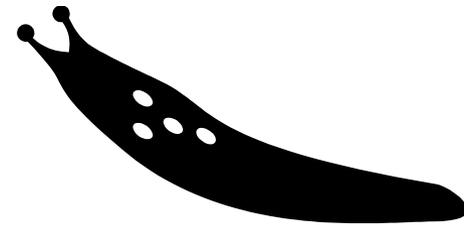
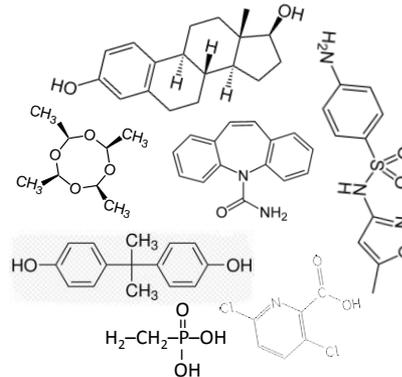


Emerging contaminants in groundwater

UK Groundwater Forum, 24th May 2011, London



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and Nicole Baran

Outline

- Definition of emerging contaminants
- Regulatory framework
- Sources and pathways for groundwater contamination
- Review of emerging contaminants in groundwater
- Focus on results from recent UK EA survey of micro-organic contamination in groundwater
- Conclusions
- Future issues

Definition of emerging contaminants

- Potentially toxic substances (aquatic ecology, human)
- Newly discovered in groundwater
- Newly developed compounds
- Newly categorised contaminants (past e.g. hormones)
- Analytical developments – broader screening tools, better detection
- Subtle distinction between emerging and ‘newly’ emerging contaminants

Past/early examples:

- Pb from fuel additives
- Endocrine disruptors (1960s[1] and 1970s[2])
- Pesticides (e.g. DDT)

[1] Stumm and Fair, 1965, [2] Garrison et al, 1971



Groups of potential contaminants



mayomedicineblog.com

- Nanomaterials – sunscreen
- Pesticides – parent compounds, metabolites
- Pharmaceuticals – human, veterinary, illicit, insect repellent
- Industrial additives and byproducts – dioxane, phthalates, bisphenols, MTBE, dioxins, musks, food additives
- Wastewater treatment by-products – THM, NDMA
- Flame retardants – alkyl phosphates
- Surfactants – PFOS & PFOA, alkyl phenols
- Hormones and sterols – estradiol, cholesterol
- Ionic liquids
- “Life style” – nicotine, caffeine



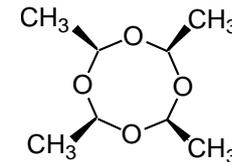
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Regulatory framework

- Water Framework Directive (2000/60/EC); Groundwater Daughter Directive (2006/118/EC); Priority Substances Directive (2008/105/EC)
- **Groundwater (England & Wales) Regulations (2009)**

Regulations 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), Scotland (2001)**
 - Pesticides (metabolites), Aromatic hydrocarbons, Chlorinated solvents and some Disinfection by-products are included
 - Drinking Water Directive is under review: proposed additional substances e.g. Bisphenol A, Nonyl-phenol (0.1 µg/L)
 - Many emerging contaminants (EC) i.e. pharmaceuticals, '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)

Get Pelletwise!

www.pelletsarepesticides.co.uk

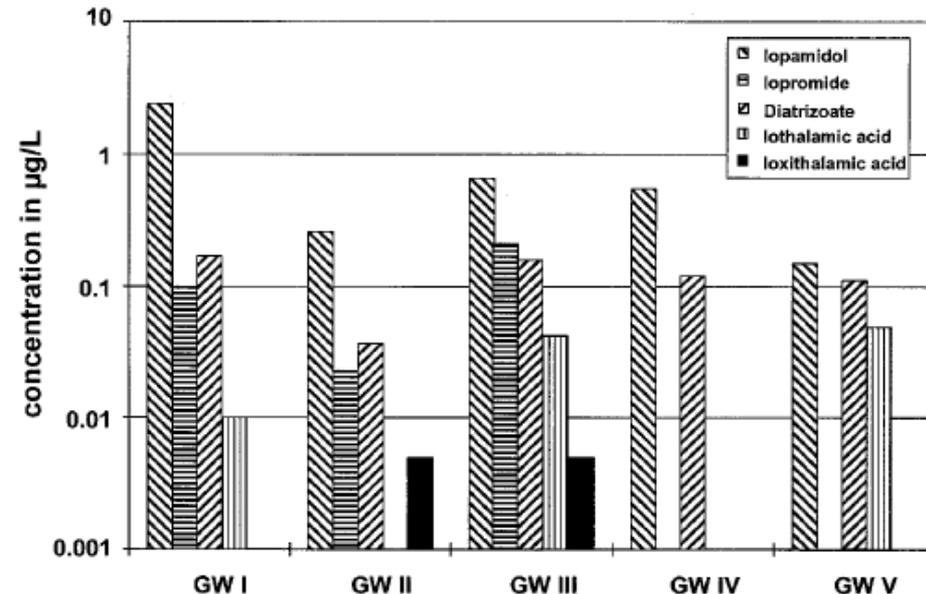
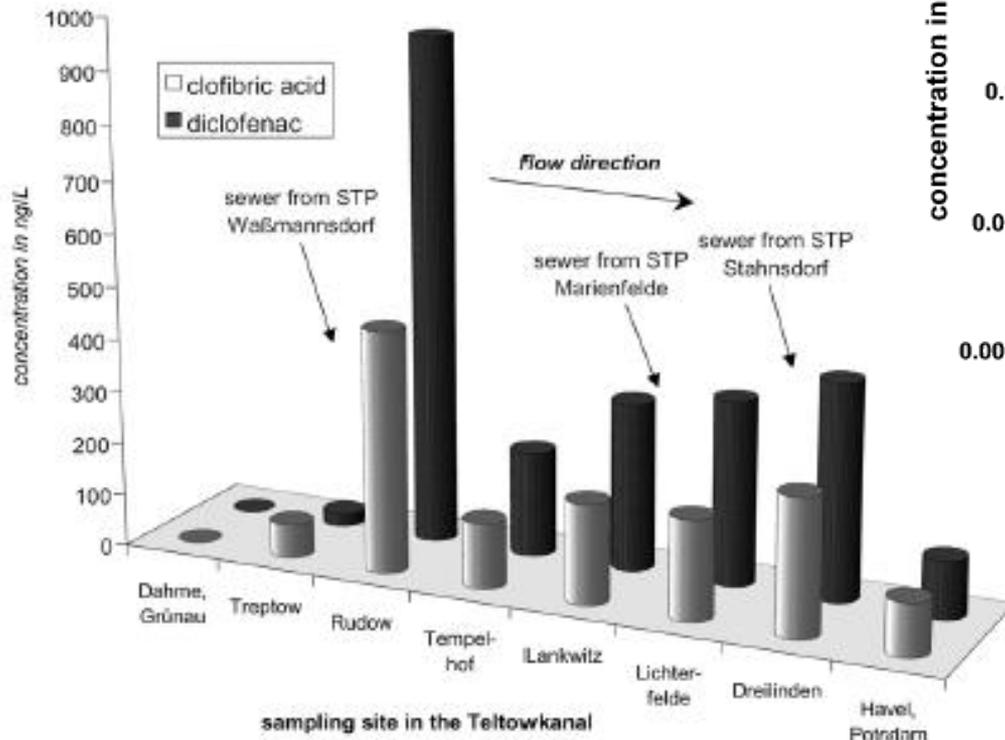


