British Geological Survey
NATURAL ENVIRONMENT RESEARCH COUNCIL

Emerging contaminants in groundwater: occurrence and risk assessment

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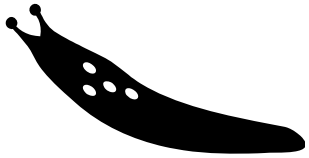
Definition of emerging contaminants

- Potentially toxic substances (aquatic ecology, human)
  - Newly developed compounds
  - Newly categorised contaminants (past e.g. hormones)
  - Newly discovered in groundwater due to analytical developments
- Past/early examples:
  - Pb from fuel additives
  - Endocrine disruptors in rivers (1960s[1] and 1970s[2])
  - Pesticides (e.g. DDT)



- Recent UK example – metaldehyde from slug pellets
  - 2007 detected in finished drinking water by Bristol Water
  - Resistance to DW treatment with low affinity for organic carbon.
  - Only emerged due to developments in analytical methods [3]
  - Accounted for around a large proportion of failures in drinking water standards in UK (2009)

[1] Stumm and Fair, 1965, [2] Garrison et al, 1971, [3] Hall (2010)

Groups of potential emerging contaminants

- Pesticides – parent compounds, metabolites
- Pharmaceuticals – human, veterinary, illicit
- “Life style” – nicotine, caffeine
- Personal care – DEET, parabens, triclosan, musks, UV filters
- Industrial additives and by-products – dioxane, phthalates, bisphenols, MTBE, dioxins
- Food additives – BHA, BHT
- Wastewater treatment by-products – THM, NDMA
- Flame/fire retardants – PBDE, alkyl phosphates
- Surfactants – PFOS & PFOA, alkyl phenols
- Hormones and sterols – oestradiol, cholesterol
- Ionic liquids
- Nanomaterials – sunscreen

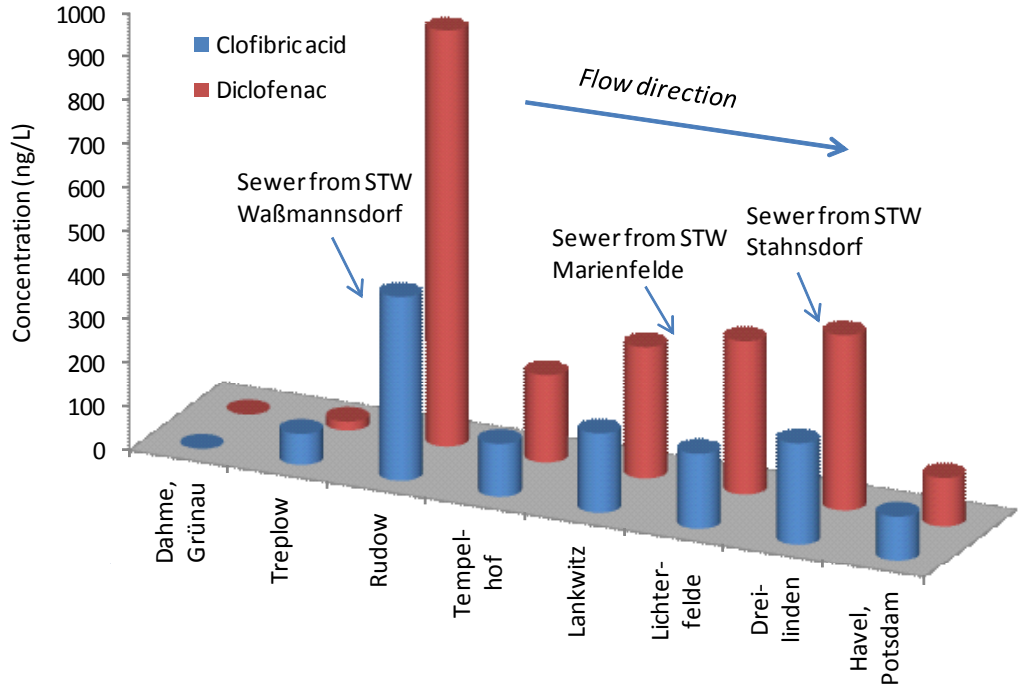
Regulatory framework

- Water Framework Directive (2000/60/EC); Groundwater Daughter Directive (2006/118/EC); Priority Substances Directive (2008/105/EC)
  - Defines 33 Priority Substances + 8 other pollutants
  - Requires setting of Threshold Values for all pollutants which put the groundwater body at risk
- **Groundwater (England & Wales) Regulations (2009)**
  - Aim to avoid pollution by preventing the input of Hazardous Substances and limiting the introduction of non-hazardous pollutants to groundwater

- Drinking Water Directive (98/83/EC)
- **Water Supply (Water Quality) Regulations, England & Wales (2000)**
  - Pesticides (metabolites), aromatic hydrocarbons, chlorinated solvents and some disinfection by-products are included
  - Many emerging contaminants i.e. pharmaceuticals, “personal care” and “lifestyle” compounds are not covered

Key sources of EC in groundwater

- Treated waste water discharge to surface water
- Artificial recharge of treated waste water and surface water
- Many ECs not completely removed by sewage treatment
- Removal can be enhanced by UV treatment or ozonolysis but does not deal with the accumulation in sludge

