



**British
Geological Survey**

NATURAL ENVIRONMENT RESEARCH COUNCIL

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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 – broader screening tools, better detection
 - Subtle distinction between emerging and “newly” emerging contaminants
- Past/early examples:
 - Pb from fuel additives
 - Endocrine disruptors in rivers (1960s^[1] and 1970s^[2])
 - Pesticides (e.g. DDT)

[1] Stumm and Fair, 1965,

[2] Garrison et al, 1971



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 byproducts – dioxane, phthalates, bisphenols, MTBE, dioxins, musks,
- Food additives – BHA, BHT
- Wastewater treatment byproducts – 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

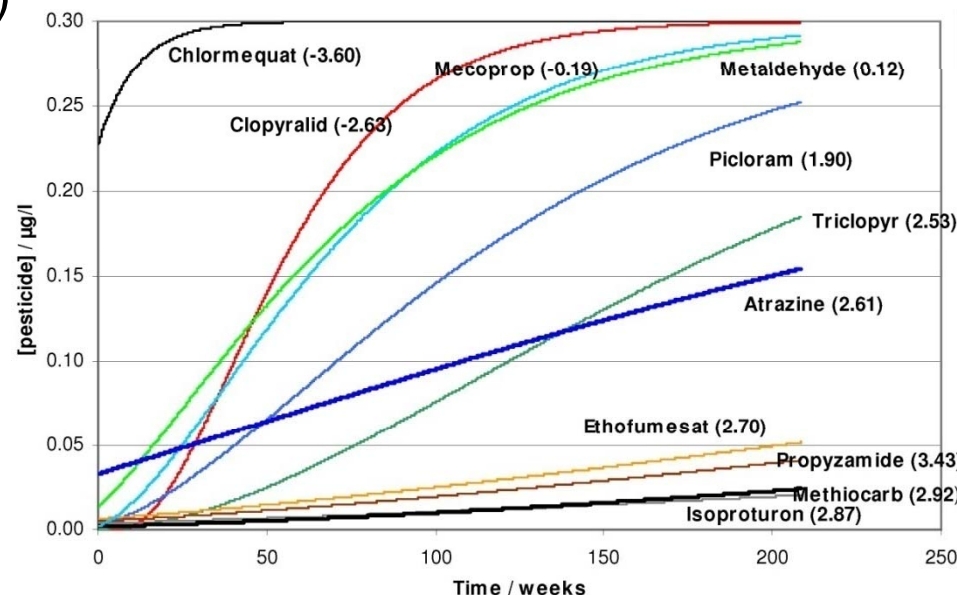
Recent UK example: Metaldehyde



- Source: slug pellets (agricultural and domestic use)
- 2007 Bristol Water detected it in finished drinking water
- Reasons for metaldehyde problem – resistance to DW treatment and difficulties of detection. Low affinity for organic carbon.
- Only emerged as a problem due to developments in analytical methods [4]
- Accounted for around a large proportion of failures in drinking water standards in UK (2009)

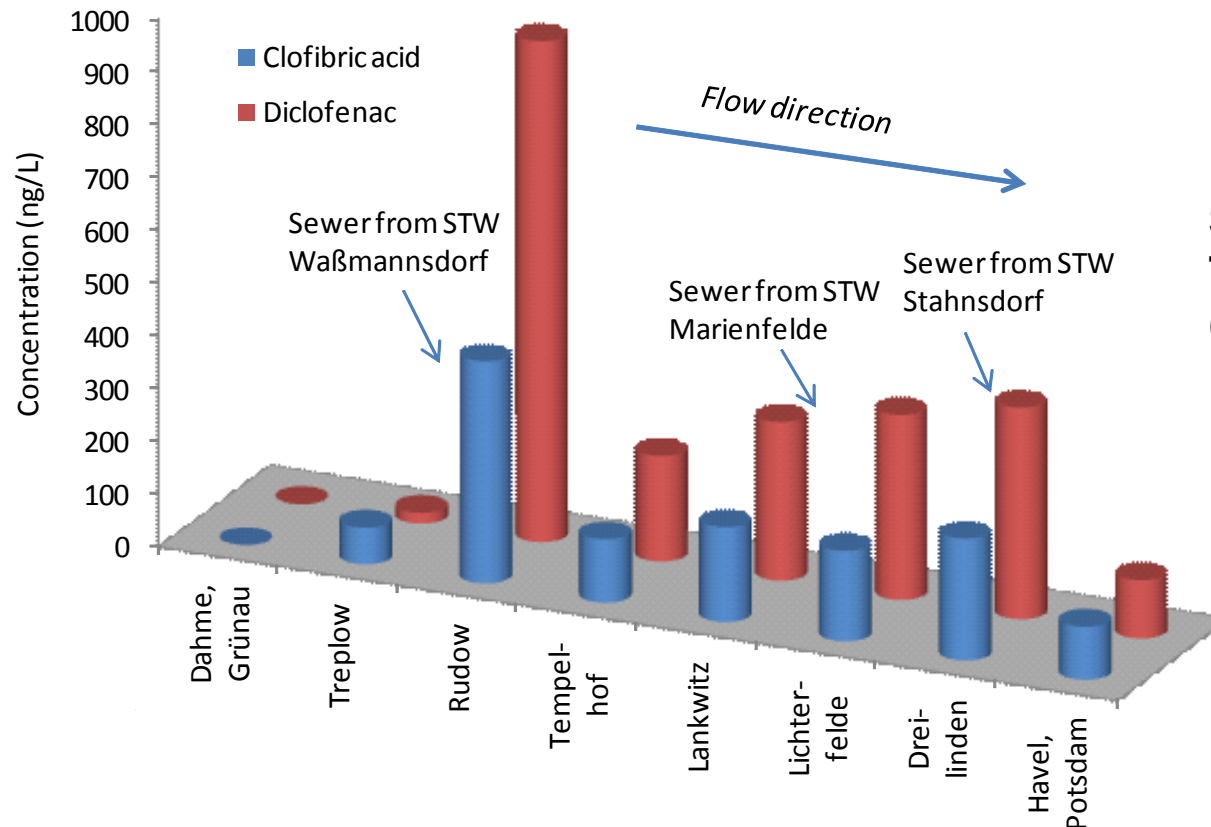


[4] Hall (2010)



