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Gateway to the Earth

Emerging contaminants in groundwater: a health risk?

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Groundwater Quality: - Public & private water supplies
Burlington House, March 2019

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Already known examples

“Toxic” or environmental effects observed

- Halogenated solvents
- Plasticisers
  - Phthalates
- Polyaromatic hydrocarbons
- Breakdown products of surfactants
  - Alkyl ethoxylates and linear alkyl benzene sulphonate
- Pesticides
  - Started with DDT
- Musk-xylene

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Emerging organic contaminants

- Anthropogenic organic compounds and their transformation products
- Emerge as result of:
  - Changes in use/new manufactured chemicals
  - Advances in analytical techniques
  - Better monitoring
- ECs in groundwater less well characterised than surface water, mainly due to lower concentrations

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Microorganic contaminants

- Pesticides – newly detected or metabolites
- Pharmaceuticals – human, veterinary, illicit
- “Life style” – caffeine, artificial sweeteners
- Personal care – DEET, parabens, triclosan, musks, UV filters
- Industrial additives and by-products – dioxanes, bisphenols, MTBE, plasticisers
- Food additives – BHT
- Flame/fire retardants – PBDE, alkyl phosphates, triazoles
- Surfactants – alkyl ethoxylates, PFOS & PFOA
- Hormones and sterols – estradiol, cholesterol

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Transformation products

- May be more toxic, polar or persistent than the parent
- For pesticides:
  - Desethyl, desisopropyl -from atrazine
  - BAM from diclobenil
  - AMPA from glyphosate
- Common TPs>parent concentrations have been:
  - Cotinine from nicotine
  - Clofibric acid from clofibrate
  - Nonyl phenol from NPE
- Cannot be reliably predicted from surface environments data due to different geochemical conditions and long residence times

Stuart & Lapworth (2014) Transformation products of emerging contaminants in the environment: analysis, processes, occurrence, effects and risks, Lambropoulou and Nollet, Wiley

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Water quality regulation and monitoring

- Drinking Water Directive
  - Limits: pesticides & metabolites, PAH, petroleum, chlorinated solvents, THM
- WFD, GWDD and PPD
  - 21 priority and 24 hazardous substances: PCP, PBDE, octyl & nonyl phenols, PAH, pesticides
  - Also “drins”, DDT and chlorinated solvents
  - Candidates: including glyphosate, AMPA, bisphenol A, musk-xylene and PFOS
  - EQS for surface water and Threshold Values for groundwater
- Watch list
  - Surface water -10 substances including 17α-ethinylestradiol, 17β-estradiol, neonicotinoids, amoxycillin
  - Groundwater - being developed by CIS WGGW

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Sample collection

- Relatively large volumes in glass bottles or filtered by SPE locally
- Sampling equipment
  - inert materials - pump tubing
- Sample collection staff
  - glove material
  - toiletries – insect repellent, sunscreen

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Occurrence in groundwater from literature, 2012

- Looked at pharmaceuticals, PCP, 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

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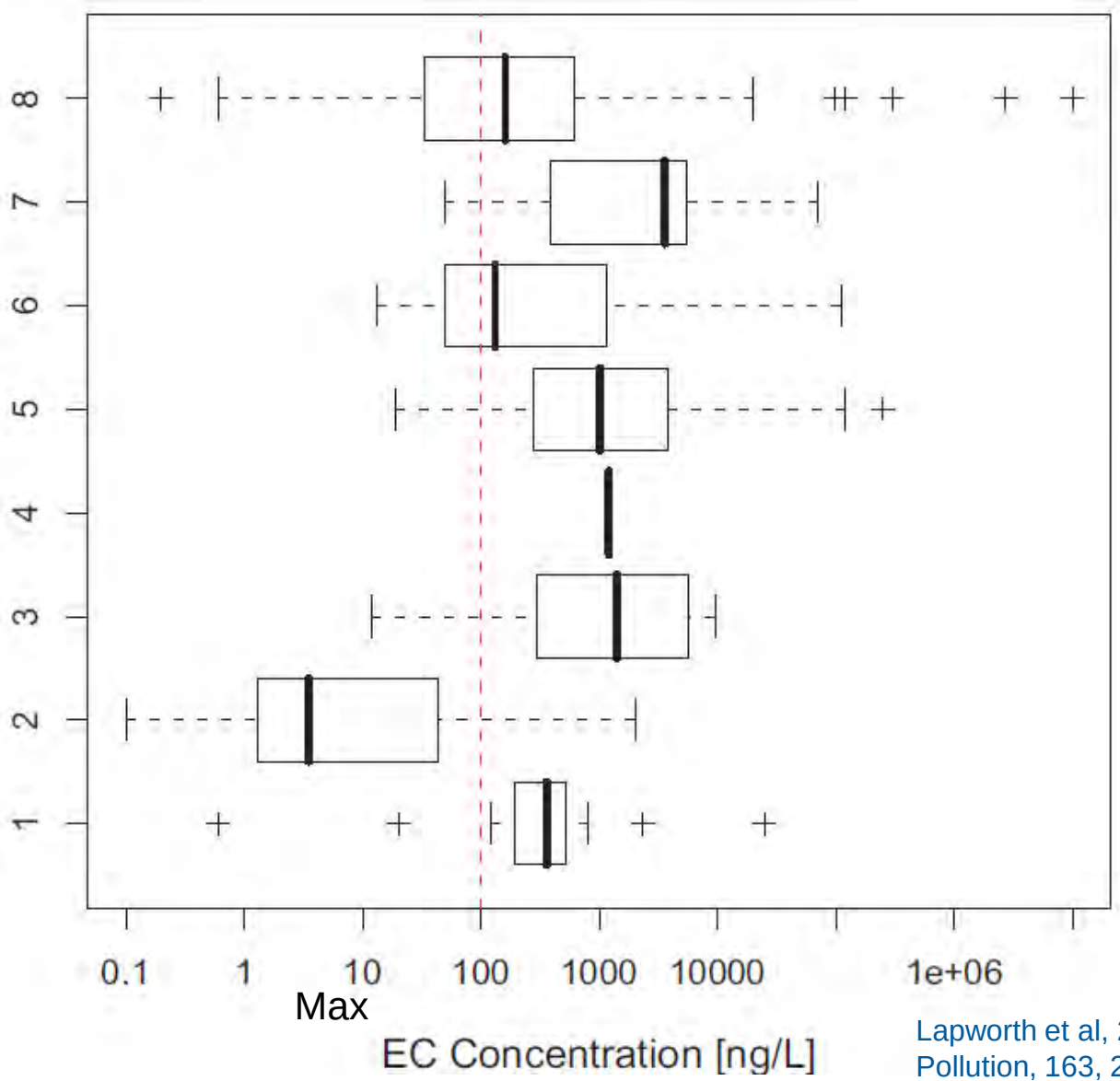
Lapworth et al, 2012 Environmental Pollution, 163, 287-303

Box plots of 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)