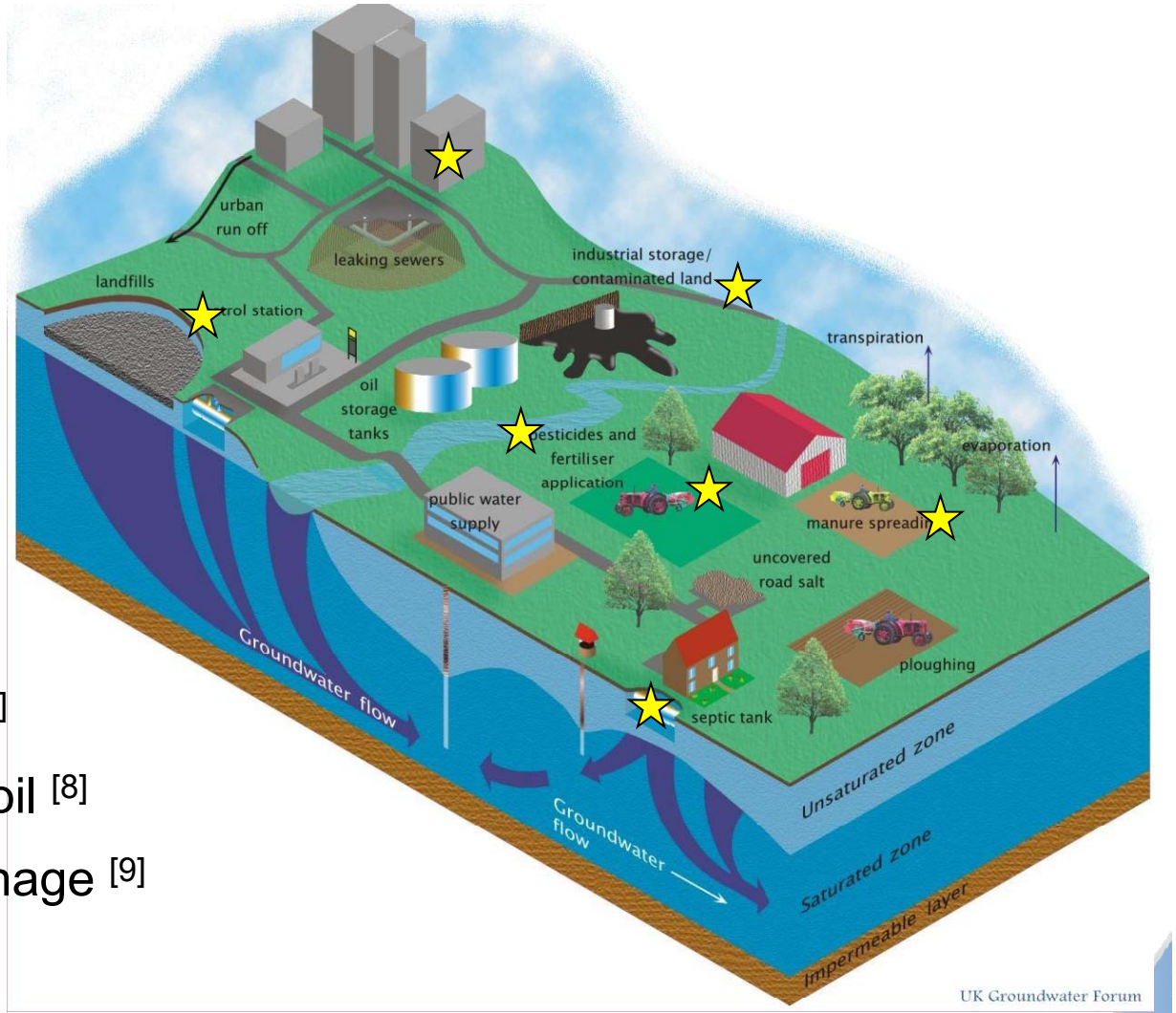


Sampling sites in the Teltowkanal, Berlin [4]

[4]Herberer (2002)

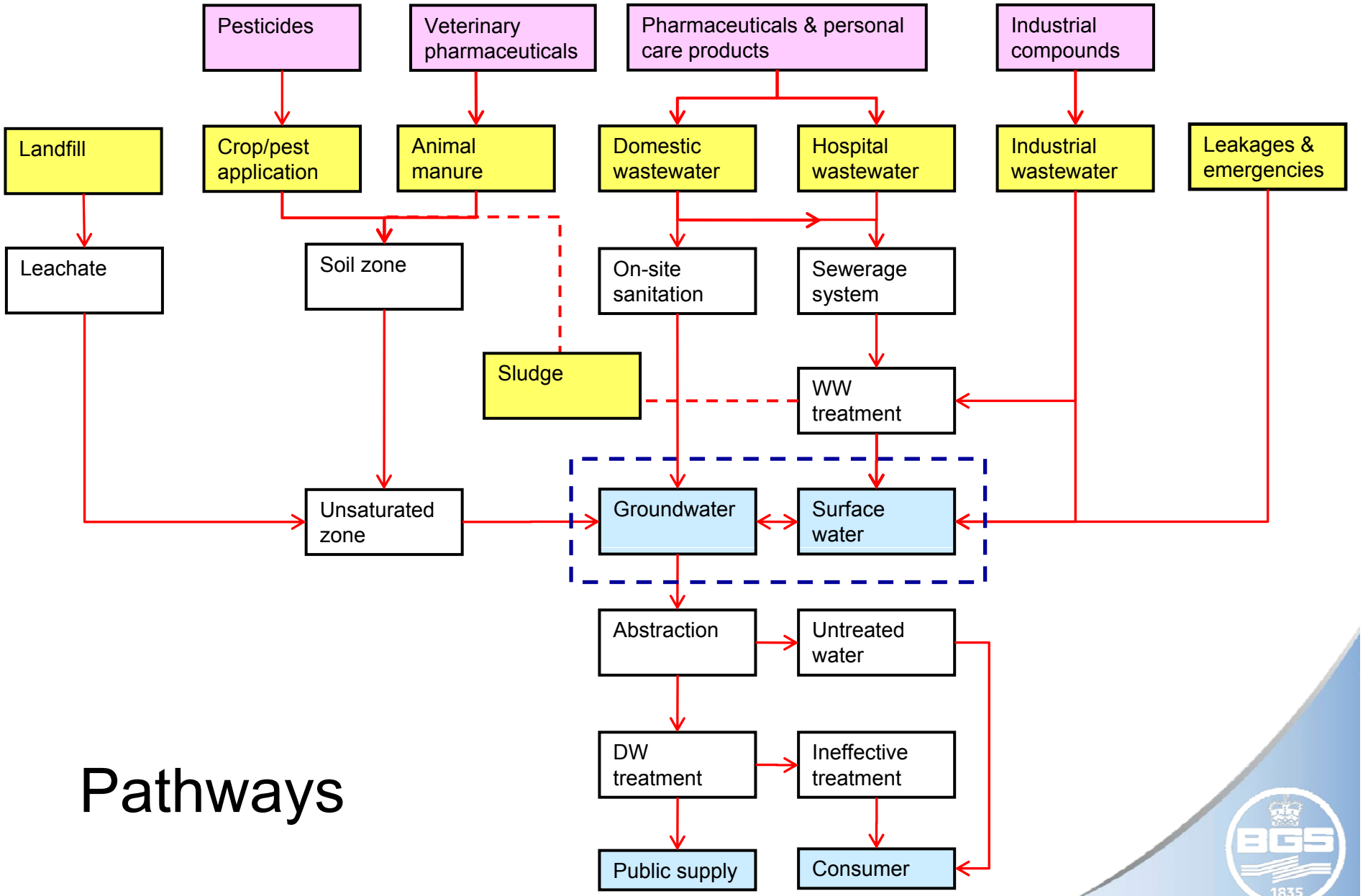
Other sources

- Water treatment
- Sludge application to soil
- Septic tanks [5,6]
- Animal waste lagoons [7]
- Manure application to soil [8]
- Urban waste water drainage [9]
- Transport networks [10]
- Landfill [11]



