Assessment of emerging groundwater contaminants

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Emerging organic contaminants (ECs)

- Anthropogenic organic compounds and their transformation products (TPs)
- 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
- Groundwater thresholds can depend on relationship with surface water

Emerging(ed) organic contaminants

- Pesticides – parents (e.g. metaldehyde), TPs
- 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

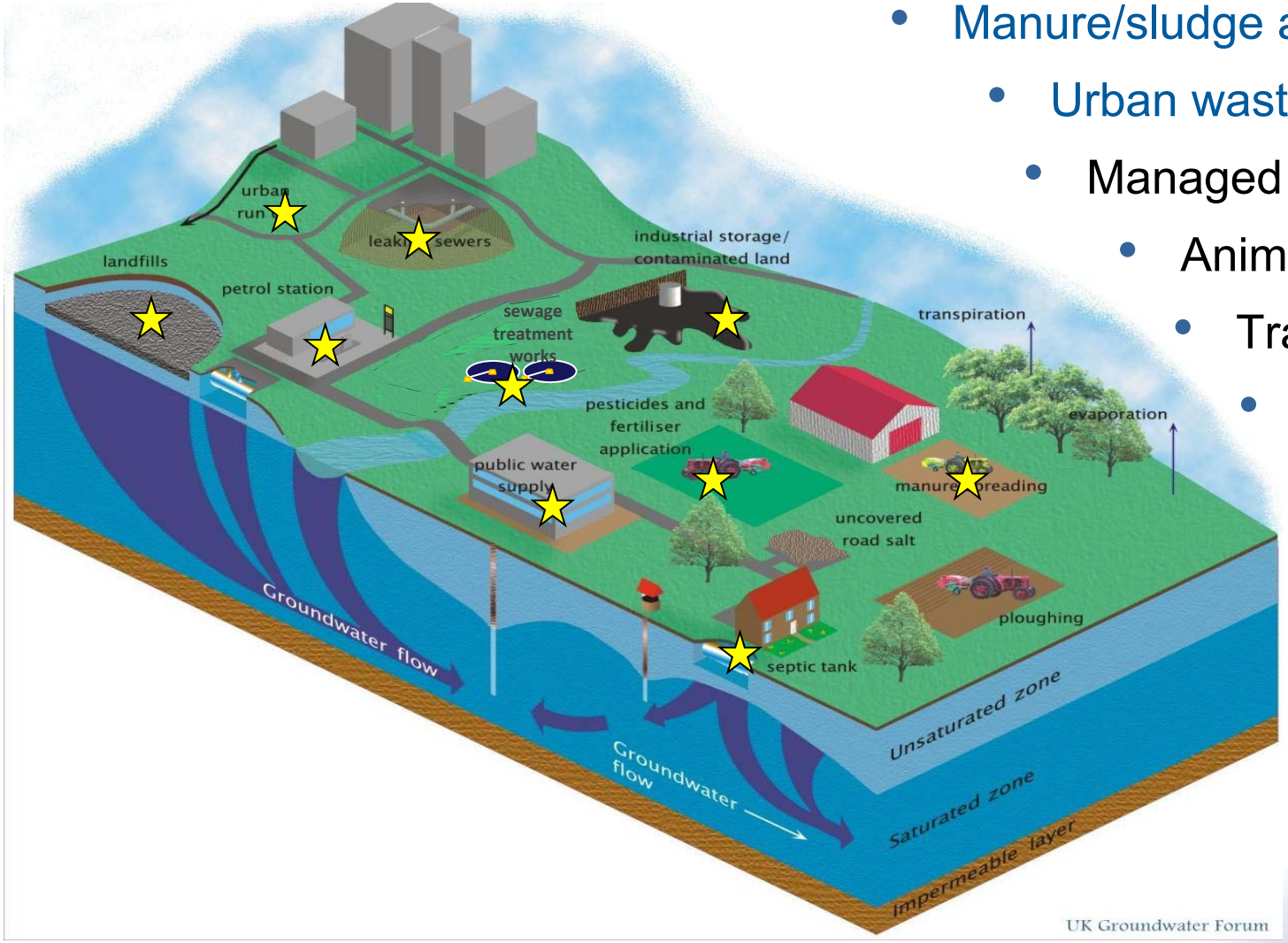
Transformation products

- 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 due to different geochemical conditions and long residence times
- Possible 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

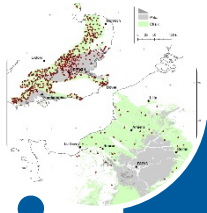


Scale

- International literature
- England and Wales
- Chalk aquifer
- Shale gas area surveys
- Site/observatory-scale

Site

Areal



Aquifer

National

Global literature

Global literature review

- Barnes et al. 2008 – USA groundwater
  - DEET, BPA, tri(2-chloroethyl) phosphate, sulfamethoxazole, 4-nonyl phenol diethoxylate, ibuprofen
- Loos et al. 2010 – Pan European study
  - DEET, caffeine, PFOA, atrazine
- Lapworth et al. 2012 – most commonly reported
  - Carbamazepine, sulfamethoxazole, ibuprofen, BPA, caffeine
- Lopez 2015 – risk matrix
  - Acetaminophen, BPA, caffeine, metformin, tolyltriazole
- Lamastra et al. 2016 – selection of environmental tracers
  - Carbamazepine, galaxolide, sulfamethoxazole

Barnes (2008) A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the United States: I) Groundwater. Sci Total Environ 402:192-200

Loos (2010) Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water. Water Research 44: 4115–26

Lapworth (2012) Emerging organic contaminants in groundwater: a review of sources, fate and occurrence. Environ Poll, 163, 287-303.

Lopez (2015). Screening of French groundwater for regulated and emerging contaminants. Sci Total Environ 518: 562-573.

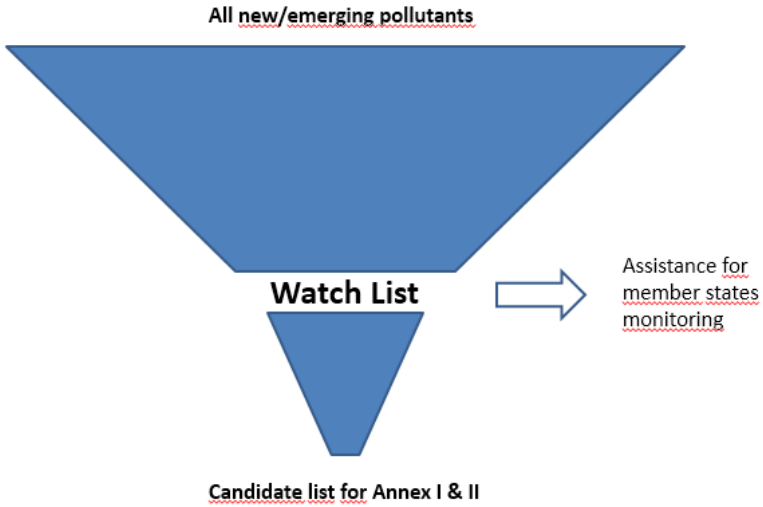
Lamastra. (2016) Inclusion of emerging organic contaminants in groundwater monitoring plans, MethodsX on line

