Emerging Contaminants: Strategies for the assessment of emerging groundwater contaminants

Marianne Stuart, Dan Lapworth, Katya Manamsa,
Emily Crane, Debbie White

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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
- Most do not have quality standards for either surface or groundwater under the Drinking Water Directive or the WFD (Priority Substances Directive)
- Groundwater thresholds can depend on relationship with surface water

Emerging(ed) organic contaminants

- Pesticides – parent compounds (e.g. metaldehyde), metabolites
- Pharmaceuticals – human, veterinary, illicit
- “Life style” – nicotine, caffeine, sweeteners
- Personal care – DEET, parabens, triclosan, musks, UV filters
- Industrial additives and by-products – dioxanes, bisphenols, MTBE, phthalates, N-butyl benzene sulfonamide (BBSA)
- Food additives – BHA, BHT
- Water and wastewater treatment by-products – NDMA, THM
- Flame/fire retardants – PBDE, alkyl phosphates, triazoles
- Surfactants – alkyl ethoxylates, PFOS & PFOA
- Hormones and sterols – estradiol, cholesterol

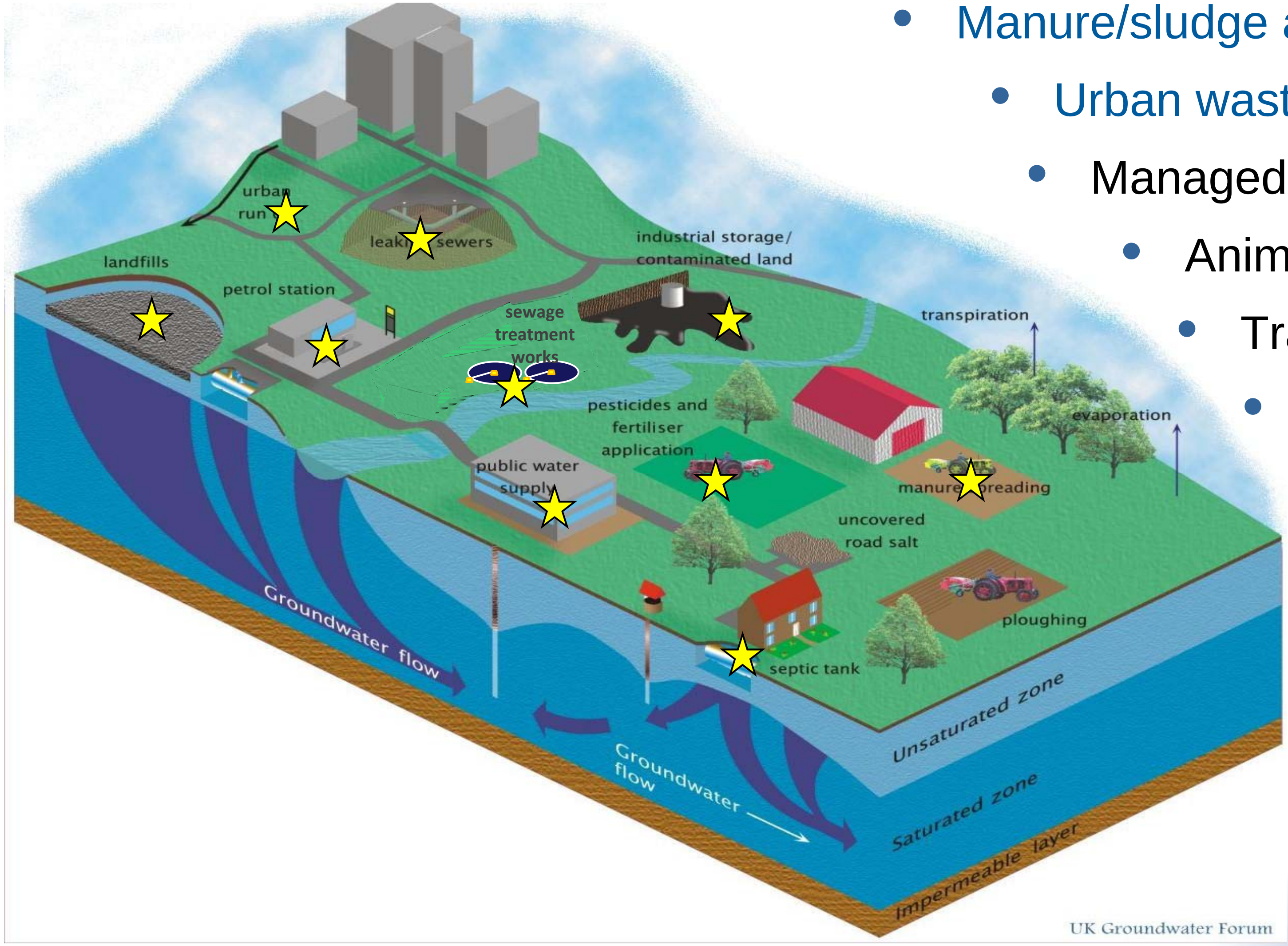
Transformation products

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

Stuart & Lapworth (2014) Transformation products of emerging organic compounds as future groundwater and drinking water contaminants. In: Transformation products of emerging contaminants in the environment: analysis, processes, occurrence, effects and risks. Wiley

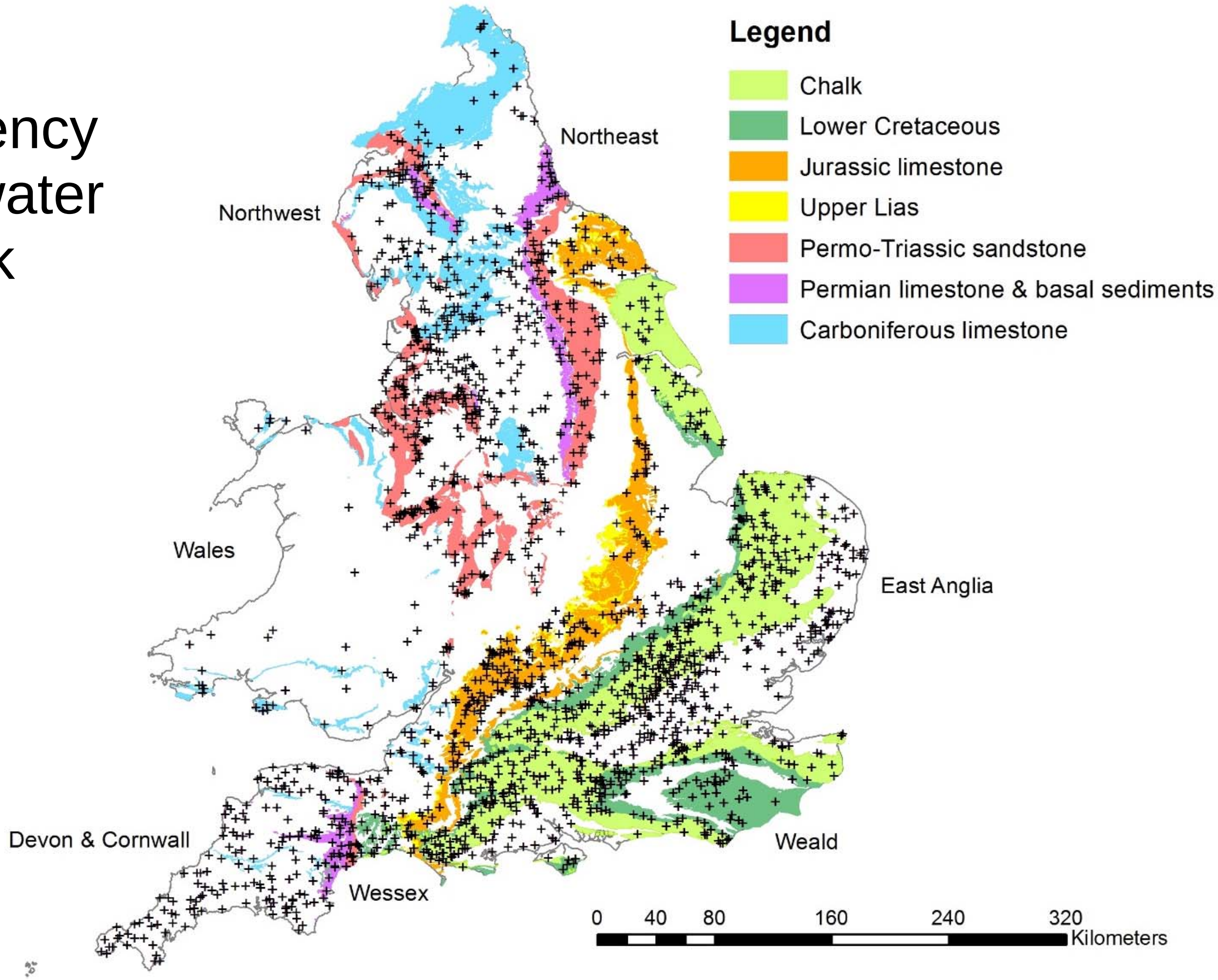
Sources of ECs in groundwater

- Treated wastewater discharge to surface water
- Manure/sludge application to soil
- Urban waste water drainage
- Managed aquifer recharge
- Animal waste lagoons
- Transport networks
- Water treatment
- Septic tanks
- Landfill



