highlighted as a risk to the environment by Boxall et al. (2003). There are a number of potential routes for these to reach the aqueous environment as shown in Figure 6.1. How these drugs are emitted during the treatment process will depend on whether the animal received the treatment topically, in feed or as an injection or bolus, and on the methods of husbandry.

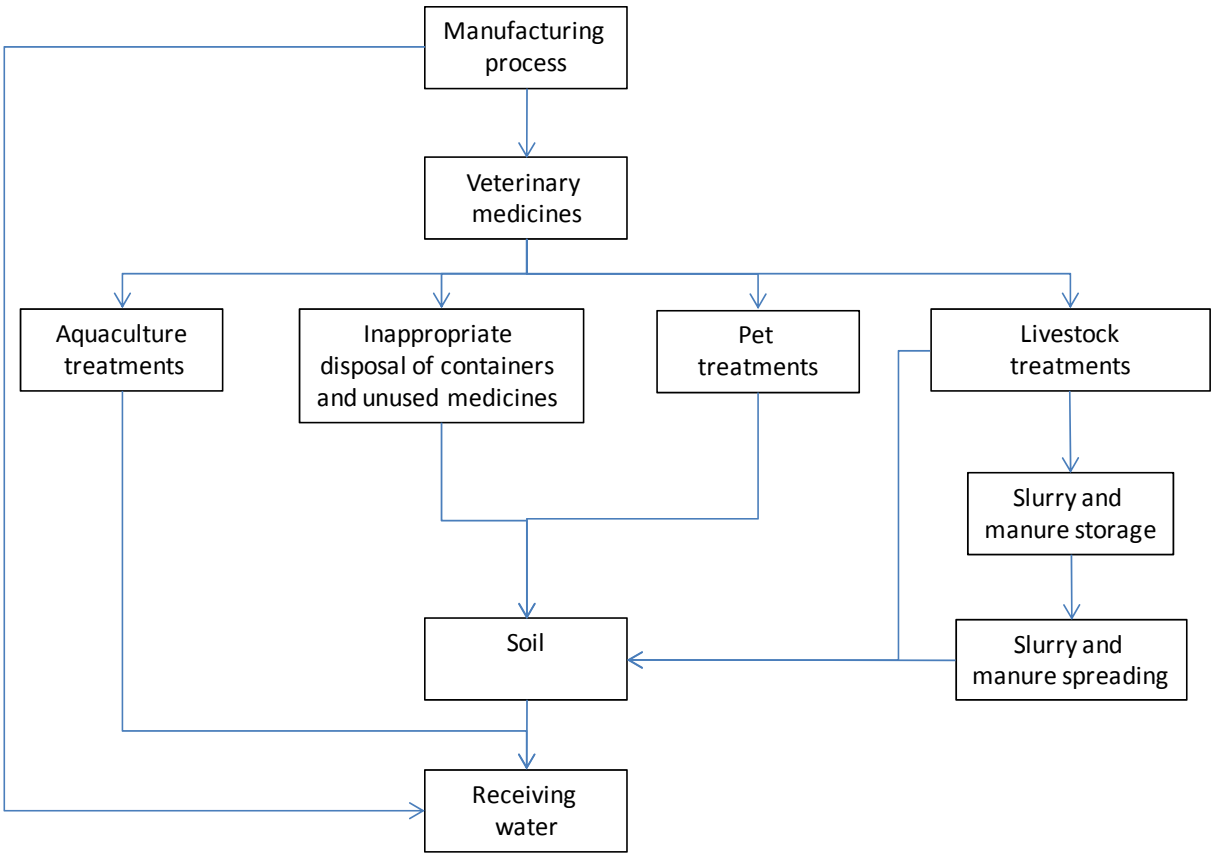

Figure 6.1 Pathways into the environment for veterinary medicines (after Boxall et al. 2003)

The most important routes for entry into the environment are likely to be the direct discharge of aquiculture products, the excretion of substances in the urine and faeces of livestock animals and the wash-off of topical treatments. There is limited or no evidence for significant contributions from the other routes.

Boxall et al. (2003b) used a two-stage assessment to assess environmental impact. An assessment of potential for these compounds to reach the environment was made using usage, pathways of entry to the environment and metabolism. For compounds that were identified by stage 1 a simple assessment of hazard was made using toxicity data in Boxall et al. (2002). Substances were classed using both aquatic and terrestrial ecotoxicity. After stage 1 a number of groups were identified which had low potential to enter the environment. These included general anaesthetics, substances with low usage, including those used to treat pets or other individual animals, and a number of individual compounds which had a high potential to be metabolised. Substances identified as having a high potential included antimicrobial compounds and sheep dip.

The assessment for the UK identified 11 compounds as high priority with a further 45 provisionally ranked (but with insufficient data available) (Table 6.1). Almost all antimicrobial and antiparasitic compounds are assessed as posing a risk to the environment by this method.

7 Emerging contaminants detected in groundwater in England and Wales: BGS analysis of Environment Agency monitoring data

7.1 INFORMATION ABOUT THE DATA SET

7.1.1 Data source

The Environment Agency has a statutory responsibility for monitoring the quality of groundwater in England and Wales. As part of their monitoring programme, samples for organic micropollutants are collected and analysed in response to WFD and Groundwater Directive requirements (Chapter 8), and for State of the Environment reporting.

Data for these parameters from the national monitoring programme were provided to BGS on 10 April 2010 in an Access database. The dataset contained 17,694 entries from 10,301 samples collected from 3963 monitoring sites. Of these 2644 had at least one analysis. Data were recorded from 1992 up to 2009. There are currently around 3300 groundwater quality monitoring sites across England and Wales.

All samples had been analysed by the National Laboratory Service. The GCMS Target Based (Multi-Residue) Screening method used allowed for almost all GC-amenable pesticides as well as hundreds of other organic pollutants to be identified from a single sample, incorporating over 850 substances and including both volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs). Chemicals could be identified at concentrations as low as 0.01µg/L using deconvolution reporting software.

7.1.2 Data processing by BGS

As provided, positive detections for all analytes for each sample from the multi-residue screening method were recorded on one line in a single text field. During data processing, the data were separated into individual lines for each separate analyte by sequential queries and some manual edits. In the processed table there were 35,604 individual lines of which 25,130 results had Chemical Abstracts Service (CAS) registry numbers. Of the sites 2633 had an analysis and of these 2285 sites had one or more result with a CAS number.

A summary of all analyte names used and their associated CAS numbers was checked for replicate entries, due to mis- or alternative spellings or punctuation, or because of incorrectly ascribed CAS numbers. This reduced the number of unique analytes from about 2000 to about 1200. About 230 of these had 10 detects or more and these were considered further.

7.2 WHAT THE DATA TELL US

7.2.1 Frequency of detection

The 30 most frequently detected compounds are shown in the barchart in Figure 7.1. This shows a number of PAH, petroleum, BTEX, triazine herbicides (atrazine, simazine, atrazine metabolites), chlorinated solvents, degradation products and THM, caffeine, DEET and industrial compounds such as bisphenol A and tributyl phosphate (solvent and plasticiser as well as a component of aircraft hydraulic fluid)**.** The 30 compounds with the highest maximum concentrations are shown in Figure 7.2. The highest concentration was for tetrahydrofuran (8000 µg/L) followed by3,5-dichlorobenzyl alcohol, nonyl phenol and chloroform.

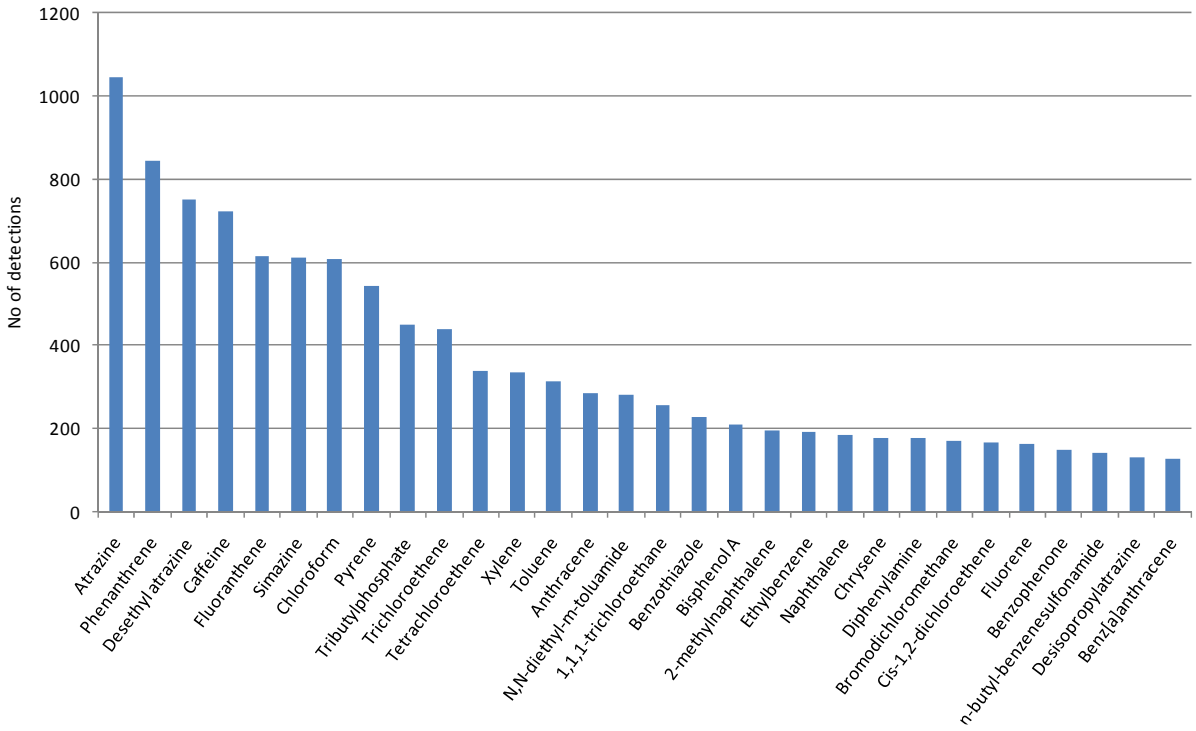

Figure 7.1 The top 30 most frequently detected compounds in the Environment Agency groundwater organic micropollutant database (excluding sulphur)

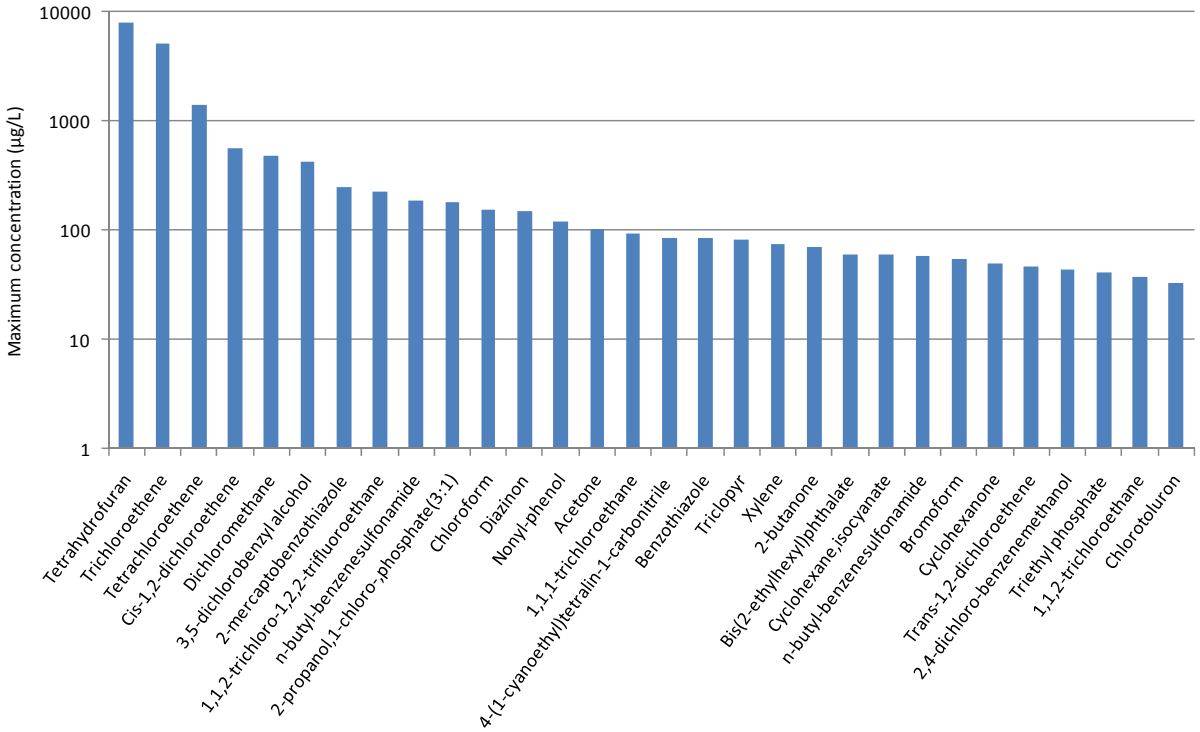

Figure 7.2 The top 30 compounds selected by maximum concentration in the Environment Agency groundwater organic micropollutant database

Summary tables of compound detections and maximum concentrations are shown in Appendix 2.

7.2.2 Spatial distribution

Examples from the top 30 compounds are used to illustrate this section. These include recognised pollutants and a number of emerging ones. Spatial plots for the remainder of the data can be found in Appendix 3.

PESTICIDES AND THEIR METABOLITES

Atrazine, with its metabolites desisopropylatrazine and desethyl atrazine, were detected at a maximum concentration of 13.0 µg/L. The majority of detections are found within the Chalk and the Jurassic in the south of England, with fewer detections within aquifers elsewhere (Figure 7.3). The distribution of all three analytes is similar. A high proportion of detects was of the lower concentrations with high concentrations predominantly detected in the Chalk in the south and east of England.

Simazine has a much higher proportion of detections in the south of England with high concentrations found predominantly within the Chalk (Section A3.4, Appendix 3). The maximum concentration detected was 2.0 µg/L; however the majority of detections were below 0.15 µg/L.

The apple scald compound diphenylamine was detected at a maximum concentration of 14 µg/L. Although the majority of detections were at the lower end of concentrations, a few high concentrations have been detected. Overall there are more detects in the south but no other patterns are obvious (Section A3.4, Appendix 3).

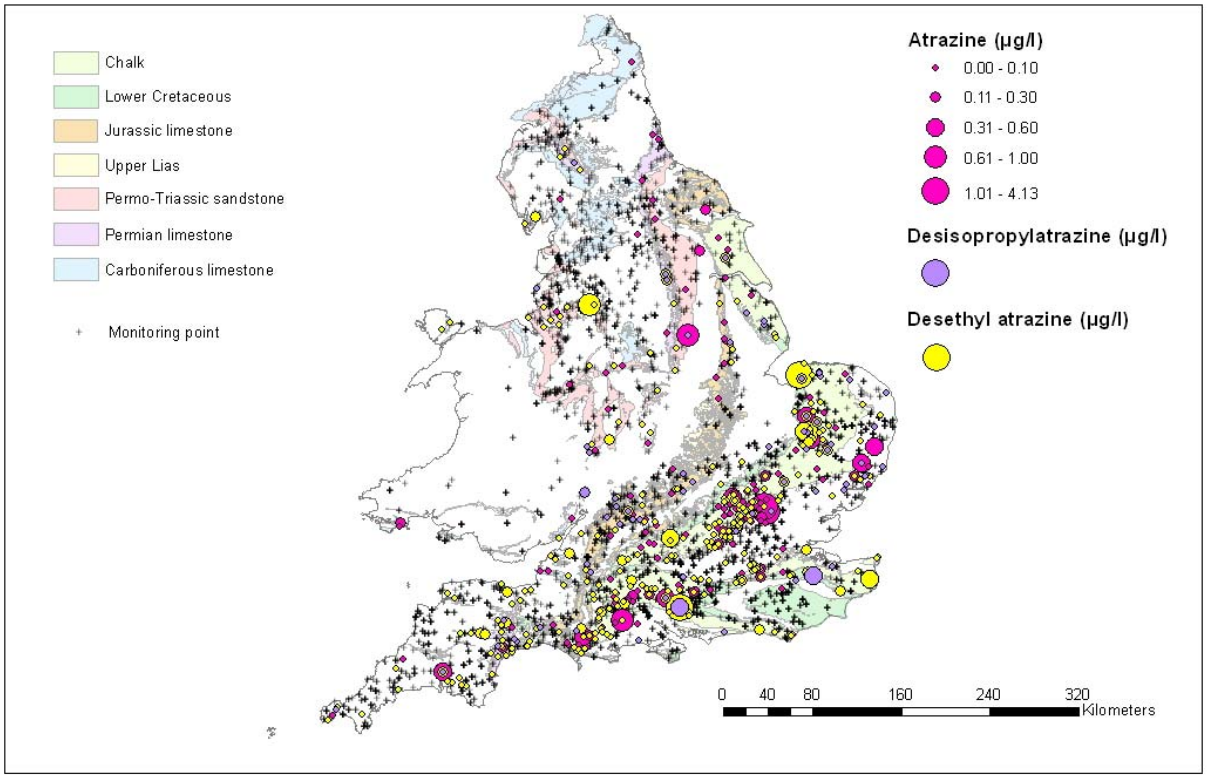

Figure 7.3 Distribution of mean concentrations of atrazine and its metabolites in the Environment Agency groundwater organic micropollutant database

CHLORINATED SOLVENTS AND TRIHALOMETHANES

Trichloroethene (TCE) has the largest maximum concentration detected of 5,132 µg/L while the maximum tetrachloroethene (PCE) concentration recorded was 1,390 µg/L. The national distribution of both contaminants is similar, with the highest density of detects being within and to the north of London (Section A3.3, Appendix 3). High concentrations of trichloroethene were also observed in East Anglia and Liverpool. High concentrations of tetrachloroethene were detected within Midlands and the north west of England.

The metabolite cis-1,2-dichloroethene had a smaller maximum concentration detected of 560 µg/L and was mainly found near Liverpool, with lower concentrations detected in the Chalk of south east England. It should be noted that overall this analyte had a smaller number of positive detects.

The pattern of distribution of 1,1,1-trichloroethane is similar to that of other solvents with the highest density of detects within the Chalk of east England, near London, having the highest concentrations (Section A3.3, Appendix 3).

The national distribution of detected chloroform concentration matches well with that of the major aquifers (Figure 7.4). The highest density of detections is for low concentrations in southern and south east England. A maximum of 155 µg/L was detected. High concentrations detected in Carlisle and Liverpool areas stand out of the national distribution which could imply industrial activity rather than the low level concentrations found elsewhere, which could be attributed to water disinfection processes.

The distribution of bromodichloromethane was similar but with fewer detections at the low end of the range. The maximum concentration detected was 14 µg/L (Section A3.3, Appendix 3).