[5] Swartz et al., 2006, [6] Carrara et al., 2007, [7] Watanabe et al., 2010, [8] Buerge et al., 2011, [9] Nakada et al., 2008, [10] Stuart et al, 2011, [11] Buszkaet al, 2009

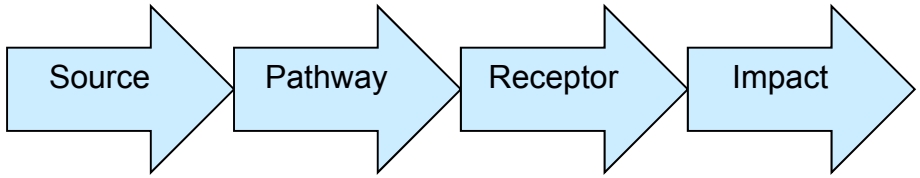
Pathways



Drinking water treatment

- Low percentage removed by clarification
- Many ECs not fully removed by combined or free chlorine and can produce undesirable by-products
- GAC or PAC filtration useful for compounds with K_{ow}>3
- Ozonation effective for compounds with double bonds, aromatic structure or heteroatoms such as N or S
- Also other advanced oxidation methods (AOP) e.g. using H_2O_2 or OH radical generated by UV, sensitised processes using semiconductors
- Membrane or nano filtration can be effective for negatively charged compounds

Risk assessment



- Need usage, persistence, leachability, water treatment recalcitrance, toxicity, bioaccumulation potential, robust sensitive analytical method
- Pesticides – have usage, solubility, K_{oc}, K_{ow}, DT_{50} and DW limit
- Pesticide metabolites - have some data on solubility, K_{oc}, K_{ow}, DT_{50}
  - Need metabolic pathway/rate and toxicity/bioaccumulation data
  - Some studies for UK
- Pharmaceuticals, personal care products and lifestyle compounds
  - Paucity of data on aquatic persistence, human and ecological effects at environmental levels
  - Some studies on properties mainly addressing treatment recalcitrance
  - Prioritisation using PEC/PNEC principles plus sales/prescription data
  - Some ADIs available
- Use surface water as early warning for groundwater

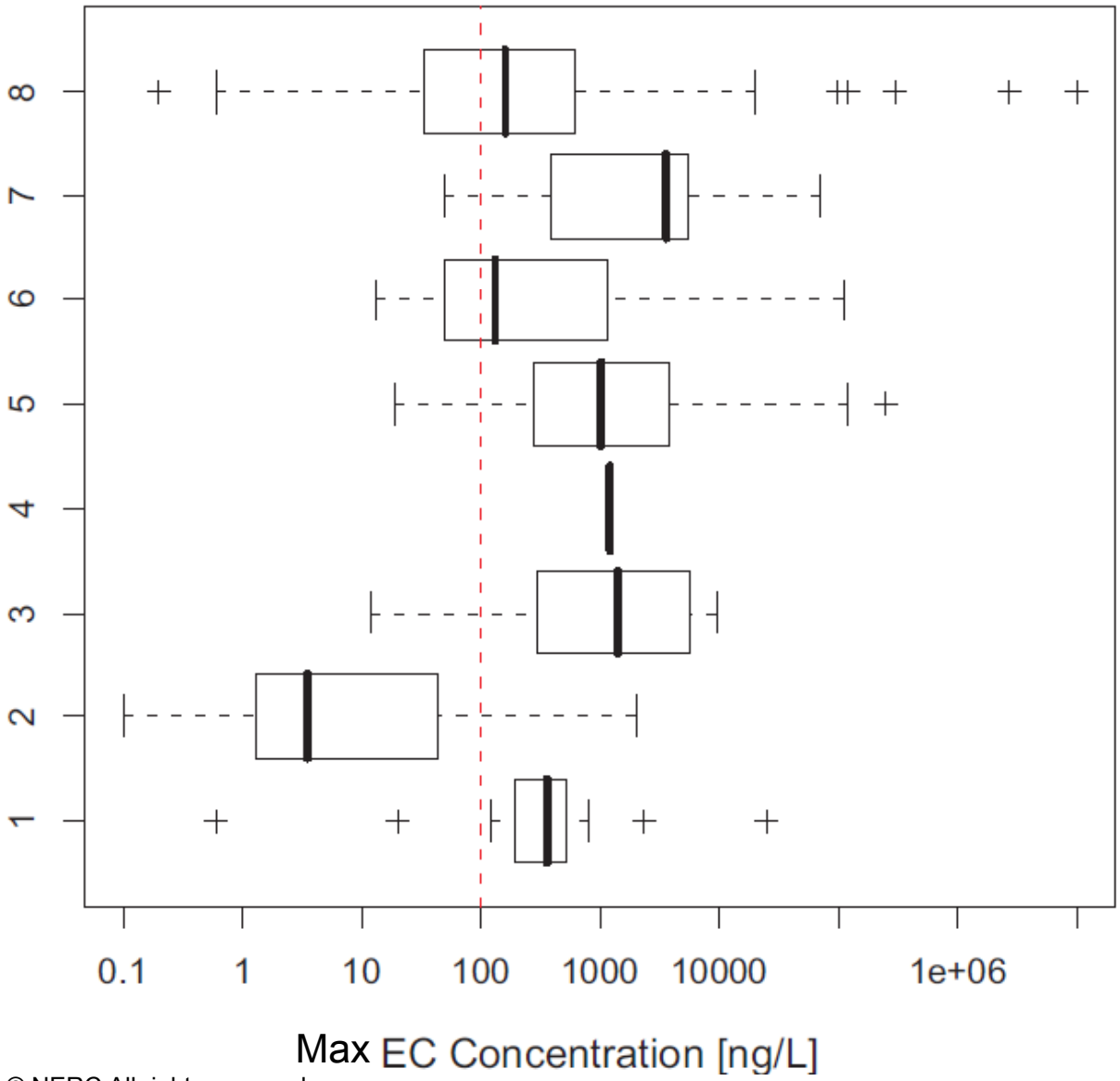
Literature review of occurrence in groundwater

- Looked at pharmaceuticals, personal care products, lifestyle products and some industrial compounds (non-regulated compounds)
- Groundwater EC occurrence from 14 countries reviewed
  - >70 published studies (reconnaissance and targeted)
  - >180 individual EC compounds
  - 23 compounds reported in ≥ 4 separate studies
  - -2 known endocrine disruptors, 6 other potential

Maximum detected concentration (ng/L) for compounds found in ≥ 10 studies:

Compounds	Group	Freq.	Lowest	Average	Highest
Carbamazepine	Anti-epileptic	21	1.64	5312	99194
Sulfamethoxazole	Antibiotic	14	5.7	252	1110
Ibuprofen	Anti-inflammatory	13	0.6	1491	12000
Caffeine	Lifestyle	12	13	9774	110000
Diclofenac	Anti-inflammatory	10	2.5	121	590

Box plots of the occurrence of groups of ECs



8: Pharmaceuticals: antibiotics, epilepsy drugs, anti-inflammatory

7: Skin care products, insecticides

6: Caffeine, nicotine and metabolites

5: Plasticisers, detergents, flame retardants

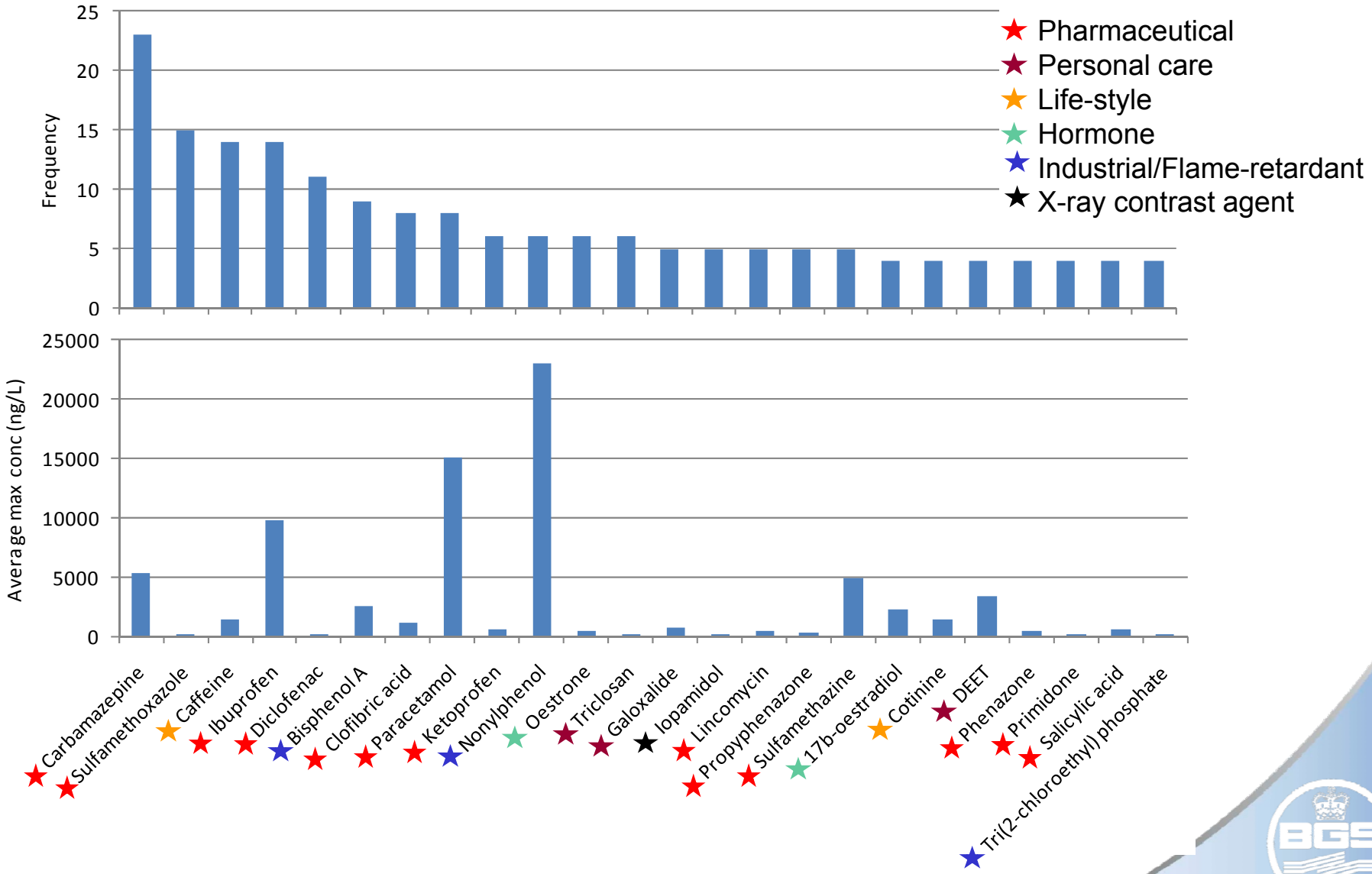
4: Illicit drugs: cocaine (n=1)

3: Food additives and artificial sweeteners

2: Steroids, hormones and metabolites

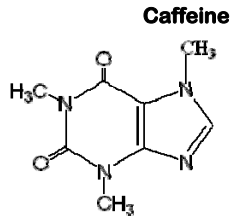
1: Veterinary antibiotics and hormones

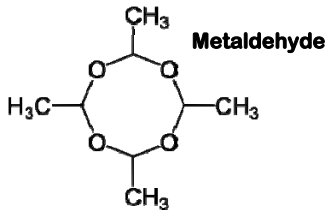
Compounds reported in ≥ 4 separate studies

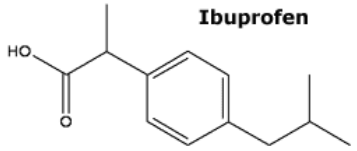


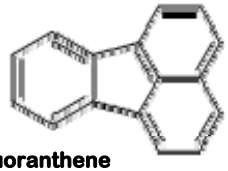
Environment Agency screening data 1993-2009

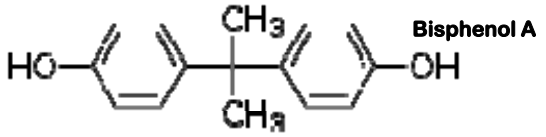
- GCMS method
- About 1200 different compounds
- Industrial intermediates & solvents
- Pesticides and metabolites
- PAH
- BTEX
- Bisphenol A
- DEET
- Pharmaceuticals
  - Carbamazepine, cocaine, lidocaine, barbituric acid, pentobarbital
  - Caffeine, nicotine, cotinine
  - Limited ibuprofen, no obvious paracetamol or sulfamethoxazole