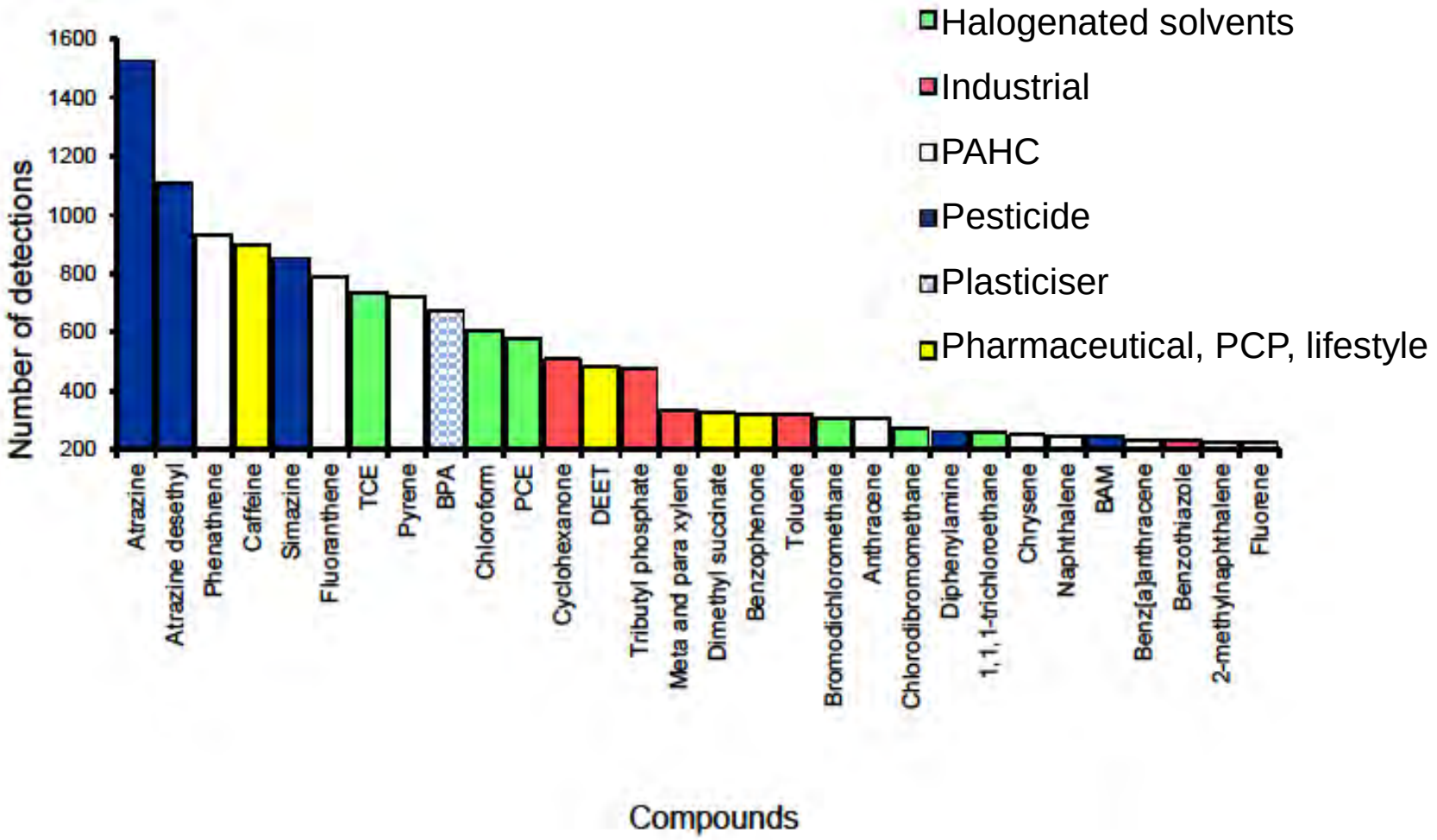
3: Food additives and artificial sweeteners

2: Steroids, hormones and metabolites

1: Veterinary antibiotics and hormones

Lapworth et al, 2012 Environmental Pollution, 163, 287-303

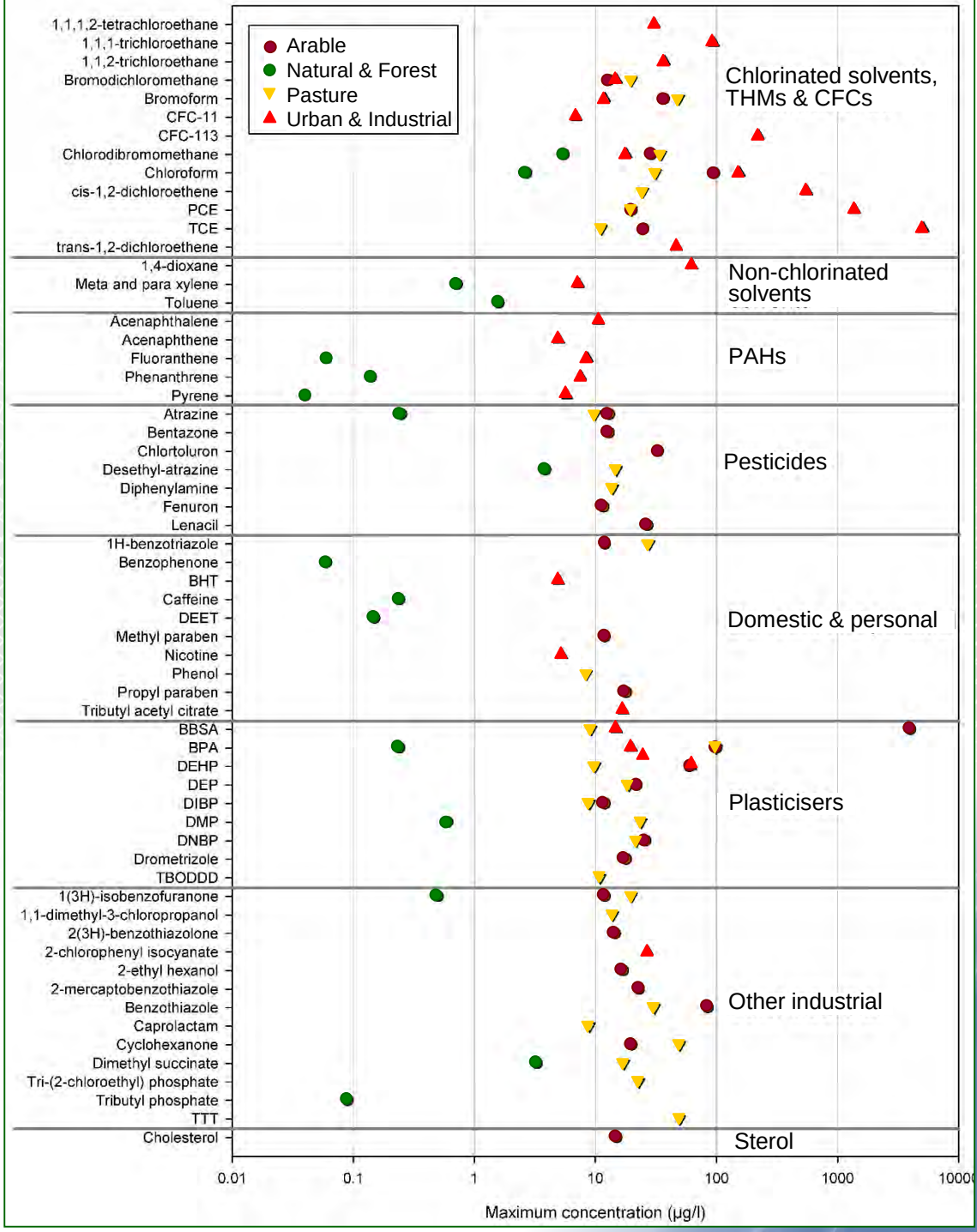
Detections in groundwater, England and Wales, 2016 study, all EA methods



Manamsa et al 2016, STOTEN, 568, 712-86

Land use

- CORINE dataset for Europe (EEA, 2006) with 60% of dominant type within 500-m radius
- Four categories:
  - Natural & Forest
  - Urban & Industrial
  - Arable
  - Pasture/grazing
- Top 30 in each land use
- Maximum concentrations