The national scale

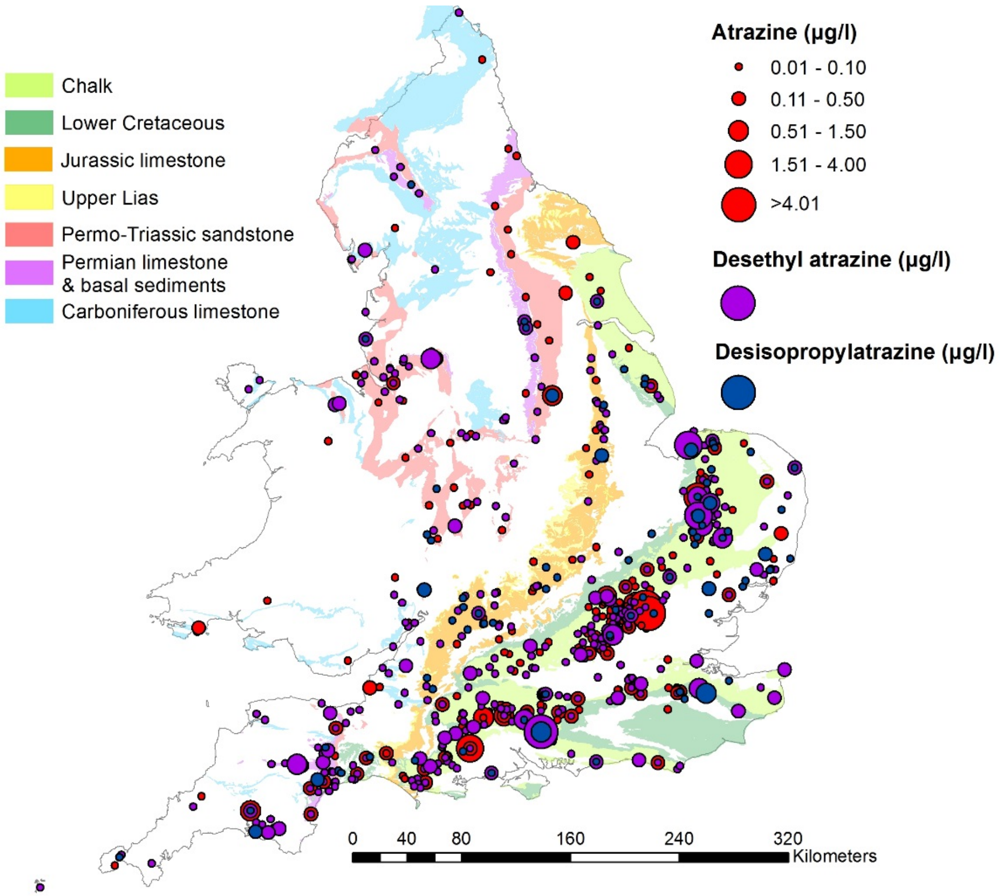
- Environment Agency national groundwater sampling network
- 2650 sites
- GCMS-screen
- Spatial plots
- Concentrations
- Frequency of detection
- Land use



Manamsa et al. (2016) A national-scale assessment of micro-organic contaminants in groundwater of England and Wales Science of the Total Environment online

Pesticides and metabolites

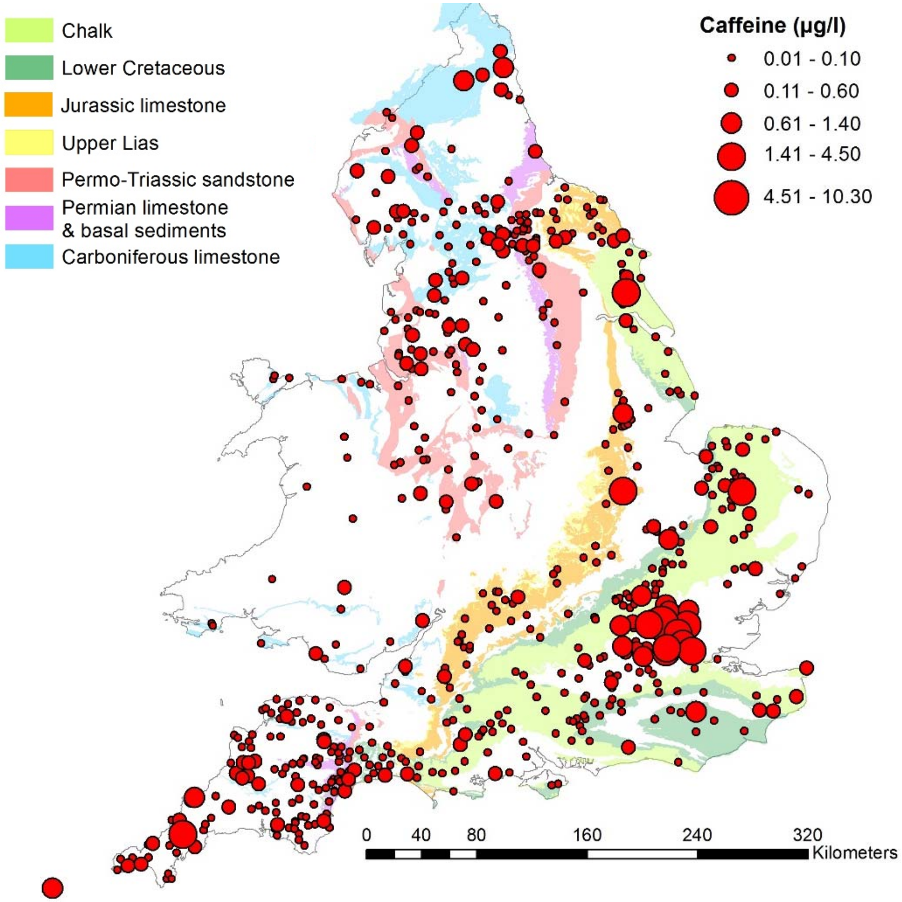
Atrazine



- Widely detected in groundwater despite being withdrawn for 2 decades
- Metabolites widespread