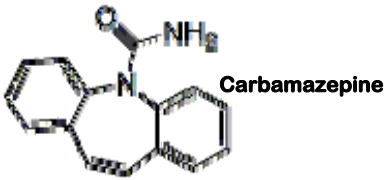


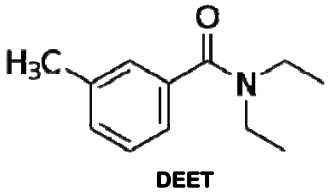




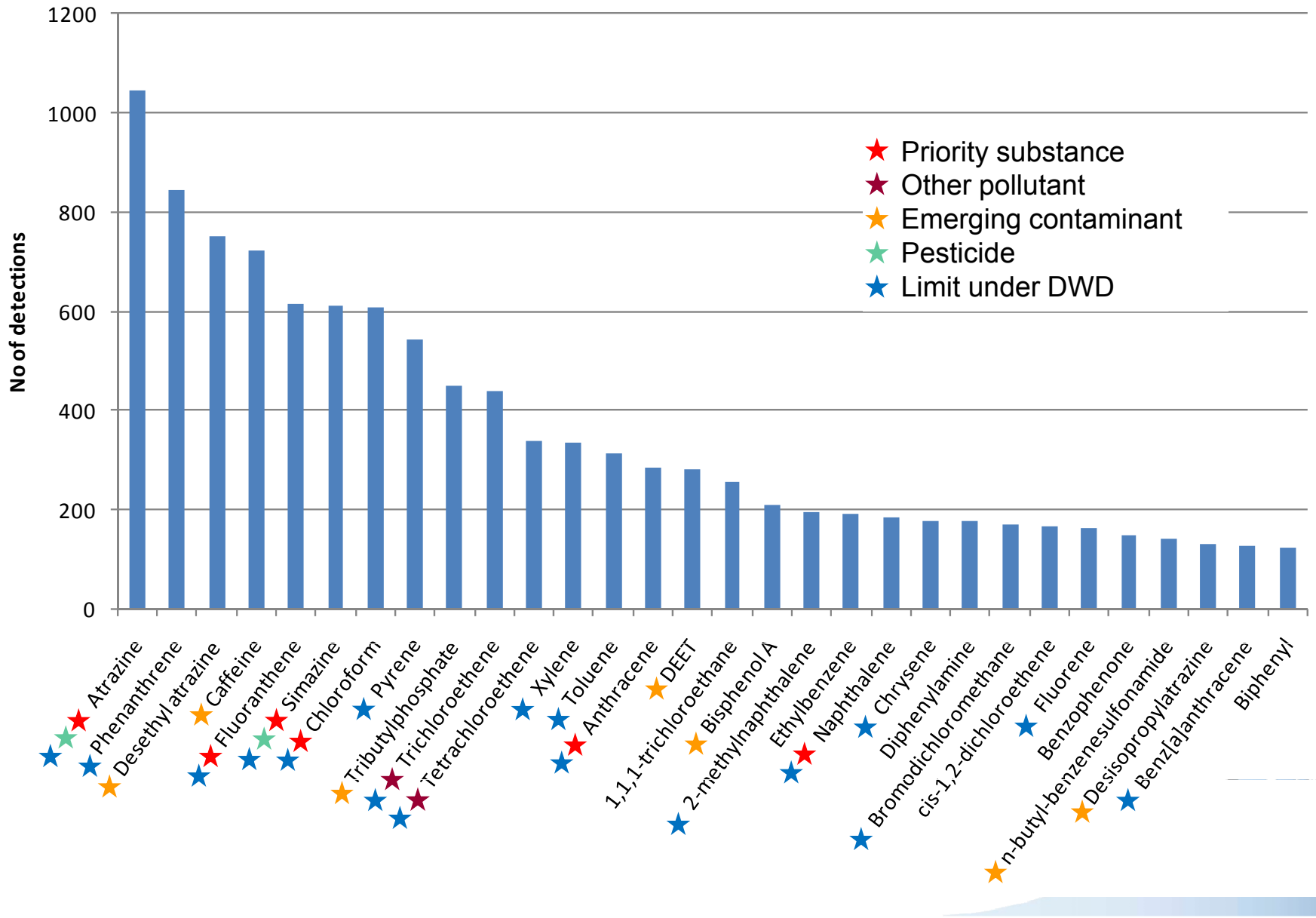