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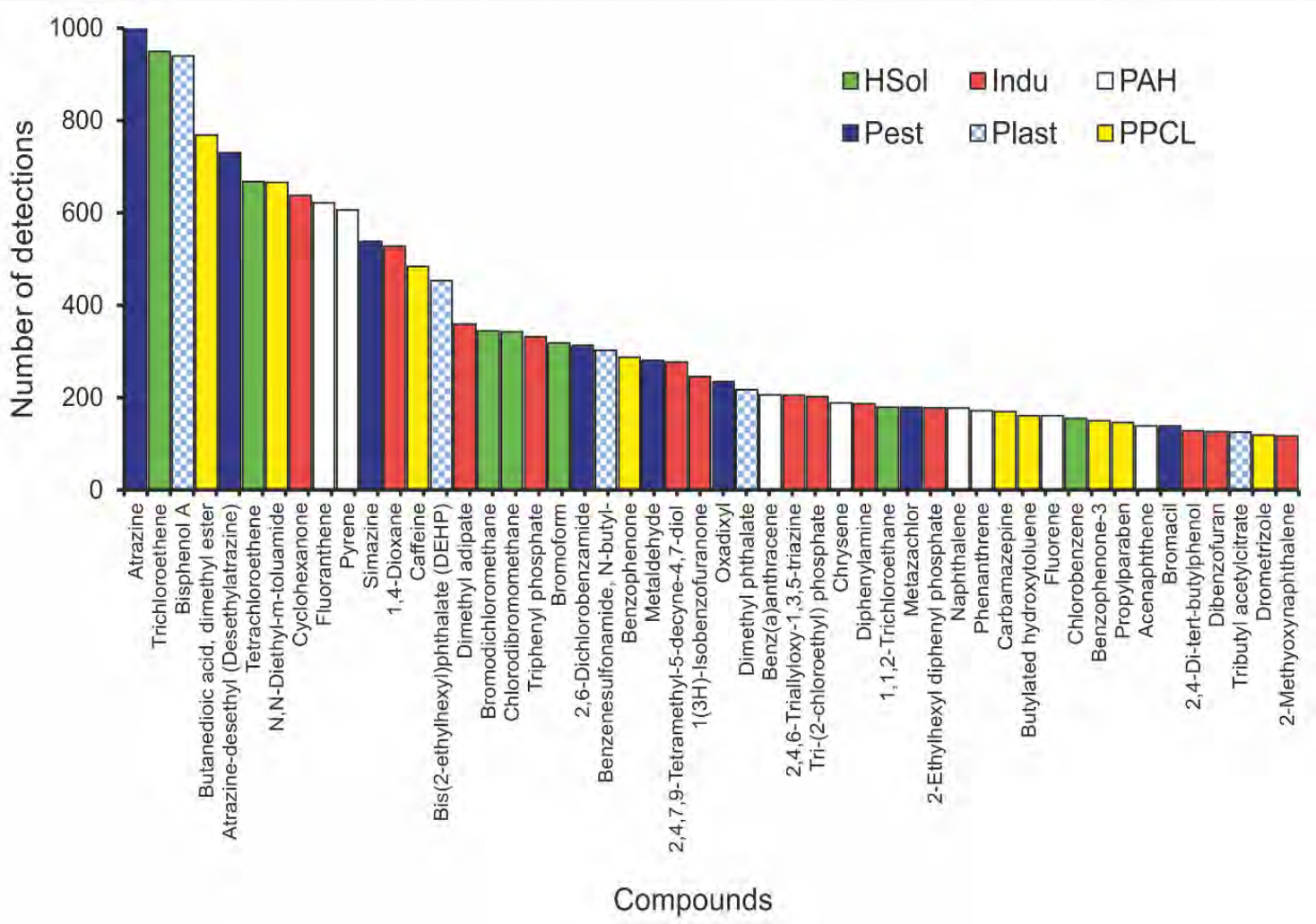
Frequency of detection in groundwater, England by GCMS, 2019



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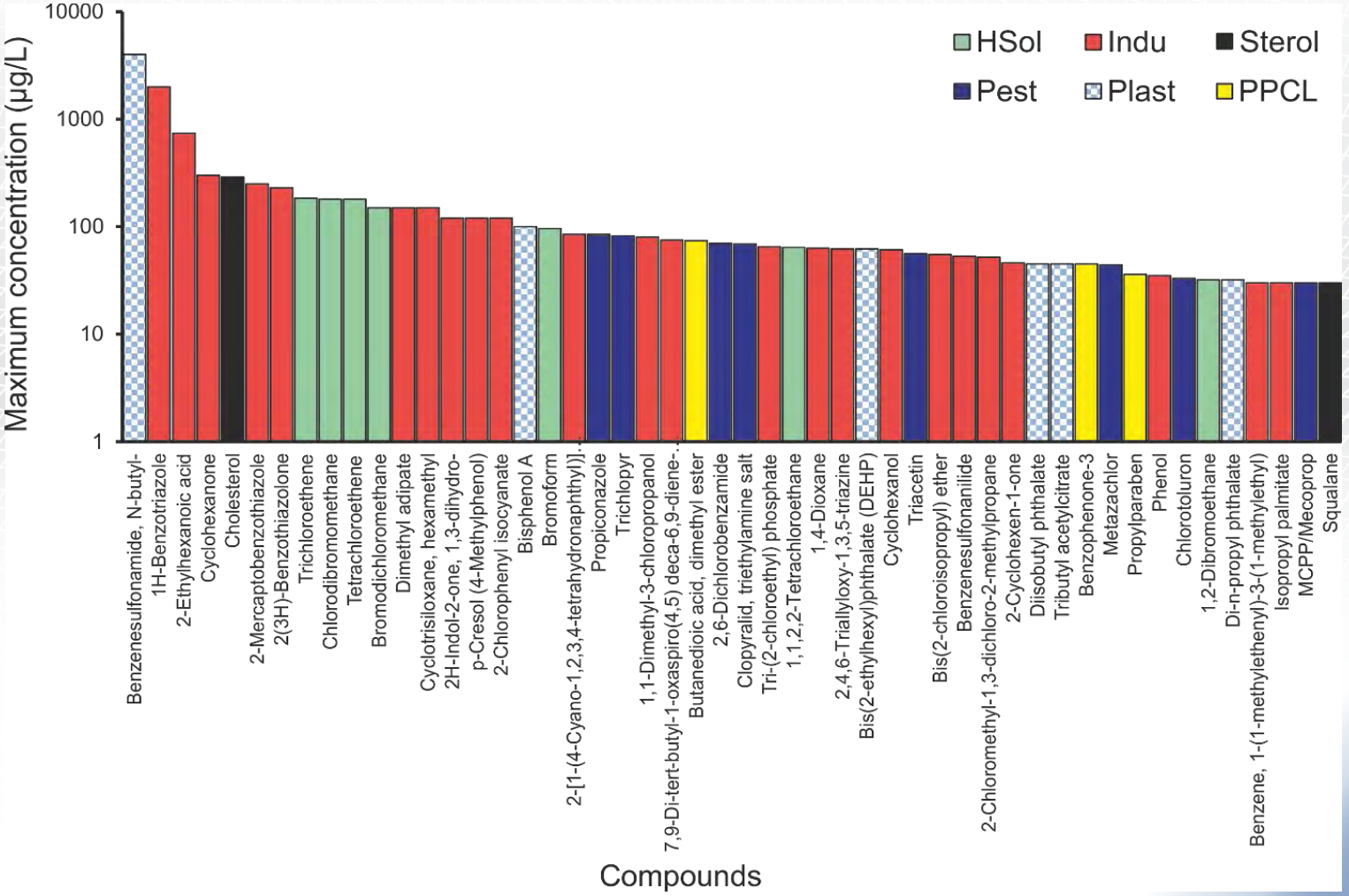