Key sources of EC in groundwater



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

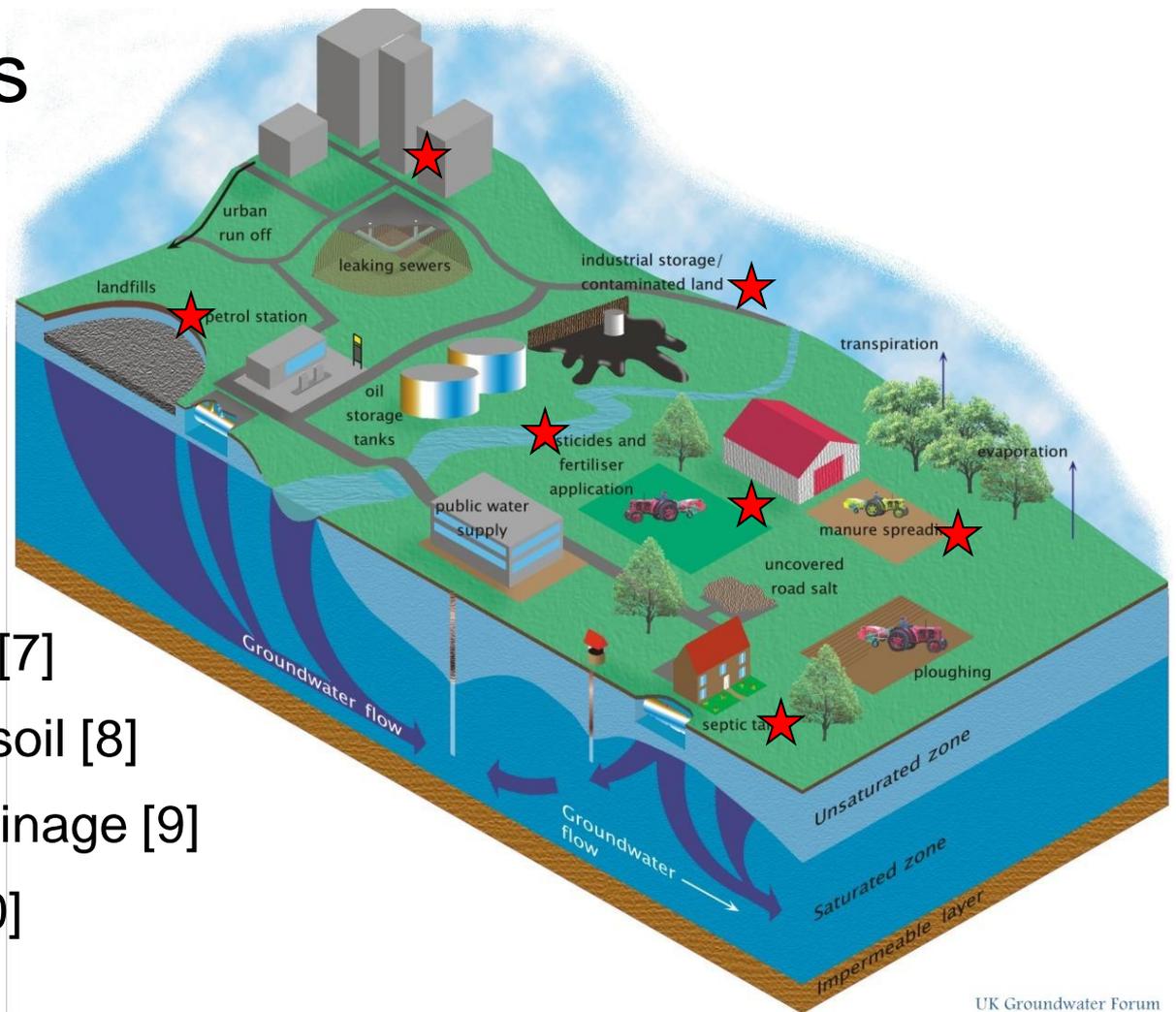
1. Surface water contamination of pharmaceuticals near Berlin [Heberer, 2002]