Priority list approach

Type	Reference	Exposure							Toxicity		Other		
		Chemical properties	Consump-tion/ use	Fate in humans	WWTP efficiency	Predicted conc. in surface water	Measured conc. in surface water	Predicted conc. in soil	Human	Environ.	LCA	Lit. occur	Multi-criteria
Domestic	Arnot 2008	●	●			●			●	●			●
Emerging pollutants	JRC 2015	●	●	●		●			●	●			
Endocrine disruptors	Calabreze 1997	●							●				
Industrial	Hansen 1999	●	●			●			●	●			●
	Öberg 2006	●							●	●			
OWC	Clarke 2011	●	●					●	●	●			
	Dickensen 2011	●					●						
	Schriks 2010	●					●		●				
Pesticides	Luchi 2010	●	●										
	Sumner 2009	●	●				●						
Pharmaceuticals	Christen 2010	●				●			●	●			
	Cooper 2008	●	●				●		●	●			
	De Vooght 2009	●										●	
	EMEA 2006	●	●	●	●	●			●	●			
	Ortiz de García 2013	●	●	●		●			●	●			
	Perazzolo 2010	●	●	●	●	●							
	Sanderson 2004	●				●				●			
Pharmaceuticals & PCP	Kumar 2010	●	●	●	●	●			●	●			●
	Muñoz 2008	●		●	●	●			●	●	●		
Storm water priority pollutants	Eriksson 2007	●					●	●		●			

Lamastra. (2016) Inclusion of emerging organic contaminants in groundwater monitoring plans, MethodsX on line

Watch lists



Surface water

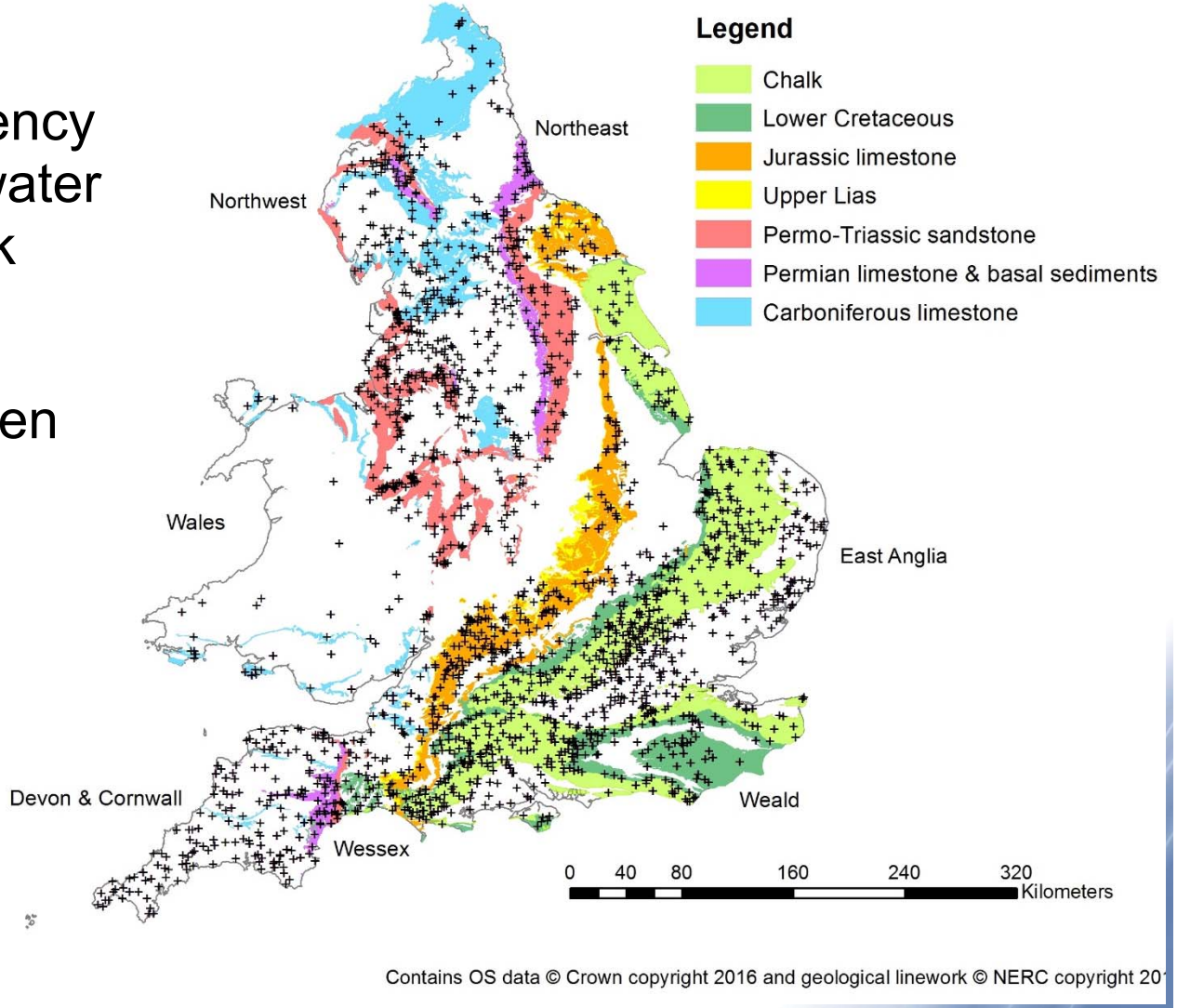
- Priority Substances Directive amendment 2013/39/EU
- Targeted EU-wide monitoring of substances of possible concern to support the prioritisation process in future reviews (10-14 in rolling programme)
- First watch list -17α-ethinylestradiol,17β-estradiol, diclofenac

Groundwater

- Groundwater Directive Recital 4
- Less developed than surface water
- Increased availability of monitoring data to facilitate identification of substances

The national scale

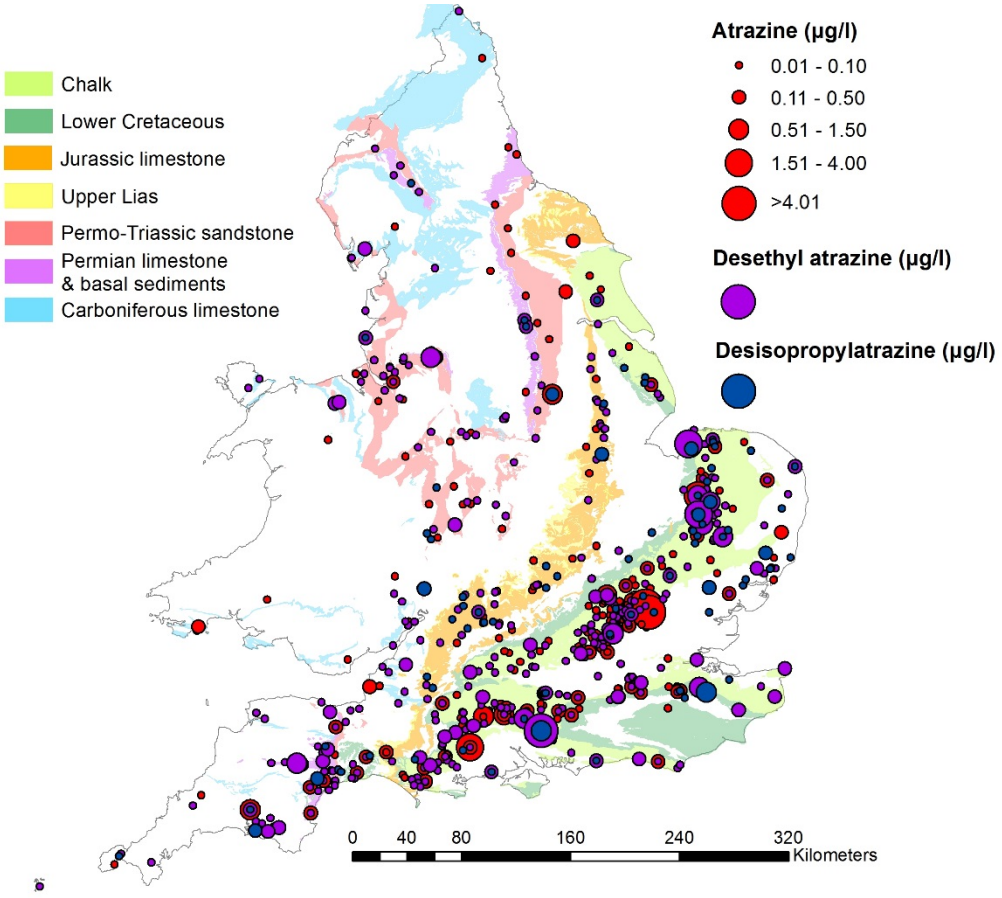
- Environment Agency national groundwater sampling network
- 2650 sites
- NLS GCMS-screen
- Spatial plots
- Concentrations
- Frequency of detection
- Land use