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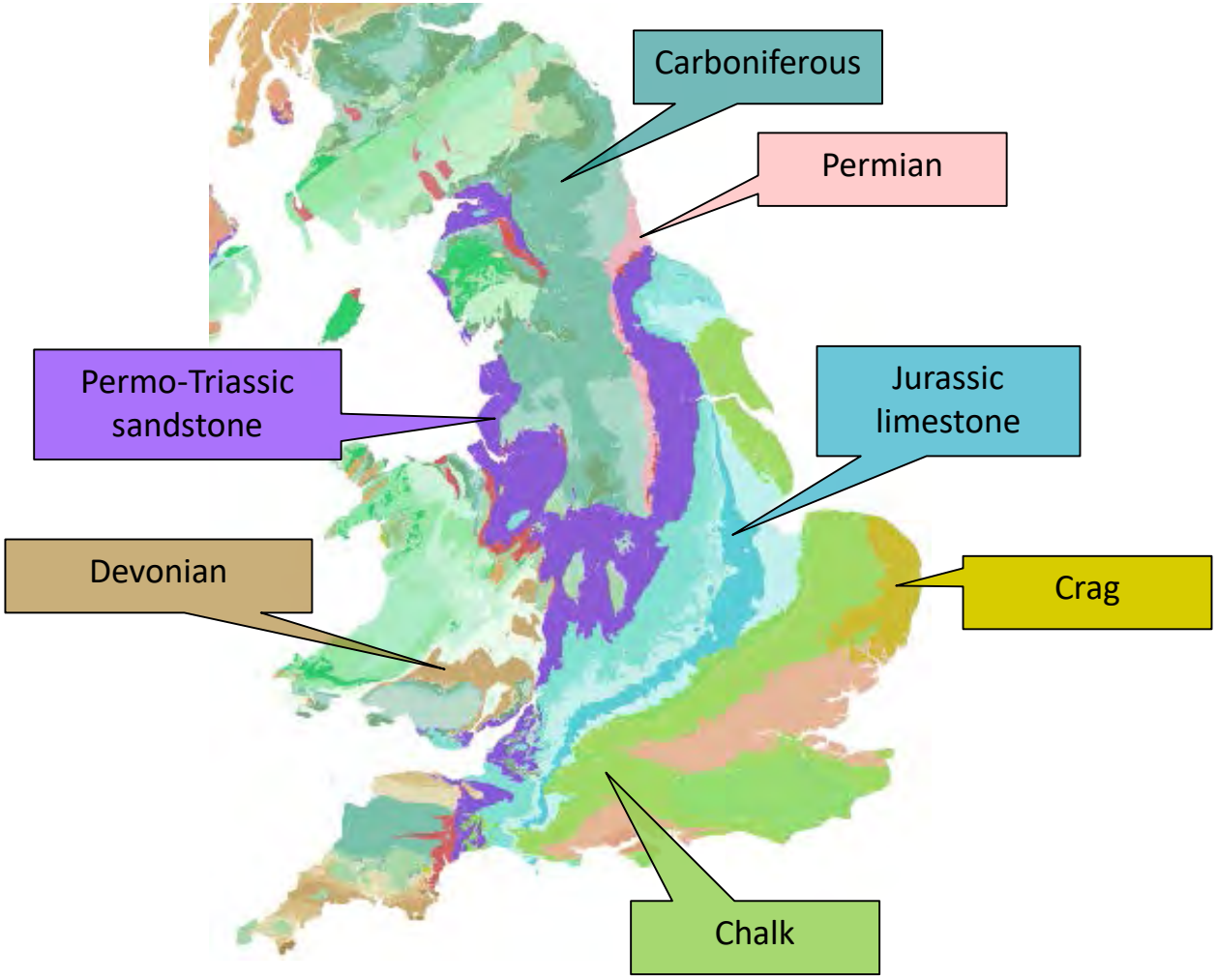
Simplified geology



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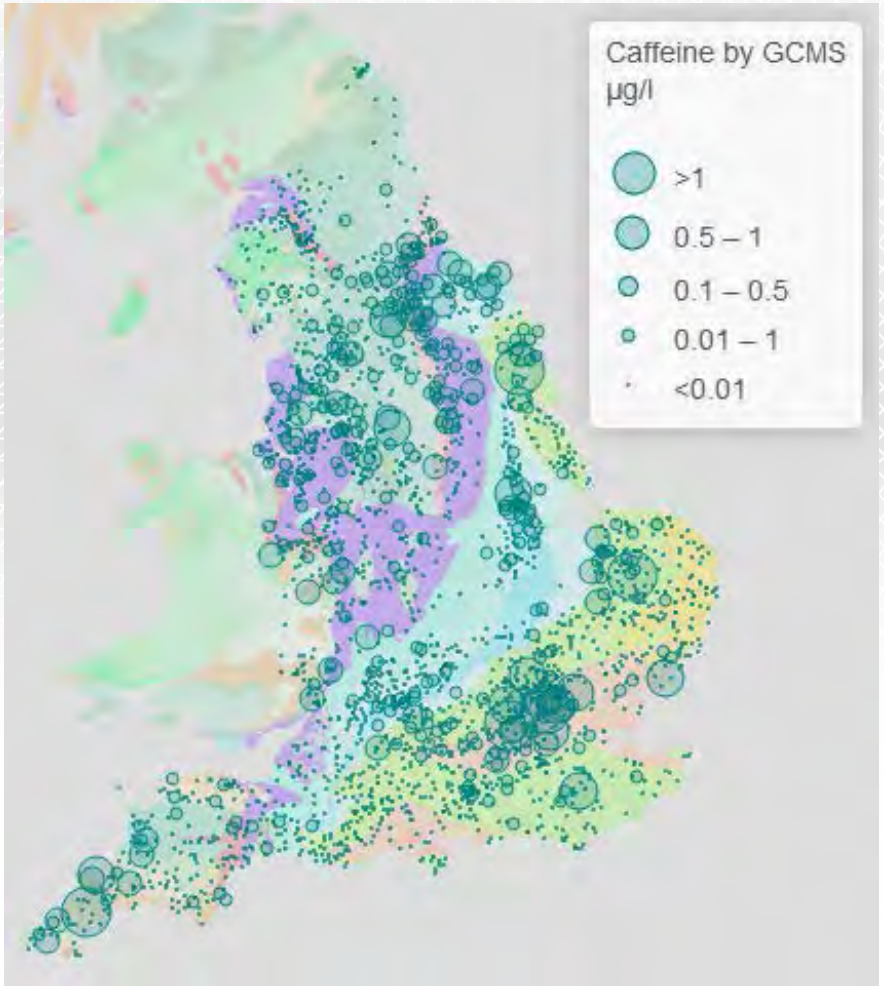
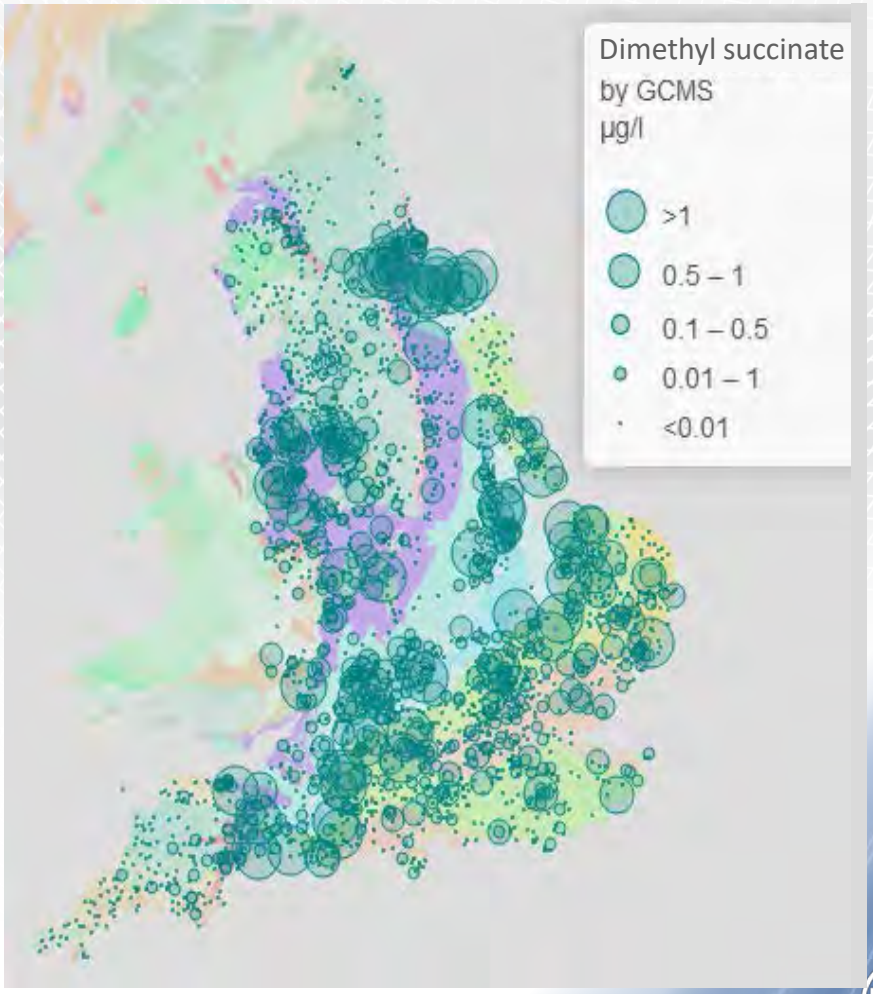
Spatial plots of caffeine and dimethyl succinate