2. Groundwater contamination by X-ray contrast agents, Frankfurt [Ternes and Hirsch, 2000]

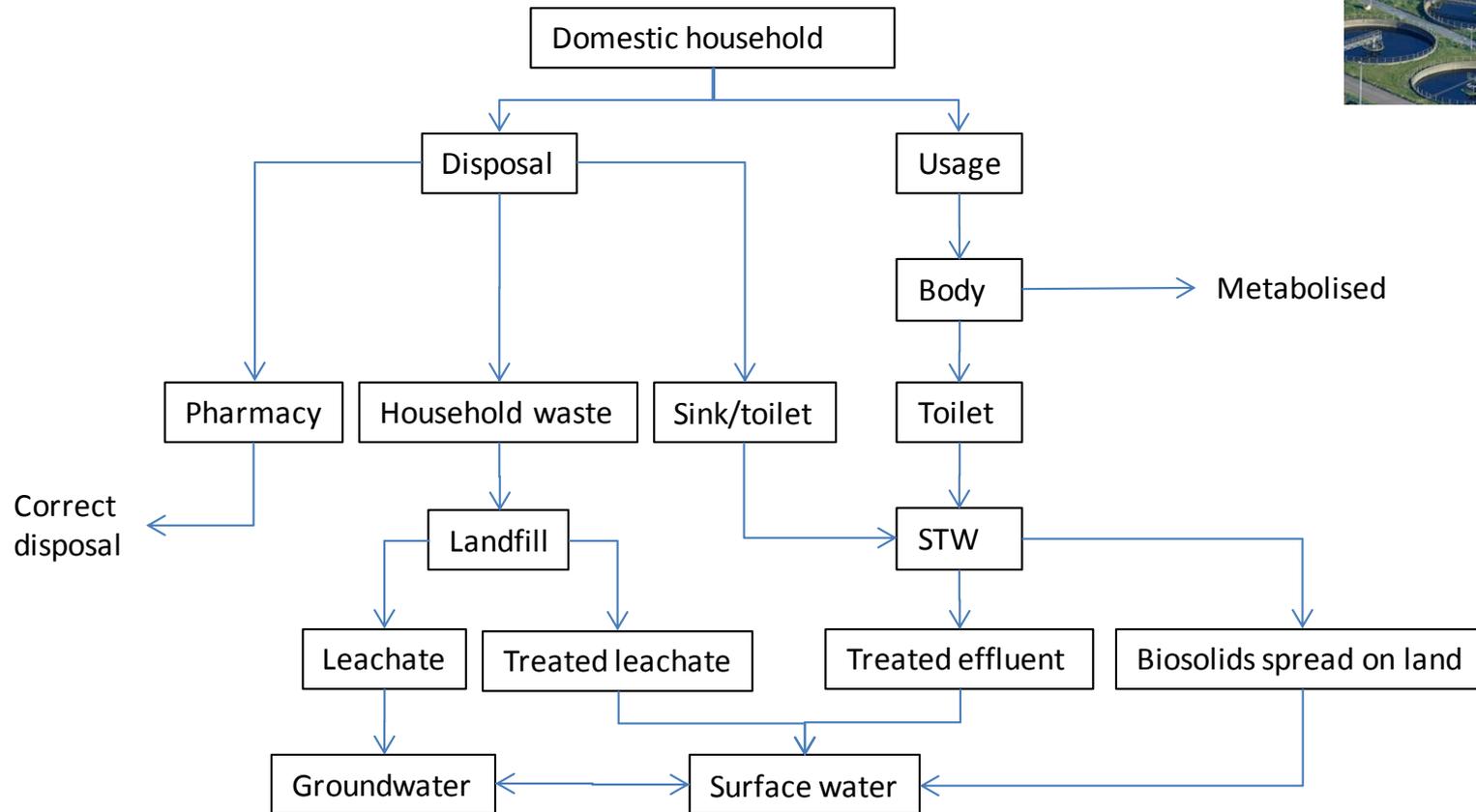
Other EC sources

- 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 for EC from domestic use



(adapted from Bound and Voulvoulis, 2005)

* Historic legacy, incorrect use and disposal, poor attenuation during treatment and migration in subsurface and indirect pathways (SW-GW exchange) are all important issues

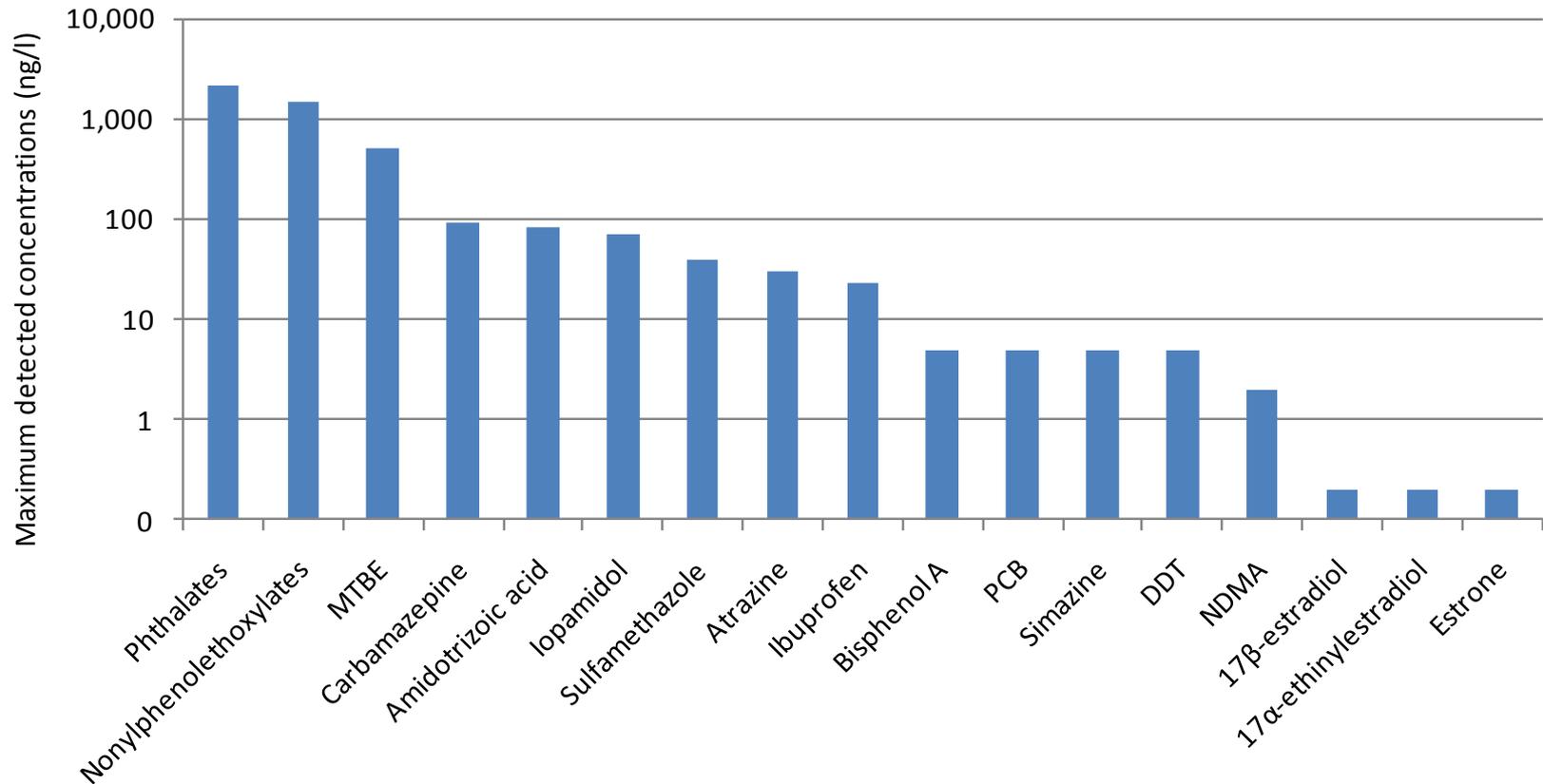
Pharmaceuticals used in the UK

- Top 8 prescription drugs in UK detected in the aquatic environment (Jones 2002) – surface water environment
- Low $\log[K_{ow}]$ indicates GAC resistance
- High PEC:PNEC indicates possible toxicological effect

Compound	Use/group	Amount (tonnes)	Log [K_{ow}]	PEC:PNEC
Paracetamol*	Analgesic	390	0.46	1.29
Ibuprofen*	Analgesic	162	3.50	0.55
Carbamazepine*	Anti-epileptic	40	2.25	0.19
Naproxen	Anti-inflammatory	35	3.18	0.01
Oxytetracycline	Antibiotic	27	-0.90	3.6
Erythromycin	Antibiotic	26	3.06	0.01
Diclofenac*	Anti-inflammatory & analgesic	26	0.70	0.01
Aspirin	Analgesic	18	1.19	0.01

* Commonly detected in groundwater studies (Lapworth et al. 2011)
 PEC = Predicted Environmental Conc. PNEC=Non-effect Conc

Netherlands treated drinking water



- Concentrations are generally orders of magnitude less than surface waters
- Pharmaceuticals are less well attenuated compared to other organic contaminants

(from Verliefde et al., 2007)