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

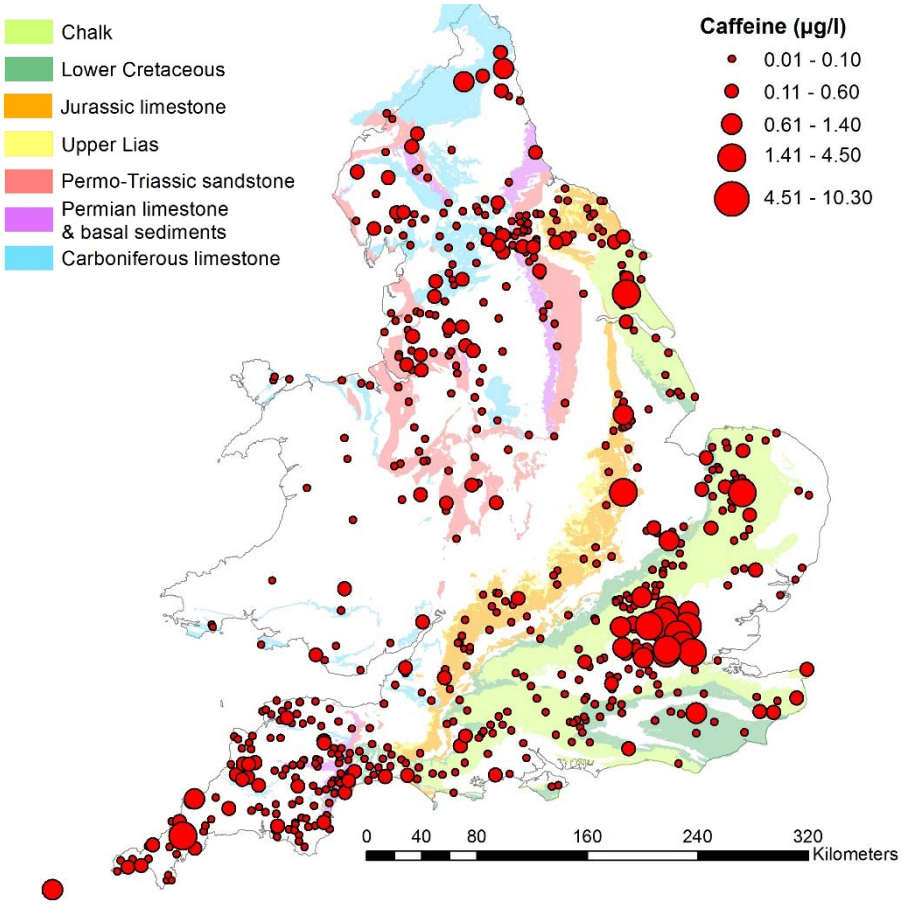
Atrazine



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

Lifestyle compounds

Caffeine and nicotine

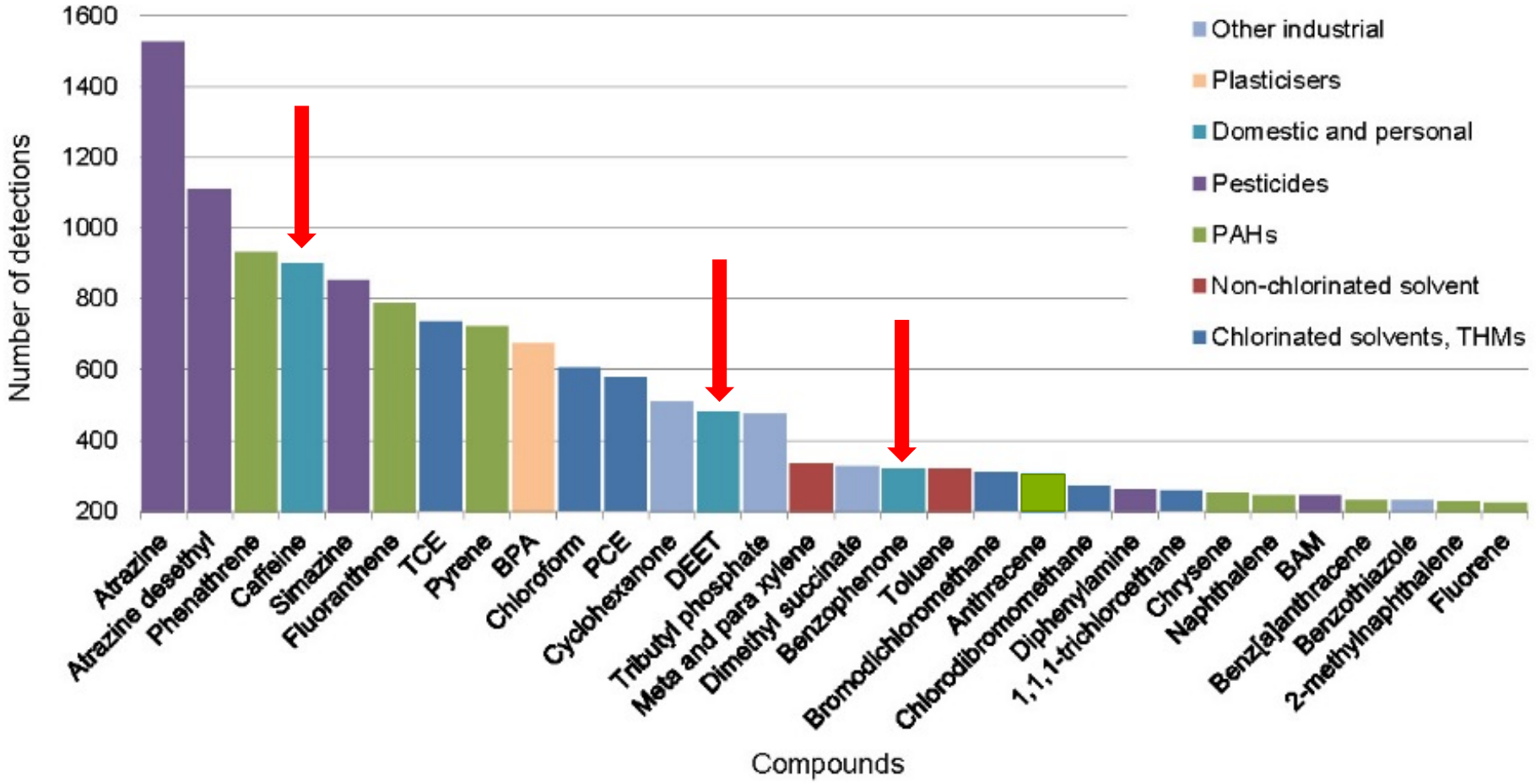


- Caffeine, nicotine and cotinine (nicotine TP), from sewage effluent, widely detected in groundwater
- Paraxanthine (caffeine TP) also found
- Dimethyl-imidazo-lidinetrione (product of caffeine chlorination) found elsewhere