Lifestyle compounds

Caffeine and nicotine



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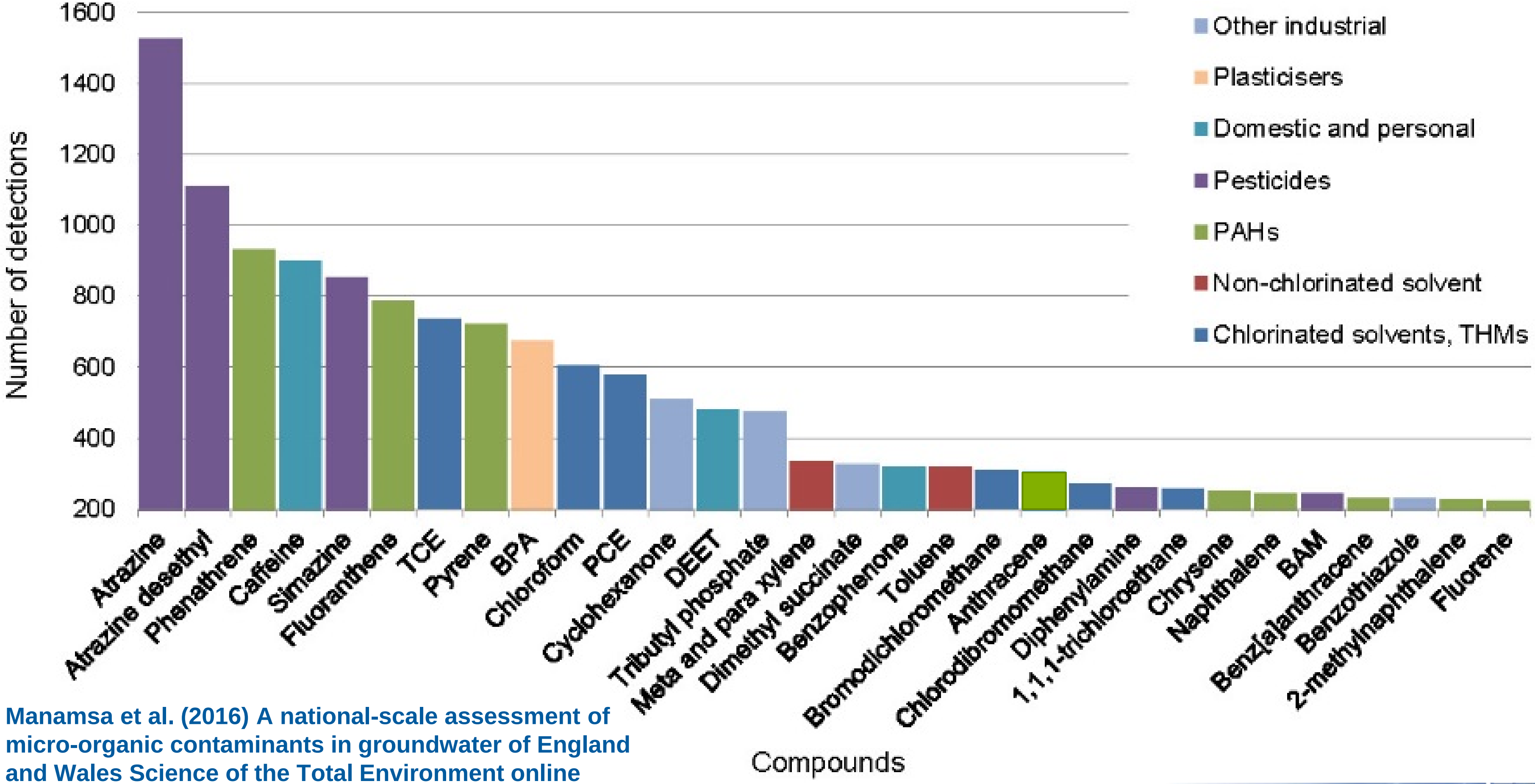
- Caffeine, nicotine and cotinine (nicotine metabolite), from sewage effluent, are widely detected in groundwater
- Paraxanthine (caffeine metabolite) also found
- Dimethyl-imidazo-lidinetrione (product of caffeine chlorination) found elsewhere

Barnes et al. (2008); Seiler et al. (1999); Swartz et al. (2006)

Top 30 microorganics in Environment Agency groundwater screening data 1993-2012

by frequency of detection



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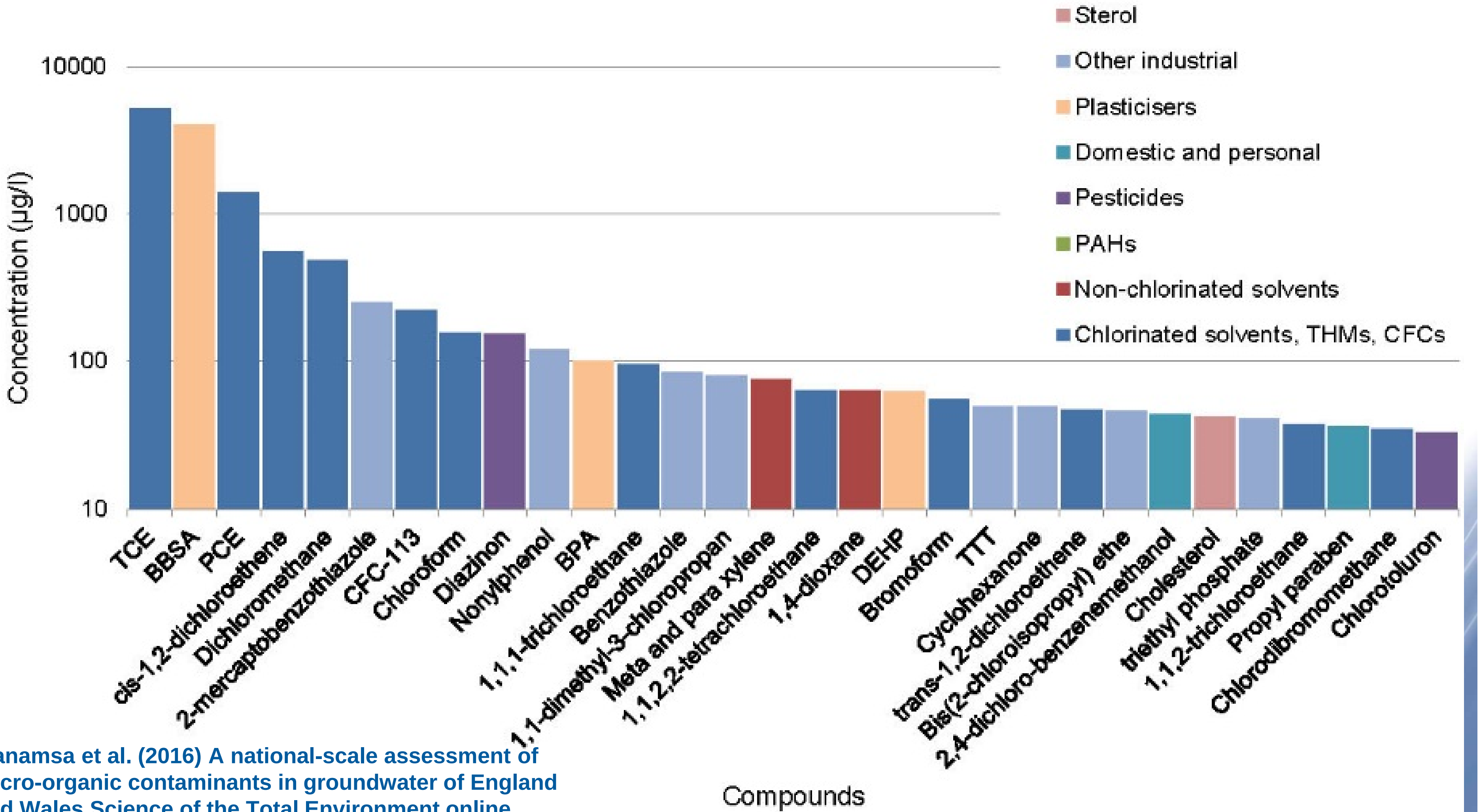
Top 30 microorganics in Environment Agency groundwater screening data 1993-2012

by maximum concentration



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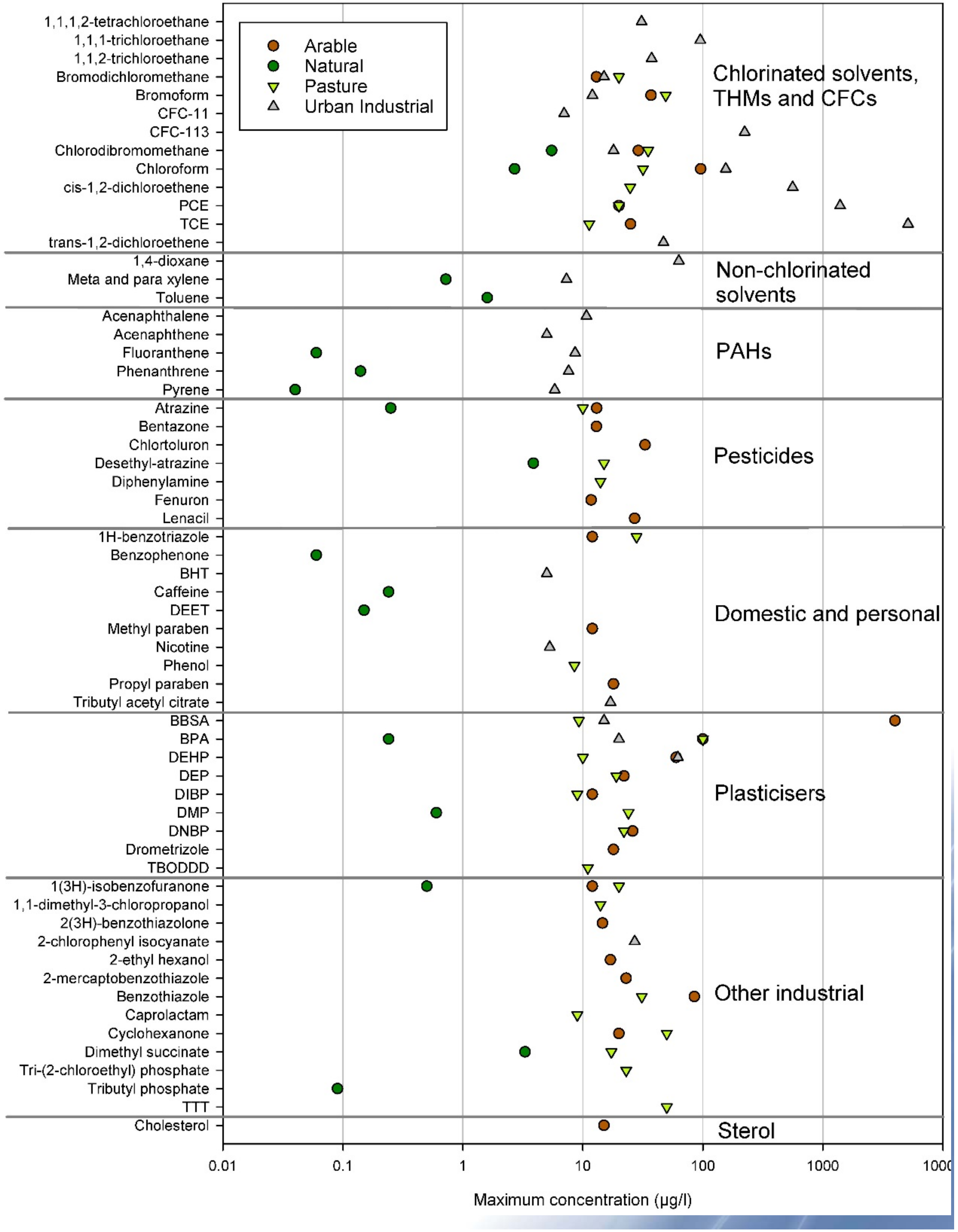
By land use