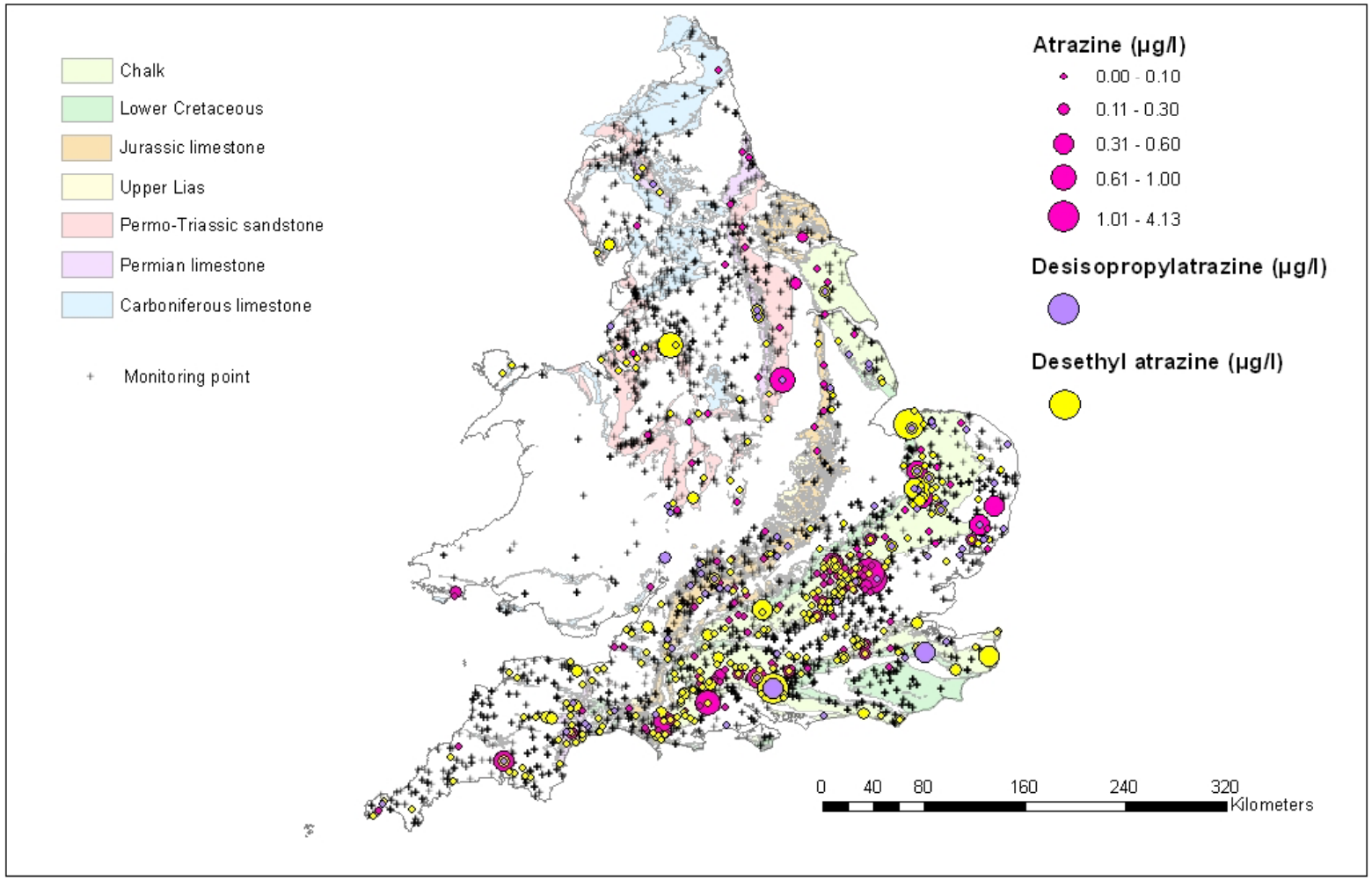




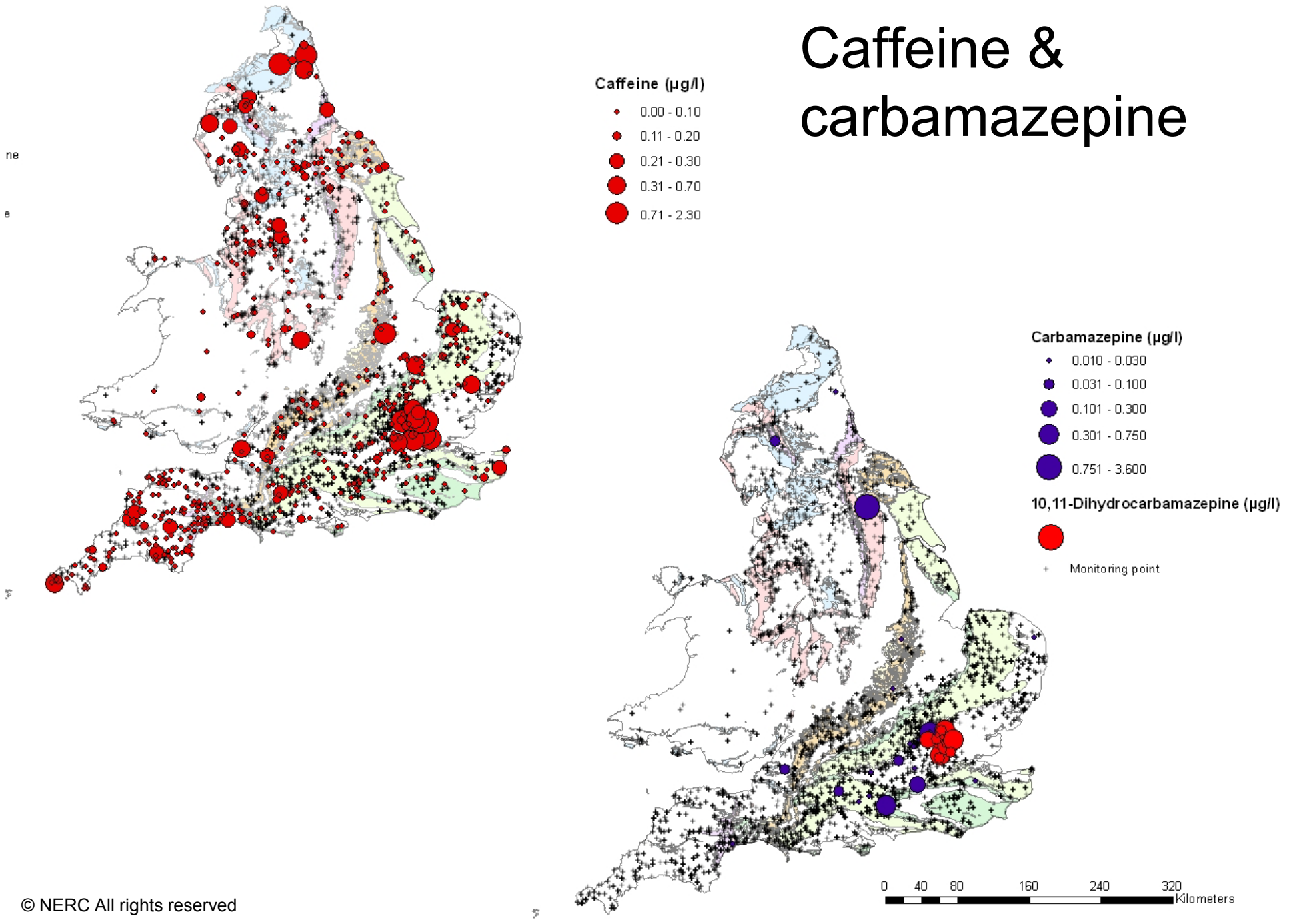
Top 30 most frequently detected compounds