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

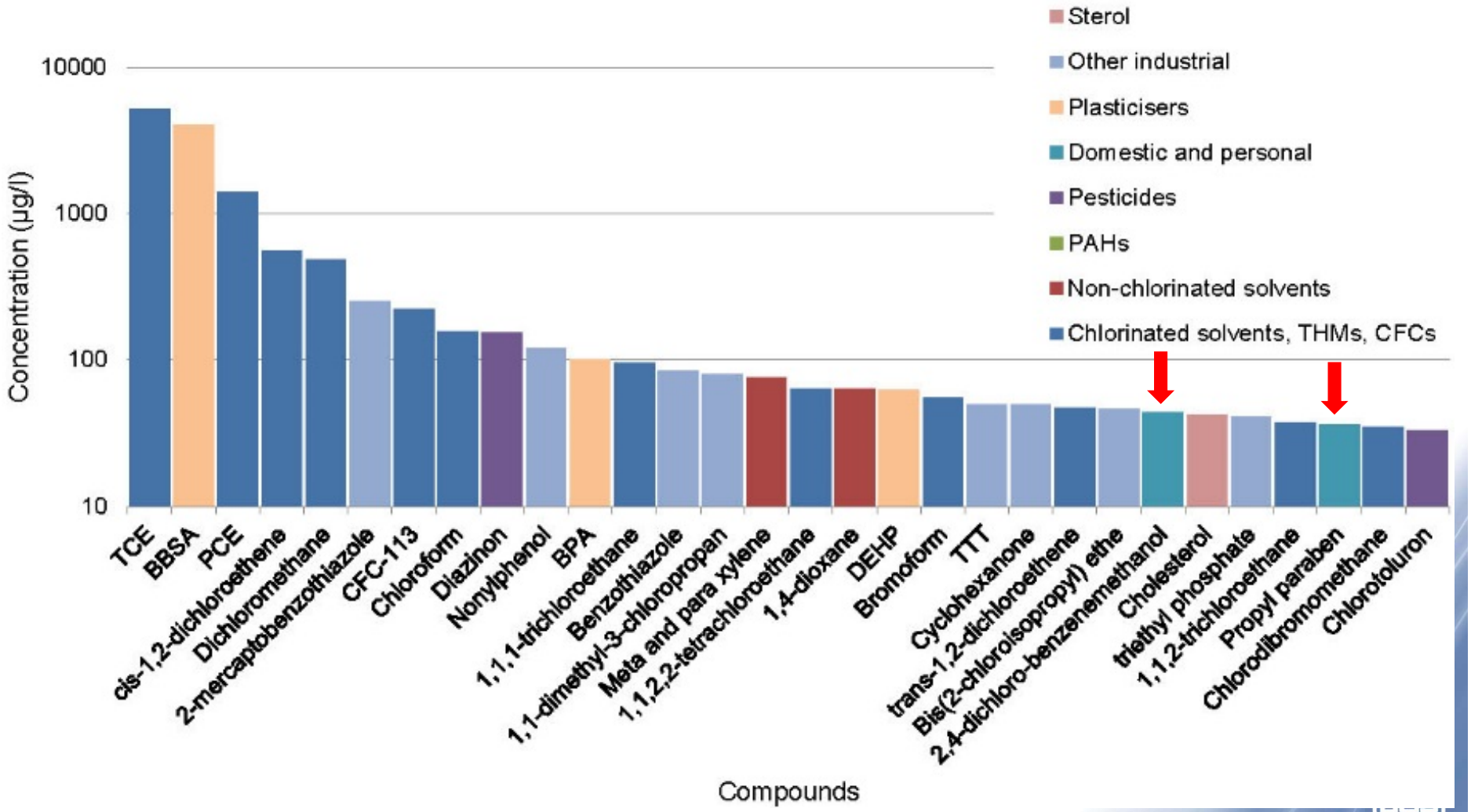
Top 30 microorganics in Environment Agency groundwater screening data 1993-2012

by frequency of detection



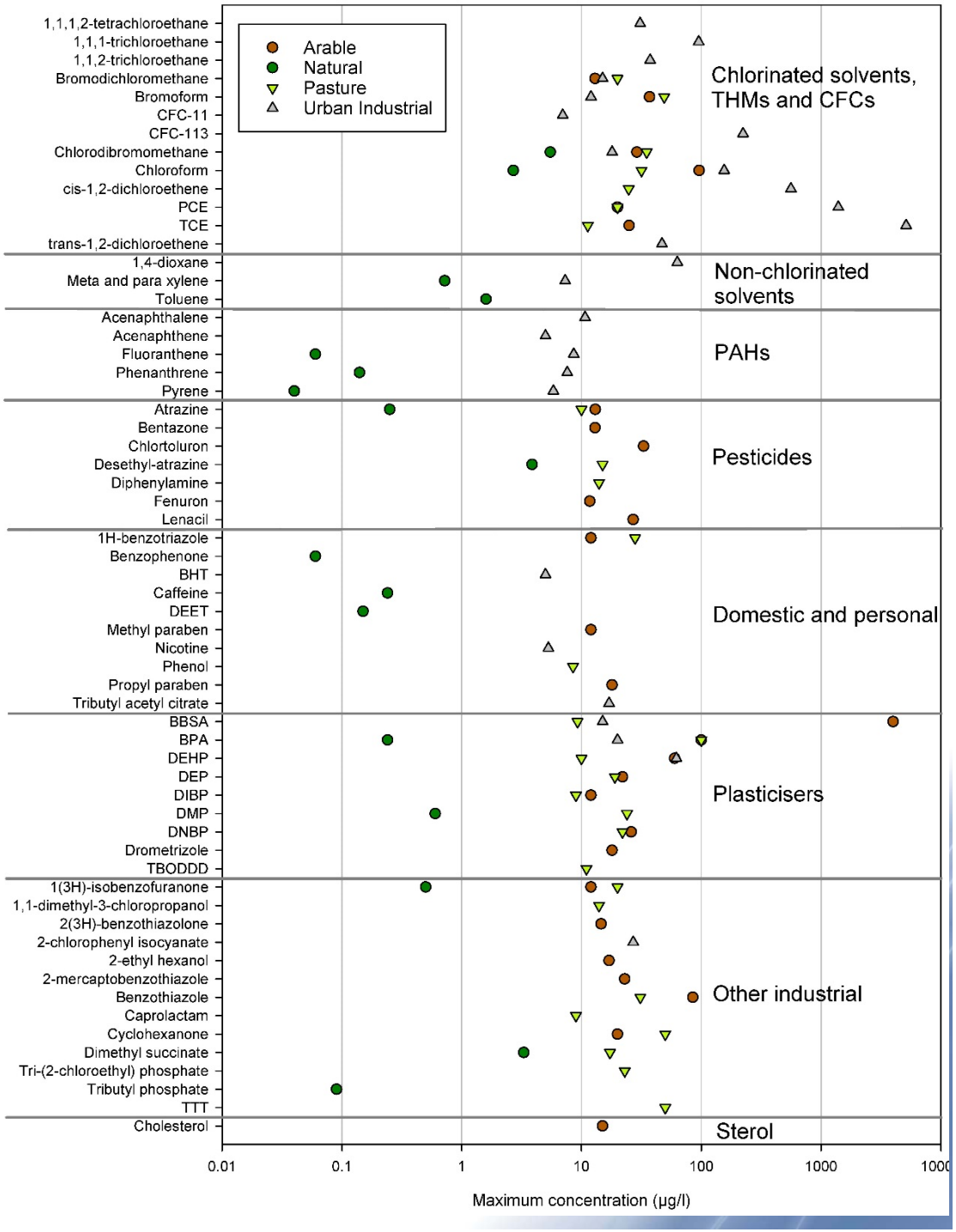
Top 30 microorganics in Environment Agency groundwater screening data 1993-2012