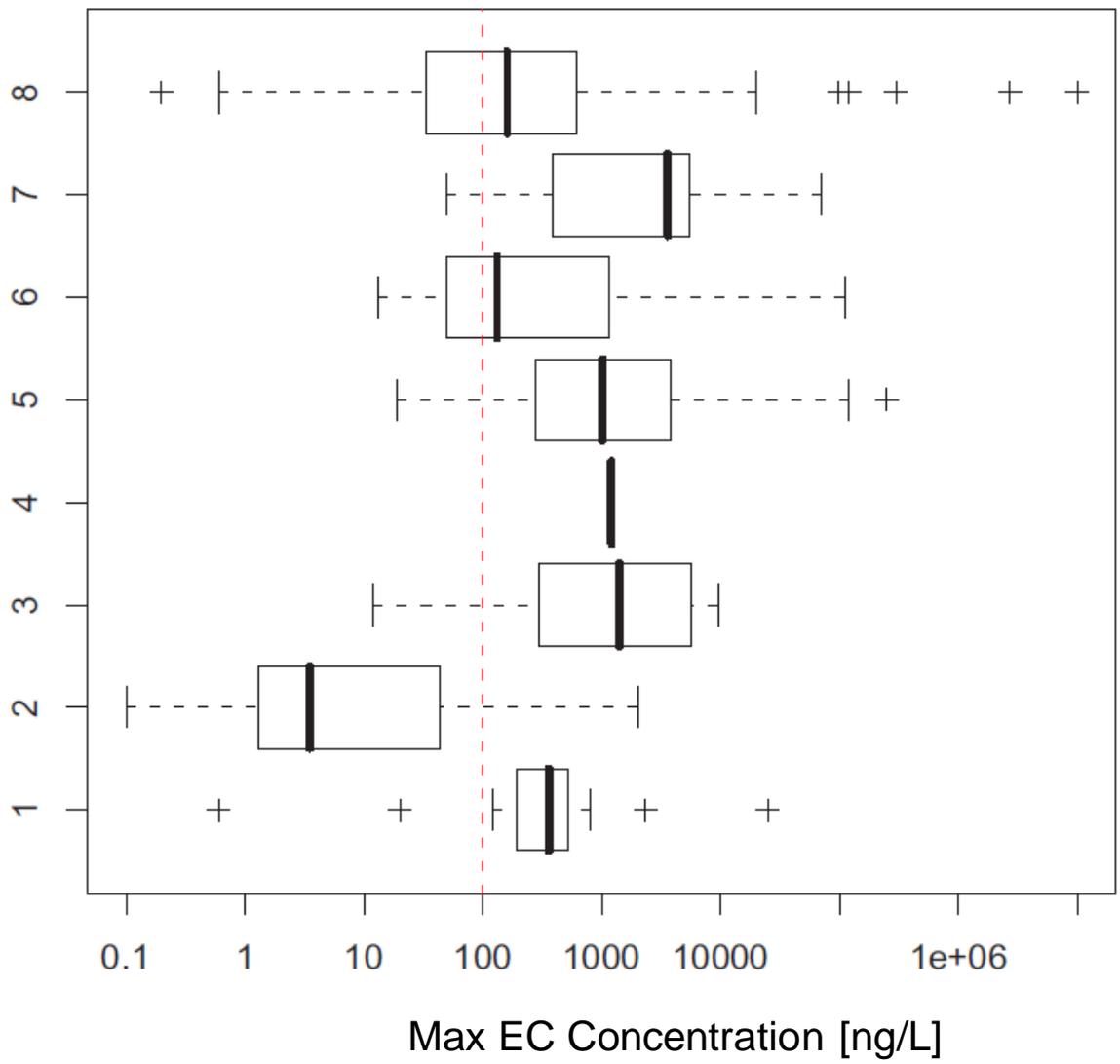
Review of EC occurrence in groundwater

- 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 EDC, 6 other potential EDC

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

Compounds	Group	frequency	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 commonly identified groups of ECs



Important groups found in groundwater

8: Antibiotics, epilepsy drugs, anti-inflammatory

7: Skin care products, insecticides

6: Caffeine, nicotine and metabolites

5: Plasticisers, detergents, flame retardants

4: Cocaine (n=1)

3: Preservatives and artificial sweeteners

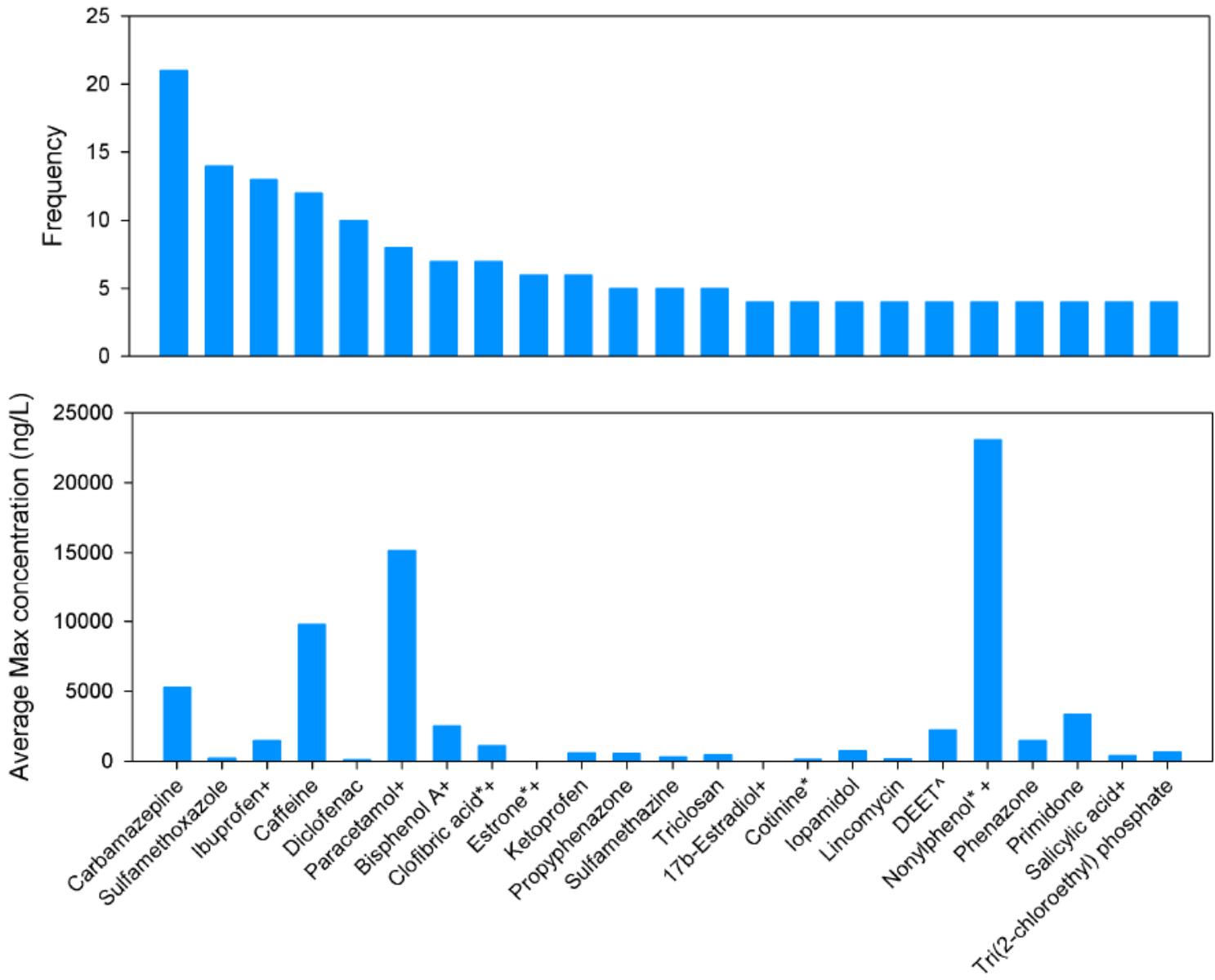
2: Steroids, hormones and metabolites

1: Antibiotics, hormones

1=Veterinary compounds, 2=Estrogenic compounds, 3=Food additives, 4=Illicit compounds, 5=Industrial compounds, 6=Lifestyle compounds, 7=Personal care products, 8=Pharmaceuticals