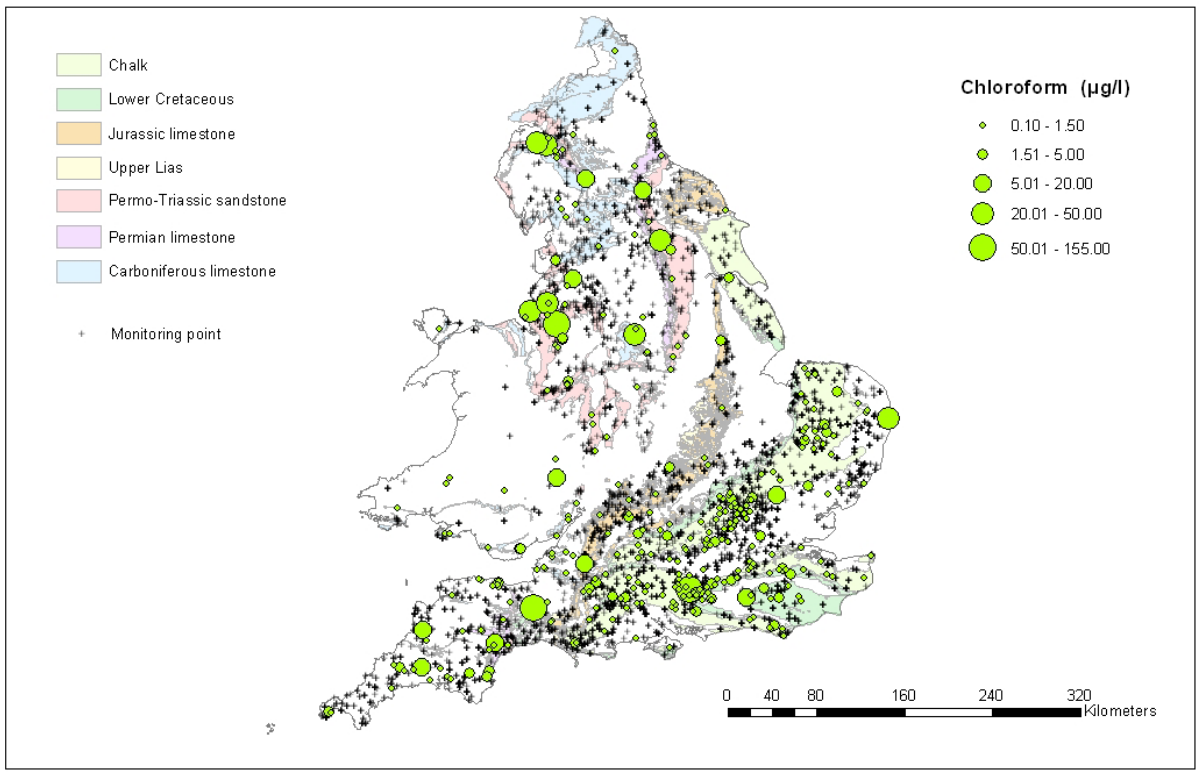

Figure 7.4 Distribution of mean concentrations of chloroform in the Environment Agency groundwater organic micropollutant database

POLYCYCLIC AROMATIC HYDROCARBONS (PAH)

These pollutants are by-products of fuel combustion and include, in order of decreasing solubility, fluoranthene, phenanthrene, napthalene, pyrene, anthracene, chrysene, fluorene, 2-methylnaphthalene and benz[a]anthracene.

The spatial distribution of detections is similar for the first two analytes in this group fluoranthene and phenanthrene. They have highest detection density around London within the south of England with noticeable clusters within the Chalk in East Anglia and Jurassic of the south west (Figure 7.5). There are fewer detections in the north and Midlands. The maximum concentration detected was 8.6 µg/L for fluoranthene and 7.61 µg/L for phenanthrene. Naphthalene has fewer detections when compared with the first two of the group with low concentrations being responsible for most detections within the Jurassic and the Chalk of the south England. There are fewer detections in other parts of the country with higher concentrations even less common. The maximum concentration detected for this analyte is 6.15 µg/L. The maximum concentration detected for pyrene was 5.8 µg/L. With relatively high detection density the distribution of high concentrations does not appear to follow a pattern. However the majority of high concentration detections were still recorded within Jurassic and Chalk aquifers of south England.

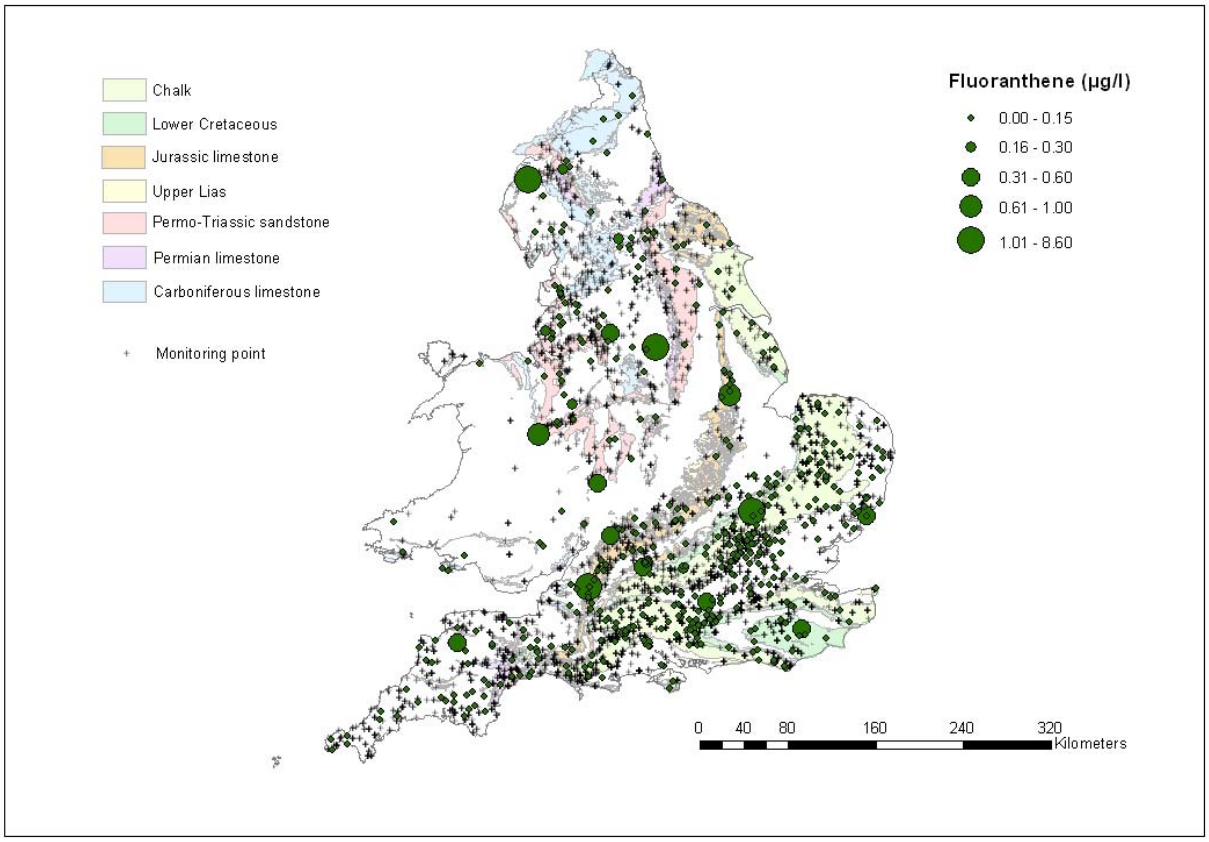

Figure 7.5 Distribution of mean concentrations of fluoranthene in the Environment Agency groundwater organic micropollutant database

The maximum concentration detected for anthracene was 6.14 µg/L. Detections are distributed predominantly in the south of England with an identifiable cluster around London. The distribution of high concentrations does not seem to follow a pattern. Chrysene distribution appears to be random apart from a cluster of detections around London with a maximum concentration of 2.01 µg/L. Fluorene has a number of detections in the Chalk and Jurassic but the overall distribution does not appear to follow a pattern. 2-methylnaphthalene

and benz[a]anthracene detection distributions also does not appear to follow a pattern. Lack of pattern could be due to sparsity of data or a different control of movement of pollutants to and through the aquifer.

BTEX

Toluene, ethylbenzene and xylene have been detected to maximum concentrations of 7.48 µg/L, 2.58 µg/L and 76 µg/L respectively. The distribution of all three analytes is similar on a national scale, in that a number of detects fall within high end of concentrations and appear to follow some of the major routes. For example, within the ethylbenzene distribution high concentration a linear feature in the south follows the route of A34 and in the north-west a linear cluster appears to follow the route of the A69/A596 (Figure 7.6). The spatial proximity of high concentrations to the A1 is also apparent. Similar patterns are noticeable within the xylene distribution but it has greater number of small concentrations when compared to ethylbenzene. These patterns are not as obvious within the toluene distribution although a high proportion of large concentrations of toluene occur within the Chalk and Jurassic of the Southern England.

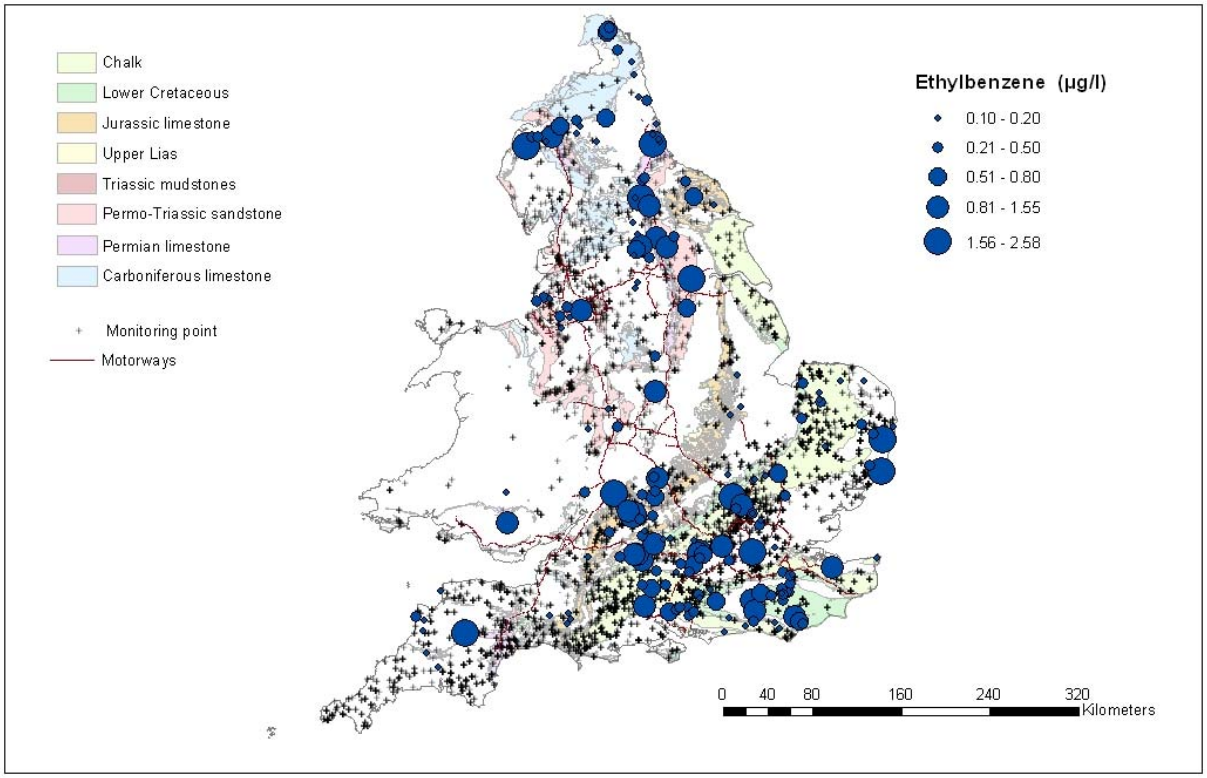

Figure 7.6 Distribution of mean concentrations of ethyl benzene in the Environment Agency groundwater organic micropollutant database

CAFFEINE

Caffeine is not often thought of as a pollutant as it is only harmful to humans in relatively high dosage. However the effects of high concentrations on the environment are not well understood. This analyte shows a number of high concentrations around the urban areas of London and Newcastle. Lower concentrations are detected across much of the rest of the country (Figure 7.7).

PHARMACEUTICALS AND PERSONAL CARE

DEET is used as an insect repellent (Section 3.3). The maximum concentration detected was 6.5 µg/L, however the majority of detects were in the range of 0.01 to 0.1 µg/L. The majority of detections are within the south of England (Section A3.5, Appendix 3). A cluster of high concentrations have been detected in the area surrounding Shrewsbury.

OTHER CONTAMINANTS

Benzothiazole was predominantly detected in one area but these data are considered to be an artefact of a faulty batch of sample containers should be discarded. Benzophenone follows a similar distribution and may possibly have the same explanation for its occurrence/detection and distribution (Section A3.6, Appendix 3).

The maximum concentration of bisphenol A detected was 20 µg/L and of its glycidal ether 3.95 µg/L. Otherwise, the distribution of detections is split clearly into two groups, southern England and Midlands. No clear patterns are present (Section A3.6, Appendix 3).

The polymer plasticiser NBBS was almost exclusively detected in groundwater in the southeastern parts of England. The maximum concentration detected was 190 µg/L (Section A3.6, Appendix 3).

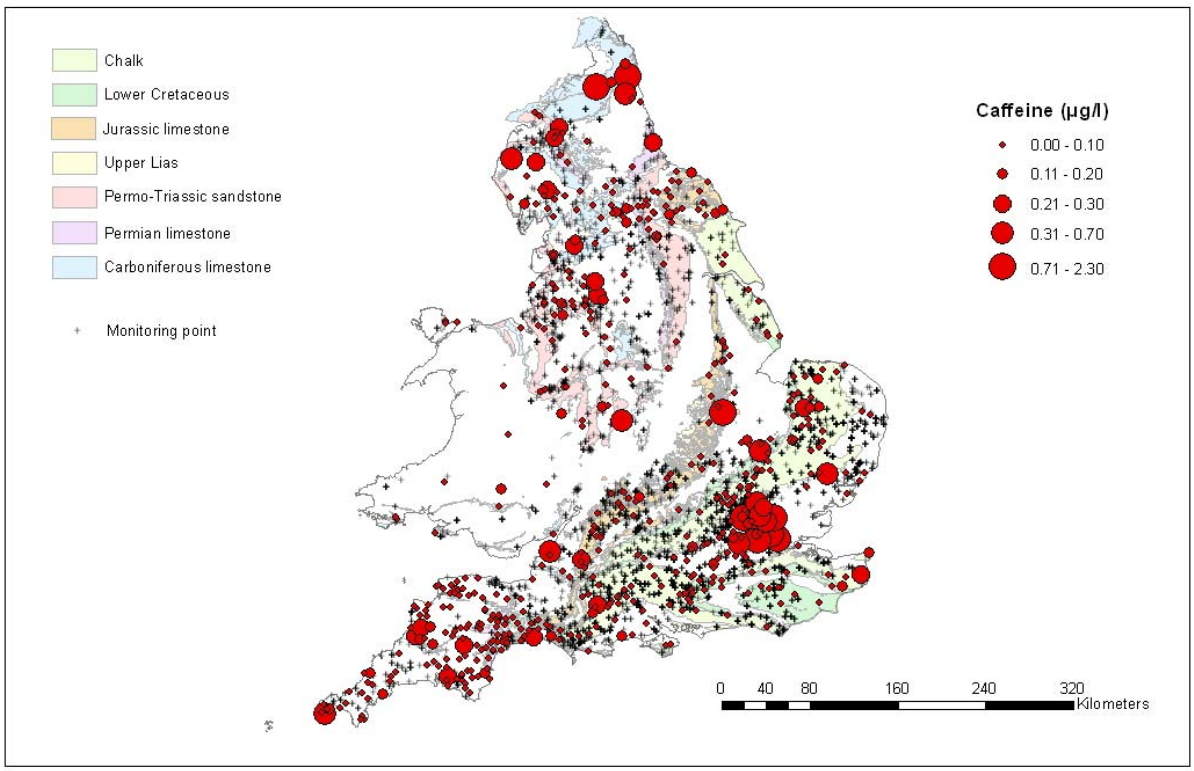

Figure 7.7 Distribution of mean concentrations of caffeine in the Environment Agency groundwater organic micropollutant database

7.2.3 Specific priority compounds

Summaries of numbers of detections and sites where detected are shown in Appendix 2. Data for compounds with 10 or more detects has been evaluated rigorously, while other data were only visually assessed.

CURRENTLY LICENSED PESTICIDES

The most significant detections using this method are for a triazine herbicide and a range of triazole fungicides (Table A2.1, Appendix 2),. It is possible that the analytical method which is not focussed to specific pesticides is not as effective as for some other groups of compounds. Compounds with significant numbers of detections are terbuthylazine (triazine herbicide), epoxiconazole, flutriafol, flusilazole, propiconazole, tebuconazole and triadimenol (triazole fungicides), fluazifop-p-butyl (aryloxyphenoxypropionate herbicide), dichlobenil (benzonitrile herbicide), metalaxyl (phenylamide fungicide), oxadiazon (oxydiazole herbicide), bentazone (benzothiadiazinone herbicide), metribuzin (triazinone herbicide), prochloraz (imidazole fungicide), chlorothalonil (chloronitrile fungicide), pirimicarb (carbamate insecticide), fenpropidin (piperidine fungicide), pendimethalin (dinitroaniline herbicide), triallate (thiocarbamate herbicide) and napropamide (alkanamide herbicide).

Metabolites detected are the desethyl metabolite of terbuthylazine, the methyl metabolite of bentazone, the deamino and deamino-deketo metabolites of metribuzin and the butoxyethyl and methyl esters of triclopyr (pyridine herbicide).

A number of compounds are shown as being detected at concentrations of >1 µg/L. Those also in the above list are flusilazole, flutriafol, chlorothalonil, metribuzin, napromide, dichlobenil, oxadiazon, pendimethalin, triallate and these may be considered to pose the greatest risk. Others are chlopropham (carbamate), chlorotoluron (uron), ethofumesate (benzofuran), metazachlor (chloroacetamide), propyzamide (benzamide) and trichlopyr (pyridine).

NON-LICENSED PESTICIDES

Compounds with significant detections, apart from the triazine herbicides atrazine and simazine and their metabolites, include other triazine herbicides, terbutryn, propazine and trietazine, as well as oxadixyl (phenylamide fungicide), mephosfolan (organophosphate insecticide), the previously widely-used uron herbicide isoproturon and also fenuron, methoxychlor and dieldrin (organochlorine insecticides), trifluralin (dinitrianailine herbicide) and dinoseb (dinitrophenol) (Table A2.2, Appendix 2),. Of these atrazine, dinoseb, fenuron isoproturon, methoxychlor, oxadixyl, simazine and terbutryn also were detected at <1 µg/L. Others detected at this concentration were diazinon, prometryne and propachlor. A few low detections of the metabolites of the insecticides DDT and endosulfan are also recorded.

Again the data demonstrate the persistence of the triazine herbicides in groundwater and the reason why compounds in this section are not or are no longer licensed for use.

PHARMACEUTICALS AND PERSONAL CARE PRODUCTS

Compounds with significant detections are the personal care products methyl and propyl paraben (Table A2.3, Appendix 2), oxybenzone, carbamodithioic acid-dimethyl-, methyl ester, isopropyl myristate, lilial and 2-phenoxy-ethanol, and the pharmaceuticals trimipramine (antidepressant), carbamazepine (antiepileptic) and its impurity, 1,3-dicyclohexylurea (hypertension) triclosan (antibacterial) coumarin (anticoagulant) and crotamitron (scabies treatment).

Drometrizole (sunscreen), ibuprofen (analgesic) and ethyl paraben are also detected. There are no detects for acetaminophen (paracetamol), aspirin or sulfamethoxazole.

It is difficult to comment on the significance of the concentrations detected as unlike pesticides these compounds have either very different limits or no limits in the environment. The highest maximum concentrations are for personal care products and galaxolide. For pharmaceuticals the highest concentrations are for crotamitron, carbamazepine and triclosan.

VETERINARY MEDICINES

There are few detections of compounds used specifically as veterinary medicines, with a limited number of detections of possible sheep dip compounds (Table A2.4, Appendix 2).

LIFESTYLE AND FOOD ADDITIVES

The main detections are for caffeine, nicotine and its metabolite, and the food additives BHT, phthalide, vanillin and p-acetyl acetophenone. All these compounds are found at relatively high concentrations (Table A2.5, Appendix 2).

ENDOCRINE DISRUPTORS

The main endocrine disruptor detected is bisphenol A by a large margin with both OP and NP also found (Table A2.6, Appendix 2). There were no detections of the ethoxylated derivatives.