by maximum concentration



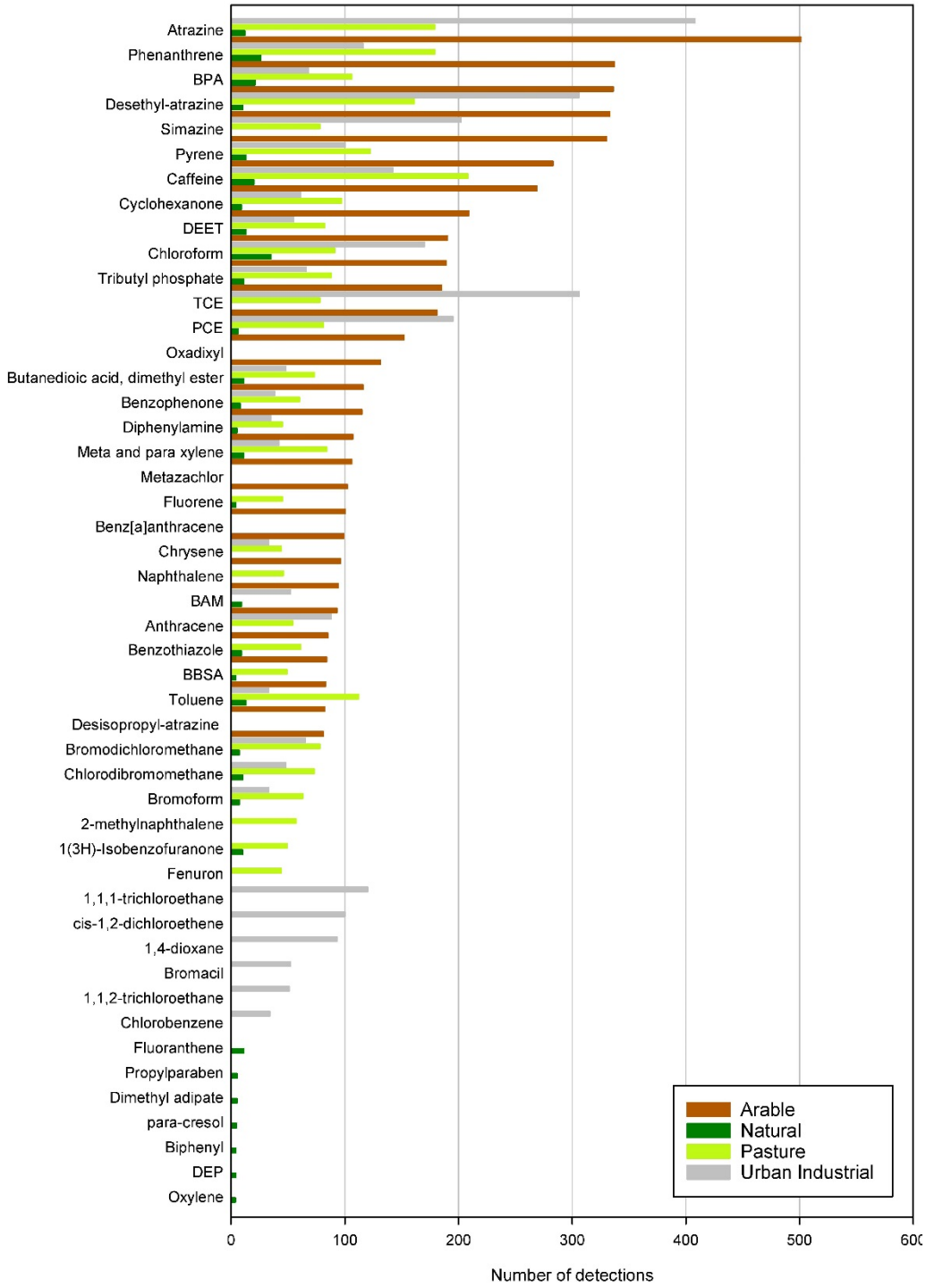
By land use

- 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



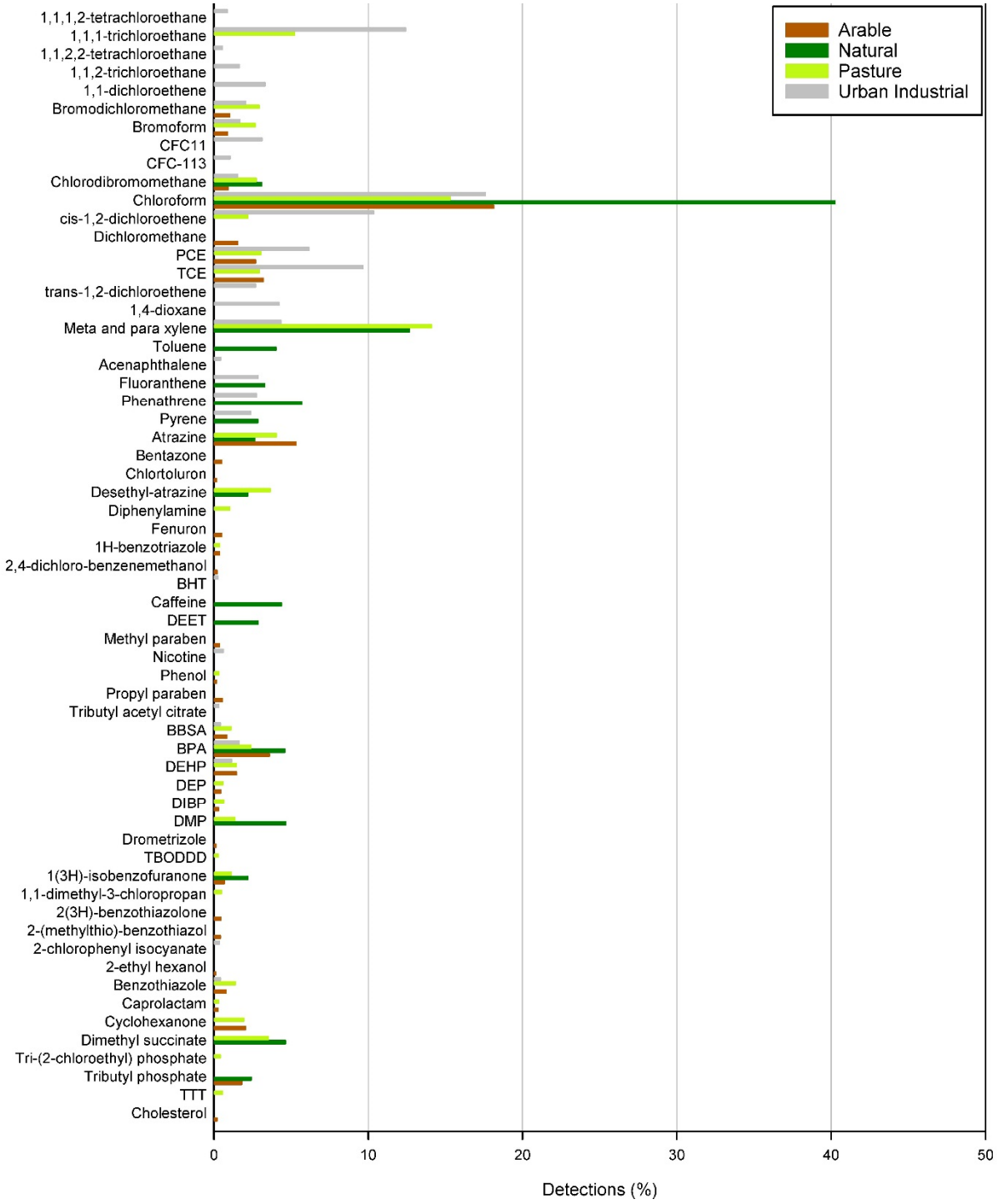
By landuse

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

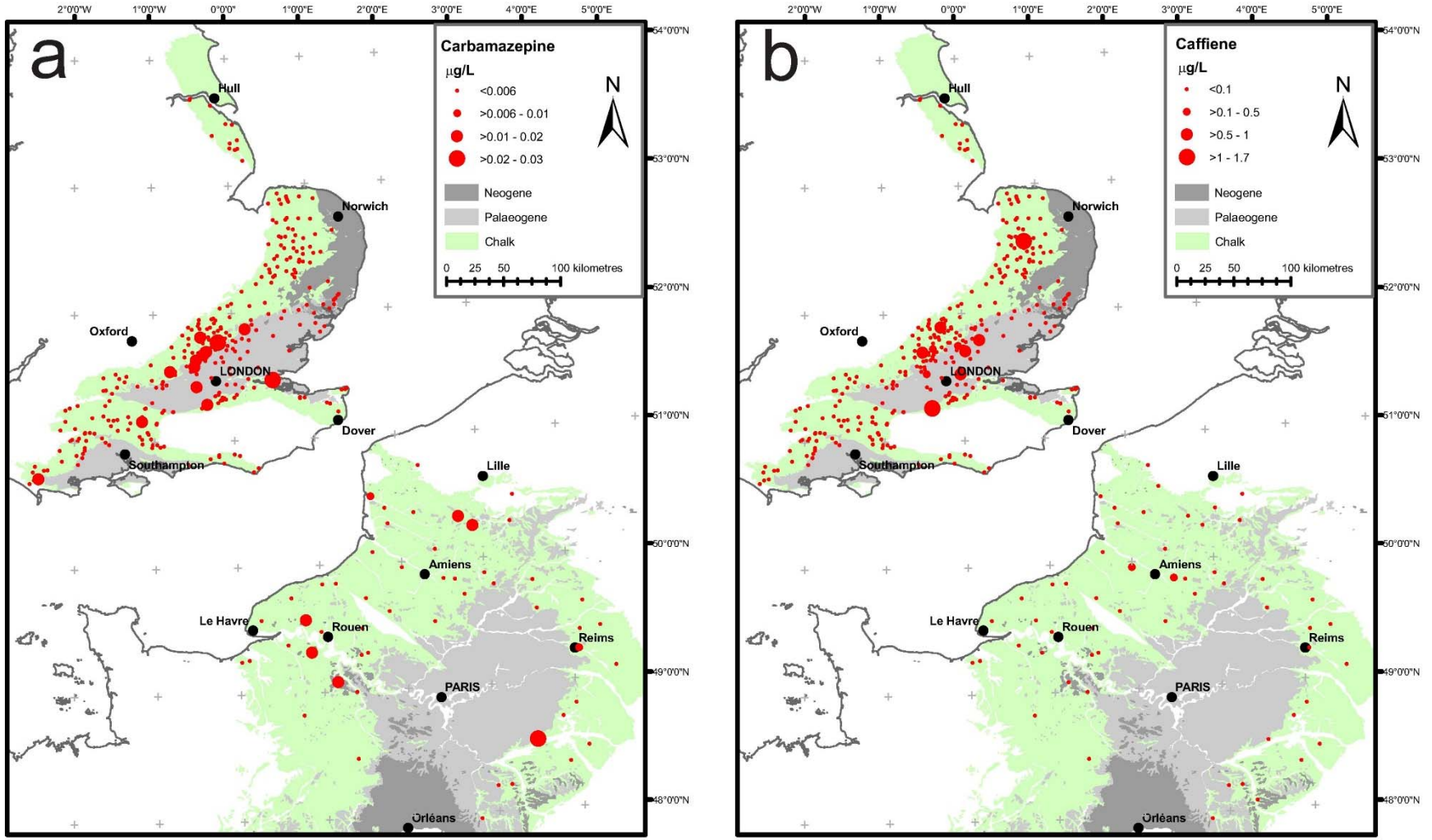


By land use

- By frequency of detection
- Normalised to each land use
- Chloroform and xylenes prominent
- Chloroform can have natural origin
- Caffeine and DEET only in Top 30 within Natural