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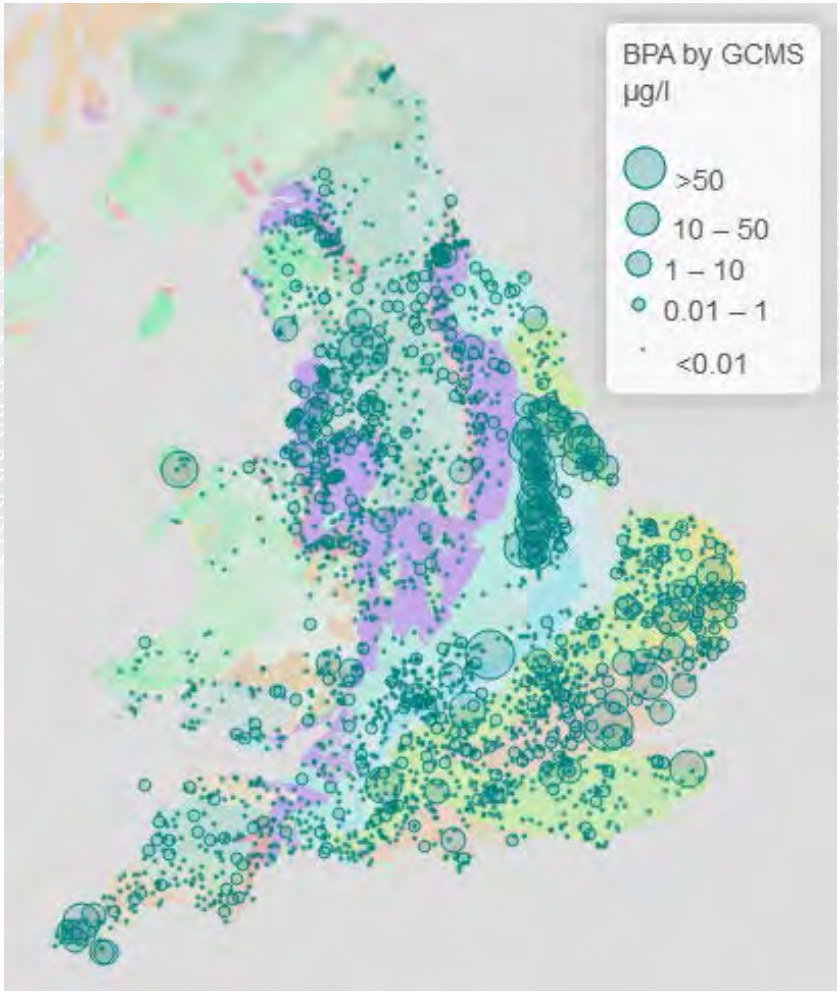
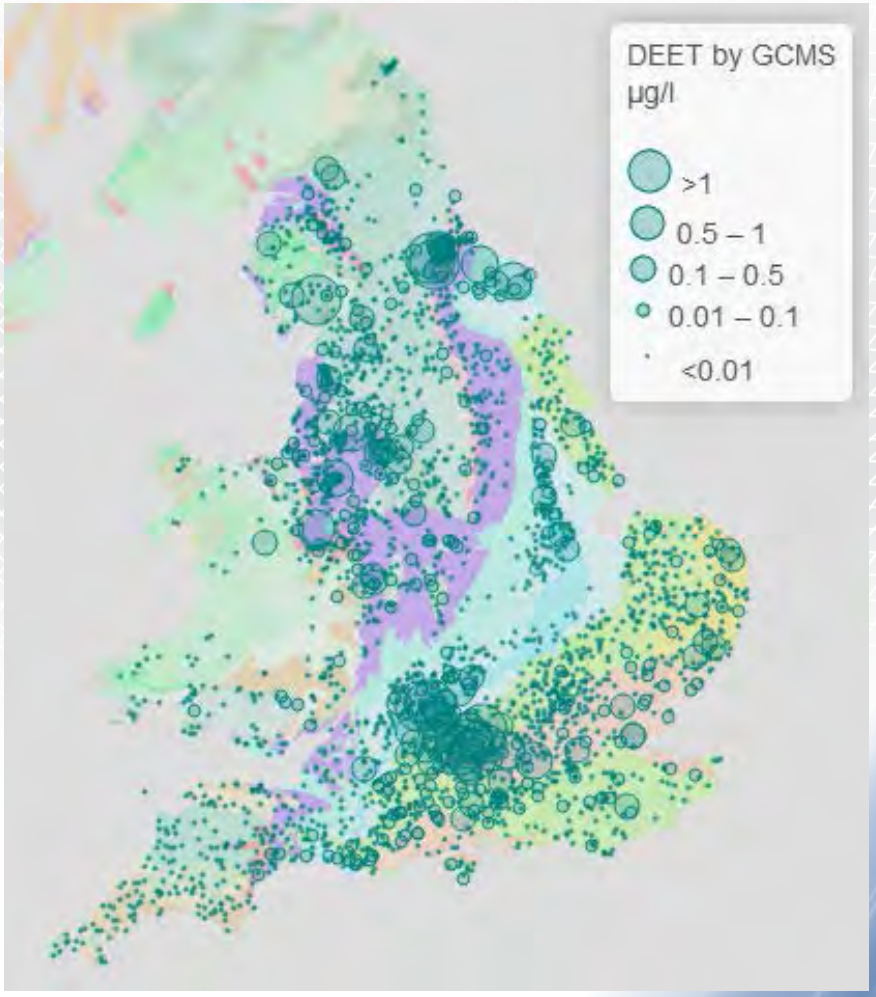
Spatial plots of bisphenol A and DEET