ALKYL PHOSPHATES

The main compounds detected were tributyl phosphate (Table A2.7, Appendix 2), 2-ethylhexyl diphenyl phosphate and tris (2-dichloroethyl) phosphate. The highest individual concentration was for triethyl phosphate.

PLASTICISERS

The main compound detected was NBBS, but a number of phthalates were also found, namely bis(2-ethylhexyl), dimethyl, diethyl and dibutyl (Table A2.8, Appendix 2).

7.2.4 Hotspots

Hotspots, i.e. a high density of high concentrations of a particular compound in a small area, may indicate point source contamination.

Data hotspots for some of these compounds are indicated in the following figures. The highest concentrations of DEET have been detected in the Shrewsbury area (Figure 7.8). Bisphenol A is detected in a number of boreholes in along the catchment of the River Waveney in East Anglia (Figure 7.9).

A large group of caffeine detections are seen in North London (Figure 7.10). The majority are close to the River Lea and it could be speculated that these are associated with artificial recharge which has been carried out in this area. However the similarity to the cluster of ethyl paraben and 10,11-dihydrocarbamazepine detections in this same area suggests this could also be a sampling artefact, perhaps from a batch of sample containers. The other parabens are highest in boreholes in the Winchester and Basingstoke area (Figure 7.11).

There is a cluster of sites with detections of carbamazepine, triclosan and/or BHT in north Yorkshire.

The metribuzin metabolites detected are all from the same site near Thirsk, Yorkshire.

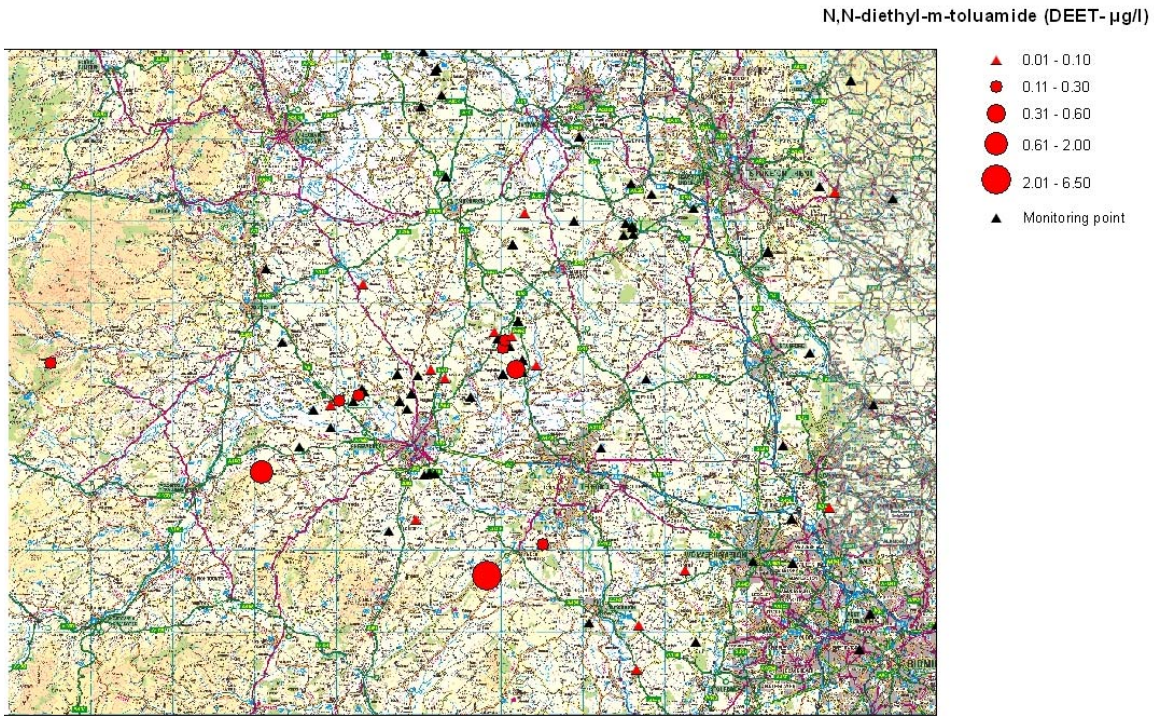

Figure 7.8 Hotspot of DEET detections in the Shrewsbury area

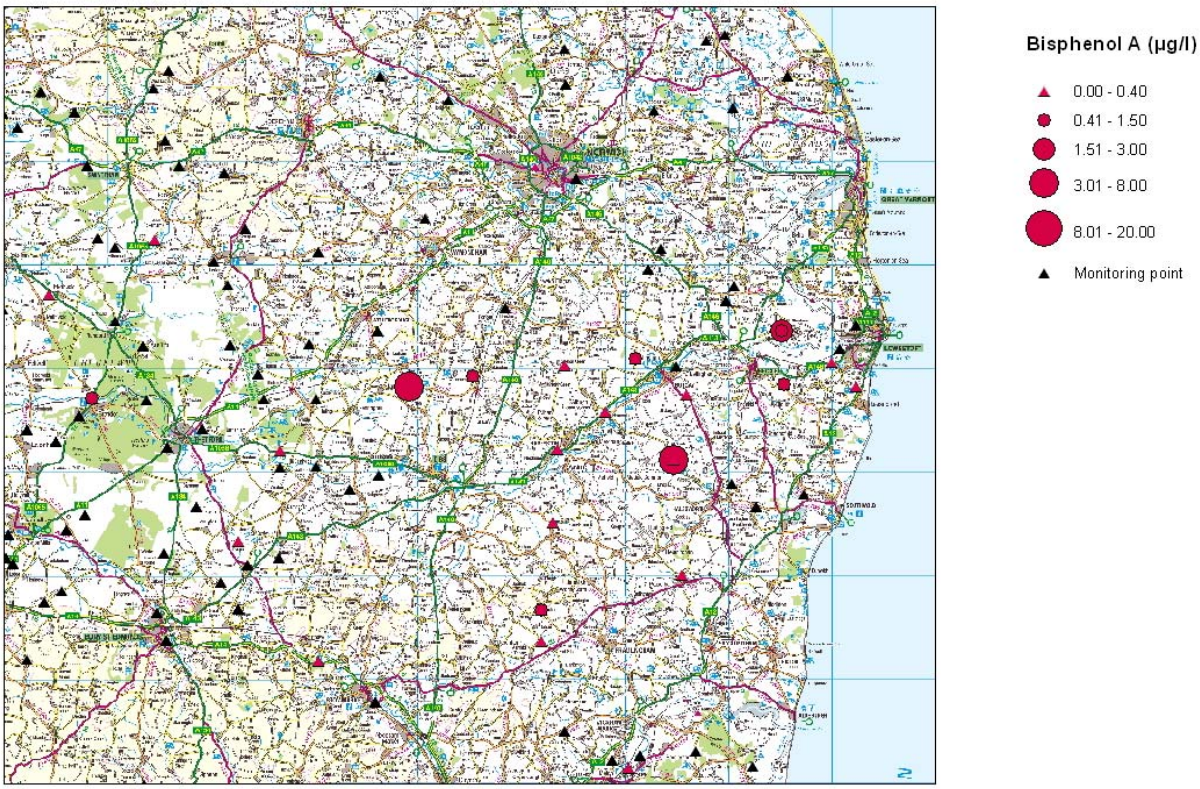

Figure 7.9 Hotspot of bisphenol A detections in the Waveney catchment, East Anglia

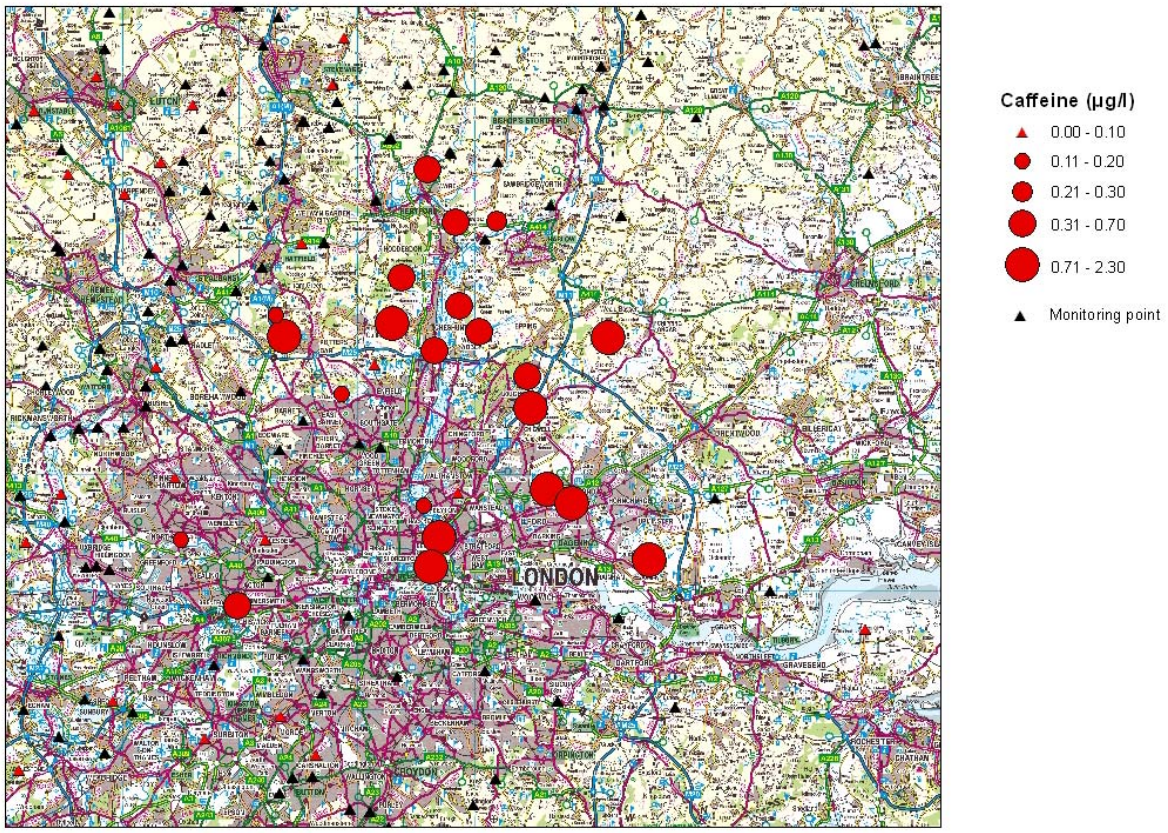

Figure 7.10 Hotspots of caffeine detections in north London and the Lea Valley

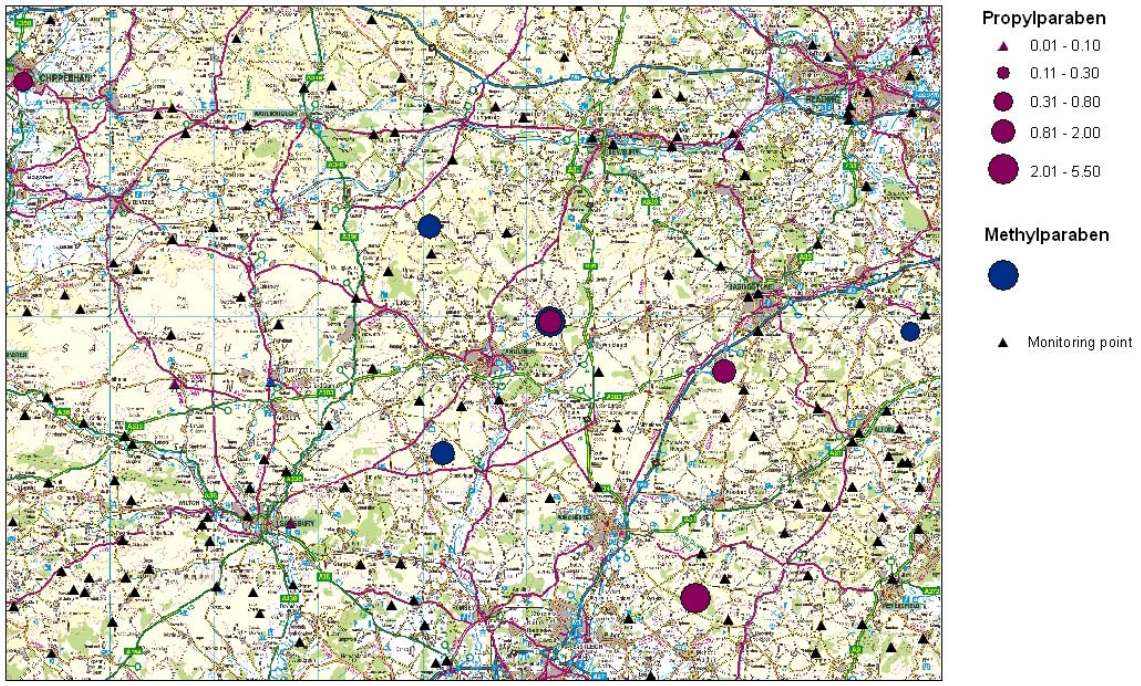

Figure 7.11 Hotspots of paraben detections in Hampshire

7.3 CONCLUSIONS FROM ENVIRONMENT AGENCY MONITORING DATA

In addition to established groundwater pollutants, a number of emerging contaminants have been detected on multiple occasions in UK groundwater. It is difficult to assess the significance of the concentrations observed in the absence of regulatory limits.

Possible emerging pollutants which could be suitable for further study based on our analysis of existing UK data include:

- pesticide metabolites: terbuthylazine, metribuzin and triclopyr
- pharmaceuticals: carbamazepine, triclosan, parabens and DEET
- life style: caffeine
- food additives: BHT
- endocrine disruptors: bisphenol A
- alkyl phosphates: tributyl phosphate
- NBBS.

8 Regulatory setting

8.1 WATER FRAMEWORK DIRECTIVE (2000/60/EC) AND PRIORITY SUBSTANCES DIRECTIVE (2008/105/EC)

The Water Framework Directive (WFD) requires that all necessary measures are taken to progressively reduce pollution of the water environment by priority substances and stop the emissions and discharges of priority hazardous substances. The control policy associated with this objective is set out in Article 16 of the WFD. This article also requires the establishment of a list of the so-called priority substances and a procedure for the identification of priority substances/priority hazardous substances (Annex X).

Priority Hazardous Substances are a subset of Priority Substances and are considered extremely harmful. Compliance with Priority Substance standards will be used to define 'good chemical status' for the Water Framework Directive (WFD). Concentrations of Priority and Priority Hazardous Substances in water must meet the WFD environmental standards by 2015 in order to achieve 'good chemical status'. In addition Priority Hazardous Substances emissions must be phased out by 2025.

No substances were defined in Annex X at the time of the publication of the WFD, instead a daughter directive - the Priority Substances Directive (2008/105/EC) – defines the Priority Substances and Priority Hazardous Substances replace Annex X. This Directive also sets out the Environmental Quality Standards for surface water for the 33 Priority Pollutants plus 8 other pollutants. The other pollutants include carbon tetrachloride, trichloroethene and tetrachloroethene and the organochlorine pesticides. All other pollutants defined in the WFD (Annex VIII) also need to be considered with standards being set at Member State level using a risk-based approach.

8.2 GROUNDWATER DAUGHTER DIRECTIVE (2006/118/EC)

The Groundwater Daughter Directive is formally known as the Groundwater Directive on the Protection of Groundwater against Pollution and Deterioration (2006/118/EC). This establishes groundwater quality standards for the first time (nitrates and pesticides) and introduces the concept of threshold values for groundwater for other WFD pollutants and indicators. A minimum list is set out which includes trichloroethene and tetrachloroethene but others must be indentified on the basis of the risk of failing to meet the WFD's environmental objectives. This directive also sets out the criteria for determining trends in pollutant concentrations and also the requirements to prevent and/or limit the inputs of pollutants to groundwater.

8.3 GROUNDWATER (ENGLAND AND WALES) REGULATIONS 2009

The Groundwater Regulations (GWR) 2009 promulgate the above EC directives. The regulations aim to reduce pollution by preventing the input of hazardous substances and limiting the introduction of non-hazardous pollutants to groundwater. Under the regulations it is a criminal offence to discharge hazardous substances and/or other nonhazardous pollutants onto or into land, without a permit.

The substances controlled under the regulations fall into two broad groups:

- hazardous substances are the most toxic and must be prevented from entering groundwater. Hazardous substances correspond to the Annex VIII pollutants in Table 8.1

Table 8.1 Pollutants established under the WFD

Annex X		**Annex VIII**
Priority Hazardous Substances	**Priority Substances**	
Anthracene	Alachlor	Organohalogen compounds and substances which may form such compounds in the aquatic environment.
Pentabromodiphenylether	Atrazine	Organophosphorous compounds.
Cadmium and its compounds	Benzene	Organotin compounds.
C10-13-chloroalkanes	Chlorfenvinphos	Substances and preparations, or the breakdown products of such, which have been proved to possess carcinogenic or mutagenic properties or properties which may affect steroidogenic, thyroid, reproduction or other endocrine-related functions in or via the aquatic environment.
Endosulphan	Chlorpyrifos	Persistent hydrocarbons and persistent and bioaccumulable organic toxic substances.
Hexachlorobenzene	1,2-Dichloroethane	Cyanides.
Hexachlorobutadiene	Dichloromethane	Metals and their compounds.
Hexachlorocyclohexane	Di(2-ethylhexyl)phthalate	Arsenic and its compounds.
Mercury and its compounds	Diuron	Biocides and plant protection products.
Nonyl-phenols	Fluoranthene	Materials in suspension.
Pentachlorobenzene	Isoproturon	Substances which contribute to eutrophication (in particular, nitrates and phosphates).
Polyaromatic hydrocarbons 5 named PAH)	Lead and its compounds	Substances which have an unfavourable influence on the oxygen balance
Tributyltin compounds	Naphthalene	
	Nickel and its compounds	
	Octyl- phenol	
	Nonyl-phenol	
	Pentachlorophenol	
	Simazine	
	Trichlorobenzenes (all isomers)	
	Trichloromethane	
	Trifluralin	

- non-hazardous pollutants are less toxic but could be harmful to groundwater, and the entry of these substances into groundwater must be limited. They include substances that contribute to eutrophication (abnormal growth of algae), in particular nitrate and phosphates, and compounds such as ammonia.

8.4 DRINKING WATER DIRECTIVE (98/83/EC),

Under the present Drinking Water Directive, promulgated as the Water Supply (Water Quality) Regulations, England & Wales 2000 and Scotland 2001, a few organic micropollutants have limits set (Table 8.2). These can broadly be grouped into pesticides, aromatic hydrocarbons, chlorinated solvents and disinfection by-products.

The Drinking Water Directive is currently under review (Fawell, 2010). Proposed changes to the Directive related to organic micropollutants are shown in Table 8.3. These include additional disinfection by-products and endocrine disruptors.

Table 8.2 Organic substances with limits set under the DWD (98/83/EC)

Organic parameters	**Limit**
Pesticides-individual (µg/L)*	0.1
Pesticides-total (µg/L)	0.5
Benzene	10
Polycyclic aromatic hydrocarbons (µg/L)	0.1
Benzo(a)pyrene (ng/L)	10
Tetrachloromethane (carbon tetrachloride) (µg/L)	3
Trichloroethene and tetrachloroethene (µg/L)	10
Trihalomethanes (µg/L)	100
1,2-dichloroethane	3
Vinyl chloride (µg/L)	0.5
Epichlorohydrin (µg/L)	0.1
Acrylamide (µg/L)	0.1

*except aldrin, dieldrin, heptachlor and heptachlor epoxide where the limit is 0.03 µg/L

Table 8.3 Proposed additional substances and limit changes

Compound	**Proposed limit**
NDMA (ng/L)	10
Total haloacetic acids (µg/L)	80
Trichloroethene (µg/L)	10
Tetrachloroethene (µg/L)	40
Oestradiol (µg/L)	0.01 precautionary value
Bisphenol A (µg/L)	0.1 precautionary value
Nonyl-phenol (µg/L)	0.1 precautionary value

9 Conclusions and recommendations

9.1 CONCLUSIONS

A wide range of organic micropollutants have been detected in the aqueous environment. These include nanomaterials, pesticides, pharmaceuticals, industrial additives and by-products, personal care products and fragrances, water treatment by products, flame/fire retardants and surfactants, as well as caffeine and nicotine metabolites and hormones. Many of the compounds are relatively small and/or polar molecules which can often not be effectively removed by conventional drinking water treatment using activated carbon. Many of these compounds are also toxic or are classed as endocrine disruptors.