Key sources of EC in groundwater

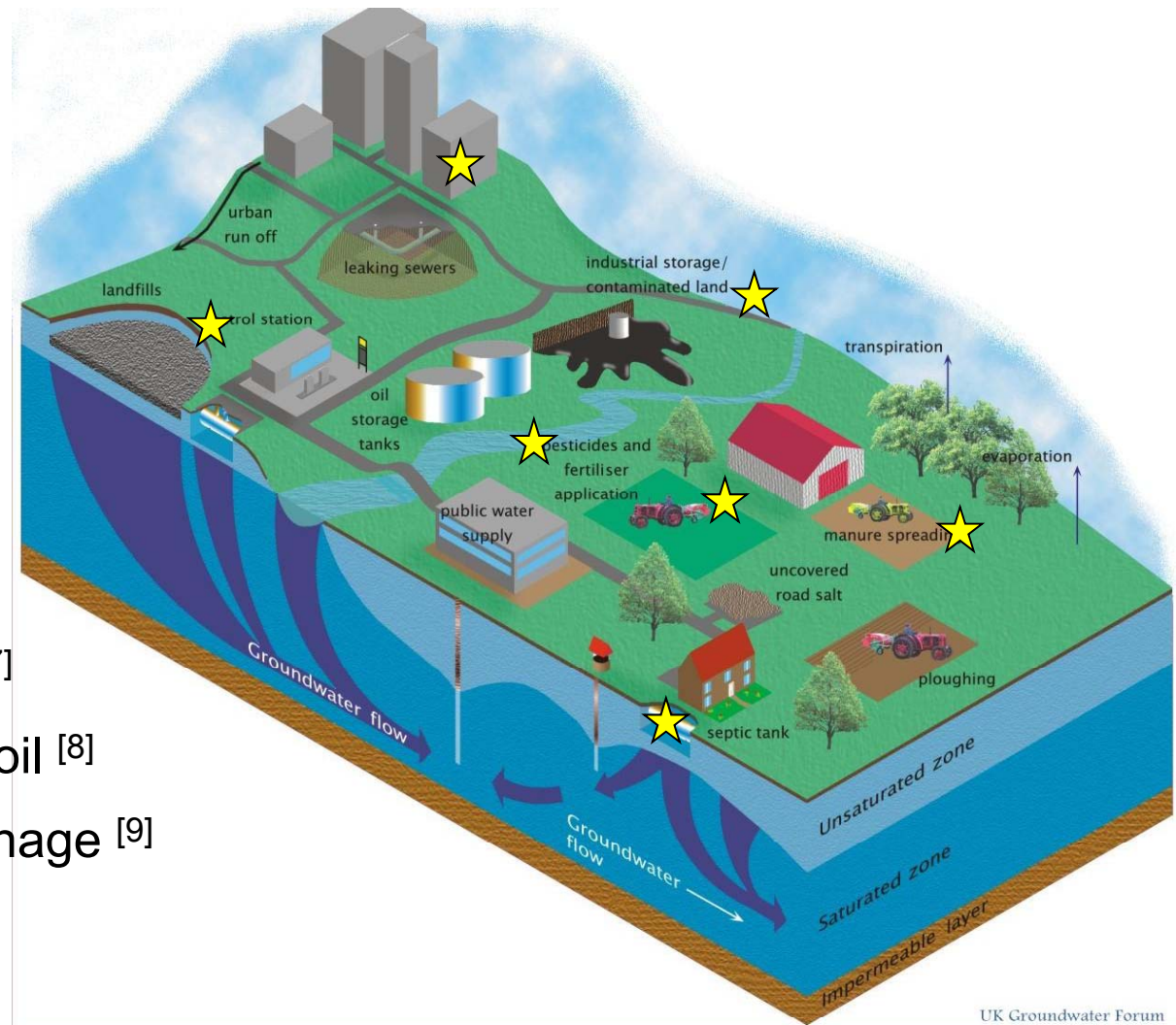
- Treated waste water discharge to surface water
- Artificial recharge of treated waste water and surface water