Compounds reported in ≥ 4 separate studies

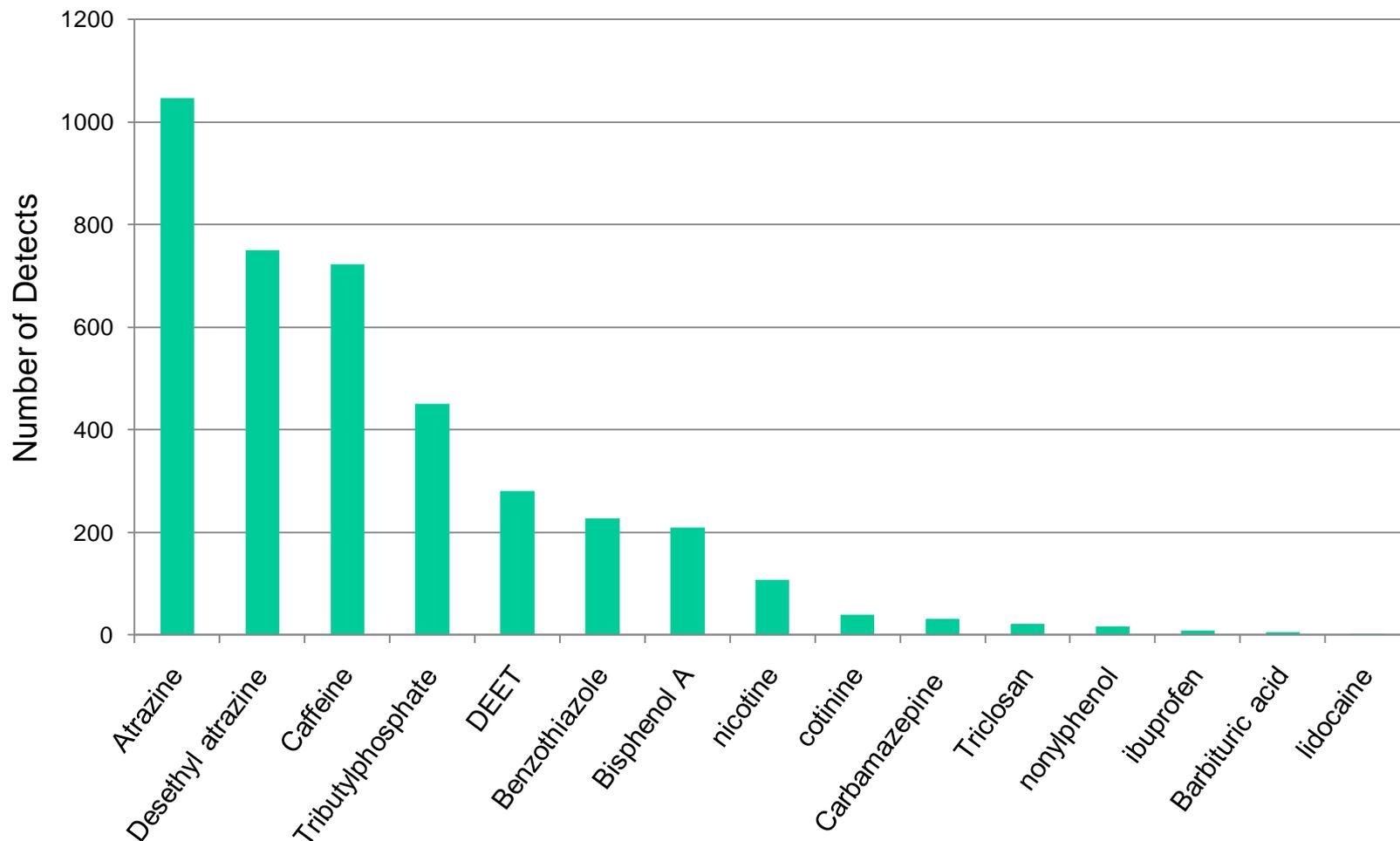


UK Environment Agency screening data: 1993-2009

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

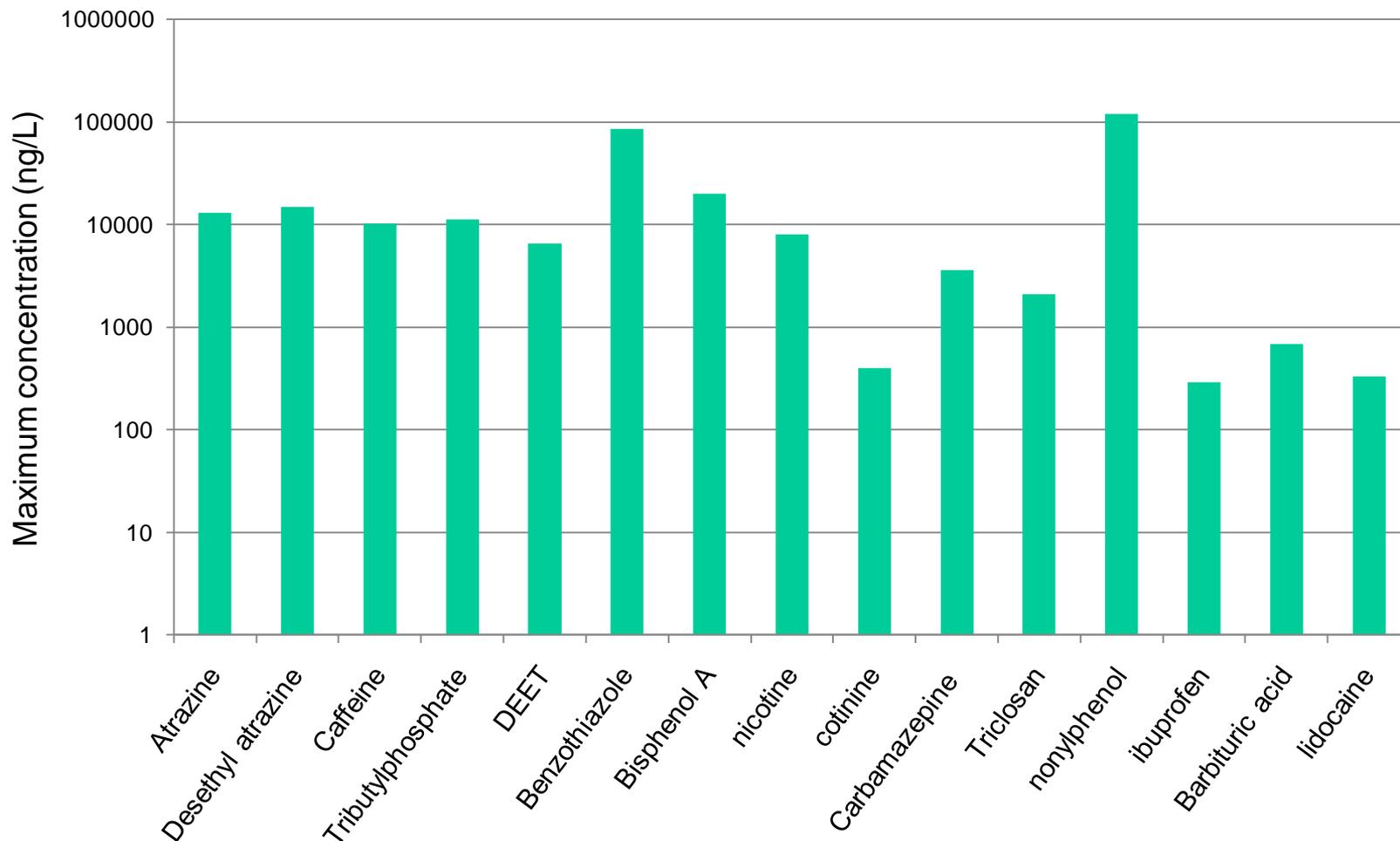


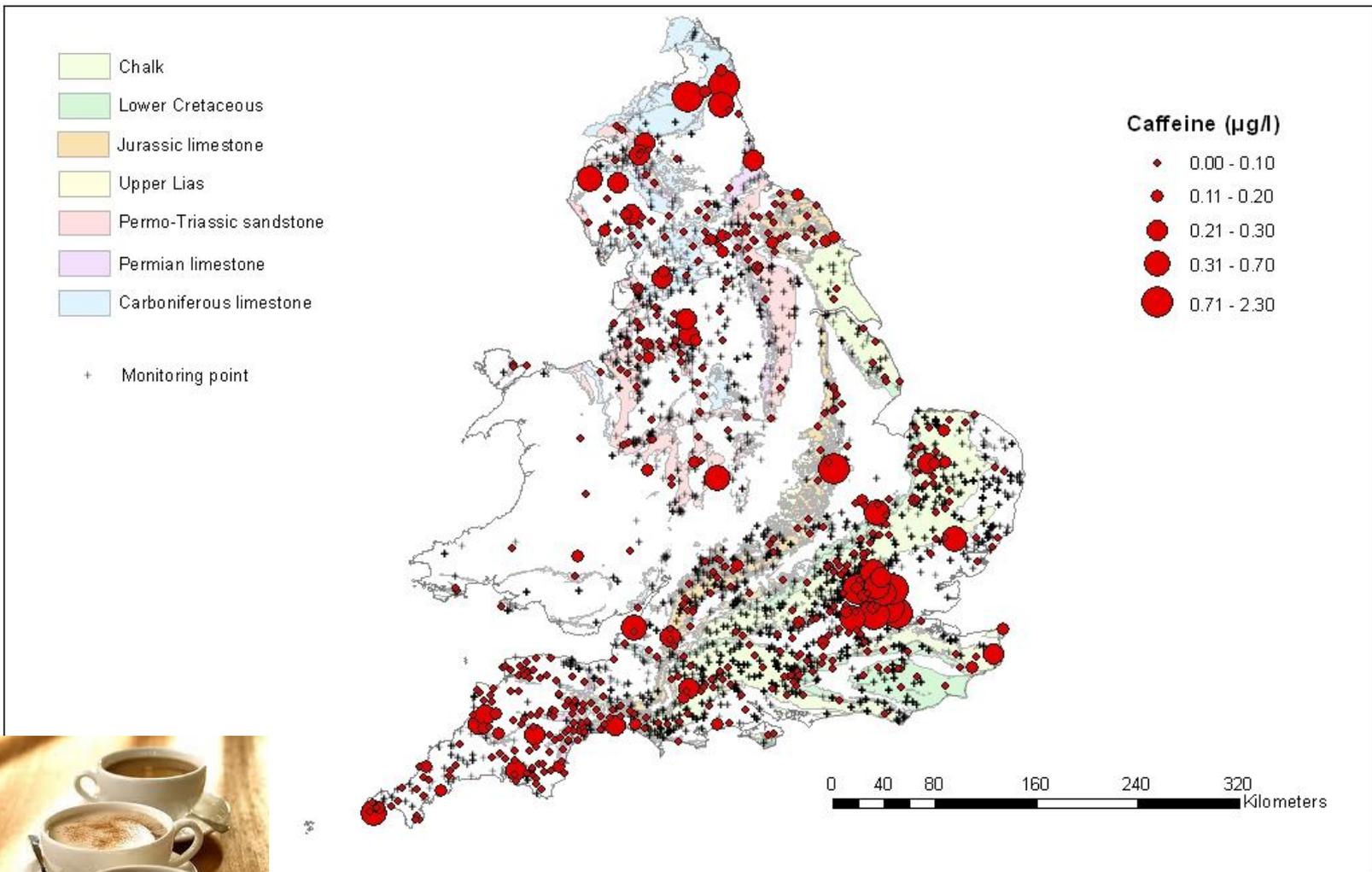
Selected ECs in UK groundwater



* Atrazine and metabolite shown for comparison

UK maximum concentrations for selecte ECs

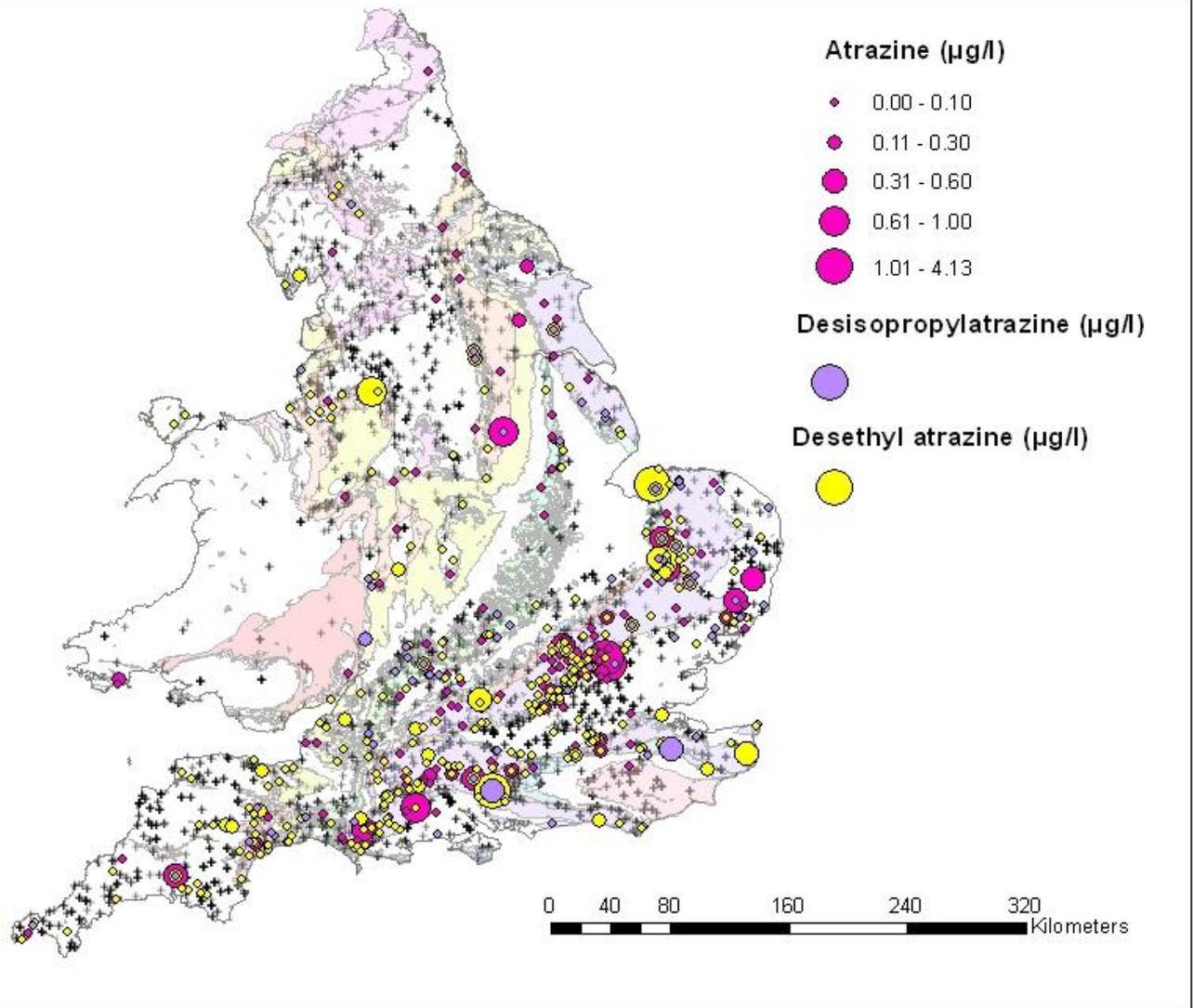