- CORINE landuse dataset for Europe (EEA, 2006) with a 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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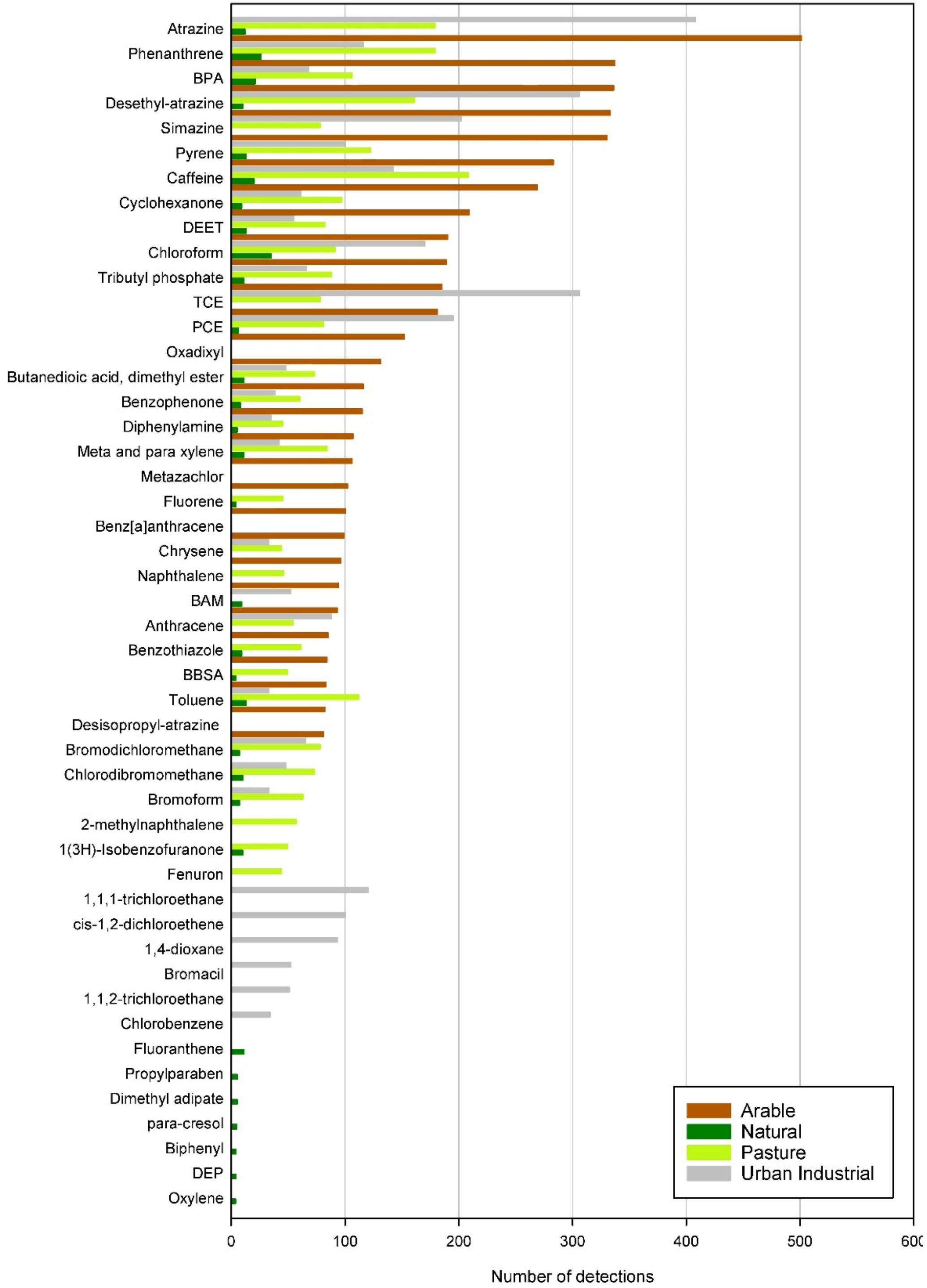
By landuse

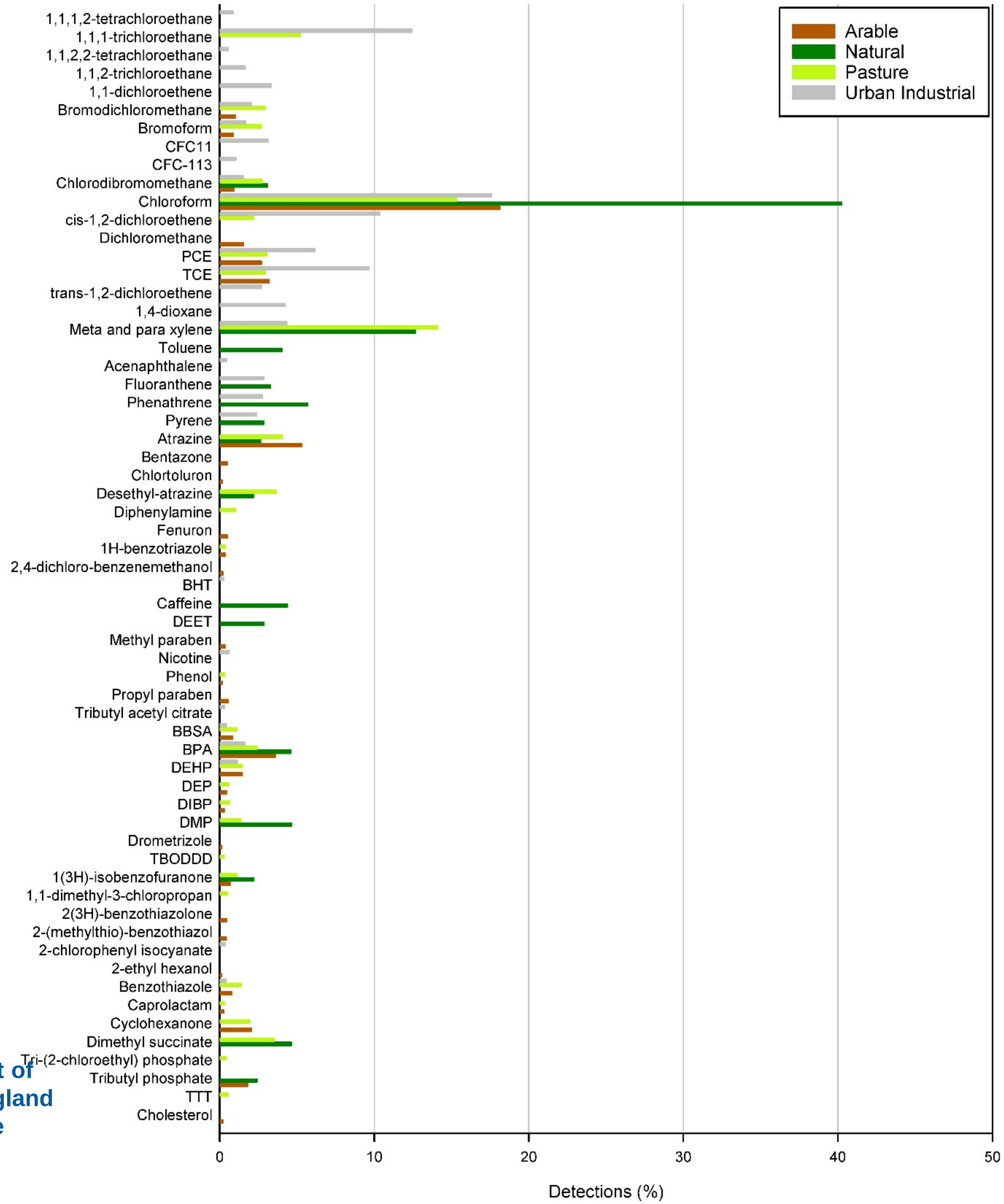
- By number of detections
- Similar to national pattern except natural/forest
- Does not take account of different number of sites