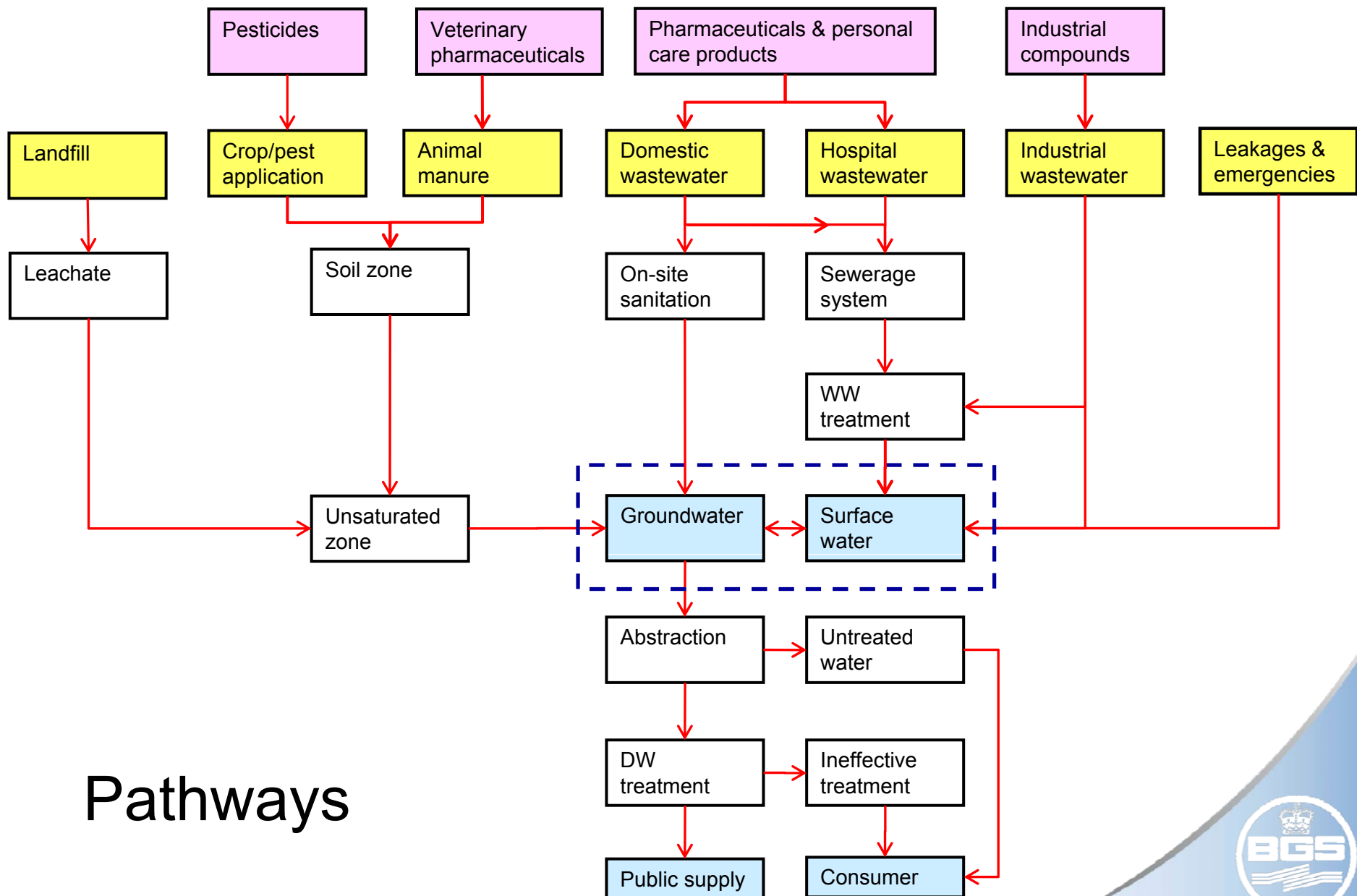
Sampling sites in the Teltowkanal, Berlin (from Herberer, 2002)

Other sources

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

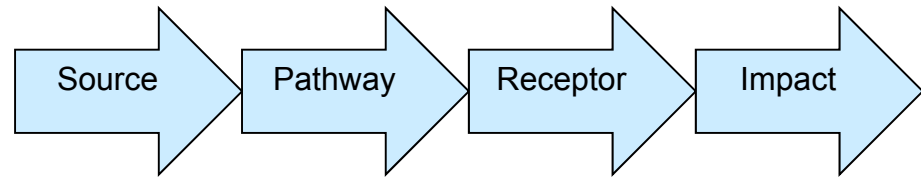


[5] Swartz et al., 2006, [6] Carrara et al., 2007, [7] Watanabe et al., 2010, [8] Buerge et al., 2011, [9] Nakada et al., 2008, [10] Stuart et al., 2011, [11] Buszka et al., 2009



Pathways

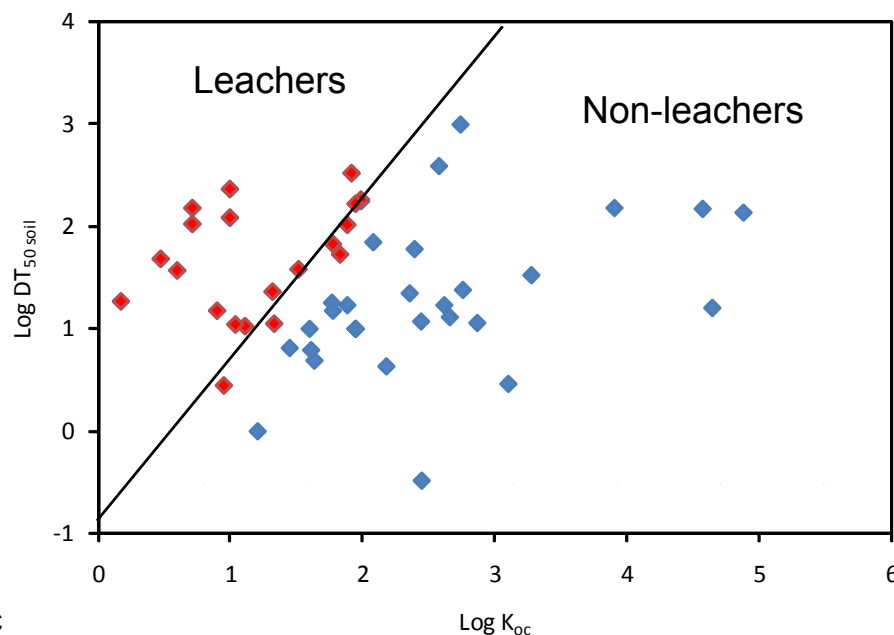
Risk assessment



- 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
- Use surface water as early warning for groundwater

Risk assessment for pesticide metabolites

- Use simple approach [12]
- Model using estimate of parent compound usage, formation rates in soil, persistence, mobility, toxicity, pesticidal activity and drinking water removal efficiency identified metabolites of aldicarb, chlorothalonil, cyanazine, atrazine and methomyl [13]
- Some metabolites more persistent or harmful than parent compound