Pesticides and some industrial compounds are presently covered by the Water Framework Directive, the Groundwater Regulations and the Drinking Water Directive. Additional parameters, such as bisphenol A and NP are anticipated to be covered by revisions to the Drinking Water Directive.

In order to assess the hazards presented by such compounds information on usage, persistence in soil and water, leachability indicated by sorption coefficient and a robust and suitably sensitive analytical method is required. The recent metaldehyde problem was not originally discovered due to lack of analysis and was exacerbated by a low K_{ow} and consequent recalcitrance in water treatment. For many pesticides the above requirements are fulfilled and an assessment of risk of leaching to groundwater can be made. However, for pesticide metabolites this information can be sparse and for compounds such as pharmaceuticals aspects can be completely lacking.

A simple hazard assessment for pesticides was made using usage, persistence, the organic carbon/water partition coefficient and published indices, such as GUS or SCI-Grow. Using this method the following currently approved compounds were assessed as having the greatest potential for leaching to water: 2,4-D, amidosulfuron, bentazone, clopyralid, dicamba, florasulam, fosthiazate, imazaquin, iodosulfuron-methyl-sodium, maleic hydrazide, MCPA, MCPP-P, metribuzin, metsulfuron-methyl, quinmerac, oxamyl, triclopyr with a further 46 also having potential. Of these, 19 had a K_{ow} less than that of metaldehyde and therefore are likely to be incompletely removed by water treatment.

For metabolites several assessments of hazard to groundwater have already been made. A simple assessment based only on K_{oc} and persistence data in this study gave results which agreed in principle. Most potentially problematic metabolites are derived from less hazardous parents. The different approaches indicate that the metabolites of chlorothalonil, cyanazine, diflufenican, flufenacet, iodosulfuron-methyl-sodium, metaldehyde, metazachlor and metsulfuron-methyl are likely to pose the greatest risk to drinking water. In many cases these metabolites are derived from parents which have a lesser risk.

Other organic micropollutants such as pharmaceuticals cannot as yet be assessed in the same way due to a lack of persistence data. The majority of persistence studies have been directed at water treatment. A range of organic micropollutants from urban settings have been detected in ground and surface water. Commonly detected compounds include: bisphenol A, caffeine, carbamazepine, DEET, galaxolide, ibuprofen, iopamidol, phthalates, phenyl ethoxylates, and sulfamethoxazole. Case studies show that a small number of contaminants may be used to characterise the contaminant loading and also be used to assess the migration pathways in urban areas.

Data from the Environment Agency monitoring programme (interpreted by BGS) for organic pollutants indicates that the 30 most frequently detected compounds includes both recognised

and emerging contaminants comprising a number of polyaromatic hydrocarbons, petroleum compounds, triazine herbicides, chlorinated solvents, degradation products and THMs, caffeine, DEET and industrial compounds such as bisphenol A and tributyl phosphate. Specific determinands include a range of currently licensed and phased out pesticides with a few metabolites, pharmaceuticals including carbamazepine and triclosan, caffeine, nicotine and food additives and alkyl phosphates. These data exhibit hot spots which may indicate possible research areas.

9.2 RECOMMENDATIONS FOR FURTHER RESEARCH

9.2.1 Selection of study compound

Research should focus on a compound identified in the literature and detected by Environment Agency monitoring. Possible topics could be:

- the metaldehyde accumulation in the unsaturated zone
- emerging pesticide metabolites
- carbamazepine or triclosan
- caffeine
- DEET
- bisphenol A
- alkyl phosphates
- NBBS

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Glossary of acronyms

Acronym	In full
AHTN	tonalide (polycyclic musk)
AMPA	aminomethylphosphonic acid (metabolite of the pesticide glyphosate)
APEs	alkyl phenol ethoxylates
BTEX	benzene, toluene, ethylbenzene, and xylenes. These compounds (all VOCs) are found in petrol and other petroleum derivatives and are used as indicators of contamination from such sources.
CAS	CAS Registry Numbers are unique numerical identifiers assigned by the '**C**hemical **A**bstracts **S**ervice' to every chemical described in the open scientific literature" (http://en.wikipedia.org/wiki/CAS_registry_number)
DAS	4,4-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)amino]stilbene (fluorescent whitening agent)
DDE	1,1-dichloro-2,2-bis(4-chlorophenyl)ethene (metabolite of DDT)
DDT	1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (discontinued pesticide)
DEET	*N*,*N*-diethyltoluamide (insect repellent)
DSBP	4,4-bis(2-sulphostyryl)biphenyl (fluorescent whitening agent)
DTPA	diethylenetriamine pentaacetic acid
DWT	drinking water treatment (process or works)
ECOSAR	Ecological Structure Activity Relationships (software used to estimate the aquatic toxicity of industrial chemicals)
EDCs	endocrine disrupting compounds
EDTA	ethylenediamine tetraacetic acid
EU	European Union
GAC	granulated activated carbon (used for water treatment)
GIS	geographic information system
GUS	groundwater ubiquity score (a leachability index)
HAA	halo acetic acid
MCPP	methylchlorophenoxypropionic acid (pesticide also known as mecoprop)
MRL	maximum residue limits
MTBE	methyl tertiary-butyl ether (fuel oxygenate additive to lead-free petrol)
NBBS	n-butylbenzenesulfonamide
NDMA	*N*-nitrosodimethylamine (water disinfection by-product)
NDMAFP	*N*-nitrosodimethylamine formation potential
NP	nonyl-phenol

NPE1C	nonyl-phenoxy acetic acid
OP	octyl-phenol
PAC	powdered activated carbon (used for water treatment)
PAH	polyaromatic hydrocarbons
PCBs	polychlorinated biphenyls
PEC	predicted environmental concentration
PEIAR	Pharmaceuticals in the Environment, Information for Assessing Risk (database with information for assessing risks to aquatic resources from drugs)
PFAs	perfluorinated acids
PFOA	perfuorooctanoic acid
PFOS	perfluorooctane sulfonate
PNEC	predicted no-effect concentration (concentration below which exposure to a substance is not expected to cause adverse effects)
PPCPs	pharmaceuticals and personal care products (as pollutants)
SCI-Grow	***S***creening ***C***oncentration ***I***n ***GRO***und ***W***ater (a screening model which is used to estimate pesticide concentrations in groundwater)
STW	sewage treatment works
SVOC	semi-volatile organic compound
TCDD	2,3,7,8-tetrachlorodibenzo-p-dioxin
TCEP	tris(2-carboxyethyl)phosphine
TDE	1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (metabolite of DDT)
TDS	total dissolved solids
THMs	trihalomethanes (by-product of water chlorination)
US	United States (of America)
UV	ultraviolet
VOC	volatile organic compound
WWT	waste water treatment (process or works)

Glossary of symbols

Symbol/shorthand	Meaning
A_{sas}	solvent accessible volume
DT_{50}	time until 50% decay (half life)
DT_{90}	time until 90% decay
K_d	partition coefficient (usually between water and a solid phase, such as an aquifer rock, with a specified initial concentration of compound in solution)
K_{oc}	partition coefficient between organic carbon and water
K_{ow}	partition coefficient between octanol and water
molref	molecular refractivity
V_{sav}	surface accessible volume
ΔH_f	enthalpy of formation
ΔH_{hyd}	hydration energy
μ	dipole moment
π	polarisability

Appendix 1 Pesticide metabolite assessments

Table A1 Pesticide metabolites selected for study by Sinclair et al. (2010)

Parent	**Metabolite**
1,3-dichloropropene	cis-3-chloroprop-2-enoic acid
	trans-3-chloroprop-2-enoic acid
Aldicarb	aldicarb sulfone
	aldicarb sulfoxide
Asulam	sulfanilamide
Atrazine	deethylatrazine
Azoxystrobin	'reference compound 10'
Carbendazim	2-aminobenzimidazole
Carbosulphan	carbofuran
Carboxin	carboxin sulfoxide
Chloridazon	5-amino-4-chloropyridazin-3(2H)-one
Chlorothalonil	3-carbamyl-1,2,4,5-tetrachlorobenzoic acid (3-cyano-2,4,5,6,tetrachlorobenzamide)
	3-cyano-6-hydroxy-2,4,5-trichlorobenzamide (2-hydroxy-5-cyano, 3,4,6,trichlorobenzamide)
	3-carbamyl-2,4,5-trichlorobenzoic acid (3-carboxy, 2,5,6-trichlorobenzamide) (R611965, SDS46851)
	2-amido-3,5,6-trichloro-4-cyanobenzenesulphonic acid (R417888)
Chlorotoluron	3-(3-chloro-p-tolyl)-1-methylurea
Cyanazine	cyanazine acid
Diflufenican	2-(3-trifluoromethylphenoxy) nicotinamide (AE 0542291)
Florasulam	5-hydroxy-XDE-570 (5-hydroxyflorasulam)
Fluazifop-P-butyl	5-trifluoromethyl-pryid-2-one
Flufenacet	FOE oxalate
	thiadone
Fosetyl-aluminium	ethanol
	phosphorous acid
Glyphosate	aminomethylphosphonic acid (AMPA)
Imidacloprid	1-(6-chloro-pyridine-3-ylmethyl)-N-nitro guanidine
Iodosulfuron methyl	4-iodo- 2-[3-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-ureidosulfonyl]benzoic acid (AE F145740)
	metsulfuron-methyl
Ioxynil	3,5-di-iodo-4-hydroxybenzamide
	3,5-di-iodo-4-hydroxybenzoic acid
Isoproturon	3-(4-isopropylphenyl)-1-methylurea
	desmethylisoproturon
Metaldehyde	acetaldehyde
Metazachlor	metazachlor oxalic acid
	metazachlor sulfonic acid

Parent	Metabolite
Methiocarb	methiocarb sulfoxide
Metoxuron	demethyl metoxuron
Metribuzin	diketo metribuzin
Metsulfuron-methyl	2-(aminosulfonyl) benzoic acid (IN-D5119)
	methyl 2-(aminosulfonyl)benzoate (IN-D5803)
Oxamyl	dimethyloxamic acid
Pendimethalin	2,6-dinitro-3,4-xylidine
	4-[(1-ethylpropyl)amino]-2-methyl-3,5-dinitro benzyl alcohol
	4-[(1-ethylpropyl)amino]-3,5-dinitro-o-toluic acid
Picalinafen	4-fluoroaniline
Pymetrozine	CGA 294849
Quinmerac	7-chloro-3,8-quinoline dicarboxylic acid (BH518-2)
	BH518-4
Simazine	deisopropylatrazine
Thiodicarb	methomyl
Triallate	diisopropylamine
Trifluralin	2-ethyl-7-nitro-5-(trifluoromethyl) benzimidazole

Table A2 Risk index for metabolites from Parsons et al. (2008)

Parent	**Metabolite**	**Risk Index**
Cyanazine	cyanazine acid	26.6
Cyanazine	cyanazine amide	24.1
Isoproturon	1-methyl-3-(4-isopropyl phenyl)-urea	7.92
Flufenacet	FOE sulfonic acid	4.67
Tebuconazole/bitertanol	1,2,4-triazole	4.51
Flufenacet	FOE oxalate	3.25
Dicamba	3,6-dichlorosalicylic acid	3.15
Atrazine/Simazine	deisopropylatrazine	2.12
Flufenacet	FOE methyl sulphone	2.03
Flufenacet	FOE thioglycolate sulfoxide	2.03
Flufenacet	thiadone	2.03
Metaldehyde	acetaldehyde	1.63
Bitertanol	bitertanol benzoic acid	1.59
Atrazine	DEHA	1.29
Propachlor	propachlor oxanilic acid	1.26
Atrazine/Simazine	DIHA	1.21
Trifluralin	α, α, α-trifluoro-2,6-dinitro-N-propyl-p-toluidine	1.10
Isoproturon	3-[4-(2'-hydroxy-2'propyl)-phenyl]-methyl urea	1.01
Bitertanol	4-hydroxybiphenyl	1.00
Linuron	demethyl linuron	0.99
Atrazine/Simazine	diaminochloroatrazine	0.89
Dimethoate	o-desmethyl dimethoate	0.81
Propachlor	propachlor ethane sulfonic acid	0.72
Trifluralin	2,2'-azoxybis (α, α, α-trifluoro-6-nitro-N-propyl-p-toluidine)	0.72
2-chloroethylphosphonic acid	ethylene	0.67
Trifluralin	α, α, α-trifluoro-2,6-dinitro-p-cresol	0.65
Trifluralin	2-ethyl-7-nitro-5-(trifluoromethyl)benzimidazole	0.62
Asulam	ionic form of asulam	0.61
Chlorothalonil	3-cyano2,4,5,6-tetrachlorobenzamide	0.61
Chlorothalonil	3-carbamyl-2,4,5-trichlorobenzoic acid	0.60
Metalaxyl	CGA-62826	0.57
Chloridazon	5-amino-4-chloropyridazine-3(2H)-one	0.54
Metalaxyl	2-N-(2,6-dimethylphenyl)-2-methoxyacetylamino propanoic acid	0.33
Trifluralin	α, α, α-trifluoro-5-dinitro-4-propyl-p-toluene-3,4-diamine	0.30
Mecoprop-P	4-chloro-2-methyl phenol	0.50

Table A3 Key metabolites for heavily used pesticides in 2008 from AERU (2010)

Compound	**Key metabolites**
Azoxystrobin	(E)-2-(2-[6-cyanophenoxy)-pyrimidin-4-yloxyl]-phenyl-3-methoxyacrylic acid
Boscalid	_
Chlormequat	-
Chlorothalonil	4-hydroxy-2,5,6-trichloroisophtalonitrile
	2-amido-3,5,6-trichlo-4-cyanobenzenesulphonic acid
	3-carbamyl-2,4,5-trichlorobenzoic acid
Cymoxanil	1-ethyl 5,6-di-2,4(1H,3H)pyridenedione
	2-cyano-2-methoxyiminoacetic acid
	3-ethyl-4-(methoxyamino)-2,5-dioxoimidazolidine-4-carboxamide
	3-ethyl-4-(methoxyamino)-2,5-dioxoimidazolidine-4-carbonitrile
Cypermethrin	3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid
	3-phenoxybenzoic acid
Cyproconazole	1,2,4-triazole
	1H-1,2,4-triazol-1-ylacetic acid
Diflufenican	2-(3-trifluoromethylphenoxy)nicotinamide
	2-(3-trifluoromethylphenoxy)nicotinic acid
Epoxiconazole	1,2,4-triazole
Fenpropimorph	fenpropimorph carboxylic acid
	cis-2,6-dimethylmorpholine
Florasulam	N-(2,6-difluorophenyl)-8-fluoro-5-hydroxy[1,2,4]triazolo[1,5-c]pyrimidine-2-sulfonamide
	N-(2,6-difluorophenyl)-5-aminosulfonyl-1H-1,2,4-triazole-3-carboxylic acid
	5-(aminosulfonyl)-1H-1,2,4-triazole-3-carboxylic acid
Flufenacet	FOE sulphonic acid
	FOE oxalate
Fluoxastrobin	HEC-5725-des-chlorophenyl
	HEC-5725-carboxylic acid
Fluroxypyr	4-amino-3,5-dichloro-6-fluoro-2-pyridinol
	4-amino-3,5-dichloro-6-fluoro-methoxypyridine
Flusilazole	bis(4-fluorophenyl)methyl silanol
Fuberidazole	1H-benzimidazole-2-carboxylic acid
Glyphosate	aminomethylphosphonic acid
Imidacloprid	1-[(6-chloro-3-pyridinyl)methyl]N-nitro-1H-imidazol-2-amine
	6-chloronicotinic acid
Iodosulfuron-methyl-sodium	2-amino-4-methoxy-6-methyl-1,3,5-triazine
	methyl 2-[3- (4-hydroxy-6-methyl-1,3,5-triazin-2-yl)ureidosulfonyl] benzoate
	metsulfuron-methyl
Lambda-cyhalothrin	(RS)-alpha-cyano-3-(4-hydroxyphenoxy)benzyl-(Z)-(1RS)-cis-3-(2-chloro-3, 3, 3-trifluoropropenyl)-2, 2-dimethylcyclopropanecarboxylate
Mancozeb	ethylenethiourea

Compound	Key metabolites
	ethyleneurea
	ethylene bisisothiocyanate sulphide
MCPP-P	2-methyl-4-chlorophenol
Mesosulfuron-methyl	2-amino-4,6-dimethoxypyrimidine
	4,6-dimethoxypyrimidine-2-yl-urea
	mesosulfuron
Metaldehyde	acetaldehyde
Metrafenone	??
Metsulfuron-methyl	methyl 2-(aminosulfonyl)benzoate
	2-(aminosulfonyl) benzoic acid
	phenylurea
	saccharin
Pendimethalin	-
Prochloraz	N-formyl-N'-propyl-N'-2(2,4,6-trichlorophenoxy)ethylurea
Propiconazole	1,2,4-triazole
	3-(2-((1H-1,2,4-triazol-1-yl)methyl)-2-(2,4-dichlorophenyl)-1,3-dioxolan-4-yl)propan-1-ol
Prothioconazole	alpha-(1,1-dimethylethyl)-beta-(2-phenoxyethyl)-1H-1,2,4-triazole-1-ethanol
	alpha-(1-chlorocyclopropyl)-alpha-o(2-chlorophenyl)methyl-1H-1,2,4-triazole-1-ethanol
Pyraclostrobin	1-(4-chlorophenyl)-3-({2 [(methoxy carbonyl)amino] benzyl} oxy)-1H-pyrazol-3-yl]glucopyranosiduronic acid
	methyl N-(2{[1-(4-chlorophenyl)-1H-pyrazol-3-yl] oxymethyl} phenyl)carbamate
Spiroxamine	-
Tebuconazole	1,2,4-triazole
Thiram	N,N dimethyl carbamosulfonic acid
Tribenuron-methyl	N-methyl triazine amine
	2-amino-4-methoxy-6-methyl-1,3,5-triazine
	saccharin
Trifloxystrobin	(E,E)-trifloxystrobin acid
Trinexapac-ethyl	trinexapac

Appendix 2 Summary of compounds detected in Environment Agency groundwater organic micropollutant database