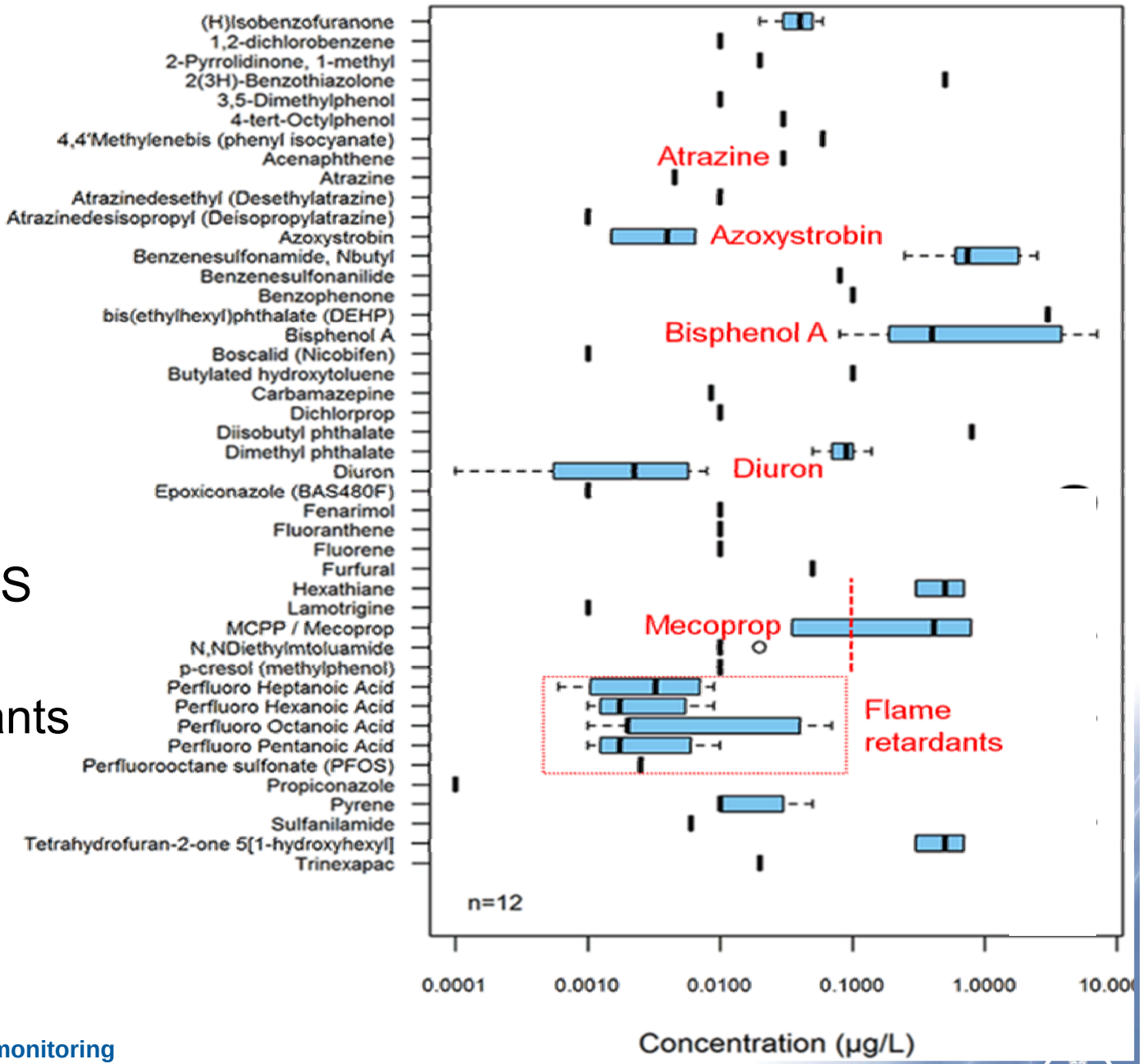
Aquifer scale - England & France Chalk



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

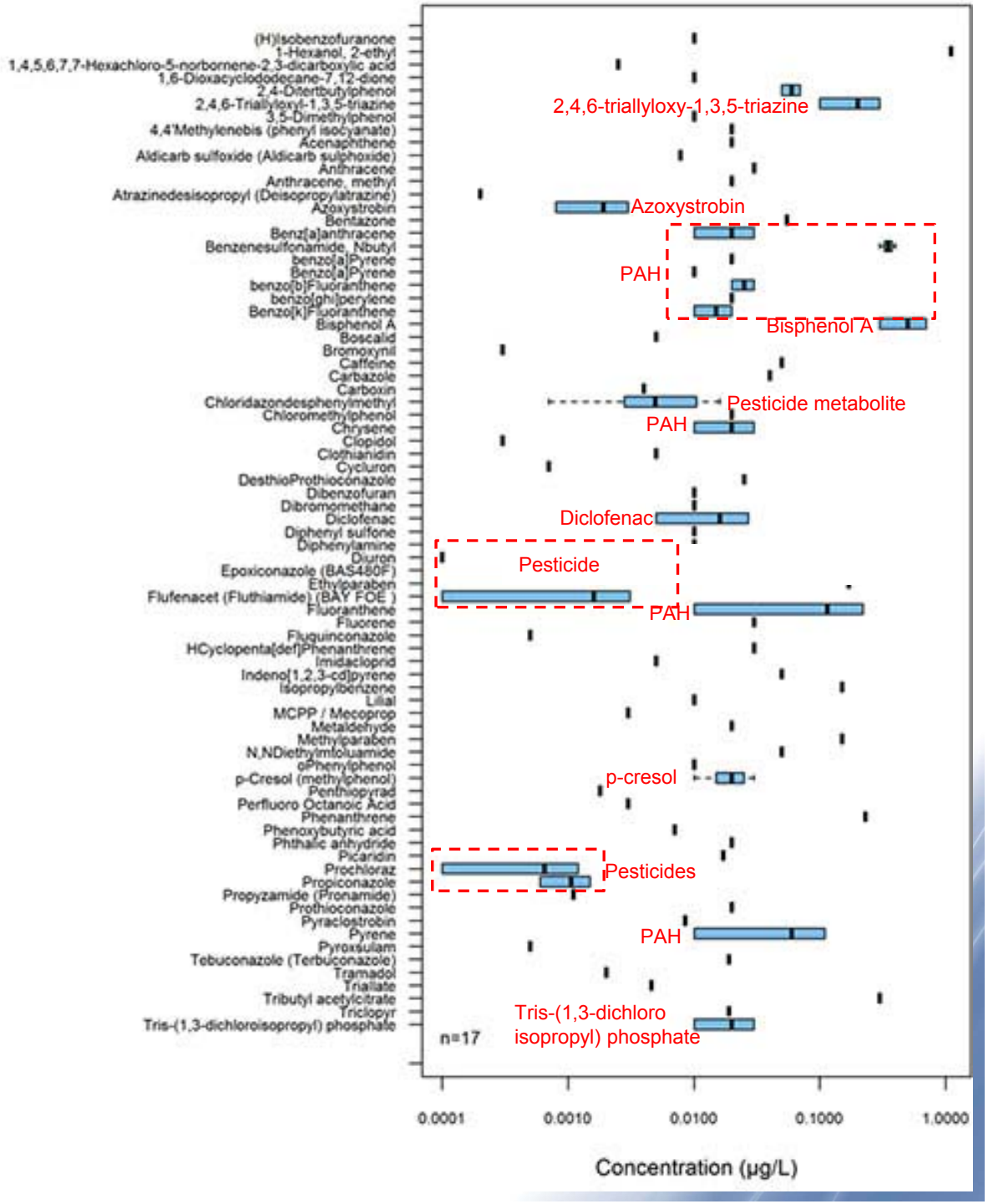
- Lancashire groundwater baseline
- Includes LCMS scan