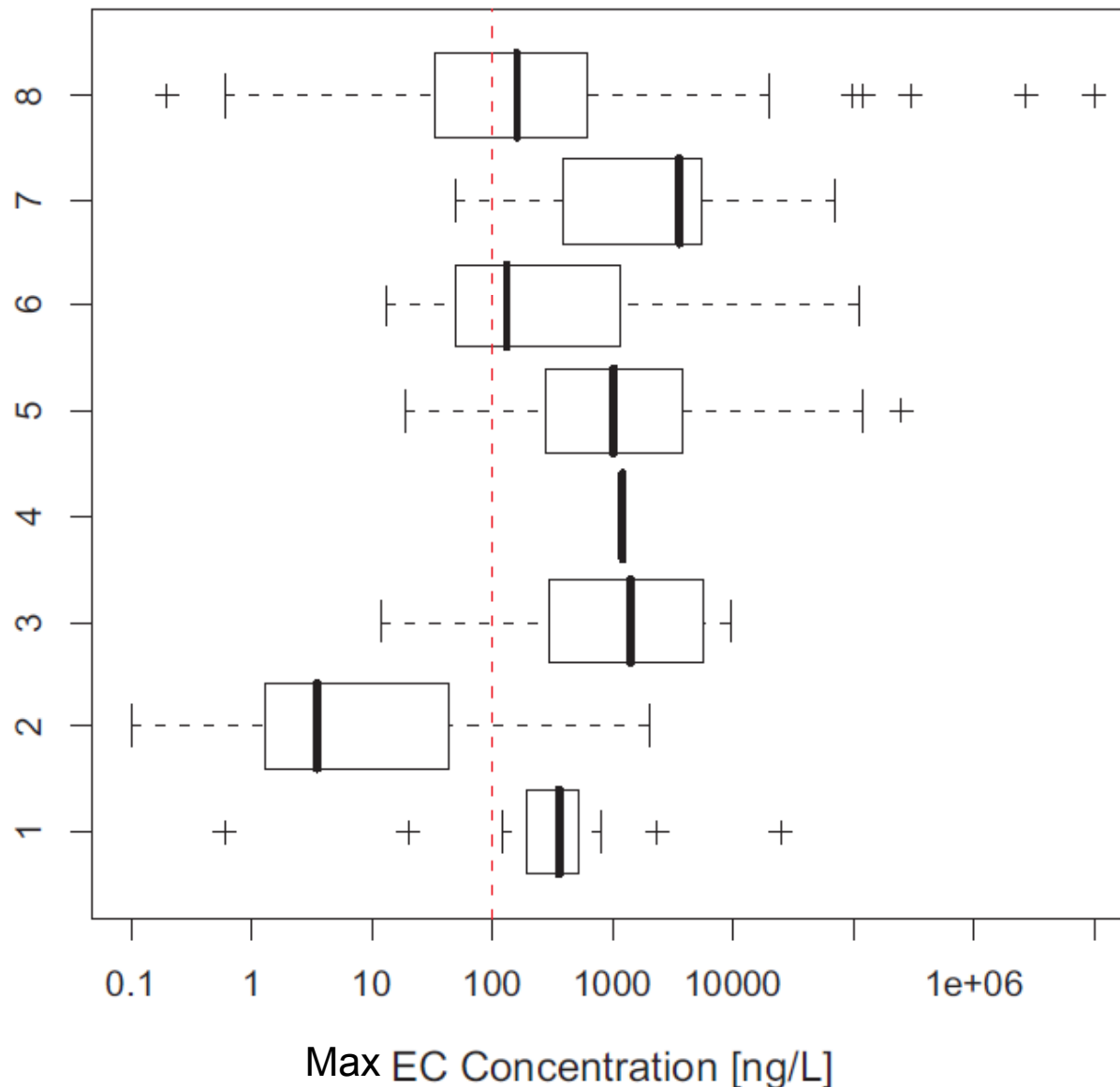
Literature review of occurrence in groundwater

- 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

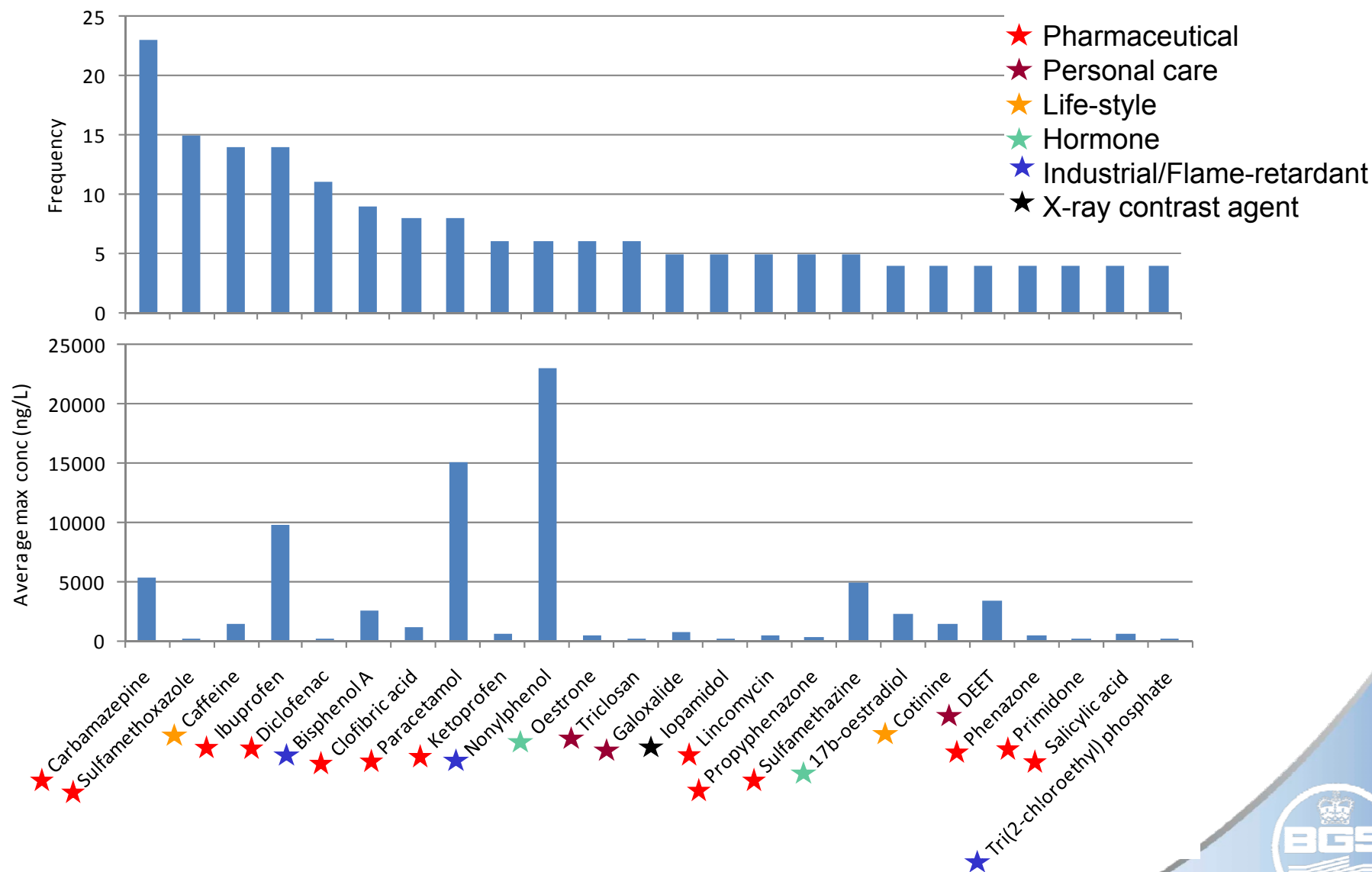
4: Illicit drugs: cocaine (n=1)