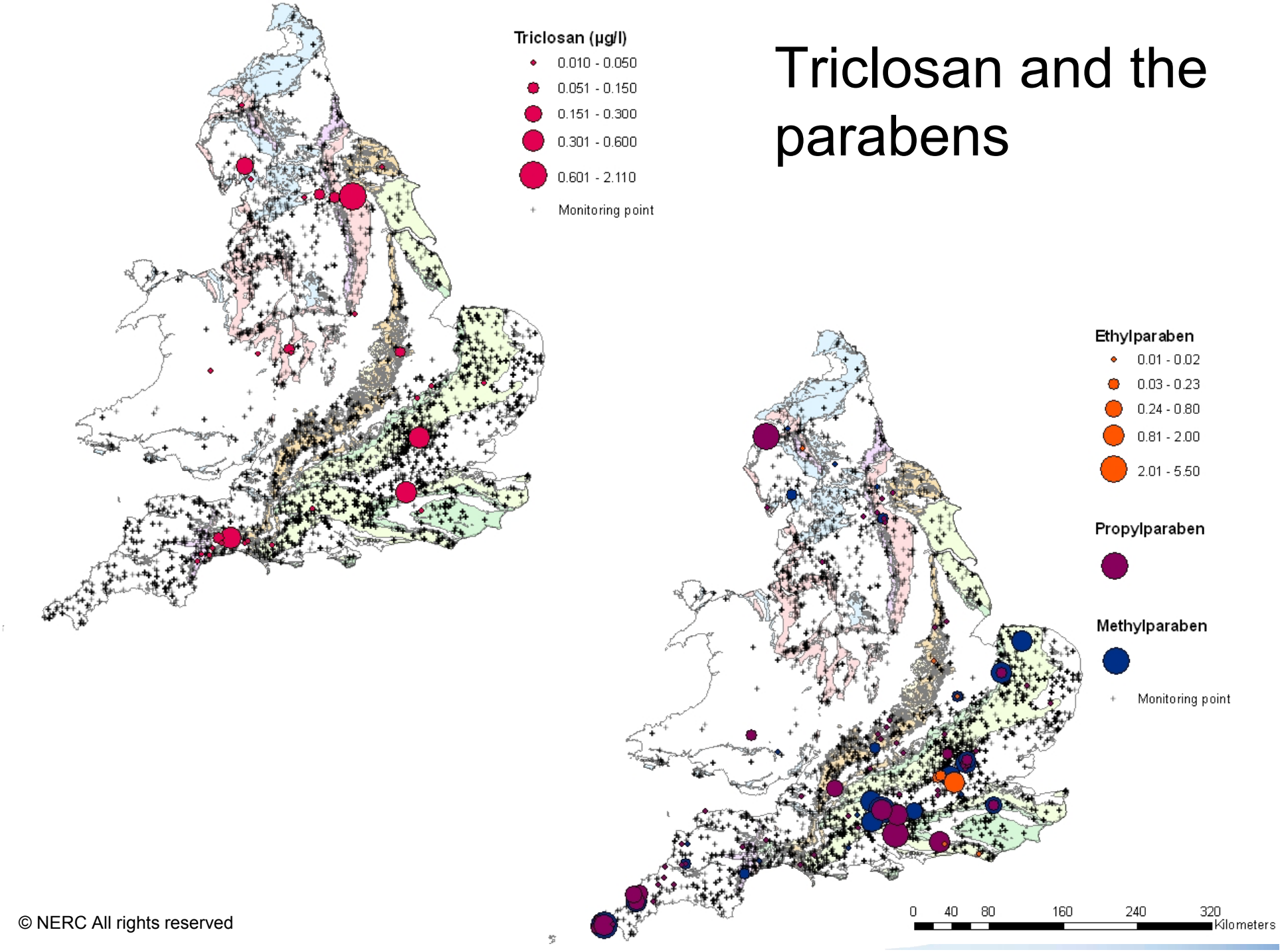
Atrazine and its metabolites



Caffeine & carbamazepine

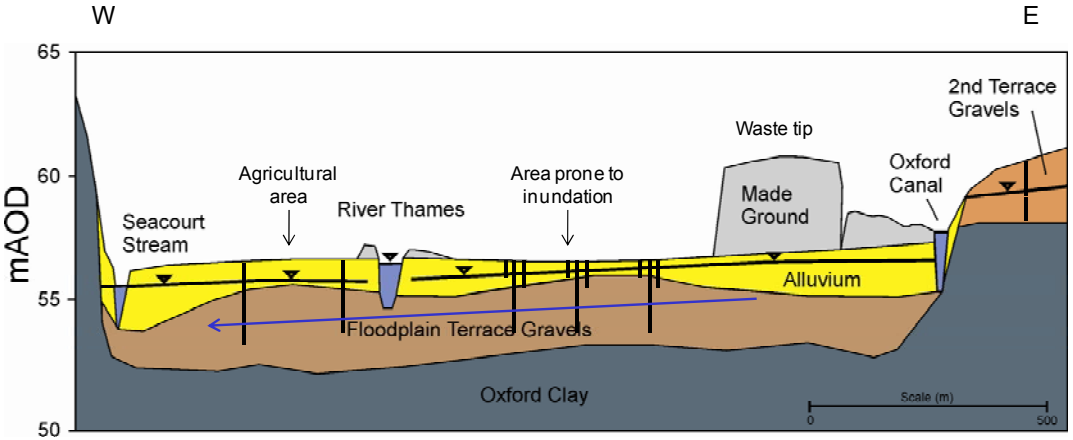


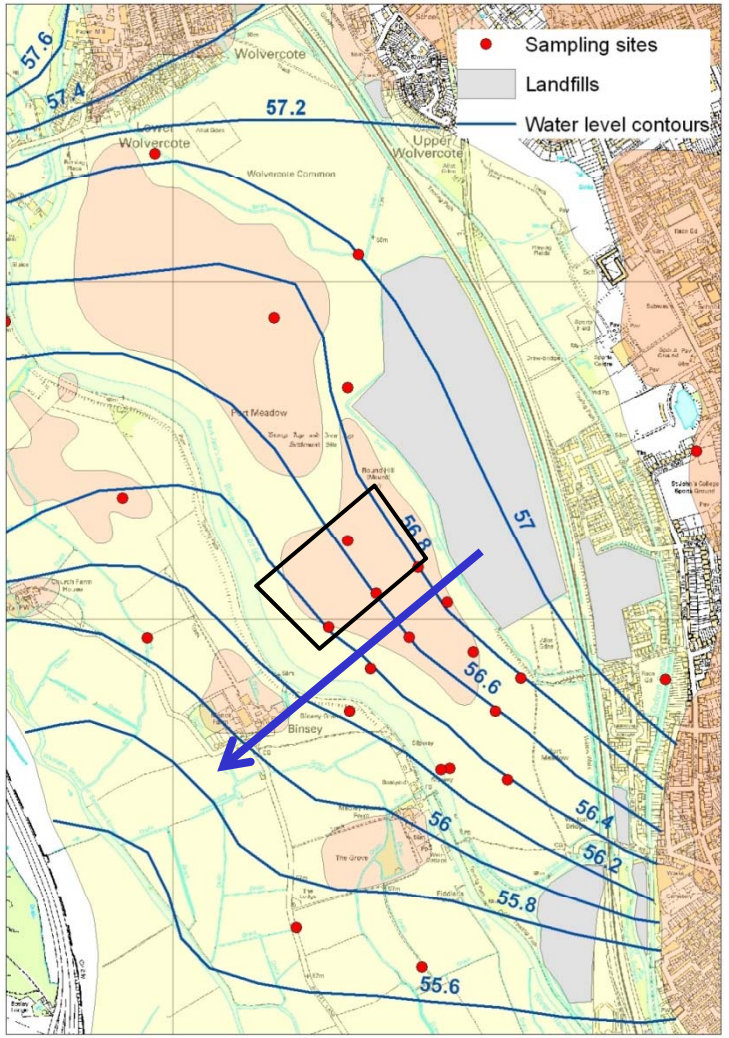
Triclosan and the parabens



Port Meadow research site

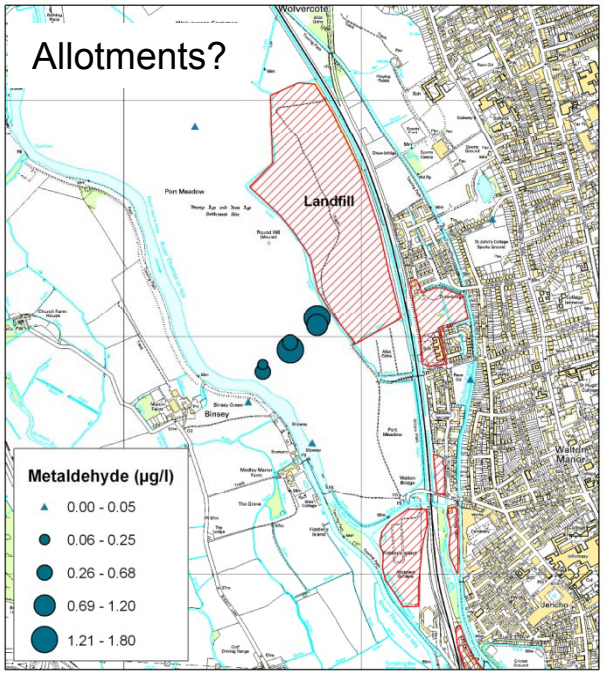
- On Thames floodplain west of Oxford
- Urban area, old landfill, agriculture
- Dynamic environment – shallow fluctuating water table, flood inundation, reversal in gradient
- Implications for attenuation of groundwater pollutants and discharge to rivers

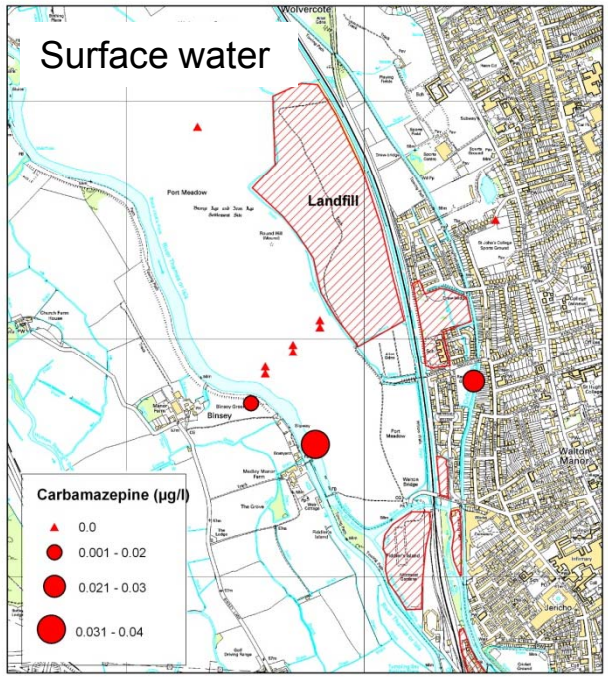


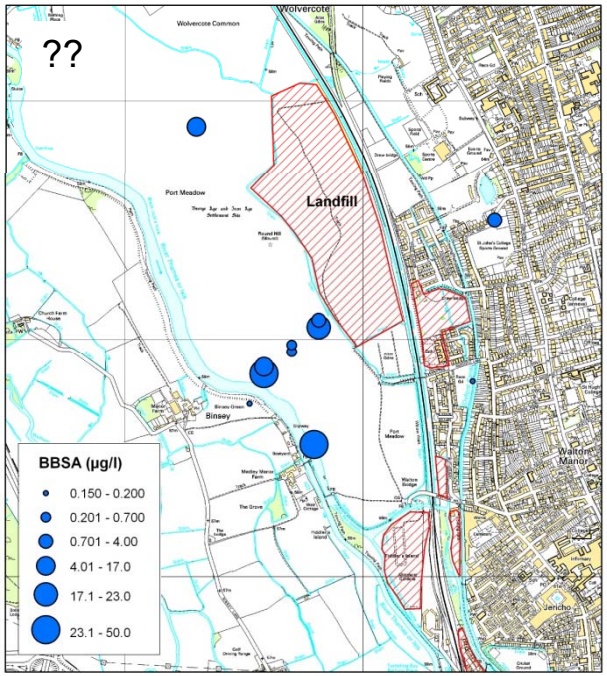


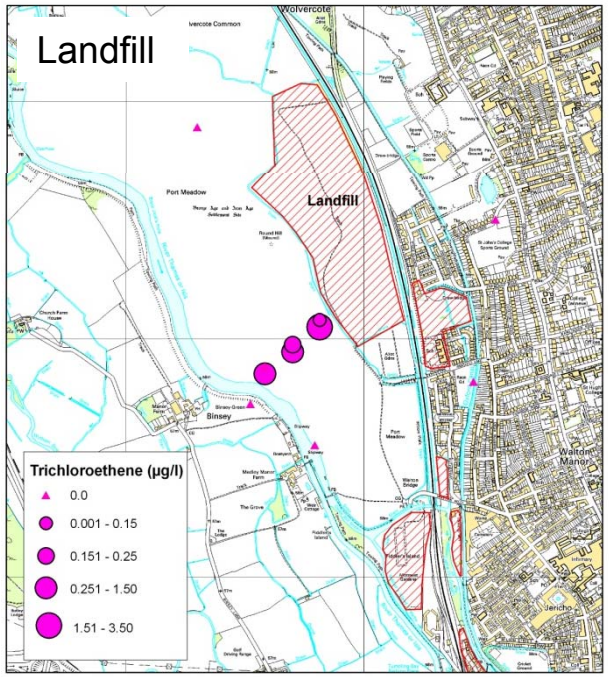
Port Meadow

- Groundwater predominantly reducing inundated areas – nitrate removal
- Impact of landfill leachate plume from NH_4, Cl, HCO_3 etc
- Microorganics fingerprint different types of water









Conclusions

- Frequently detected groups of ECs include antibiotics, lifestyle compounds, pharmaceuticals and preservatives
- Although mostly detected in low ng/L concentrations in groundwater there are many examples where high concentrations are found (in both targeted and reconnaissance studies)
- There are hot-spots of ECs groundwater contamination in several parts of the UK which warrant further investigation
- Overall there is a poor understanding of the occurrence, transport, fate, and human and ecological risk of many ECs in groundwater
- Although many ECs are not currently regulated the number of regulated contaminants will continue to grow over the next several decades -a real challenge for industry, utilities and regulators
- Ongoing need to prioritise ECs, cannot look for everything everywhere

Future research needs

- Characterisation of groundwater EC occurrence
- Fate and transport of ECs in groundwater, particularly in the unsaturated zone
- Use as novel environmental tracers (e.g. pharmaceuticals, sweeteners)
- Toxicity of multiple trace organics
- Predictive transport models –e.g. bank infiltration sites Rhine and Danube