Manamsa et al. (2016) A national-scale assessment of micro-organic contaminants in groundwater of England and Wales Science of the Total Environment online

By land use

- By frequency of detection
- Normalised to each land use
- Chloroform and xylenes prominent
- Caffeine and DEET only found within N



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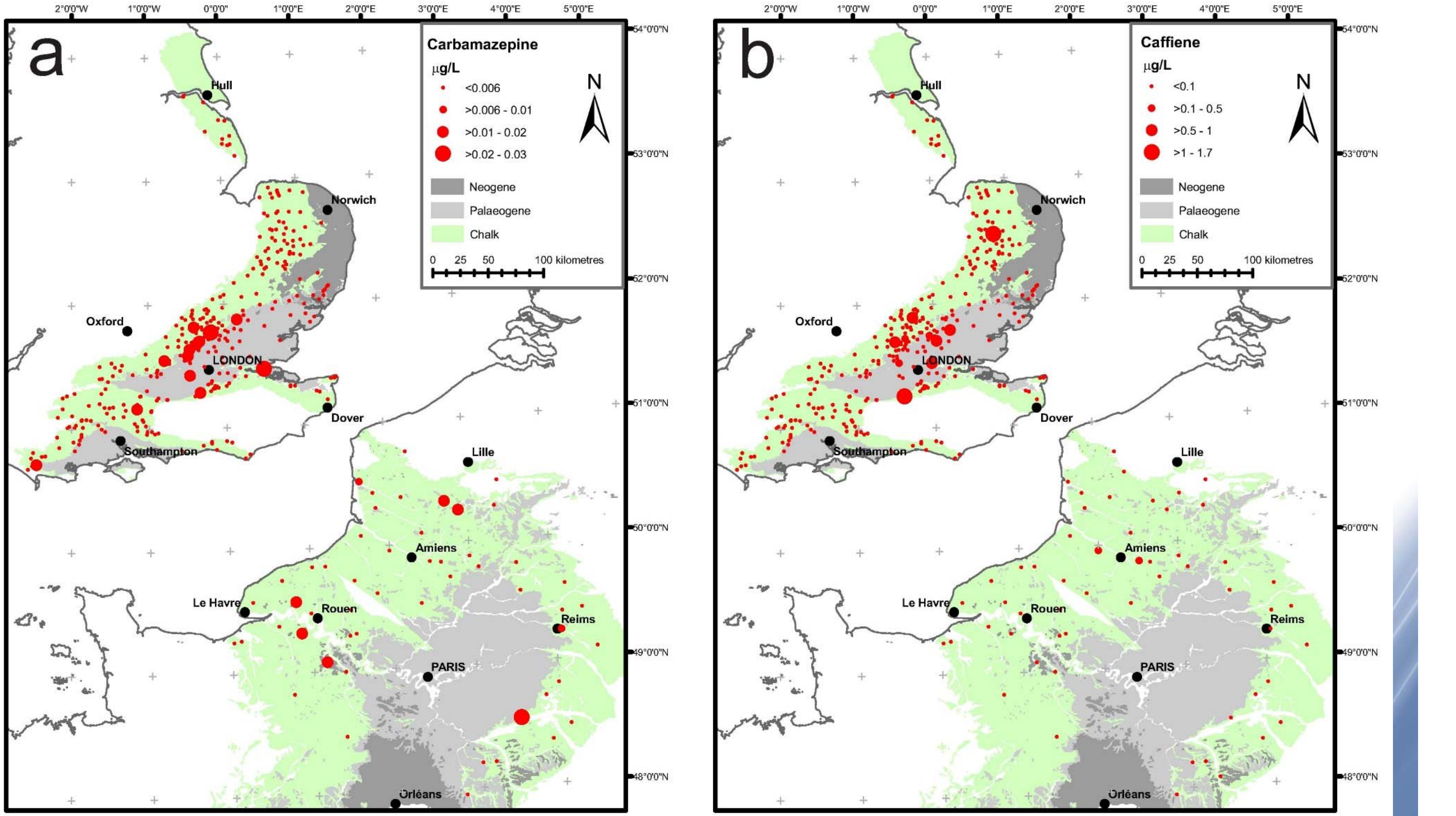
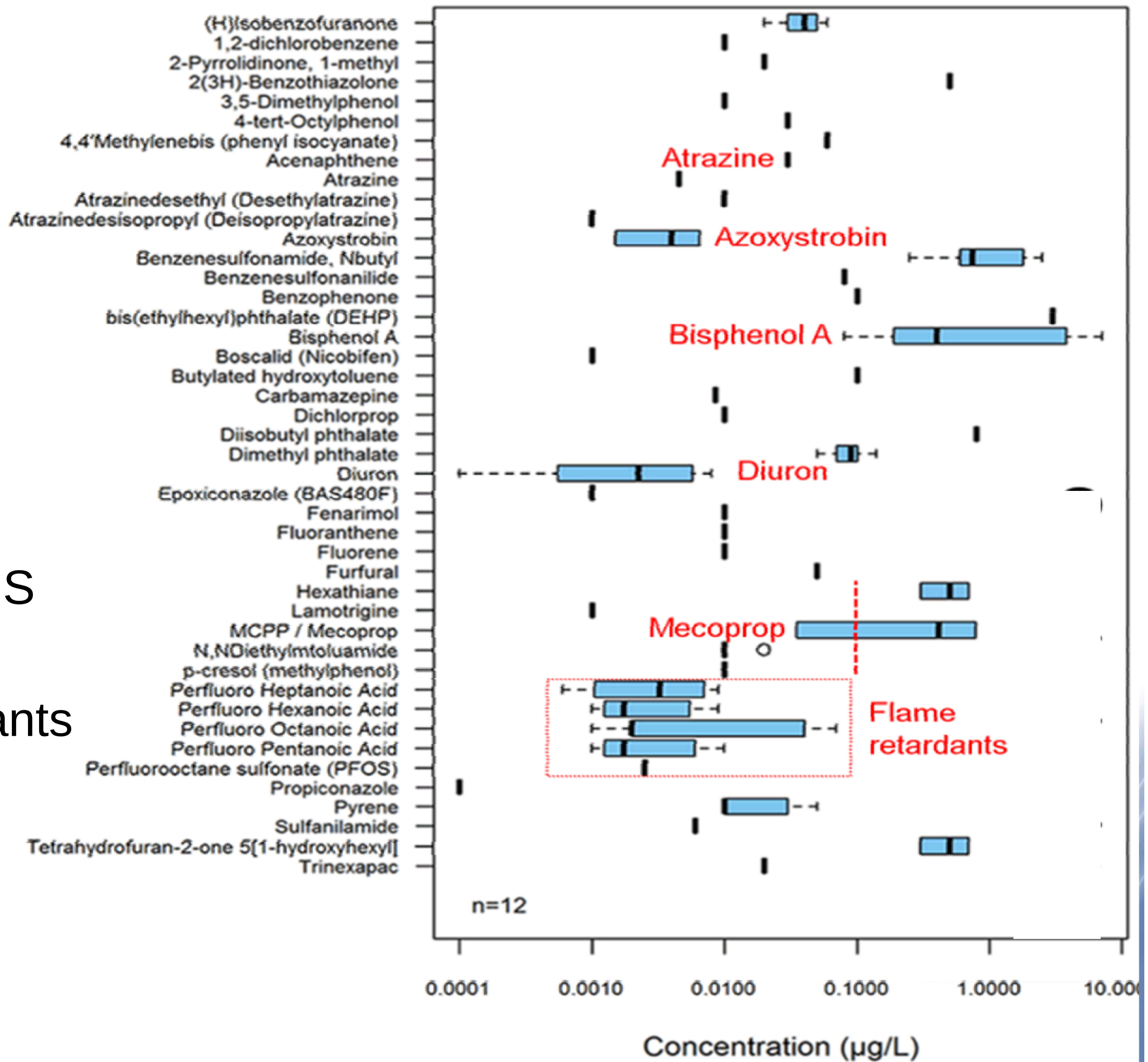
Aquifer scale - England & France Chalk



Lapworth et al. (2015) Persistent and emerging micro-organic contaminants in Chalk groundwater of England and France. Environmental Pollution, 203, 214-225..