3: Food additives and artificial sweeteners

2: Steroids, hormones and metabolites

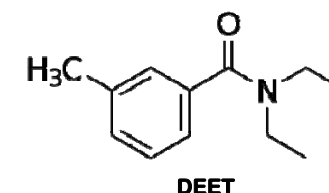
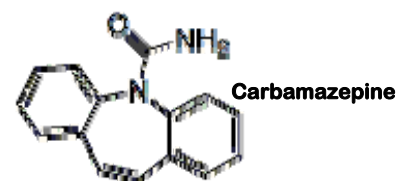
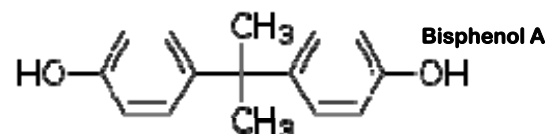
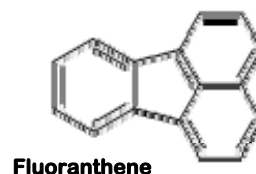
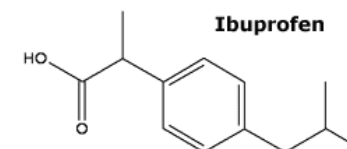
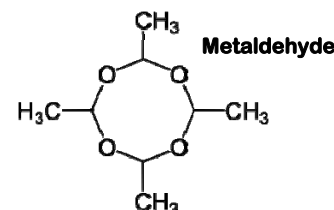
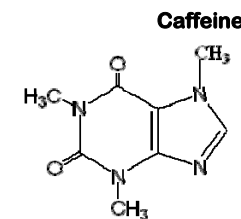
1: Veterinary antibiotics and hormones