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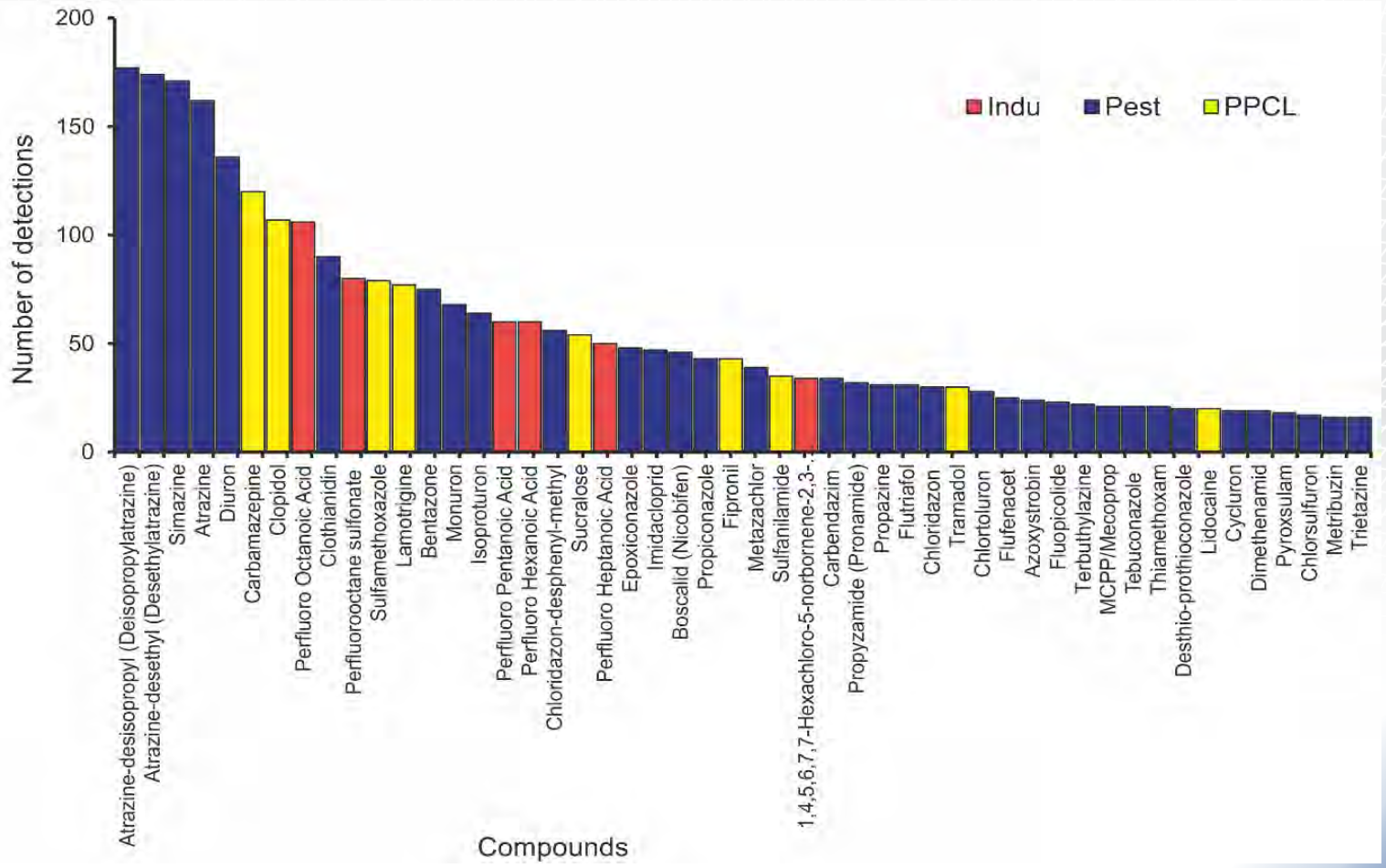
Frequency of detection in groundwater, England by LCMS, 2019



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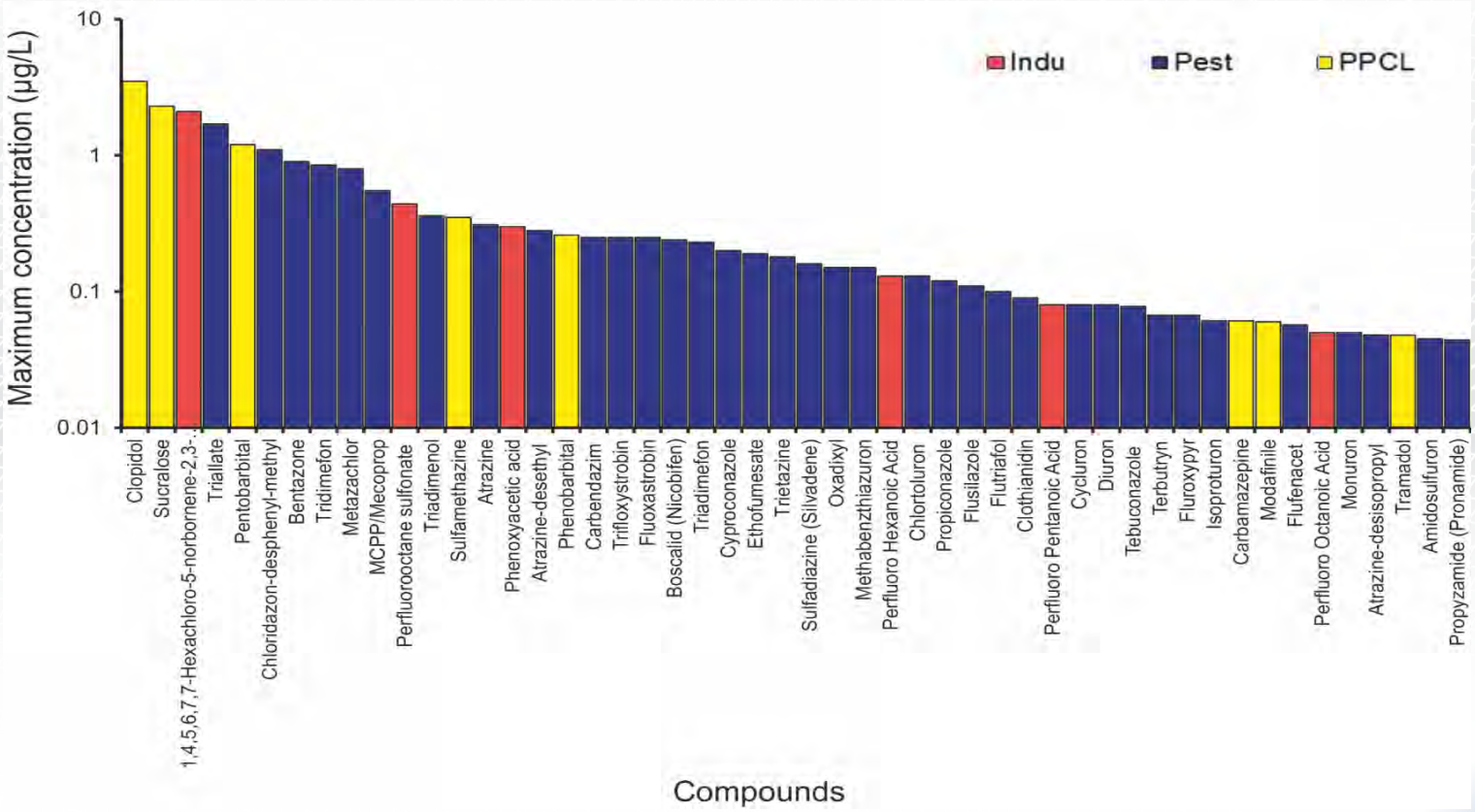
Maximum concentrations in groundwater, England by LCMS, 2019