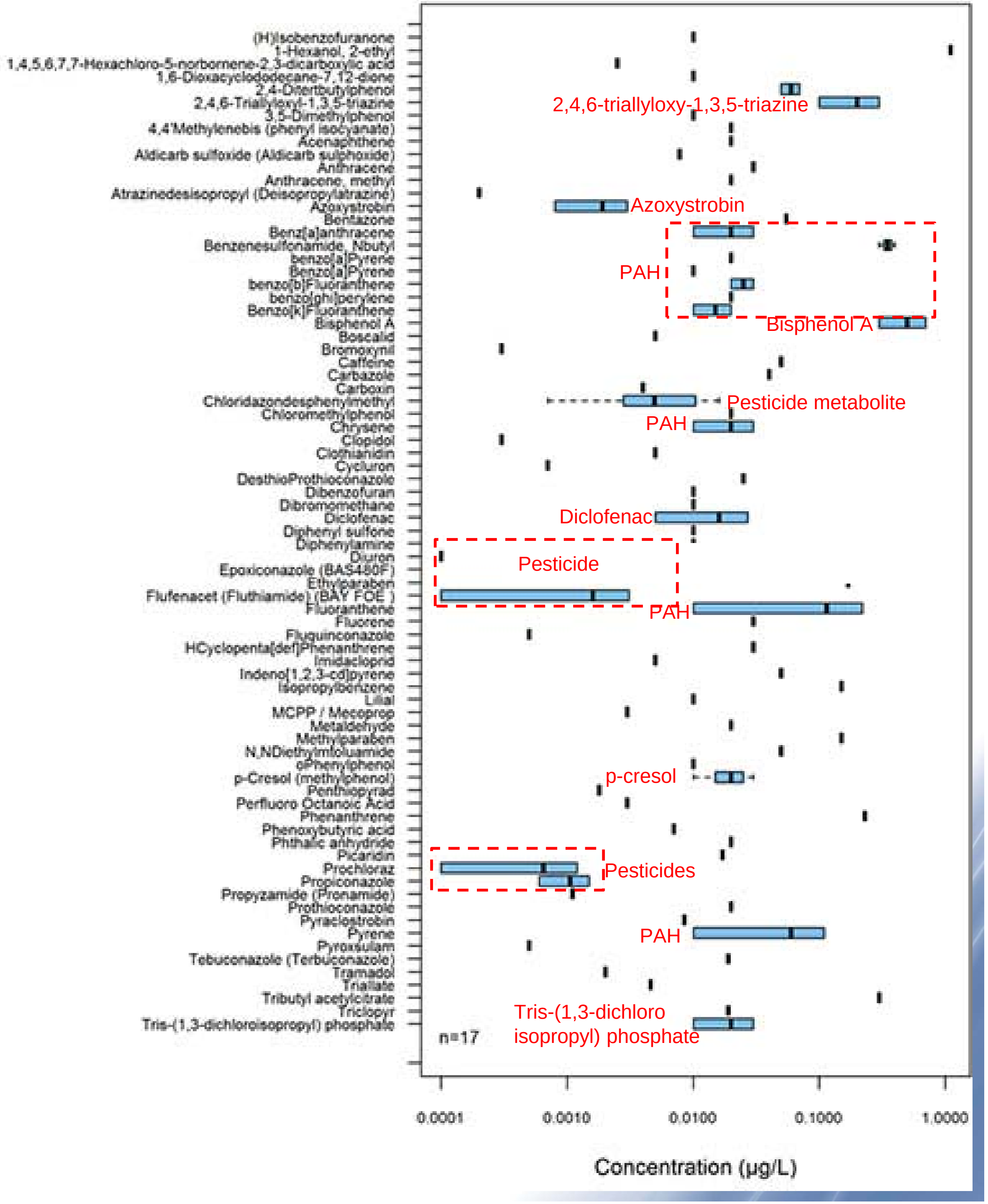
Local survey scale

- Lancashire groundwater baseline
- Includes LCMS scan
- Flame retardants frequently detected at 1-10 ng/L



Local survey scale

- Vale of Pickering groundwater baseline
- More complex mixture of compounds



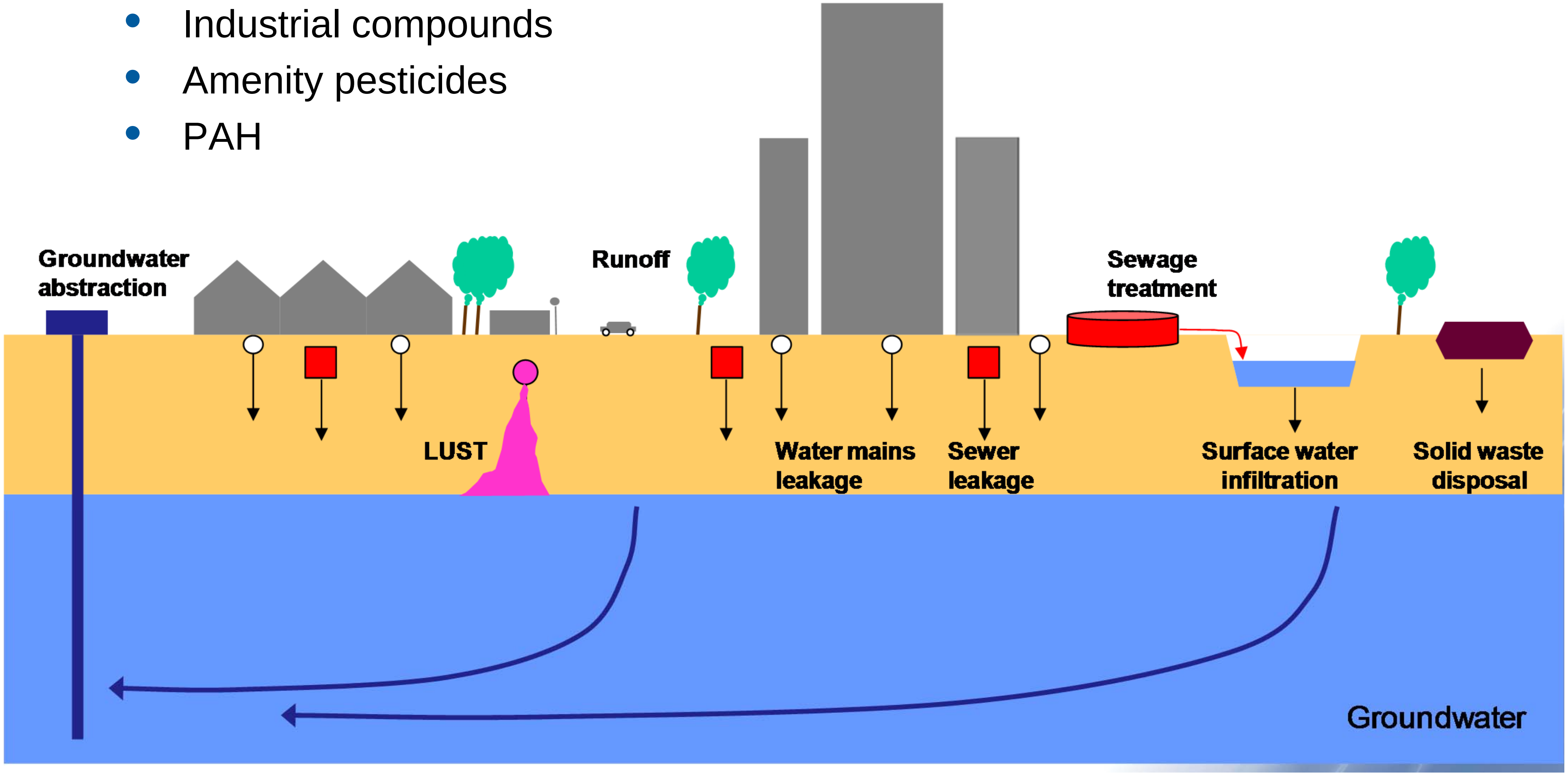
PFOS & PFOA

- PFOS (perfluoroctanesulfonic acid) – PFOA (perfluoroctanoic acid)
- Extremely persistent in the environment
- Were used as surface-active agents and in a variety of products, such as firefighting foams, coating additives and cleaning products
- Common ex-situ water treatment technologies include GAC (only for PFOA), nanofiltration and RO – then incinerate concentrated waste
- Resist most in-situ treatments
- Possibilities considered have been:
  - In-situ chemical oxidation for water with persulphate or permanganate
  - Enzyme-catalyzed oxidative humification in a reactive barrier