Compounds reported in ≥ 4 separate studies

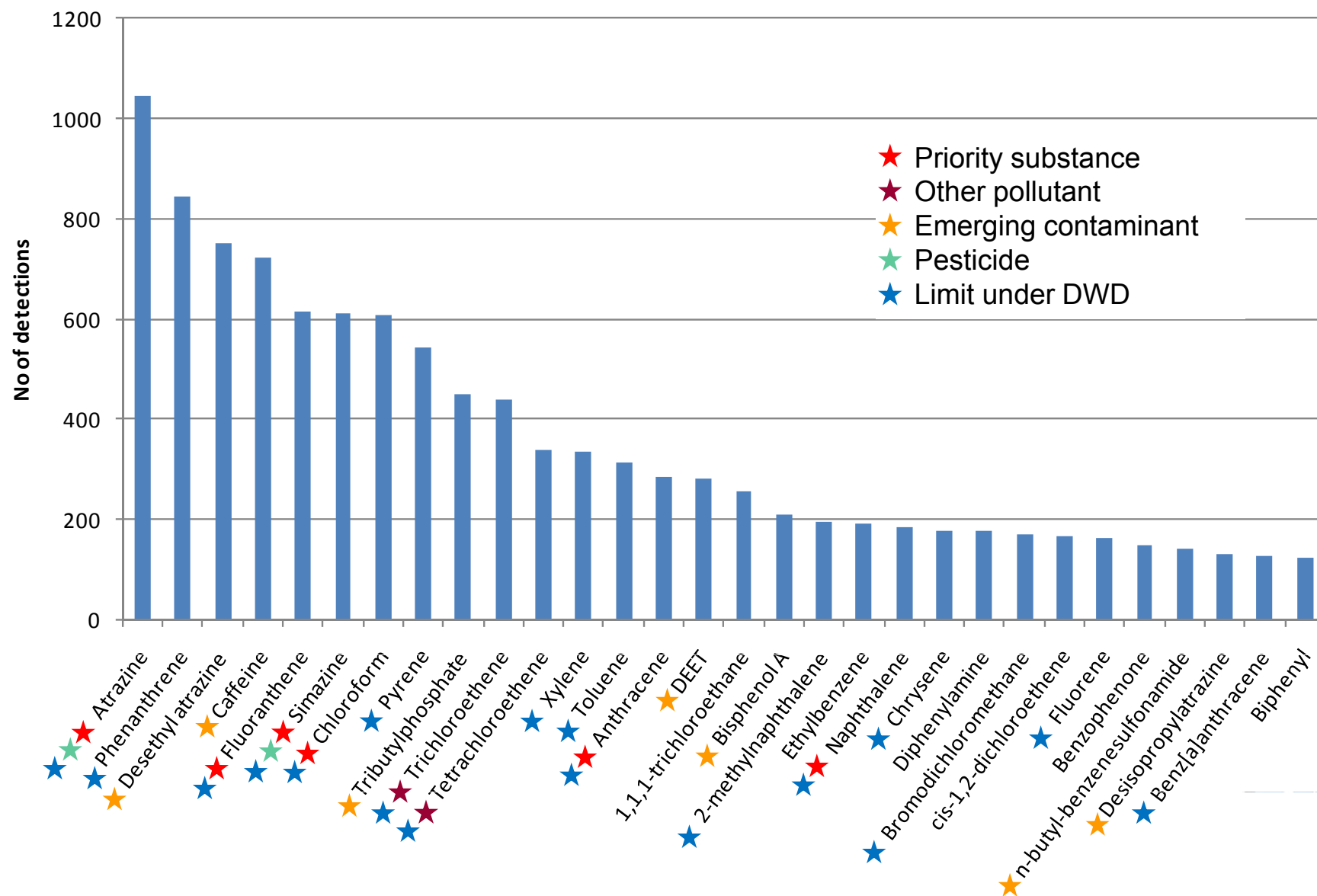


Environment Agency screening data 1993-2009

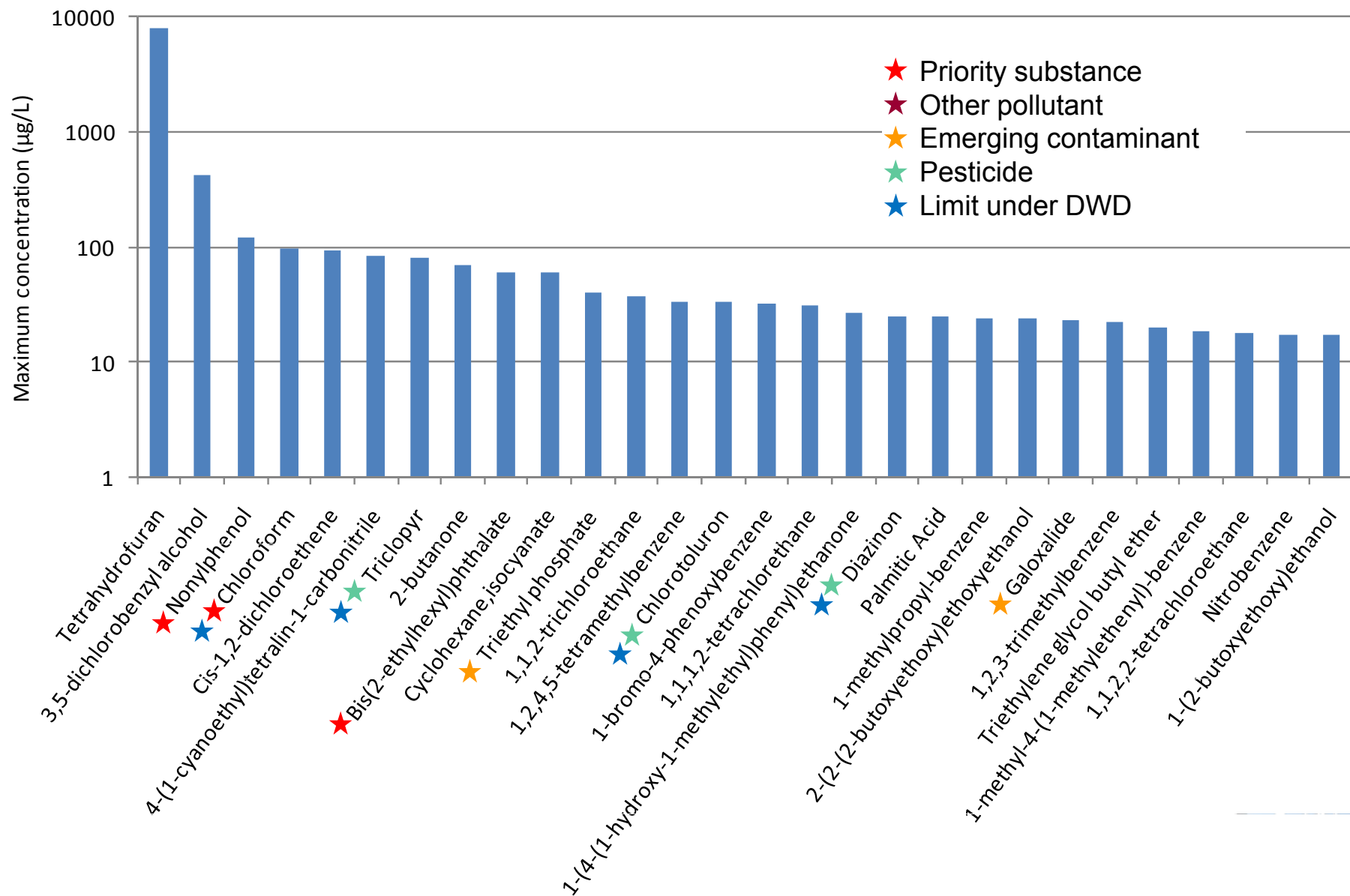
- GCMS method
- About 1200 different compounds
- Industrial intermediates & solvents
- Pesticides and metabolites
- PAH
- BTEX
- Bisphenol A
- DEET
- Pharmaceuticals
 - Carbamazepine, cocaine, lidocaine, barbituric acid, pentobarbital
 - Caffeine, nicotine, cotinine
 - Limited ibuprofen, no obvious paracetamol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