Table A2.1 Currently licensed pesticides

Name	Detects	Sites	Max. conc (µg/L)	Metabolite	Name	Detects	Sites	Max. conc (µg/L)	Metabolite
2,4-DB, methyl ester	1	1	0.02		Lenacil	9	8	3.0	
Azoxystobin	3	3	0.2		Linuron	1	1	0.9	
Bentazone	29	29	0.63	Bentazone methyl (1,1, 0.01)	Mecoprop	2	2	0.02	
Bifenthrin	3	3	0.03		Metalaxyl	36	36	3.64	
Bromoxynil	5	5	0.1		Metaldehyde	1	1	0.8	
Bupirimate	6	6	0.11		Metamitron	1	1	0.22	
Carbetamide	6	6	0.16		Metazachlor	1	1	0.12	
Chlorpropham	8	8	11.4		Metribuzin	29	28	2.9	Metribuzin-deamino-(3,3,0.19), deamino deketo (2,2,0.11)
Chloridazon	1	1	0.02		Myclobutanil	8	8	0.99	
Chlorothalonil	17	17	1.01		Napropamide	11	11	2.35	
Chlorotoluron	8	8	33		Oxadiazon	30	30	9.7	
Clomazone	5	5	0.93		Paclobutrazol	6	6	0.59	
Clopyralid	3	3	0.03		Penconazole	1	1	0.04	
Cyproconazole.	2	2	0.01		Pendimethalin	12	12	5.3	
Cyprodinil	3	3	0.86		Pirimicarb	17	17	0.16	
Dicamba, methyl ester	1	1	0.01		Pirimiphos methyl	3	3	0.09	
Dichlobenil	38	38	6.23		Prochloraz	24	24	0.86	
Diflufenican	7	7	0.2		Propamocarb	1	1	0.01	
Dimethoate	5	5	0.02		Propiconazole	22	22	0.17	
Epoxiconazole	68	66	0.03		Propyzamide	2	2	7.9	
Ethofumesate	8	8	9.14		Prosulfocarb	4	4	0.12	
Fenoxaprop-ethyl	1	1	0.49		Pyrimethanil	5	5	0.13	
Fenpropidin	14	14	0.03		Tebuconazole	14	14	0.32	
Fenpropimorph	1	1	0.16		Terbuthylazine	75	74	0.5	Desethyl-terbutylazine (8,8,0.3)
Fluazifop-P-butyl	68	66	0.01		Thiabendazole	2	2	0.15	
Flufenacet.	1	1	0.01		Tolclofos-methyl	3	3	0.04	
Fluroxypyr,1-meptylester	1	1	0.403		Triadimenol	15	15	0.27	
Flusilazole	22	21	6.0		Triallate	12	12	1.65	
Flutolanil	2	2	0.17		Triclopyr	2	2	82	Butoxyethyl ester (3,3,0.47), methyl ester (1,1,0.02)
Flutriafol	47	47	1.4						

Table A2.2 Non-licensed pesticides

Name	Detects	Sites	Max conc (µg/L)	Metabolite	Usage in Europe in 2011
Atrazine	1046	1039	13.04	Desethyl atrazine (751,747,3.87), Desisopropylatrazine (130,130, 1.25)	No
Clofenvinfos	2	2	0.16		Not listed
Cyprazine	4	4	0.06		Not listed
DDT	-	-	-	DDD & DDE isomers (5,5,0.04)	No
Demephion	3	3	0.082		Not listed
Desmetryn	3	3	0.02		No
Diallate	1	1	0.03		No
Diazinon	6	6	152*		No
Diclobutrazole	1	1	0.01		No
Dieldrin	14	14	0.79		No
Dimethenamid	2	2	0.22		Not on UK
Dimetridazole	1	1	0.97		No
Dinoseb	23	22	2.0		No
Dinoterb	8	8	0.45		No
Diuron	3	3	0.14		Not on UK
Endosulfan	-	-	-	Endosulfan I, II & ether (3,3,0.02)	No
Fenarimol.	8	8	0.18		No
Fenson	1	1	0.02		No
Fenuron	51	51	5.22		No
Fonofos	2	2	0.07		No
Hexaconazole	2	2	0.01		No
Isomethiozin	8	8	0.2		Not listed
Isoproturon	33	33	1.54		Not in UK
Lindane (isomers)	6	6	2.7		No
Mephosfolan	44	43	0.01		No
Methidathion	2	2	0.06		No
Methoxychlor	24	24	6.0		No
Monuron	5	5	0.08		No
Oxadixyl	100	98	1.66		No
Pentanochlor	1	1	0.06		No
Permethrin	2	2	0.02		No
Prometryn	6	6	1.2		No
Propachlor	1	1	1.0		No
Propazine	50	49	0.16		No
Simazine	613	611	2.0		No
Simetryn	3	3	0.07		No
Terbutol	1	1	0.01		Not listed
Terbutryn	75	74	1.94		No
Triadimefon	14	14	0.57		No
Triazophos	1	1	0.02		No
Trietazine	49	47	6.71		No
Trifluralin	13	13	0.21		No

Table A2.3 Pharmaceuticals and personal care products

Name	Detects	Sites	Max Conc (µg/L)	Use
1,3-Dicyclohexylurea	27	27	0.41	Blood pressure/hypertension
10,11-dihydrocarbamazepine	15	15	0.73	Carbamazepine impurity
2-phenoxy-ethanol	11	11	5.19	Personal care
Amobarbital	5	5	0.69	Sedative
Carbamazepine	32	32	3.6	Antiepileptic
Carbamodithioic acid, dimethyl-, methyl ester	19	19	14.6	Personal care
Chlorzoxazone	1	1	0.09	Muscle relaxant
Cocaine	1	1	1.21	Illicit
Coumarin	20	20	0.42	Anticoagulant
Coumarin, 7-(diethylamino)-4-methyl-	2	1	0.72	Anticoagulant
Crotamitron	10	10	3.9	Antipruritic
DEET	280	280	6.5	Insect repellent
Disopyramide	1	1	0.05	Antiarrhythmic
Disulfiram	1	1	0.44	Alcoholism treatment
Drometrizole	9	9	0.05	Sunscreen
Ethylparaben	7	7	0.83	Personal care
Galoxalide	4	4	23	Polycyclic musk
Hexestrol	3	3	0.09	Hormone
Ibuprofen	8	8	0.29	Analgesic/anti-inflammotory
Isopropyl myristate	22	22	0.39	Personal care
Lilial	15	15	0.07	Personal care
Methylparaben	44	44	5	Personal care
Mirtazapine	1	1	0.11	Antidepressant
Oxybenzone	32	32	3.15	Personal care
Paraldehyde	6	6	0.5	Antiepileptic/sedative
Pentobarbital	2	2	0.66	Sedative
Phenobarbital	4	4	0.11	Sedative
Propylparaben	68	68	5.5	Personal care
Tonalide	6	6	1.1	Polycyclic musk
Triclosan	22	22	2.11	Antibacterial
Trimipramine	34	34	0.26	Antidepressant

Table A2.4 Veterinary medicines

Name	Detects	Sites	Max Conc (µg/L)	Usage
Diazinon	6	6	152	Sheep dip (also pesticide)
Dimetridazole	1	1	0.964	Coccidostat (also pesticide)
Lidocaine	1	1	0.33	Sedative
Permethrin	2	2	0.02	Sheep dip (also pesticide)
Piperonyl butoxide	5	5	0.32	Sheep dip

Table A2.5 Lifestyle and food additives*

Name	Detects	Sites	Max Conc (µg/L)	Usage
1(3H)-Isobenzofuranone (phthalide)	59	56	20	Food additive
2,6-di(t-butyl)-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one (BHT analogue)	79	79	4.2	Food additive
2,6-di-t-butyl-4-methylphenol (BHT)	106	106	7.0	Food additive
3,5-Di-tert-butyl-4-hydroxybenzyl alcohol (BHT analogue)	1	1	0.7	Food additive
Caffeine	722	720	10.3	Coffee and tea
Cotinine	40	40	0.4	Nicotine metabolite
Dimethyldisufide	22	22	9.48	Food additive
Ethyl citrate	6	6	0.33	Food additive
Indole-3-aldehyde	10	10	0.27	Food additive
Nicotine	107	107	8.07	Tobacco ingredient
N-nitrosomorpholine	18	18	0.05	Tobacco ingredient
p-acetylacetophenone	30	30	9.42	Food additive
Triacetin	9	9	2.8	Food additive
Tributyl citrate	9	9	0.57	Food additive
Tributylacetylcitrate	17	16	1.81	Food additive
Vanillin	31	31	1.08	Food additive

*Some of these compounds also have industrial uses

Table A2.6 Endocrine disruptors

Name	Detects	Sites	Max Conc (µg/L)	Use
n-nonyl-phenol	17	17	119	Surfactant
4-nonyl-phenol	1	1	0.02	Surfactant
4-tert-octyl- phenol	18	18	6.9	Surfactant
4-n-octyl- phenol	1	1	0.19	Surfactant
p-tert-octyl- phenol	2	2	2.73	Surfactant
Bisphenol A	209	206	20	Resin precursor
Bisphenol A, diglycidal ester	6	6	3.95	Metabolite
2,2'-bisphenol F	6	6	0.48	Resin precursor

Table A2.7 Alkyl phosphates

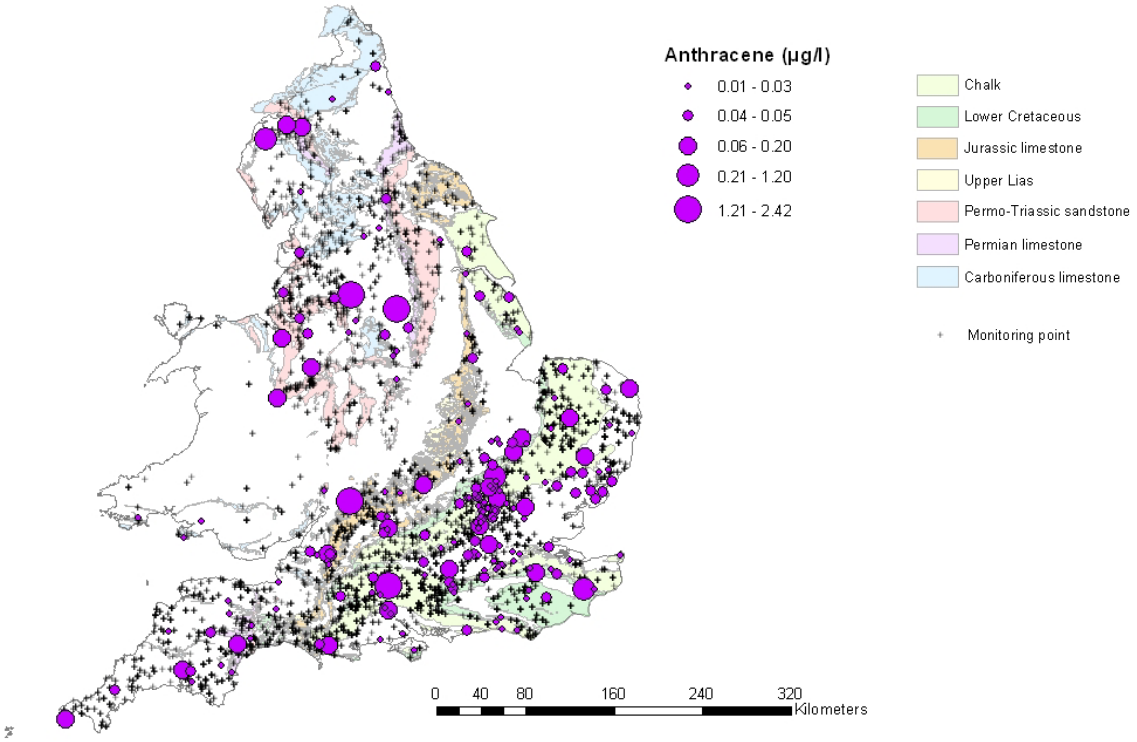
Name	Detects	Sites	Max Conc (µg/L)	Usage
2-butoxyethanol phosphate (3:1)	1	1	0.26	Flame retardant plasticiser
2-ethylhexyl diphenyl phosphate	68	68	2.7	Flame retardant plasticiser
2-propanol,1-chloro-, phosphate (3:1)	5	4	184	Flame retardant plasticiser
Cresyl diphenylphosphate	2	2	0.03	Flame retardant plasticiser
Diethyl p-nitrophenyl phosphate (Paraoxon)	1	1	0.15	Parathion metabolite, glaucoma treatment
Isopropylphenyldiphenyl phosphate	4	4	0.23	Flame retardant
Tributylphosphate	450	450	11.3	Solvent, plasticiser & anti-foaming
Triethyl phosphate	13	13	41	Plasticiser
Triphenylphosphate	5	5	0.041	Flame retardant plasticiser
Tris(1,3-dichloroisopropyl) phosphate	8	8	1.83	Flame retardant plasticiser
Tris(2-dichloroethyl)phosphate	54	54	4.9	Flame retardant plasticiser

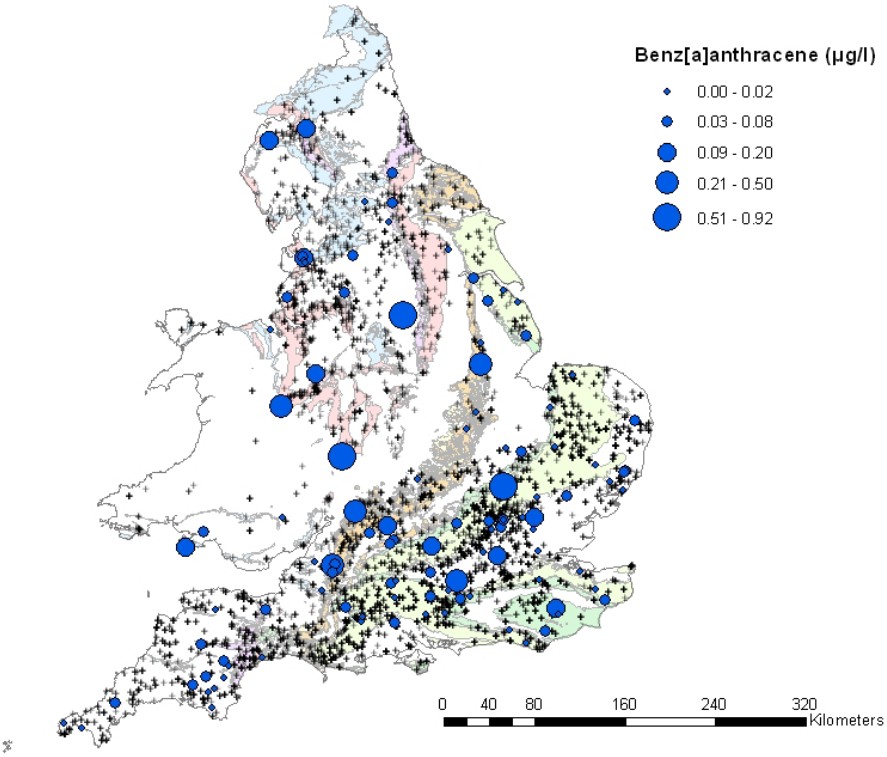
Table A2.8 Other plasticisers

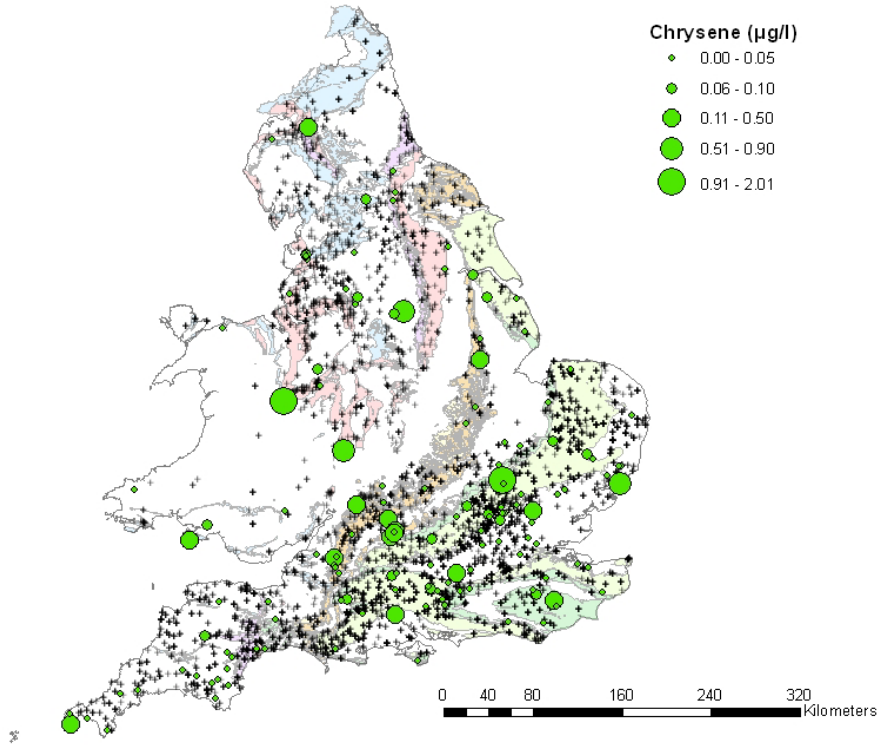
Name	Detects	Sites	Max Conc (µg/L)
2-benzothiazolesulfonamide	1	1	0.51
2-methyl-benzenesulfonamide,	2	2	0.6
4-methylbenzenesulfonamide	2	2	0.59
Benzene sulfonamide	3	1	0.32
Benzylbutylphthalate	5	5	3.5
Bis(2-ethylhexyl)phthalate	26	26	60
Dibutyl phthalate	13	13	20
Diethyl phthalate	18	18	9
Di-ethylhexyl adipate	2	2	0.35
Diisooctyladipate	1	1	1.7
Dimethyl tetrachloroterephthalate	7	7	0.6
Dimethylphthalate.	31	31	0.3
n,n-dibutyl-benzenesulfonamide	1	1	0.03
n-butylbenzenesulfonamide (NBBS)	143	143	190
n-ethyl-4-toluenesulfonamide	1	1	0.05
n-ethyl-o-p-toluenesulfonamide	1	1	0.6
n-methylbenzenesulfonamide	1	1	0.82

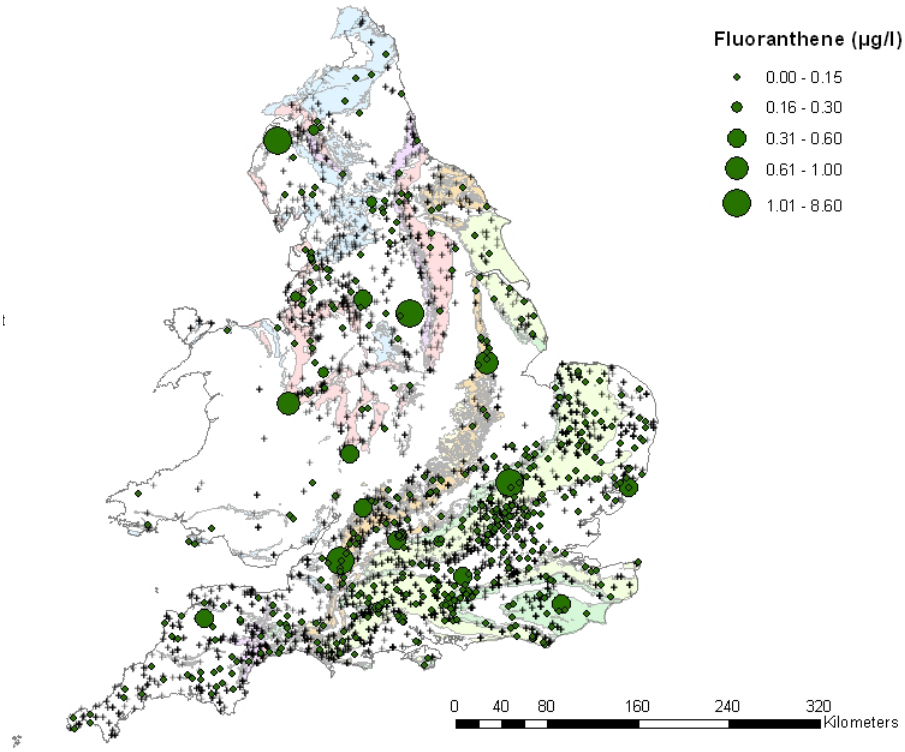
Appendix 3 Spatial distribution of mean concentrations for most frequently detected organic micropollutants from the Environment Agency database