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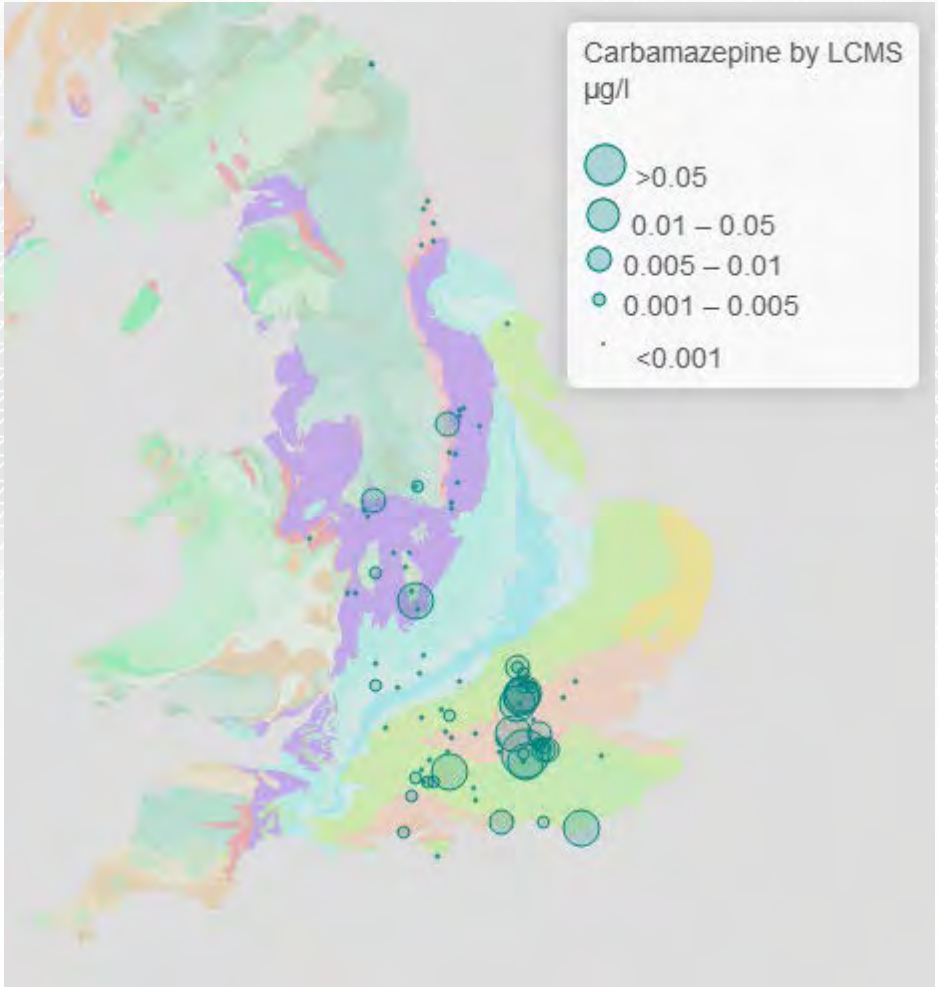
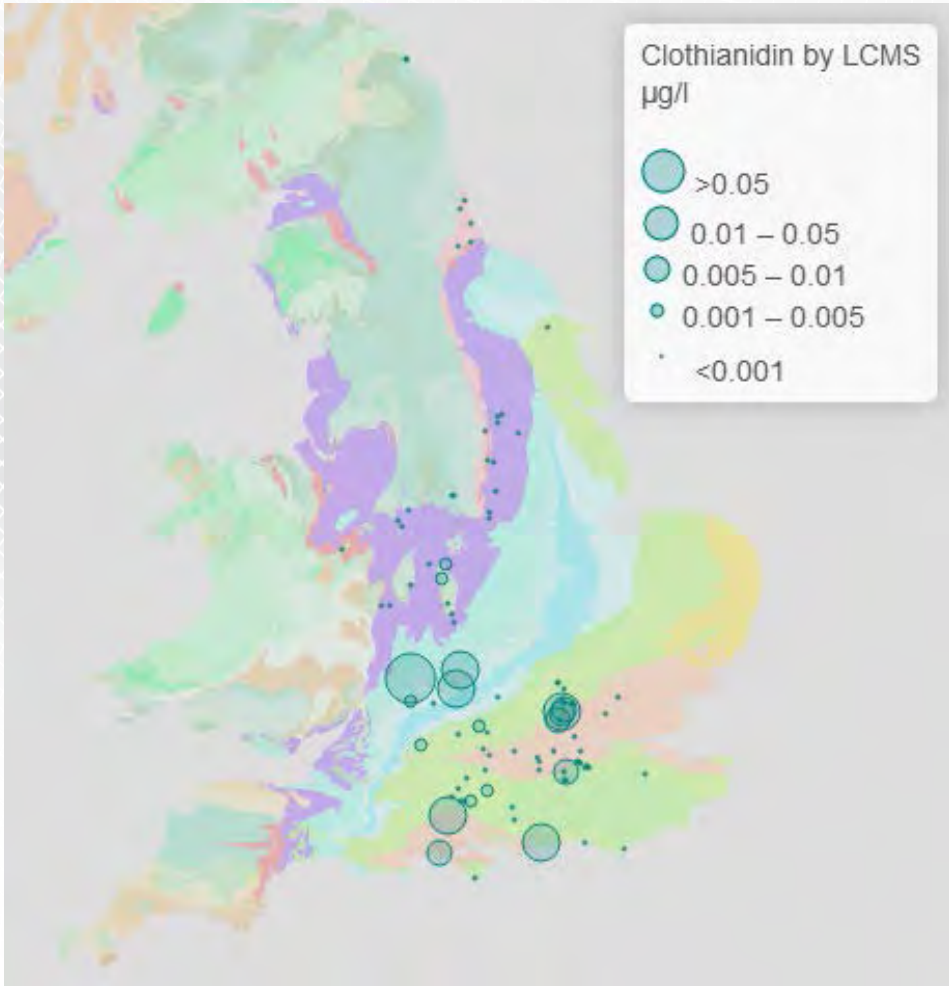
Spatial plots of carbamazepine and clothianidin





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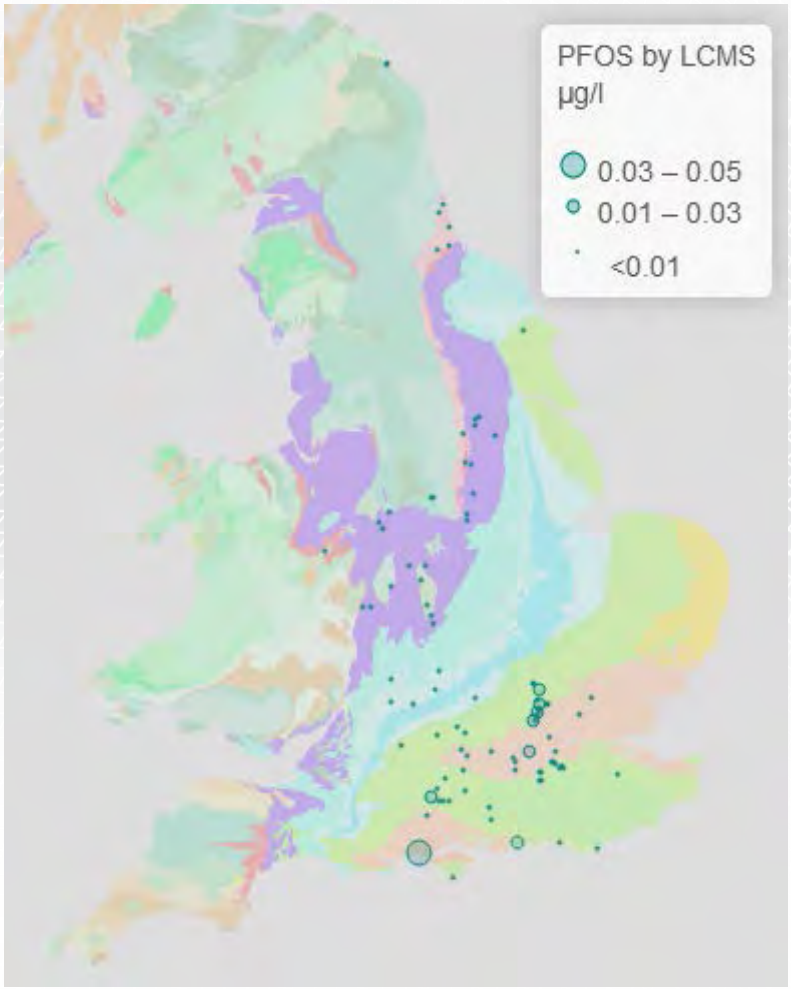
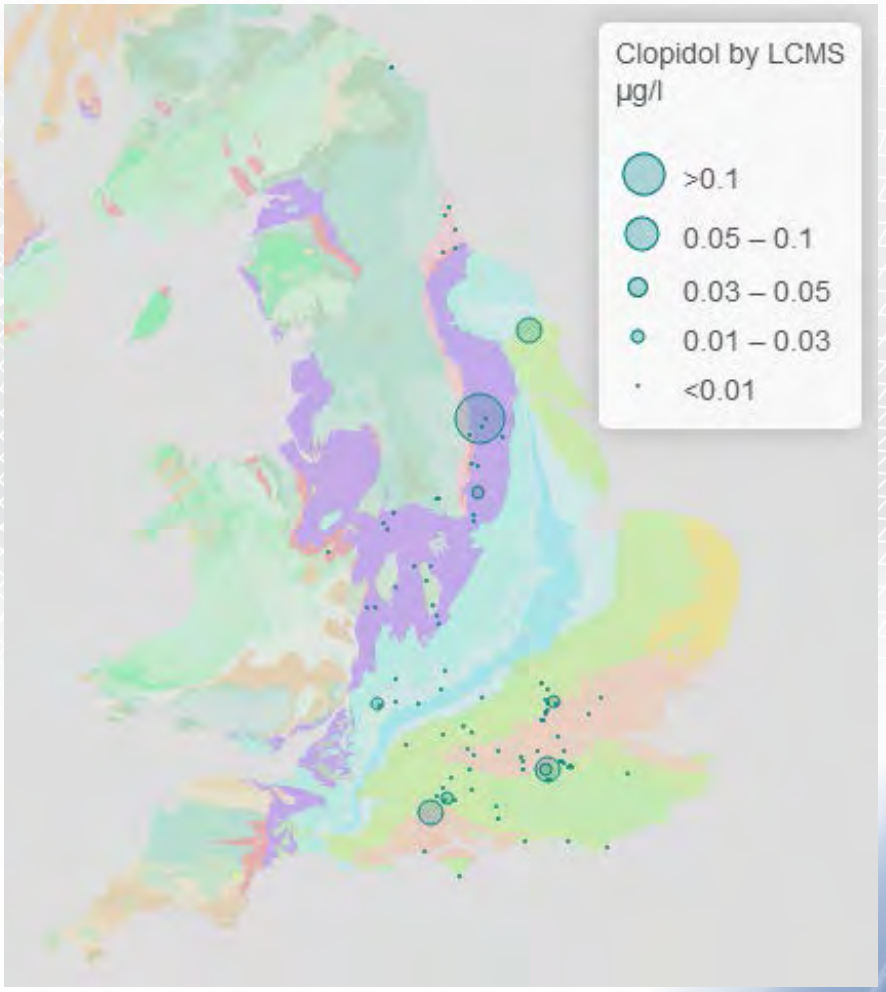
Spatial plots of PFOS and clopidol