- Flame retardants frequently detected at 1-10 ng/L



BGS website Shale gas monitoring

Local survey scale

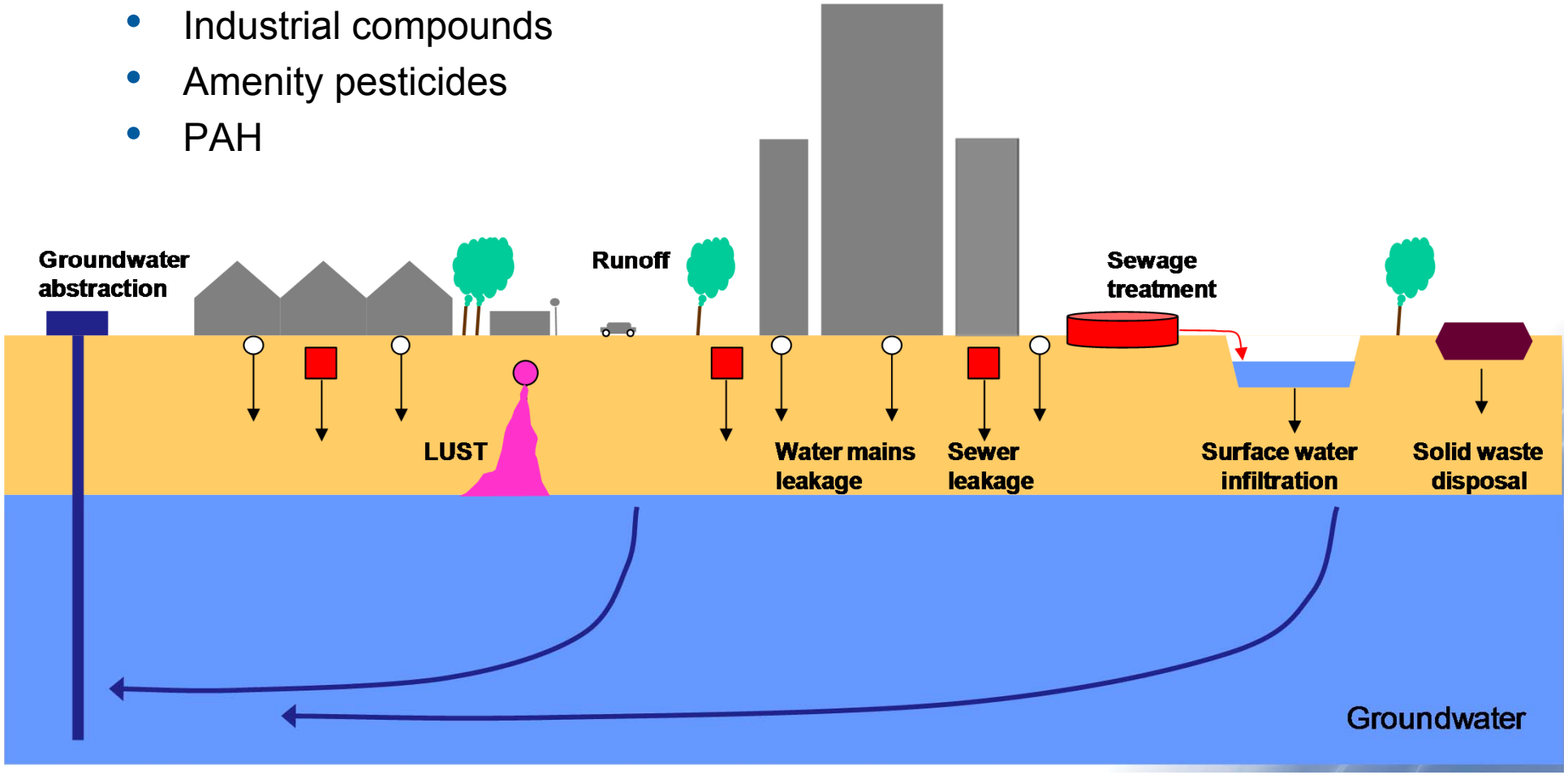
- Vale of Pickering groundwater baseline
- More complex mixture of compounds