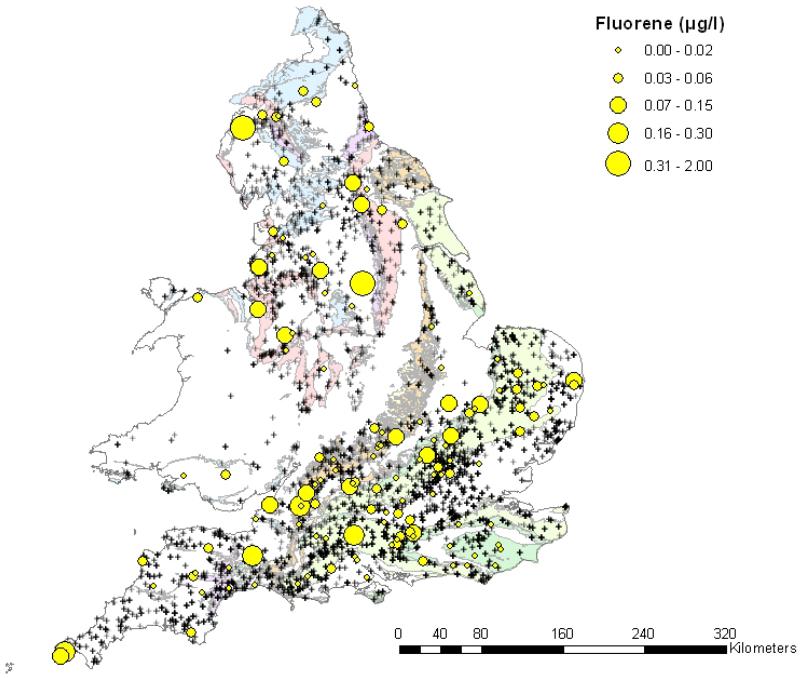
A3.1 PAH

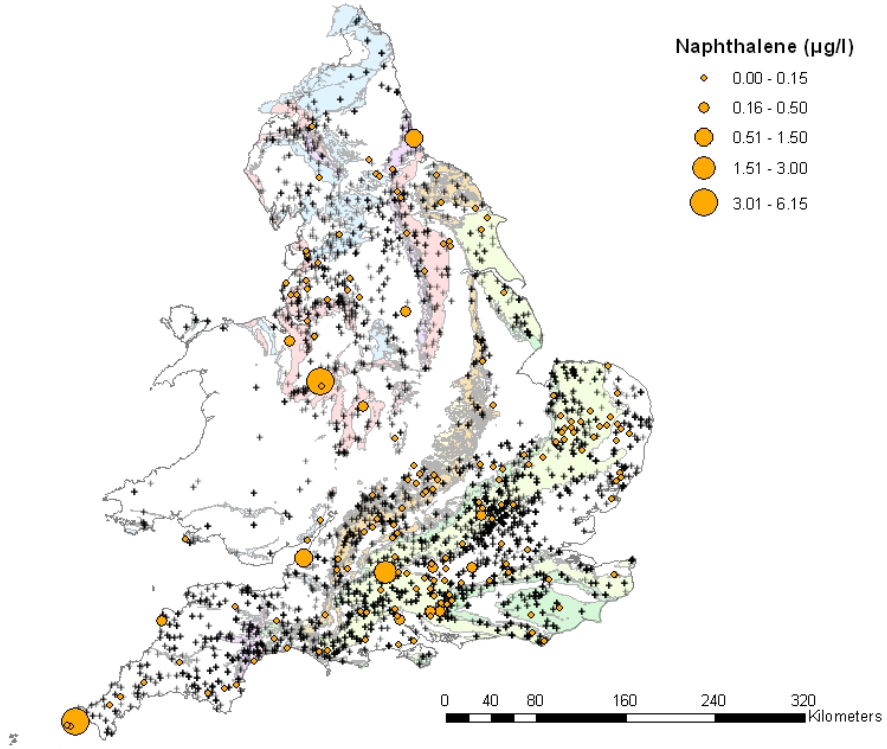


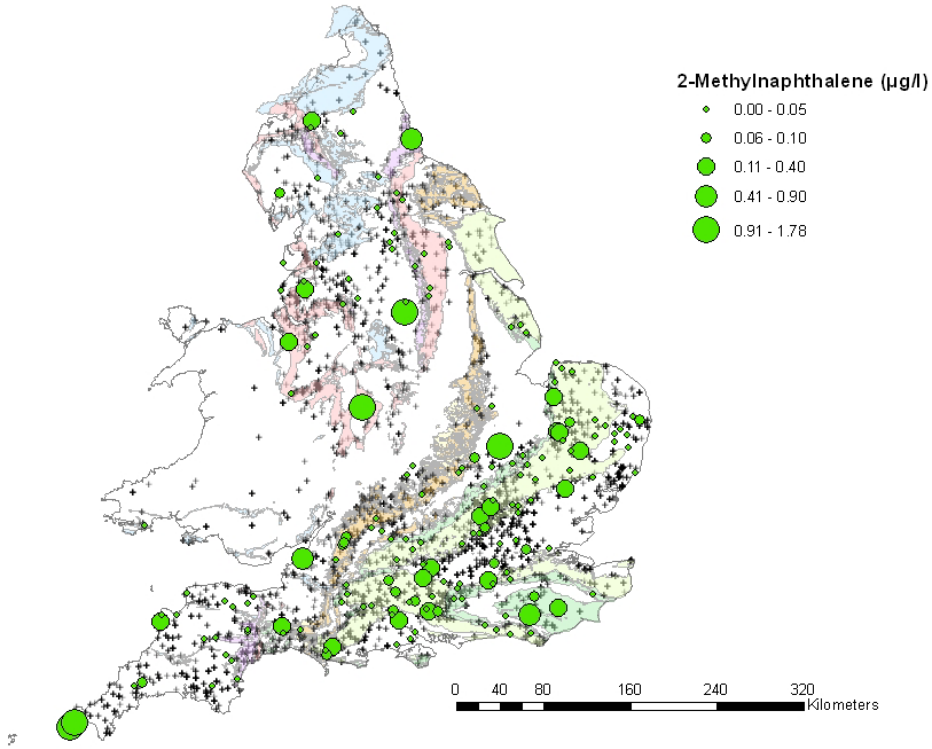


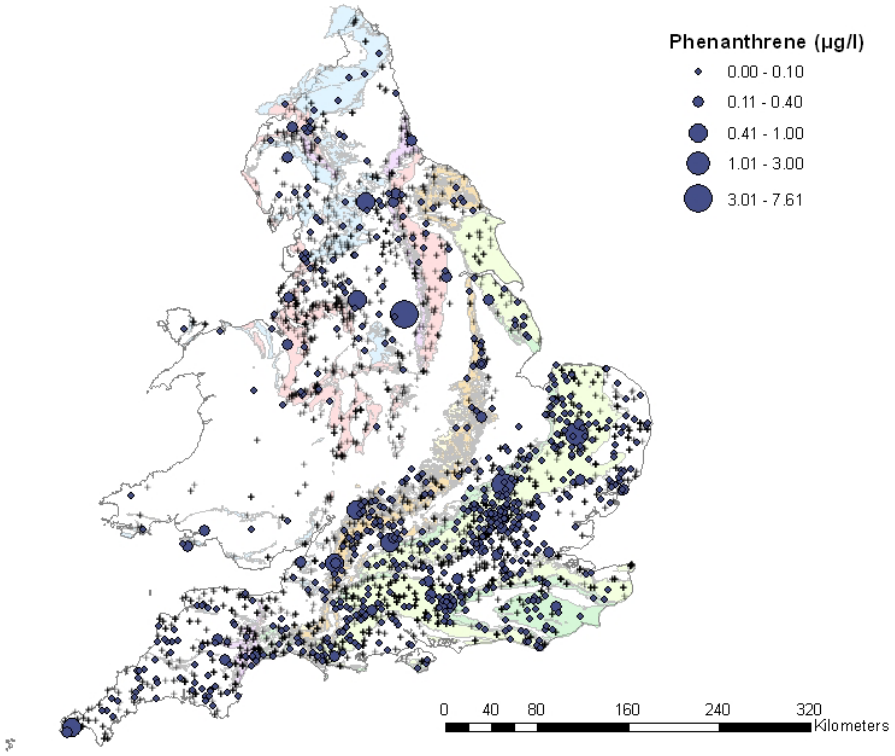

Chrysene (µg/l)
0.00 - 0.05
0.06 - 0.10
0.11 - 0.50
0.51 - 0.90
0.91 - 2.01
0 40 80 160 240 320
Kilometers

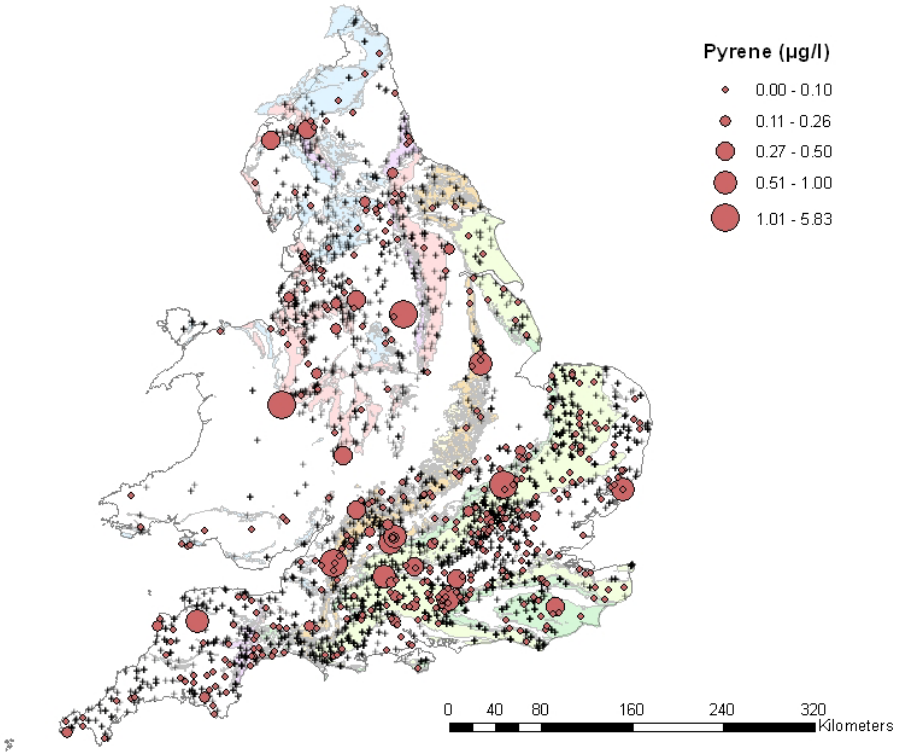

Fluoranthene (µg/l)
0.00 - 0.15
0.16 - 0.30
0.31 - 0.60
0.61 - 1.00
1.01 - 8.60
0 40 80 160 240 320
Kilometers


Fluorene (µg/l)
0.00 - 0.02
0.03 - 0.06
0.07 - 0.15
0.16 - 0.30
0.31 - 2.00
0 40 80 160 240 320
Kilometers

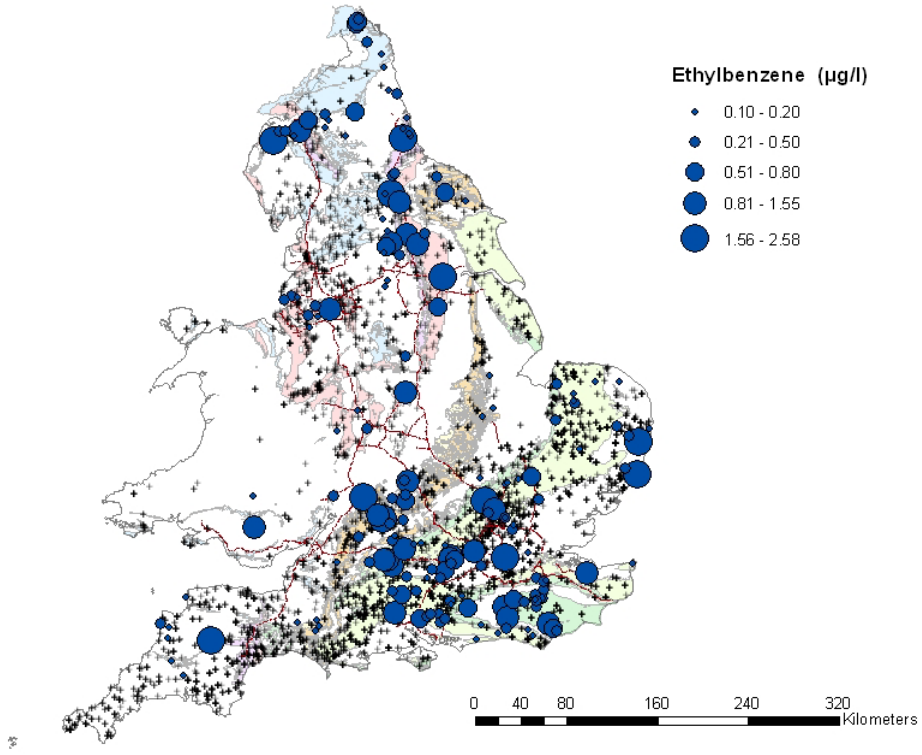

Naphthalene (µg/l)
0.00 - 0.15
0.16 - 0.50
0.51 - 1.50
1.51 - 3.00
3.01 - 6.15
0 40 80 160 240 320
Kilometers

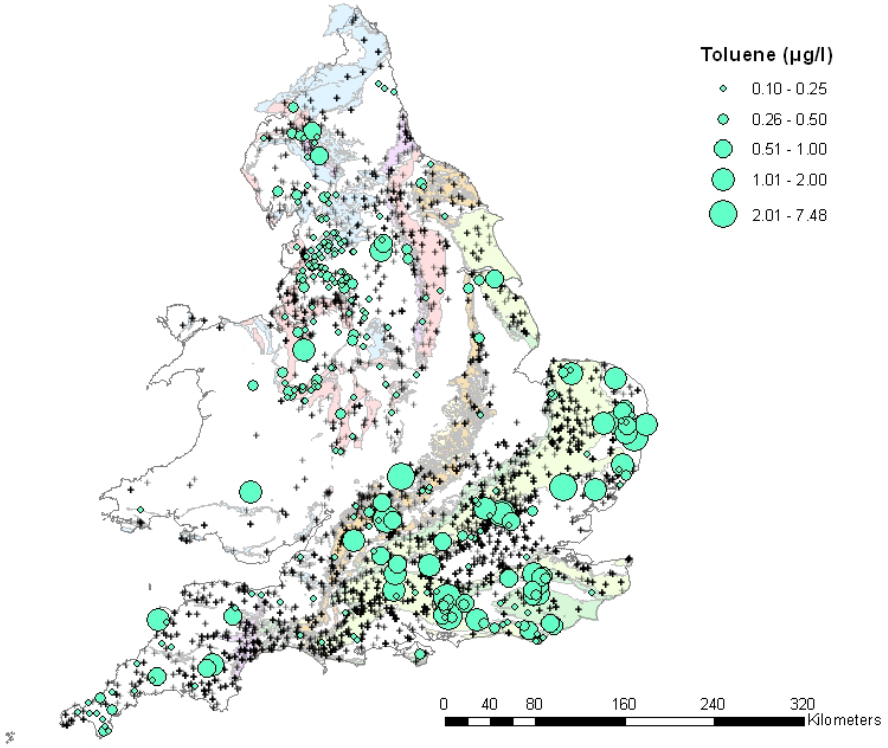

2-Methylnaphthalene (µg/l)
0.00 - 0.05
0.06 - 0.10
0.11 - 0.40
0.41 - 0.90
0.91 - 1.78
0 40 80 160 240 320
Kilometers

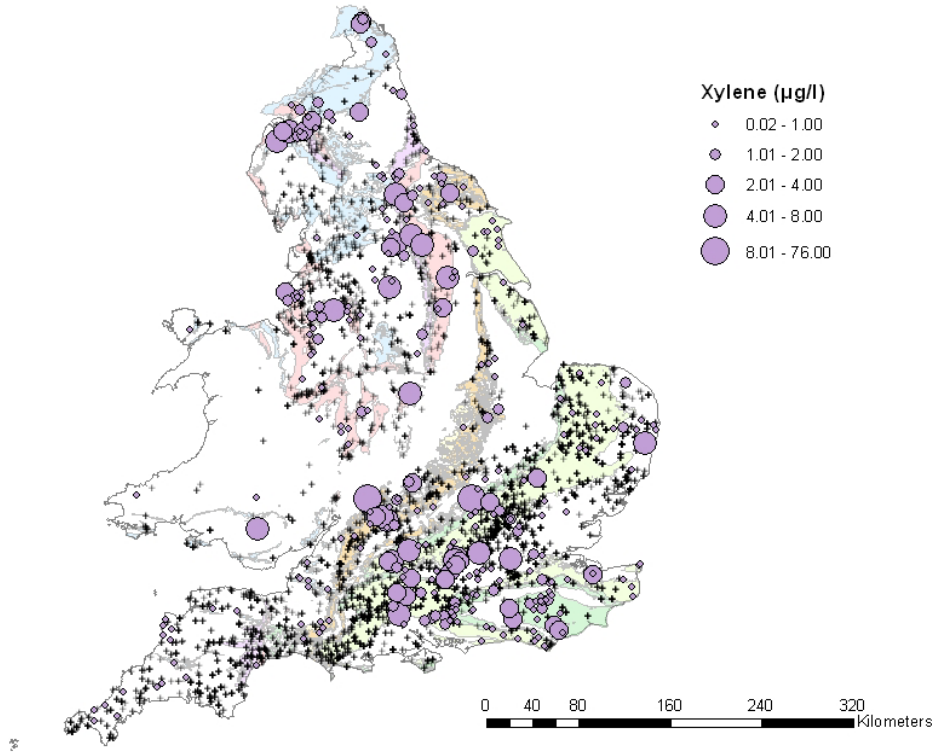

Phenanthrene (µg/l)
0.00 - 0.10
0.11 - 0.40
0.41 - 1.00
1.01 - 3.00
3.01 - 7.61
0 40 80 160 240 320
Kilometers


Pyrene (µg/l)
0.00 - 0.10
0.11 - 0.26
0.27 - 0.50
0.51 - 1.00
1.01 - 5.83
0 40 80 160 240 320
Kilometers