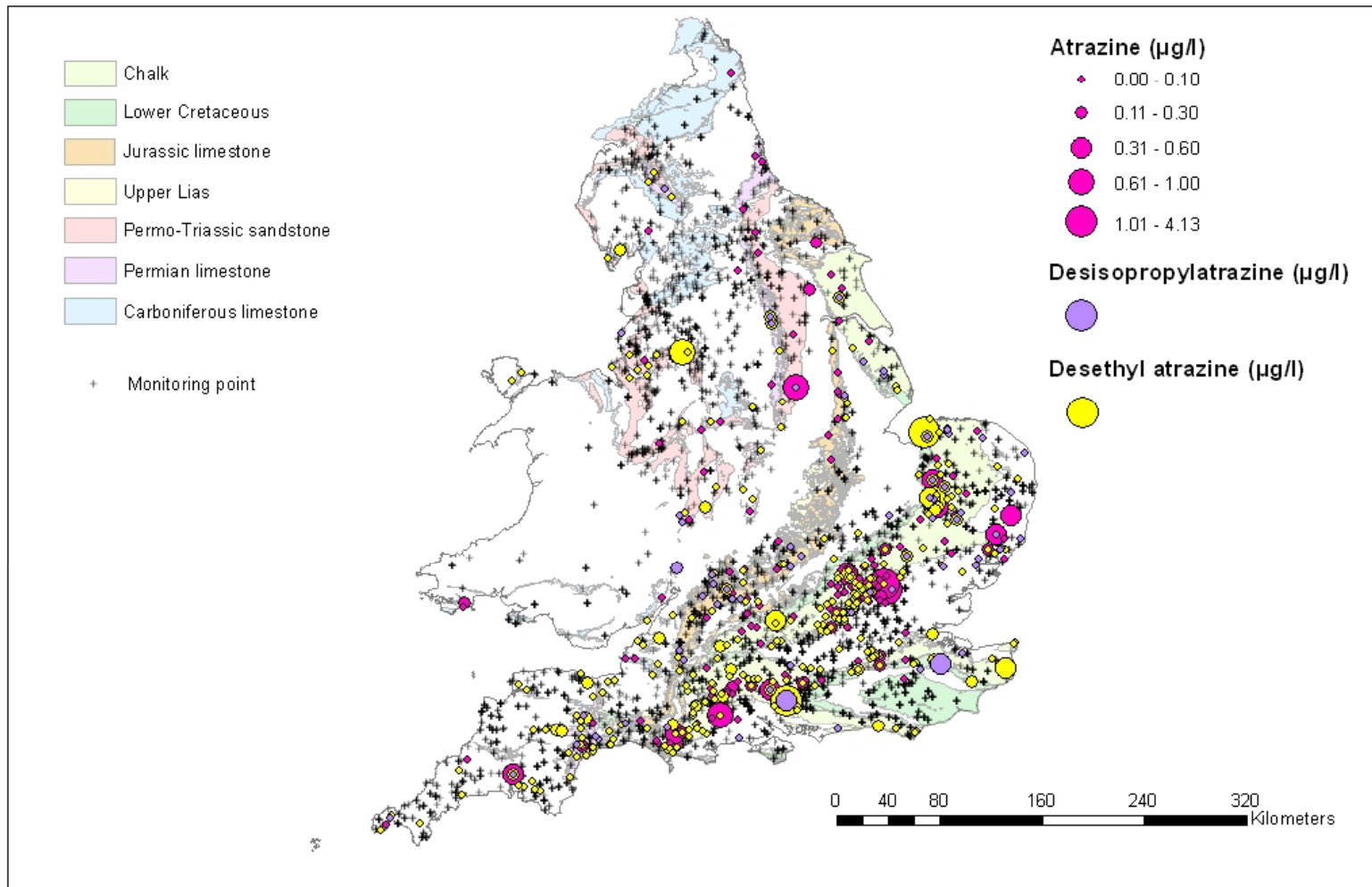
Top 30 most frequently detected compounds



Top 30 maximum concentrations



Atrazine and its metabolites

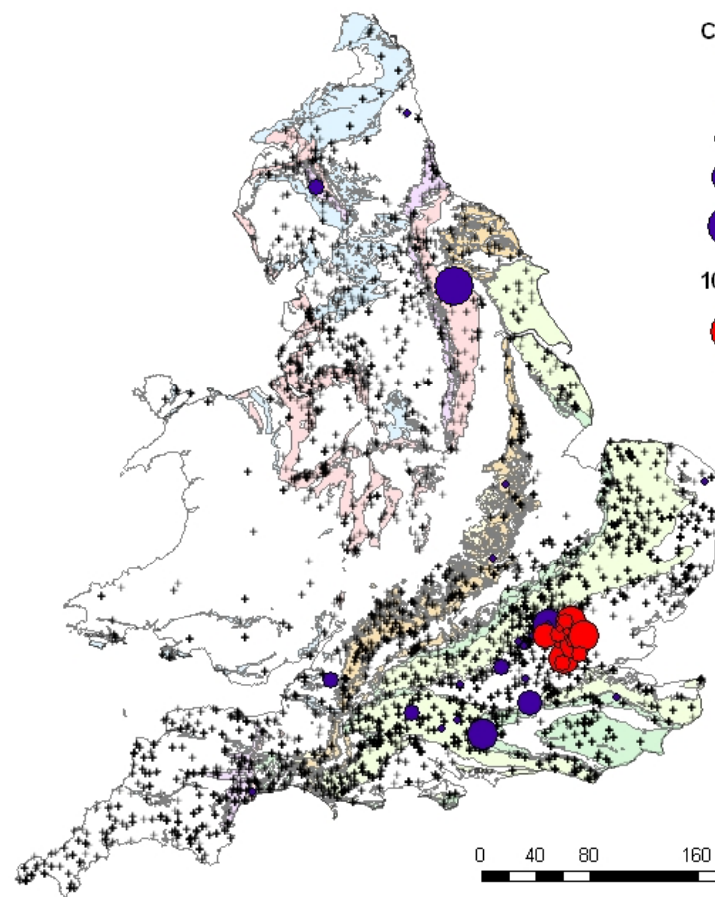


Caffeine & carbamazepine



Caffeine ($\mu\text{g/l}$)