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Health effects

- Carcinogenic, teratogenic, mutagenic, endocrine disruption and neurotoxic effects
- Lack of data for many categories for ECs
- Complex mixtures of very low concentrations
- We are not the only receptors

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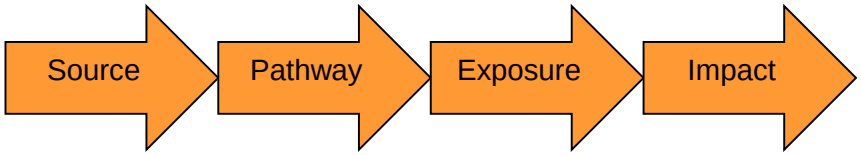
Risk assessment



- Source:
  - Usage / prioritisation using prescription/ sales data
  - Formation in environment /metabolic pathway
- Pathway/mobility/attenuation:
  - Route
  - Leachability
  - Aquatic persistence (particularly for non-pesticides)
  - Water treatment recalcitrance, both waste and potable
- Exposure:
  - Measured/predicted concentrations
- Impact on receptor:
  - Human and ecological effects at environmental levels
  - Synergistic effects
  - Use surface water as early warning for groundwater

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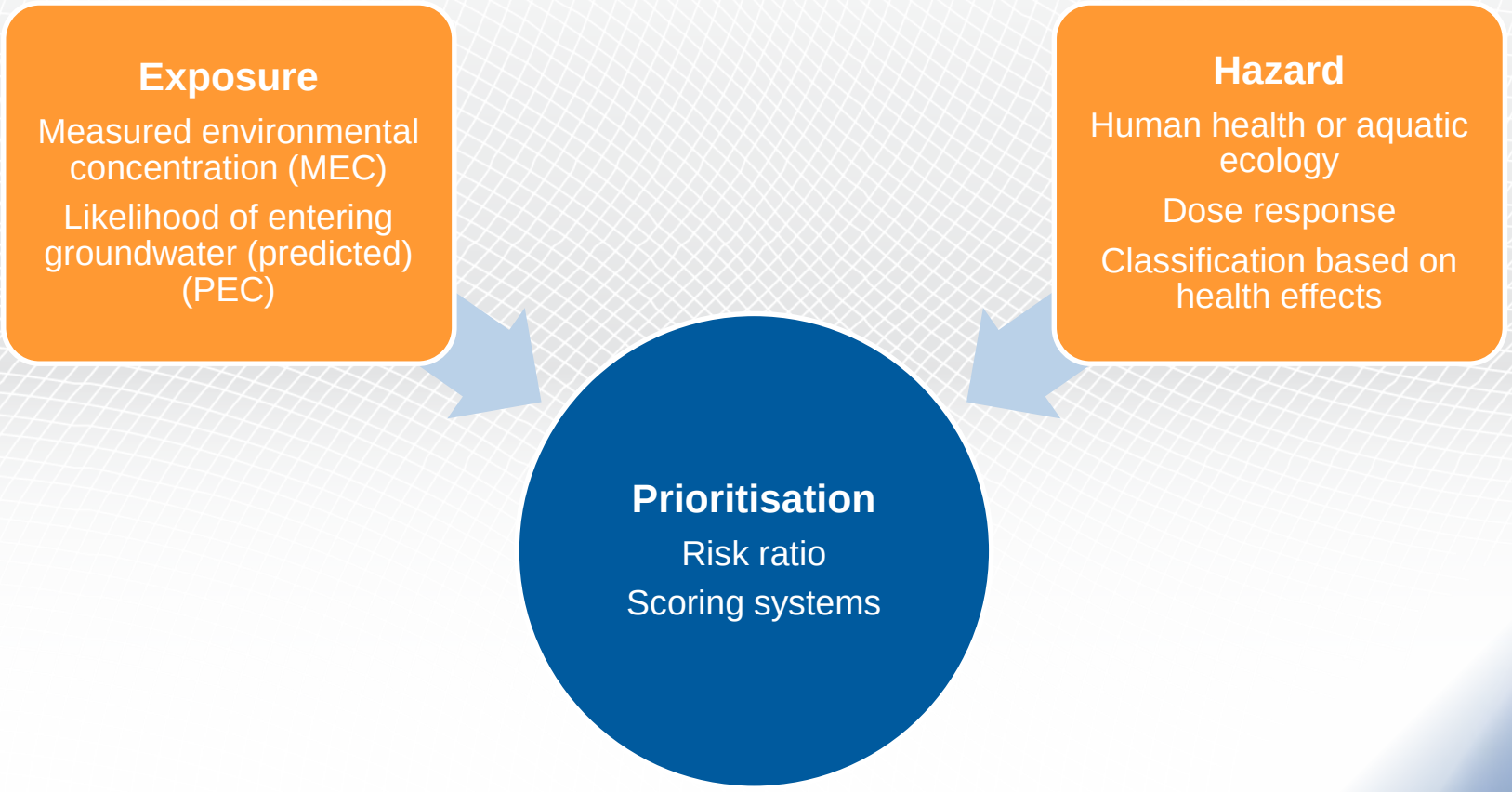
Prioritisation approaches



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Are emerging contaminants in groundwater a health risk?

- An increasing range of compounds is being detected with widespread detection of trace pharmaceuticals and pesticides
- Some are probably no threat to drinking water at such µg/L concentrations, e.g. caffeine, but there are other receptors
- Other compounds may prove to be problematic in the future
- Urban, arable and pasture areas show impact of sewage, manure/sewage sludge or industrial wastewater
- There is increasing information becoming available to allow DW limits, EQSs and TVs to be set
- Still far to go

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