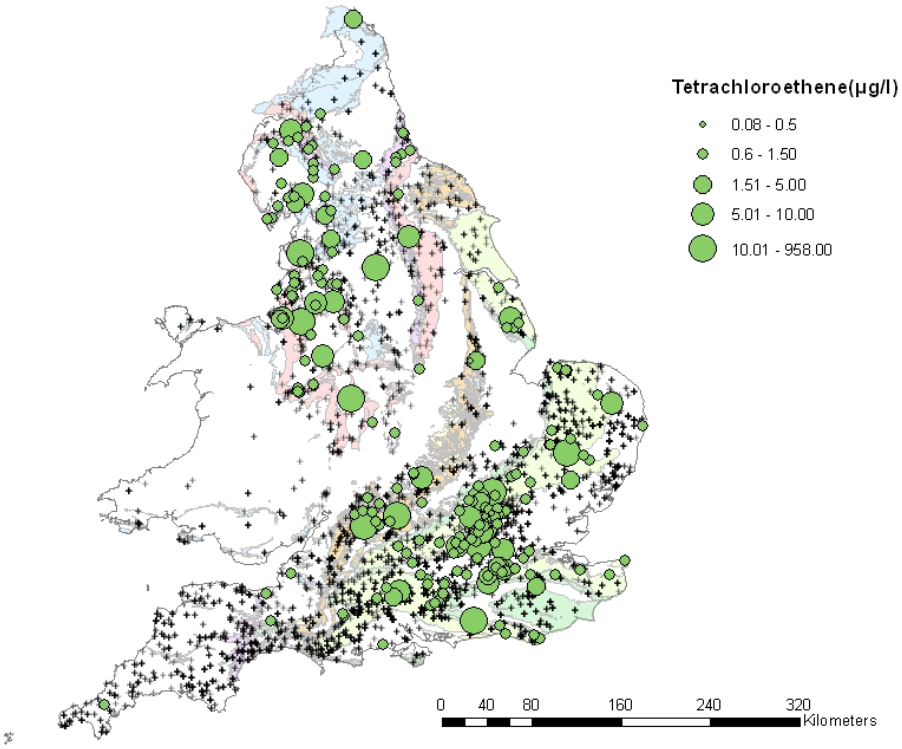
A3.2 BTEX

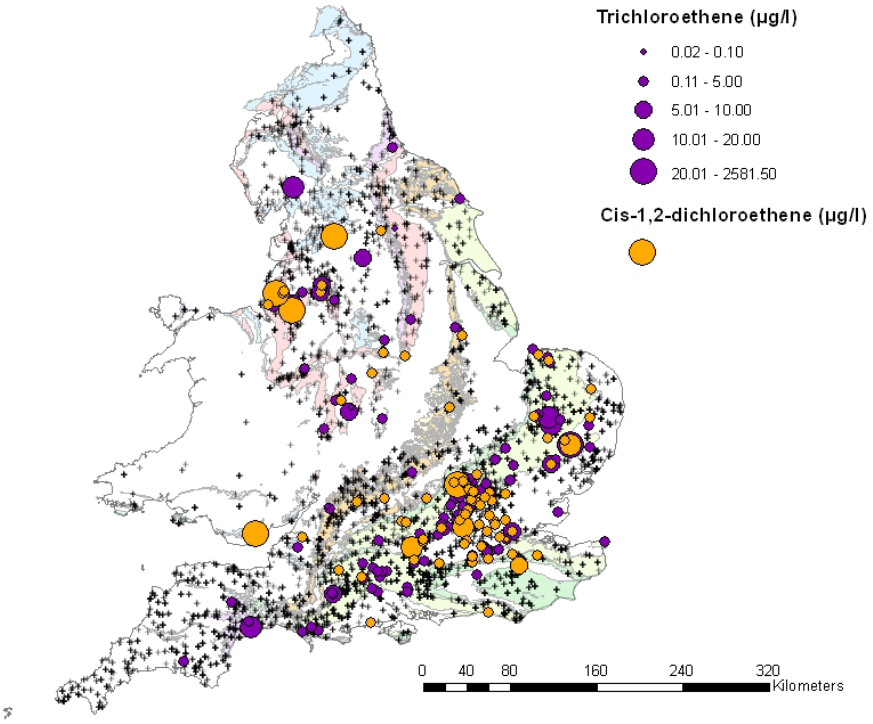

Ethylbenzene (µg/l)
0.10 - 0.20
0.21 - 0.50
0.51 - 0.80
0.81 - 1.55
1.56 - 2.58
0 40 80 160 240 320
Kilometers

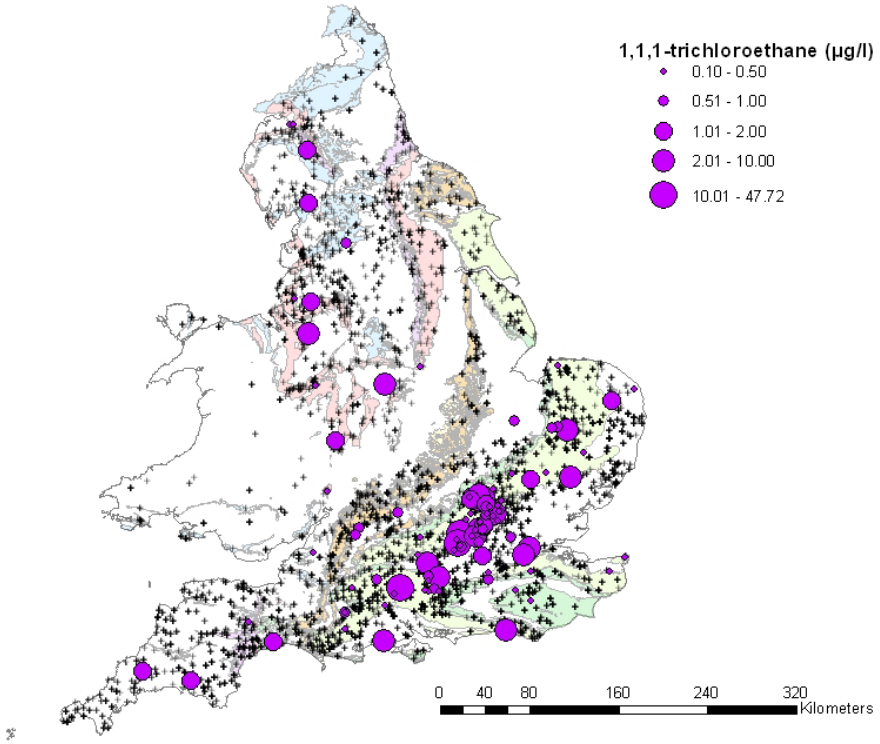

Toluene (µg/l)
0.10 - 0.25
0.26 - 0.50
0.51 - 1.00
1.01 - 2.00
2.01 - 7.48
0 40 80 160 240 320
Kilometers

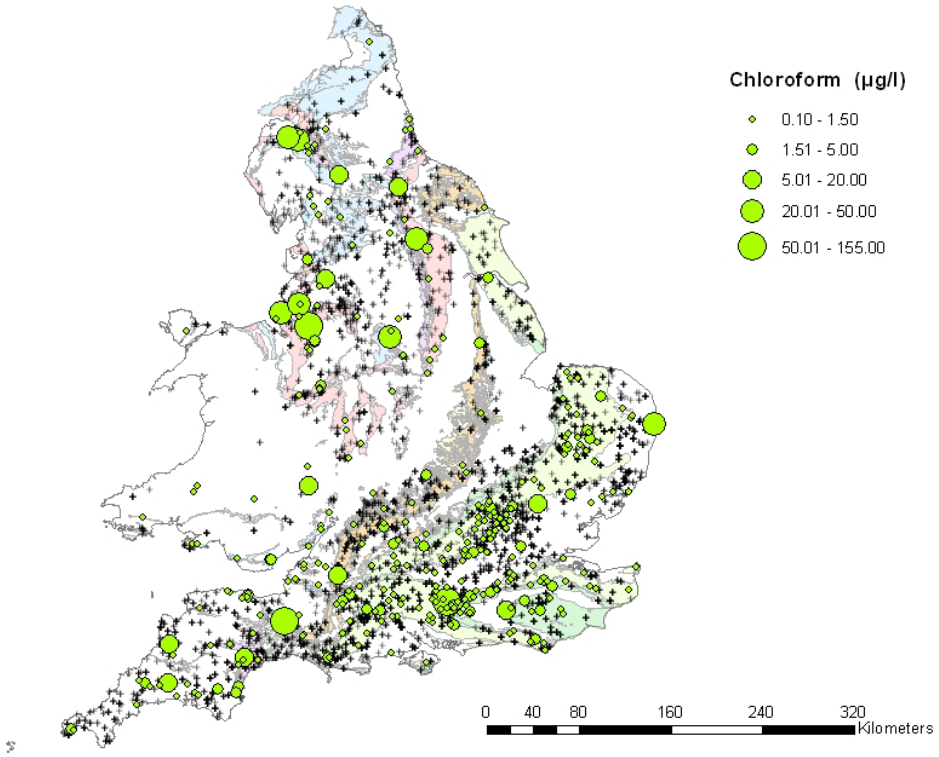

Xylene (µg/l)
0.02 - 1.00
1.01 - 2.00
2.01 - 4.00
4.01 - 8.00
8.01 - 76.00
0 40 80 160 240 320
Kilometers

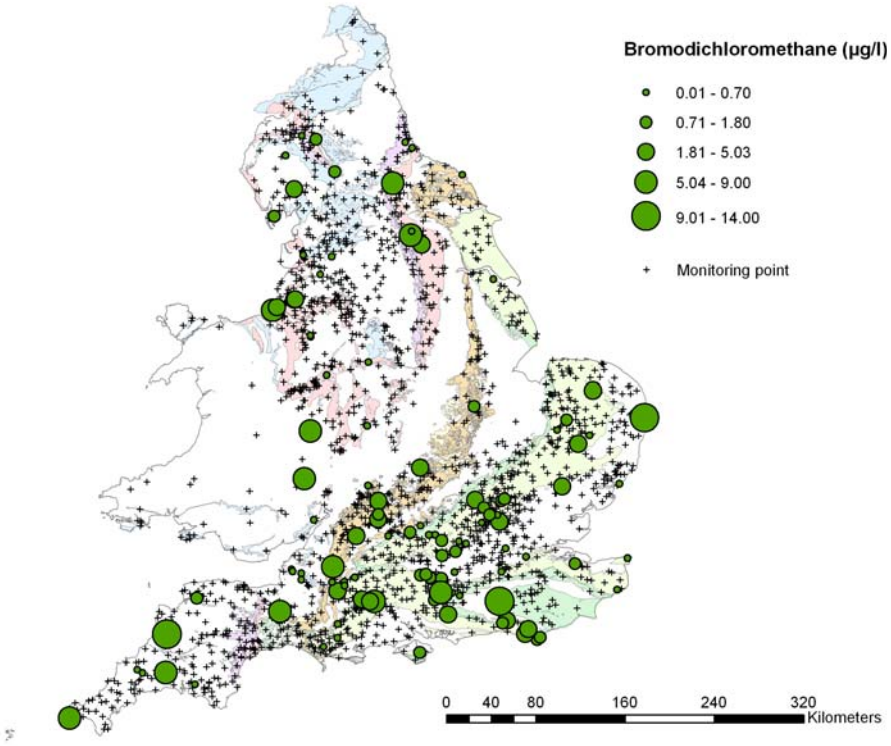
A3.3 CHLORINATED SOLVENTS & THM



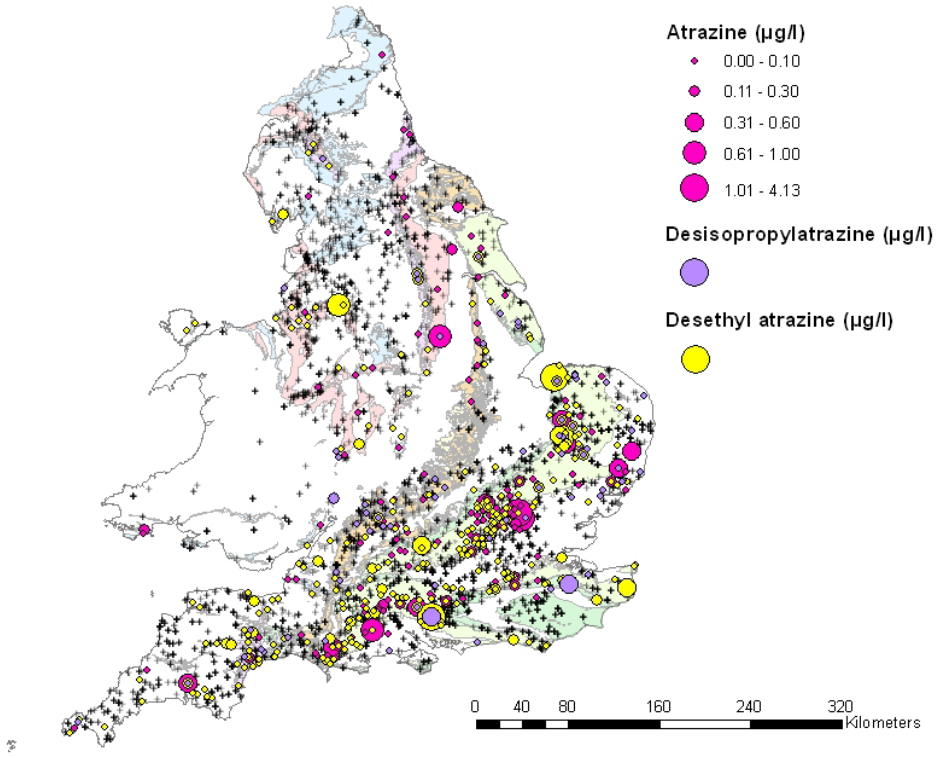


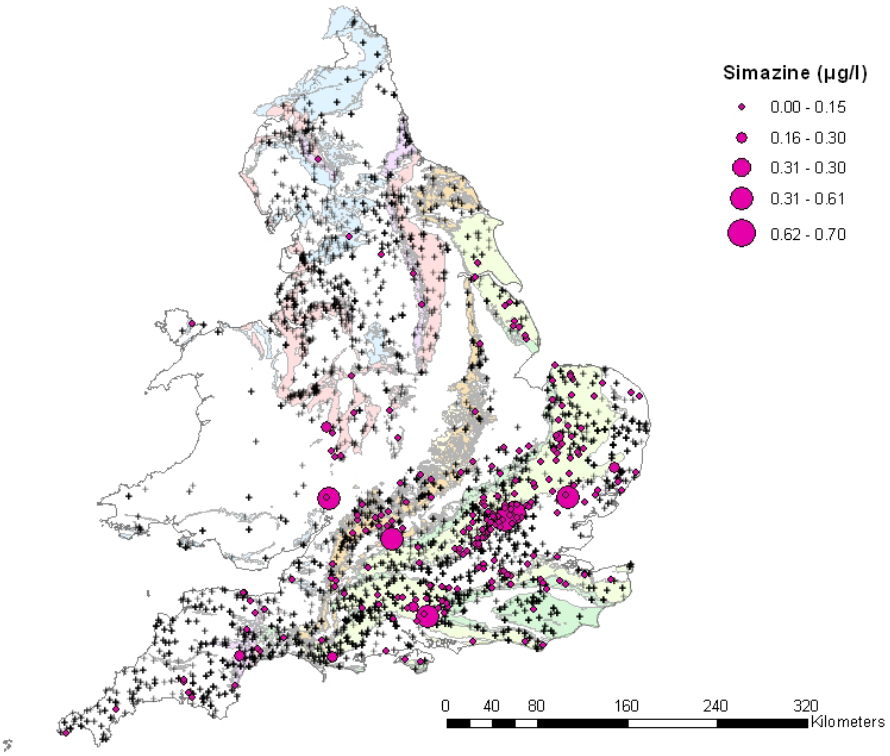

1,1,1-trichloroethane (µg/l)
0.10 - 0.50
0.51 - 1.00
1.01 - 2.00
2.01 - 10.00
10.01 - 47.72
0 40 80 160 240 320
Kilometers

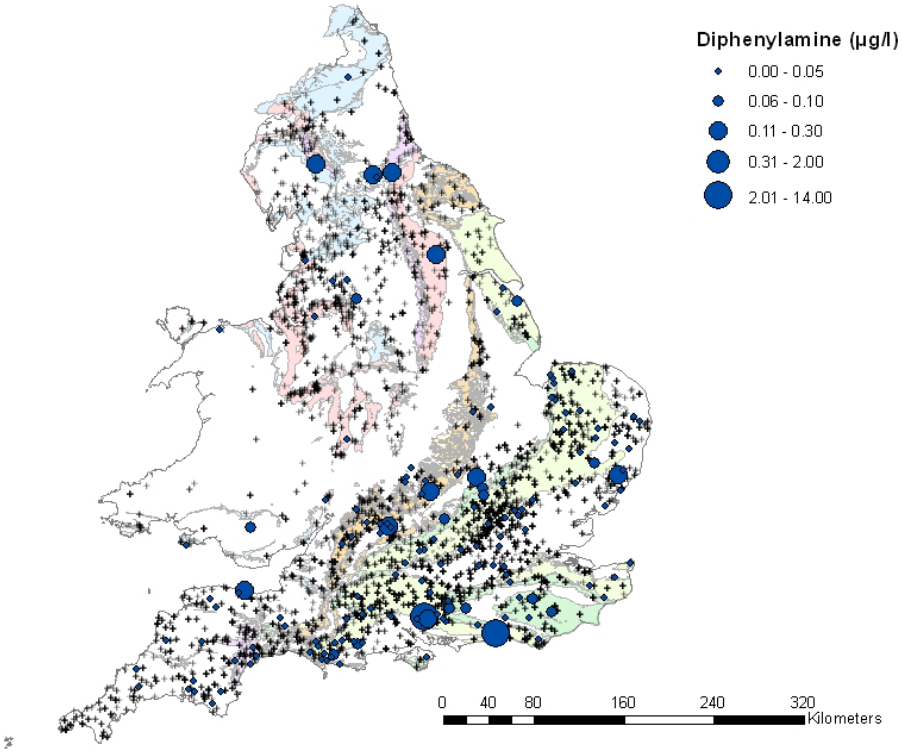

Chloroform (µg/l)
0.10 - 1.50
1.51 - 5.00
5.01 - 20.00
20.01 - 50.00
50.01 - 155.00
0 40 80 160 240 320
Kilometers



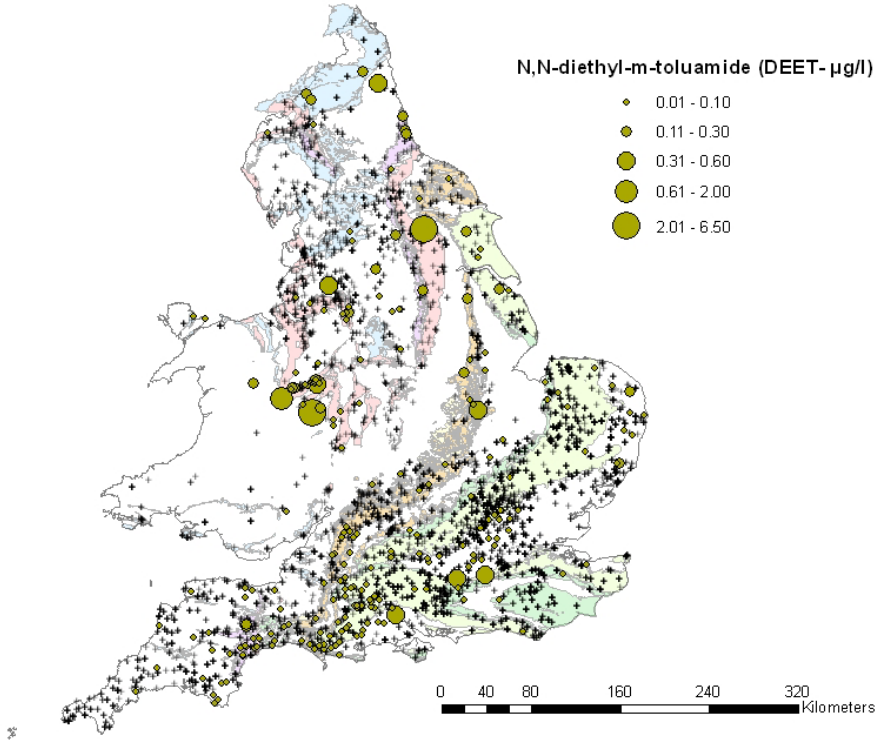
A3.4 PESTICIDES



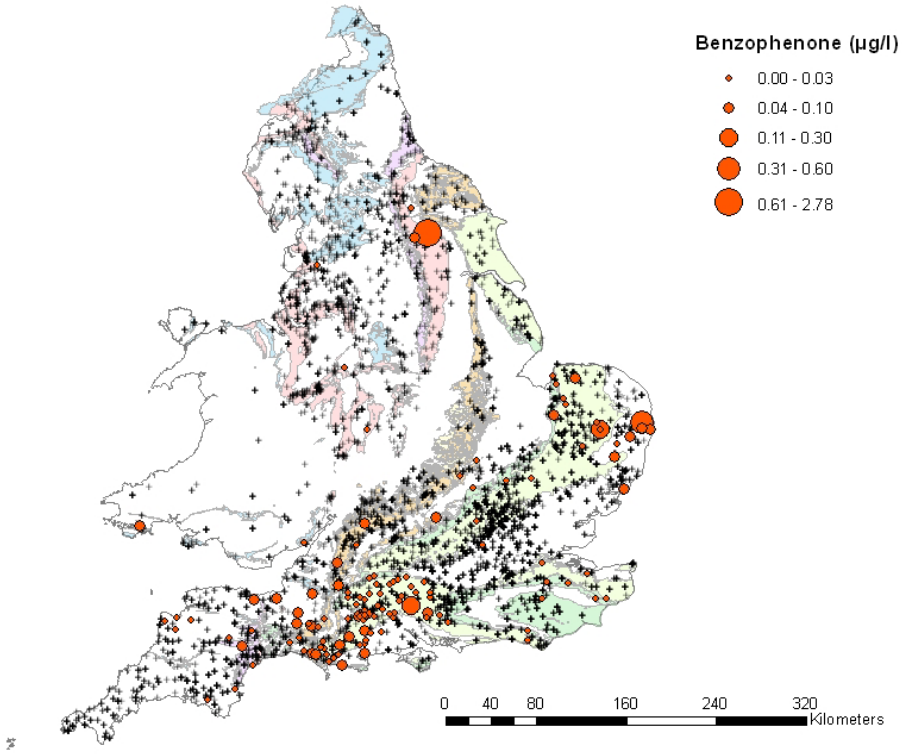

Simazine (µg/l)
0.00 - 0.15
0.16 - 0.30
0.31 - 0.30
0.31 - 0.61
0.62 - 0.70
0 40 80 160 240 320
Kilometers