- 0.00 - 0.10
- 0.11 - 0.20
- 0.21 - 0.30
- 0.31 - 0.70
- 0.71 - 2.30



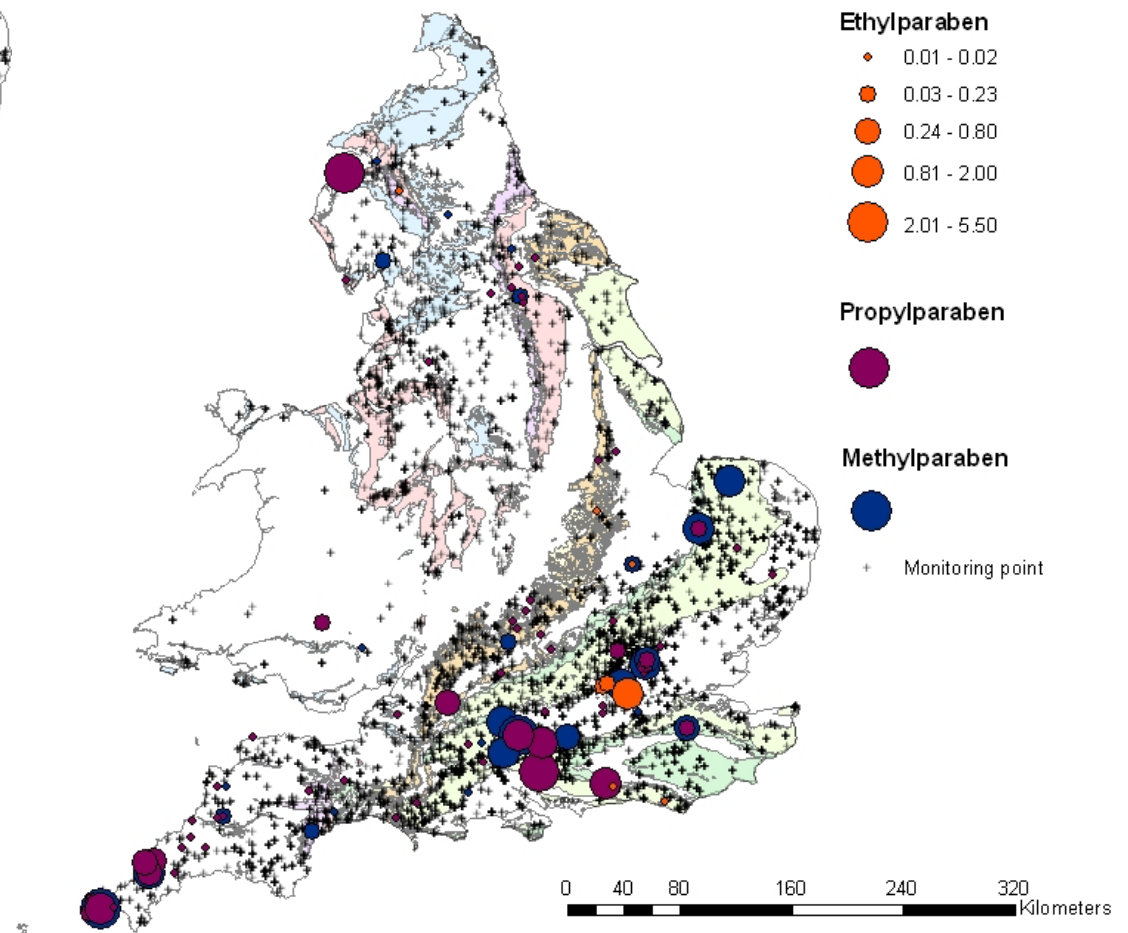
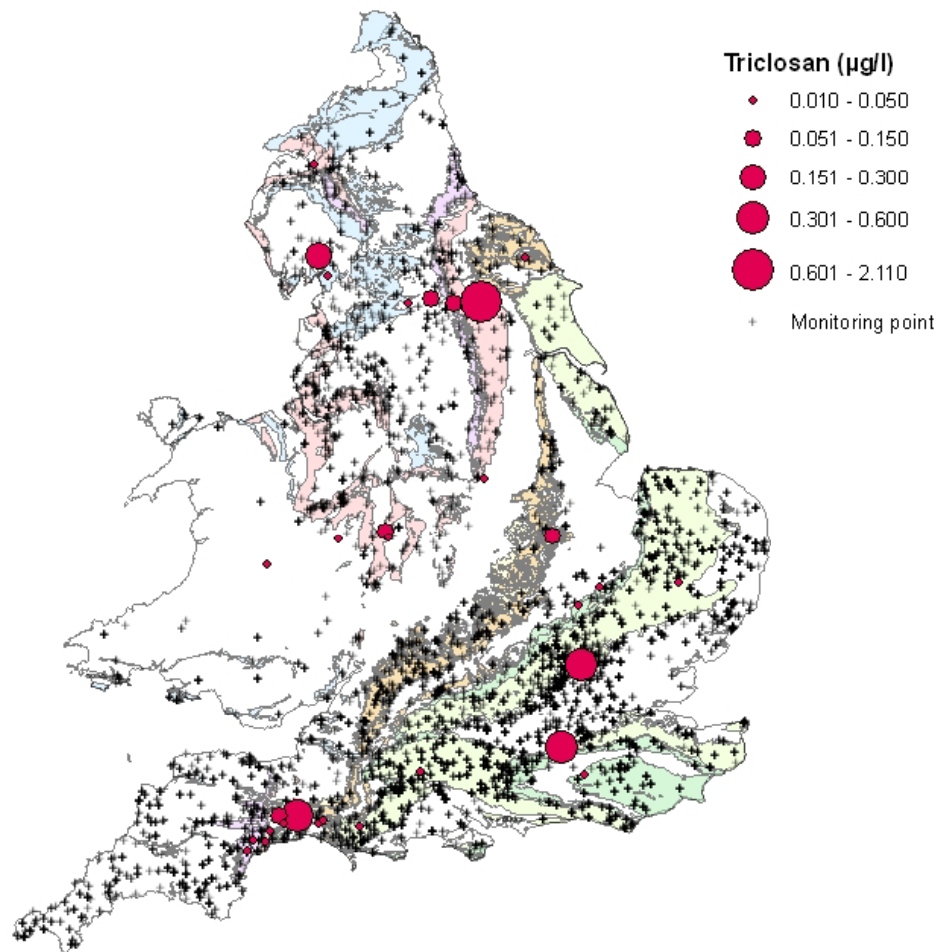
Carbamazepine ($\mu\text{g/l}$)

- 0.010 - 0.030
- 0.031 - 0.100
- 0.101 - 0.300
- 0.301 - 0.750
- 0.751 - 3.600

10,11-Dihydrocarbamazepine ($\mu\text{g/l}$)

- Monitoring point

Triclosan and the parabens



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

- Characterisation of groundwater EC occurrence
- Studies on 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