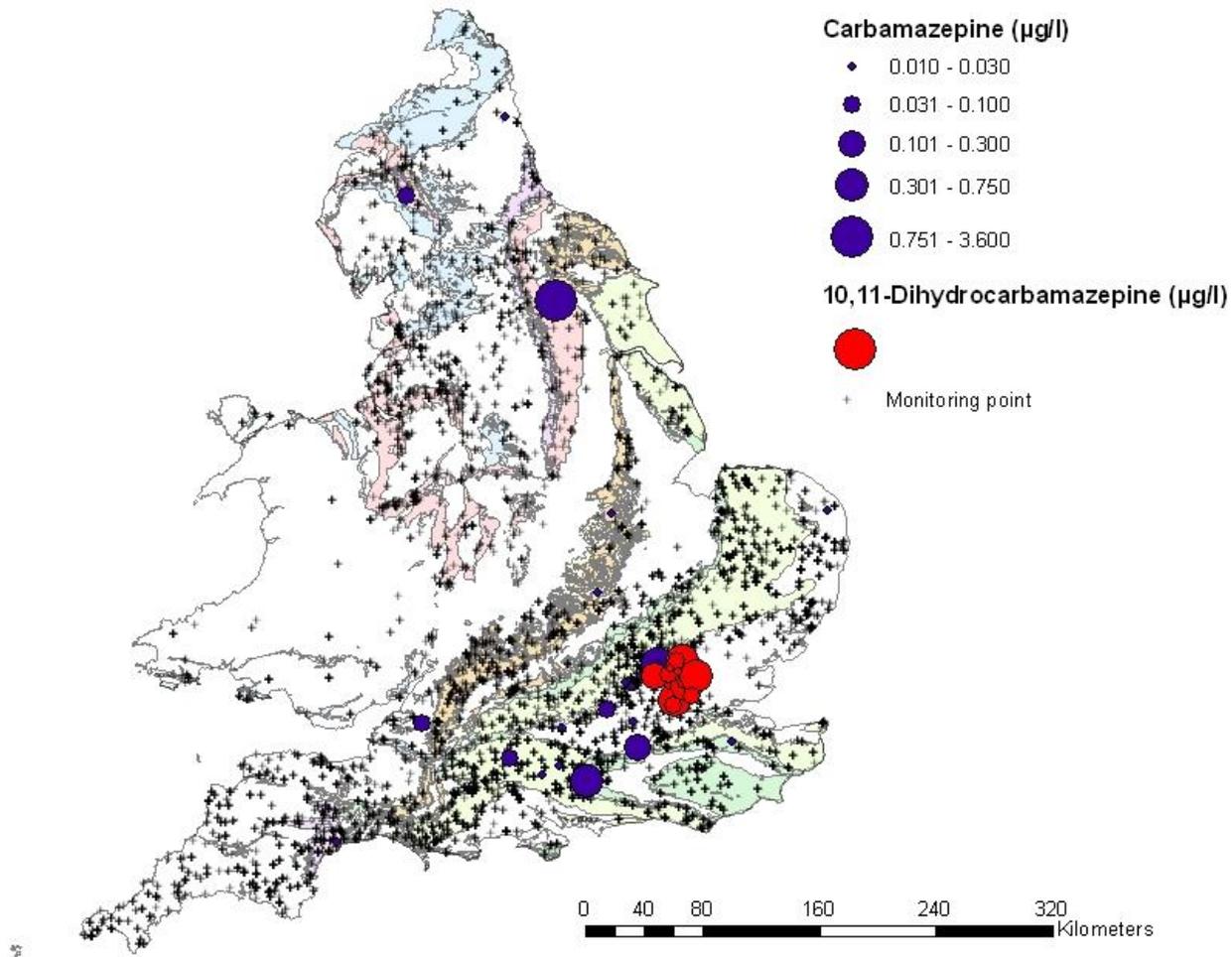


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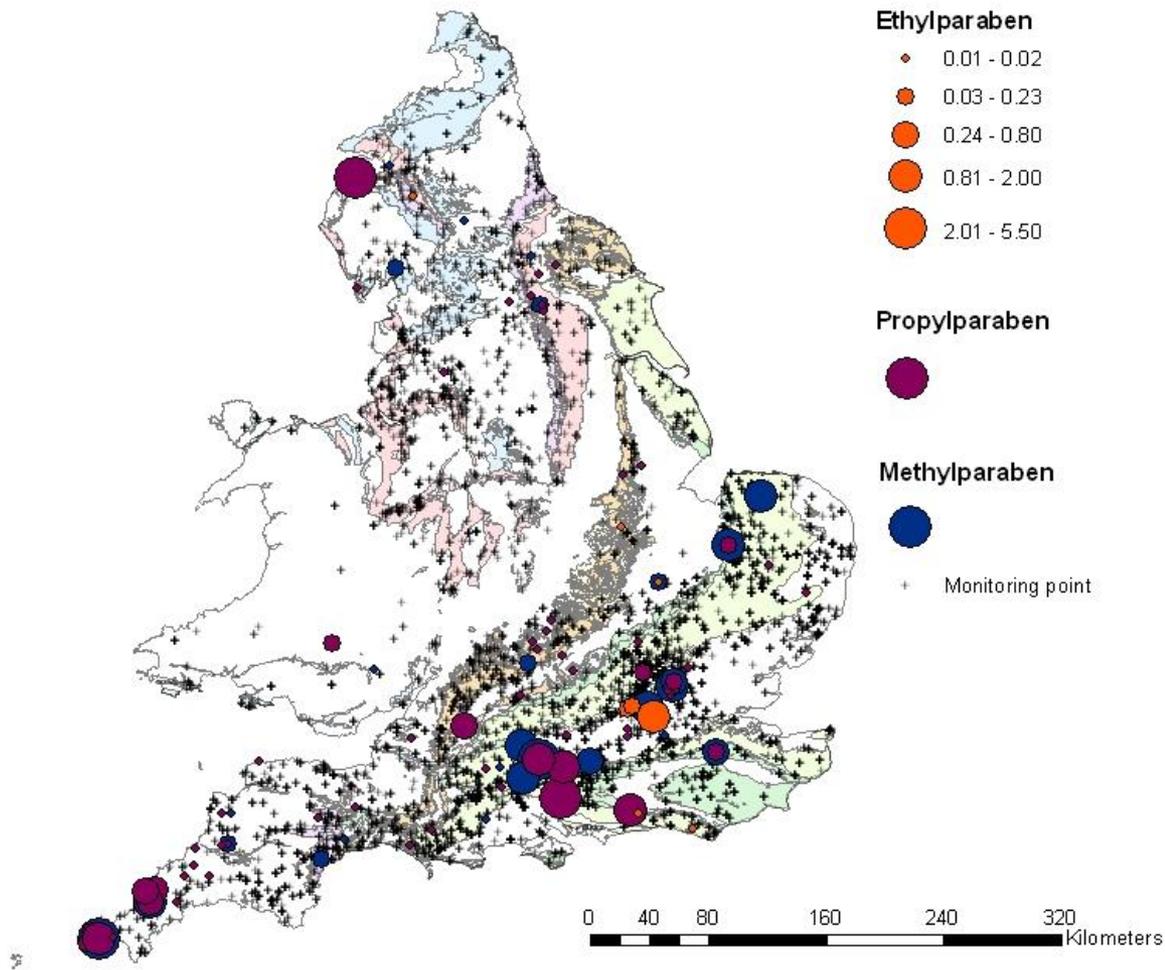




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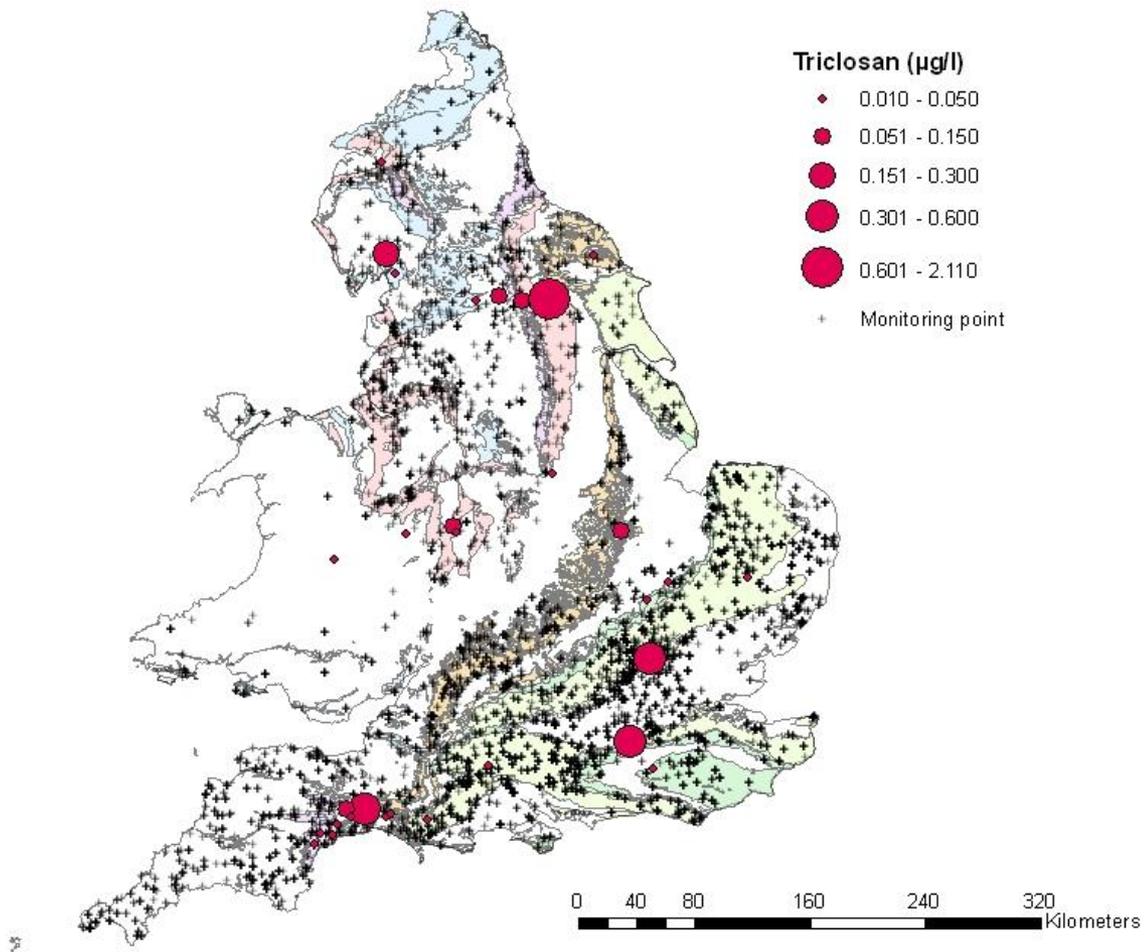




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Conclusions

- Overall there is a poor understanding of the occurrence, transport and fate of many ECs in groundwater
- Although mostly detected in low ng/L concentrations in groundwater there are lots of examples where high $\mu\text{g/L}$ concentrations are found (in both targeted and reconnaissance studies)
- Frequently detected groups of ECs include antibiotics, lifestyle compounds, pharmaceuticals and preservatives
- There are hot-spots of ECs groundwater contamination in several parts of the UK which warrant further investigation
- 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

- Groundwater EC occurrence in UK is still poorly defined
- Very few UK studies on fate, transport and occurrence of pharmaceuticals and personal care products in groundwater
- Lack of information on unsaturated zone transport processes
- Growing use as novel environmental tracers (e.g. pharmaceuticals, sweeteners)
- Toxicity of multiple trace organics is still poorly understood
- Predictive transport models – e.g. bank infiltration sites Rhine and Danube
- Newly emerging issues: engineered nano-materials (Ag, Ti, Zn)