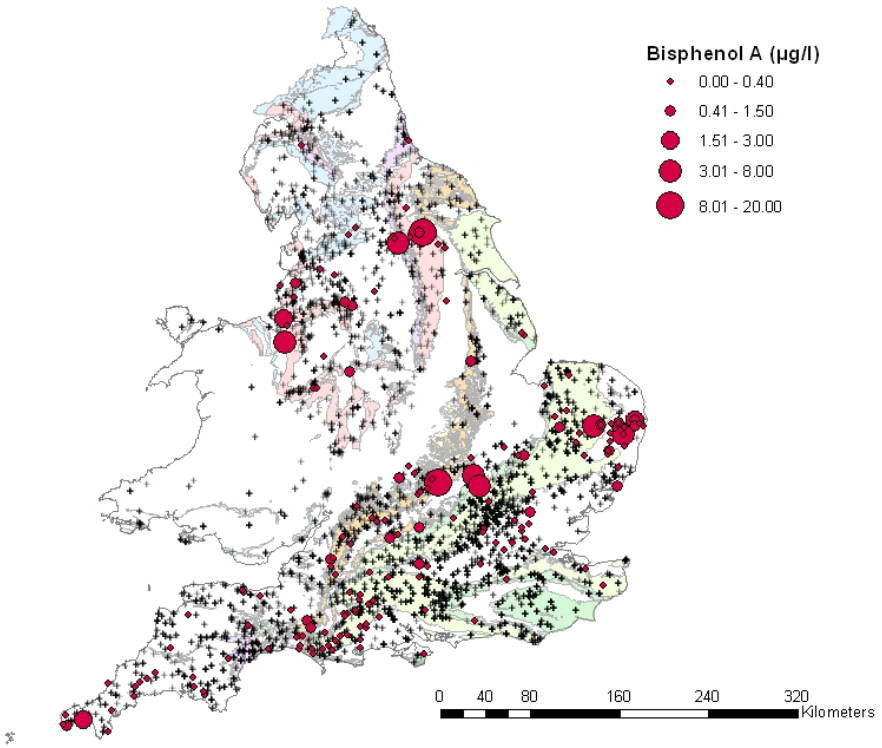

Diphenylamine (µg/l)
0.00 - 0.05
0.06 - 0.10
0.11 - 0.30
0.31 - 2.00
2.01 - 14.00
0 40 80 160 240 320
Kilometers

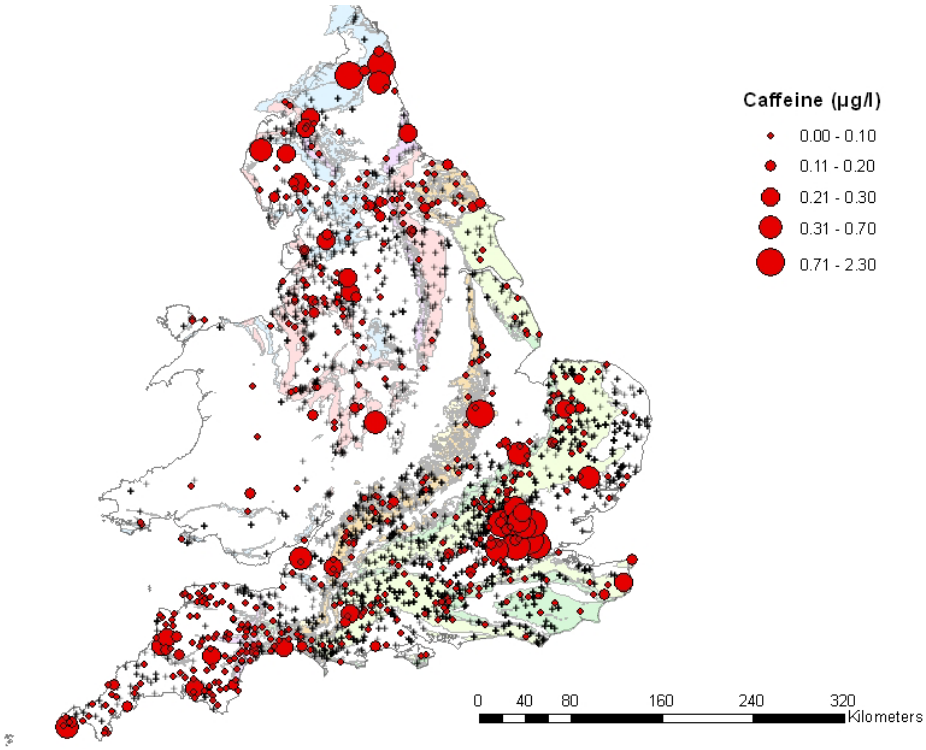
A3.5 INSECT REPELLENT

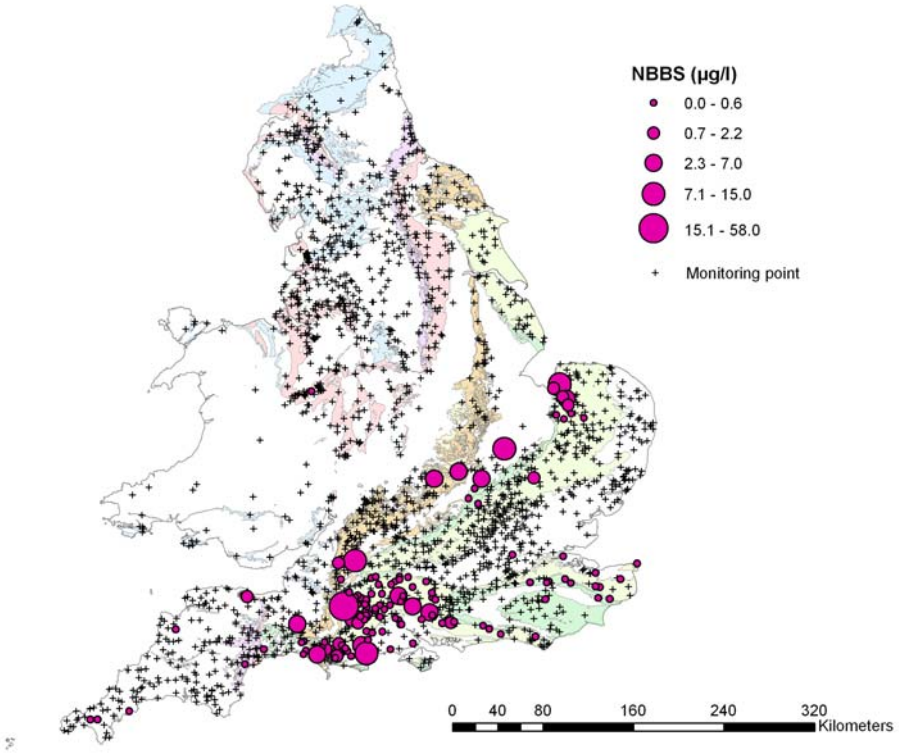


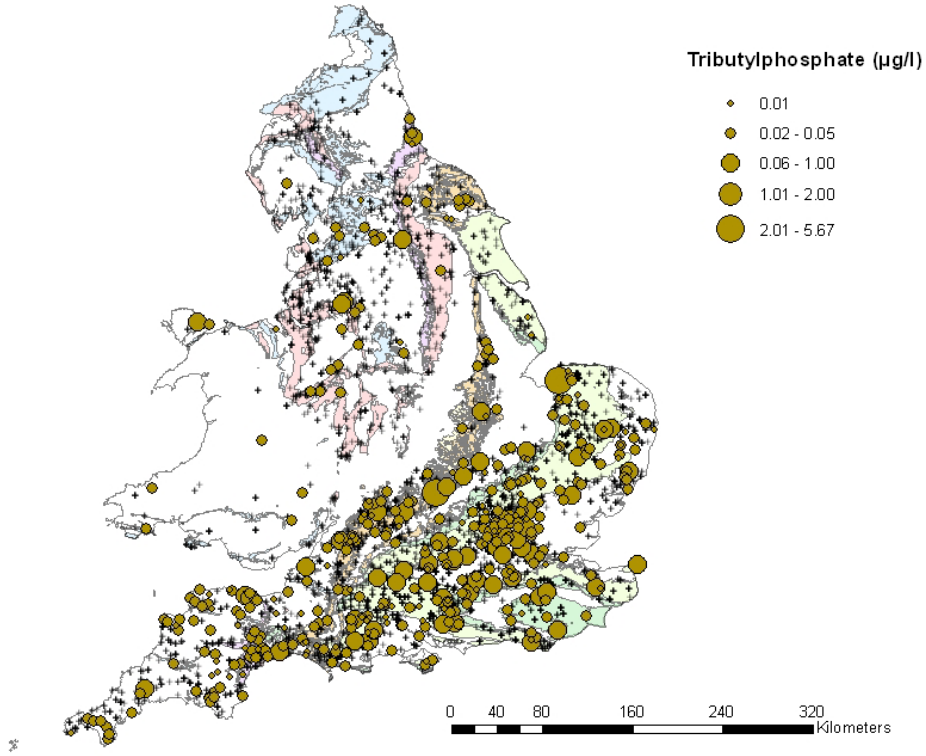
A3.6 OTHER



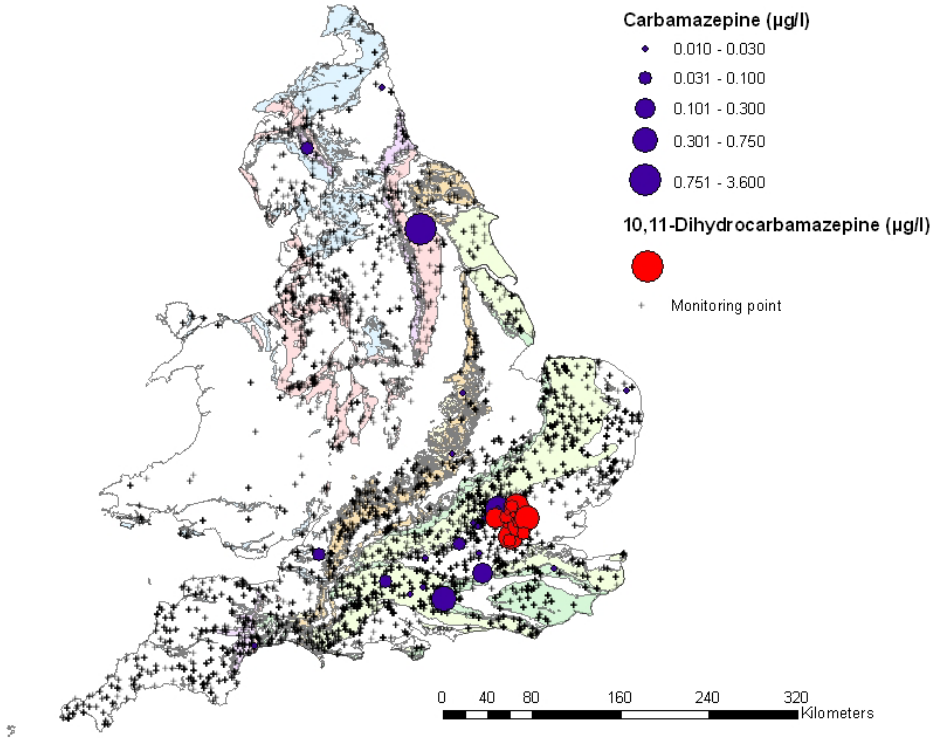

Bisphenol A (µg/l)
0.00 - 0.40
0.41 - 1.50
1.51 - 3.00
3.01 - 8.00
8.01 - 20.00
0 40 80 160 240 320
Kilometers

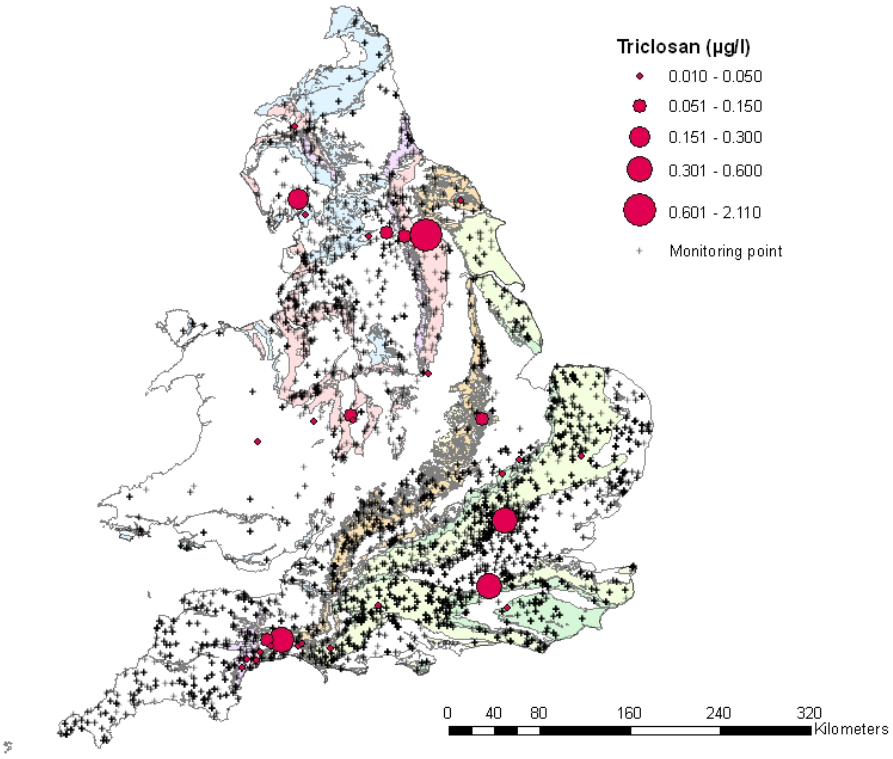

Caffeine (µg/l)
0.00 - 0.10
0.11 - 0.20
0.21 - 0.30
0.31 - 0.70
0.71 - 2.30
0 40 80 160 240 320
Kilometers

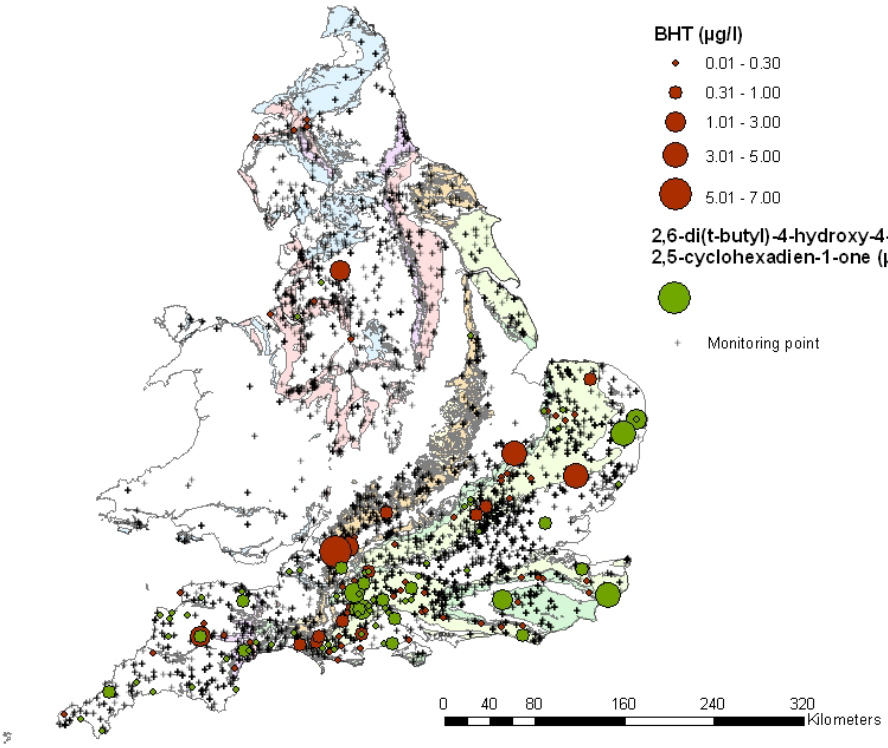

NBBS (µg/l)
0.0 - 0.6
0.7 - 2.2
2.3 - 7.0
7.1 - 15.0
15.1 - 58.0
Monitoring point
0 40 80 160 240 320
Kilometers

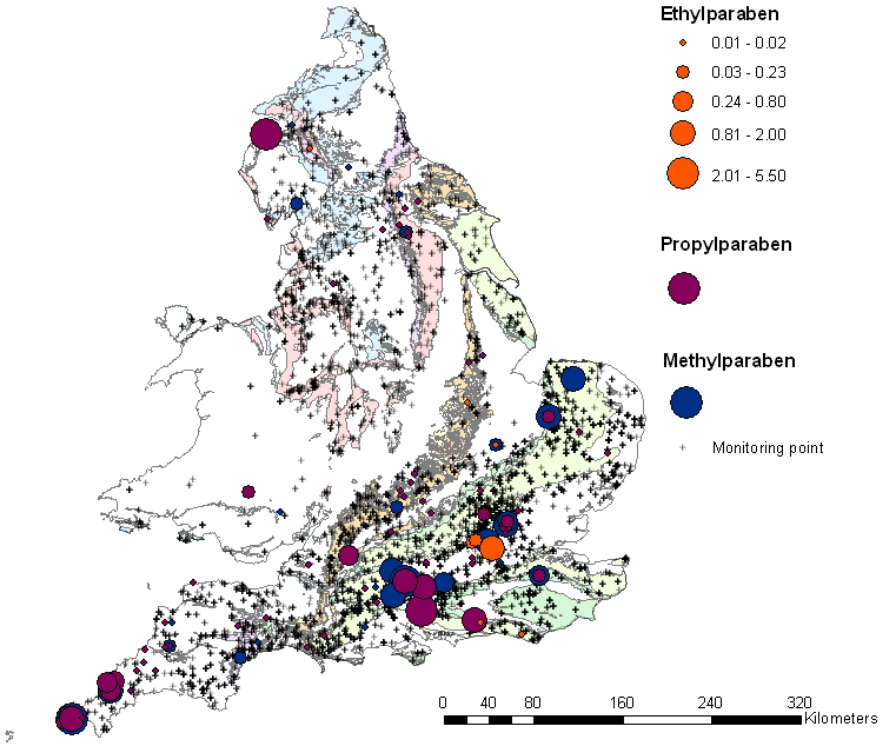

Tributylphosphate (µg/l)
0.01
0.02 - 0.05
0.06 - 1.00
1.01 - 2.00
2.01 - 5.67
0 40 80 160 240 320
Kilometers

A3.7 SPECIFIC CONTAMINANTS






BHT (µg/l)
0.01 - 0.30
0.31 - 1.00
1.01 - 3.00
3.01 - 5.00
5.01 - 7.00
2,6-di(t-butyl)-4-hydroxy-4-methyl 2,5-cyclohexadien-1-one (µg/l)
Monitoring point
0 40 80 160 240 320
Kilometers


Ethylparaben
0.01 - 0.02
0.03 - 0.23
0.24 - 0.80
0.81 - 2.00
2.01 - 5.50
Propylparaben
Methylparaben
Monitoring point
0 40 80 160 240 320
Kilometers