ECs in urban groundwater

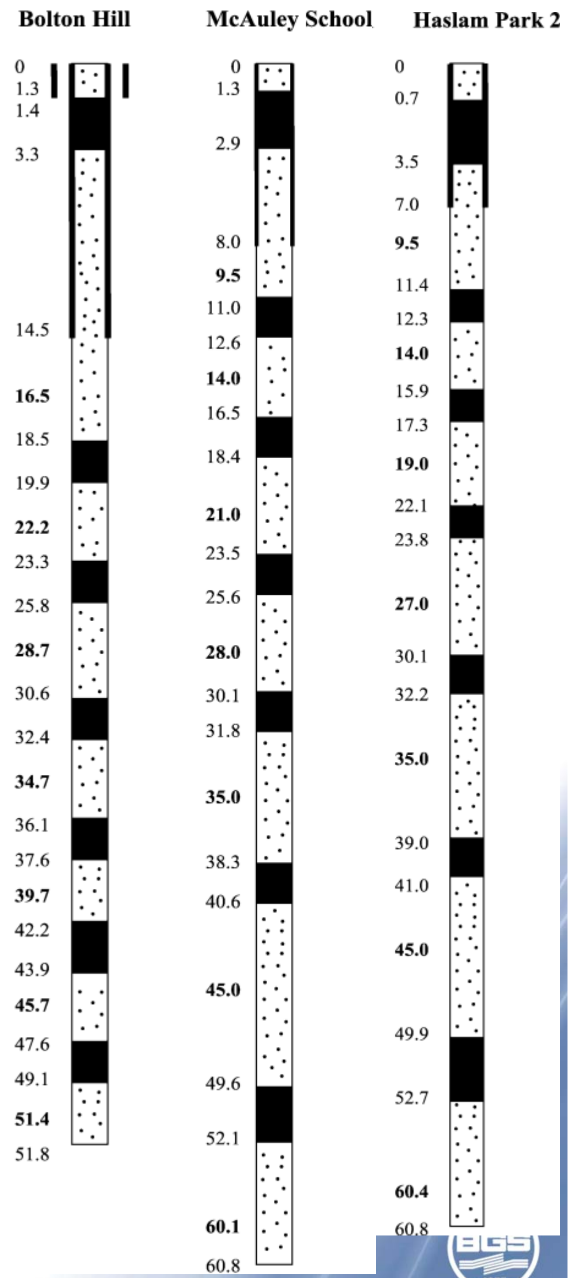
Types of compounds anticipated

- Pharmaceuticals and personal care products (PCP)
- Household compounds
- Industrial compounds
- Amenity pesticides
- PAH



Characterisation with depth

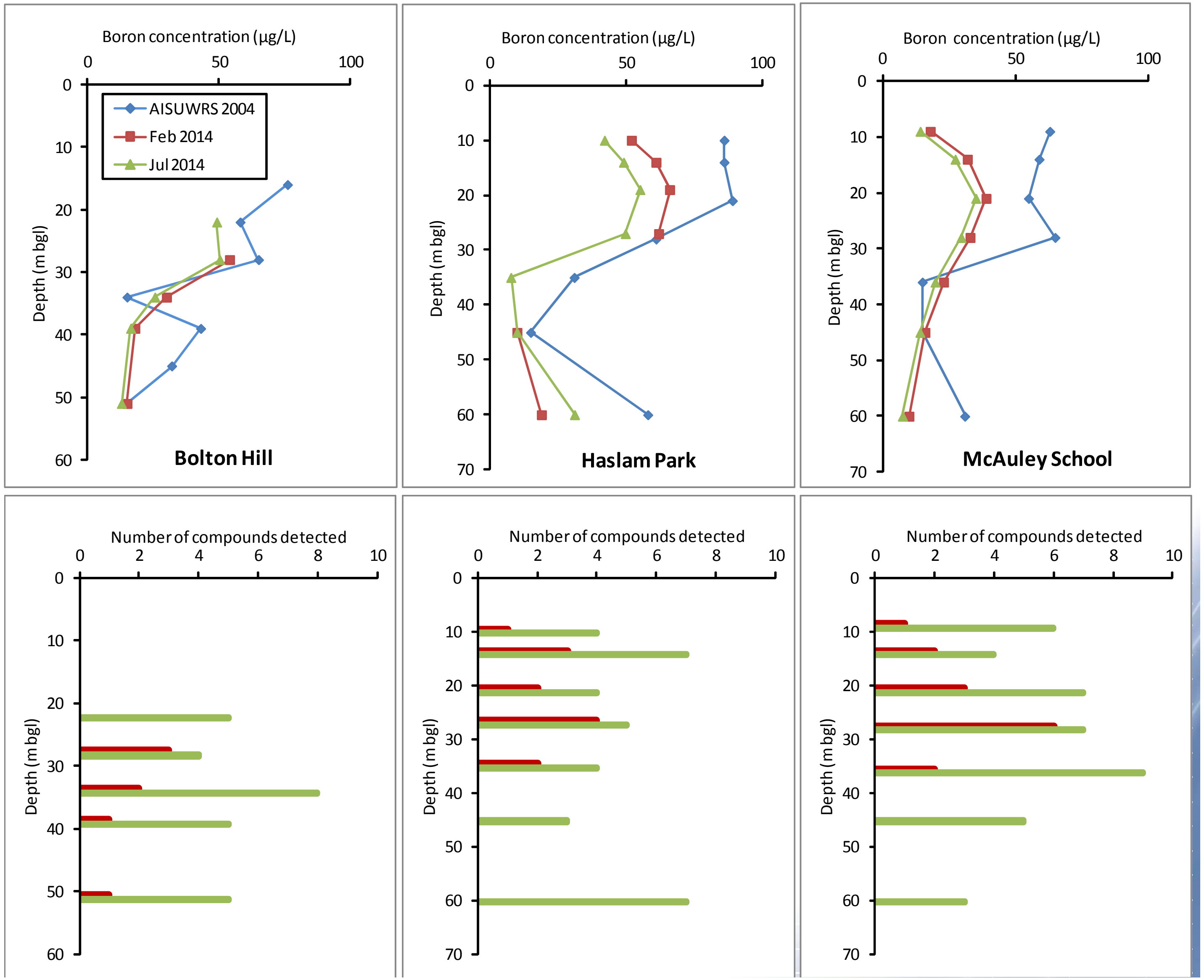
- Boreholes or multi-level piezometers
  - Measure water levels
  - Collect discrete samples at different depths
- Pump (peristaltic) or depth sampler made from inert materials
- Sherwood Sandstone
  - Doncaster & Nottingham
  - Microbial indicators were found to depths of 60 m bgl
  - Recharge estimates (mm/y) urban water approx. 30-40% of total recharge in Doncaster



White et al (2016) Hydrochemical profiles in urban groundwater systems: new insights into contaminant sources and pathways in the subsurface from legacy and emerging contaminants

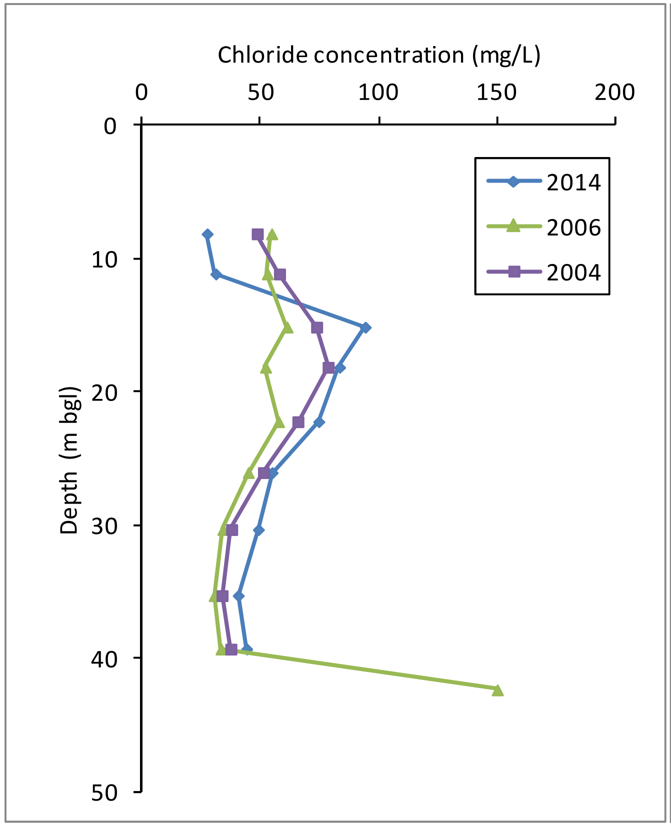
Doncaster B and MO profiles

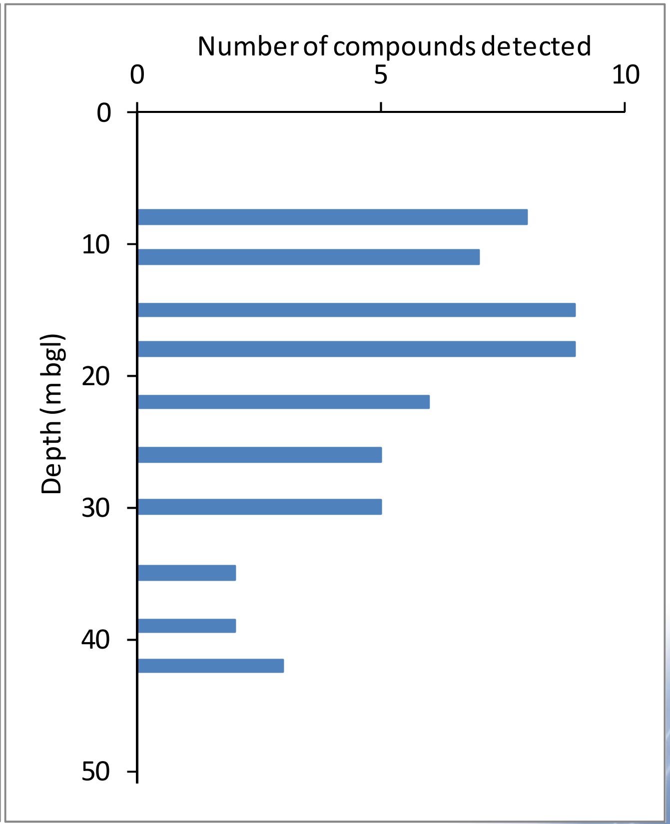
- Boron historical wastewater indicator
- Concentrations have declined with time
- MOs show similar shape
- Penetration to 50 m
- More compounds during high water levels in July



Nottingham Cl and MO profiles

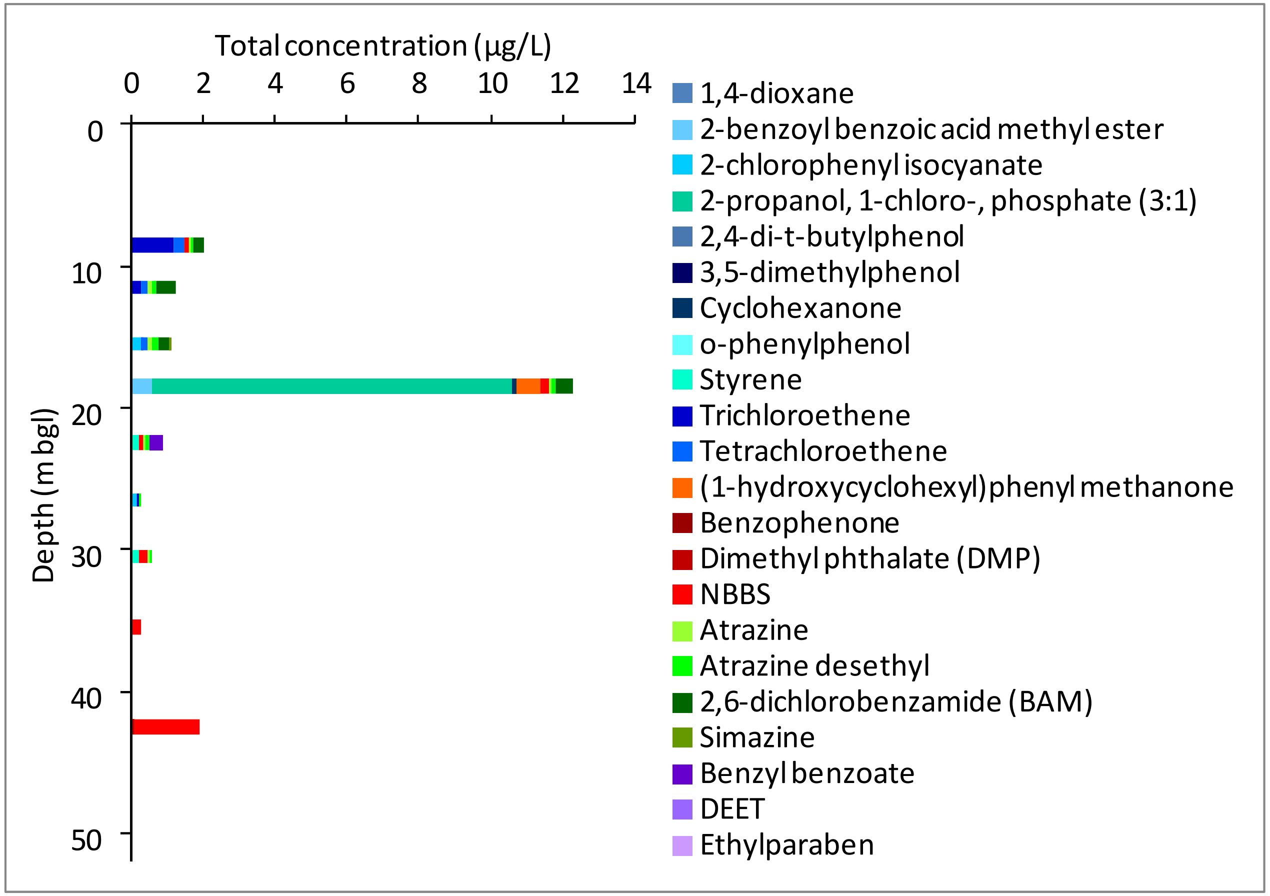
- Chloride profile similar over 10 years
- Possible evidence of Cl at depth
- ECs again show similar shape





From MSc project work by Stephanie Allcock and Nicola Moorhead

Nottingham MO concentration profile

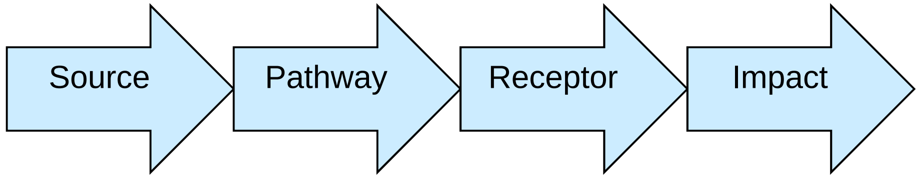


- Predominantly industrial compounds and plasticisers

Summary of compounds found

- **Industrial compounds (24):** 1-(2,3-dihydro-1H-inden-5-yl) ethanone, 1,3-dichlorobenzene, 1(3H)-isobenzofuranone, 1,4-dioxane, 2-benzoylbenzoic acid methyl ester, 2-chlorophenyl isocyanate, 2-propanol, 1-chloro phosphate (3:1), 2,4-dimethyl phenol, 2,4-di-tert-butylphenol, 3,5-dimethylphenol, 3,5-di-tert-butyl-4-hydroxyacetophenone, benzothiazole, bisphenol A, dibromomethane, cyclohexanone, furfural, isopropyl benzene, n-propyl benzene, o-phenyl phenol, styrene, triacetin, trichloroethene, tetrachloroethene
- **Plasticisers and UV stabilisers(10):** (1-hydroxycyclohexyl) phenyl methanone, 2,6-di-tert-butylphenol, 7,9-di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione, benzophenone, bis(2-ethyl hexyl) adipate, DEHP, DEP, DMP, BBSA, octabenzone
- **PCPs (4):** benzyl benzoate, DEET, ethyl paraben, octocrylene
- **Pesticides (4):** atrazine, BAM, desethyl atrazine, simazine
- **Petroleum-related (3):** indane, indene, naphthalene
- Nottingham, Doncaster, Both

Risk assessment



- Source:
  - Usage / prioritisation using prescription/ sales data
  - Formation in environment /metabolic pathway
- Pathway/mobility/attenuation:
  - Define route
  - Leachability
  - Aquatic persistence (particularly for non-pesticides)
  - Water treatment recalcitrance, both waste and potable
- Impact on receptor:
  - Human (ADI, NOEL, LDTD etc) and ecological effects at environmental levels e.g. toxicity, bioaccumulation potential
  - Synergistic effects
  - Use surface water as early warning for groundwater
- Robust sensitive analytical method
  - Likely to include concentration step + GCMS or LCMS

Are emerging contaminants in groundwater important?

- An increasing range of compounds is being detected
- Urban areas show impact of sewage and industrial wastewater
- Some ECs are probably no threat to drinking water at such µg/L concentrations, e.g. caffeine
- Others may prove to be in the future
- There is little information on their impact on other groundwater receptors in the environment
- We are still far from understanding which of these compounds could be important