ECs in urban groundwater

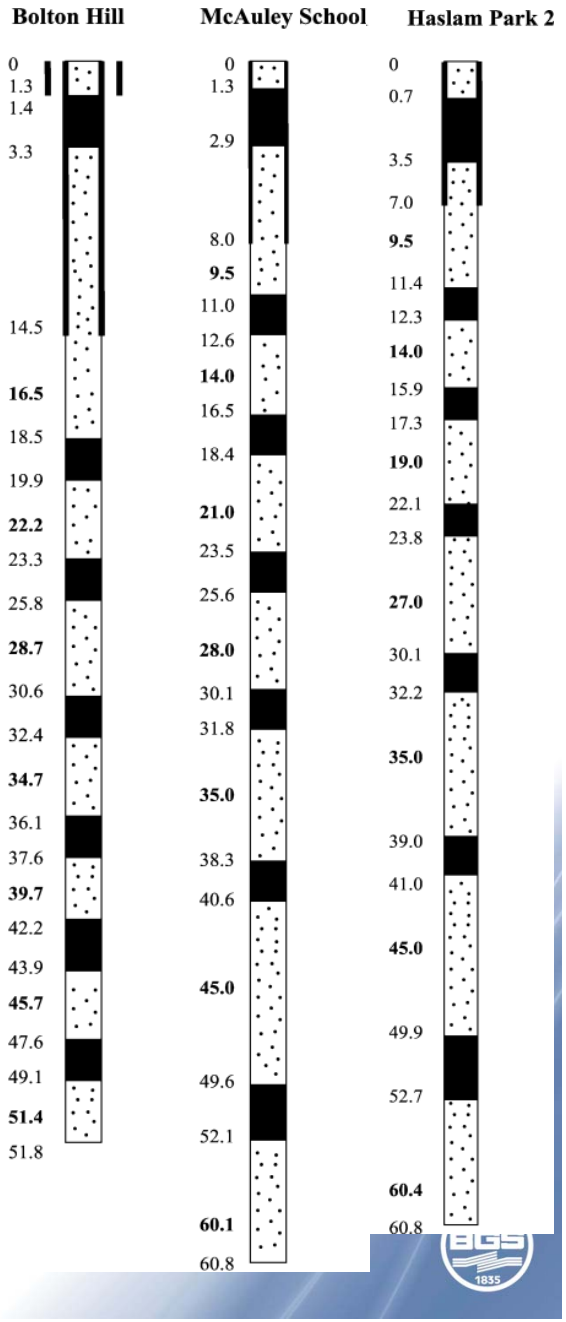
Types of compounds anticipated

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



Site scale

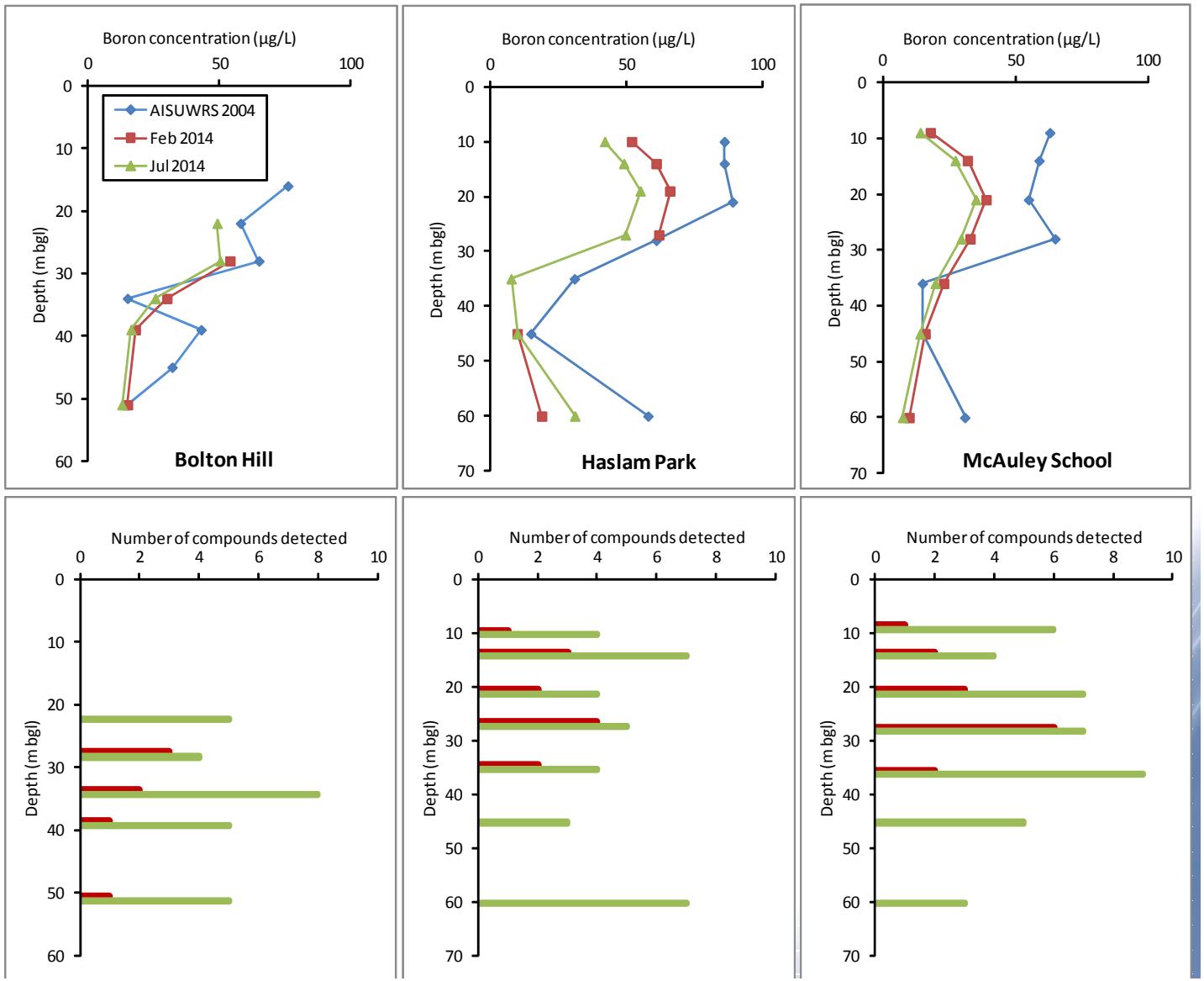
- Characterisation with depth
- Boreholes or multi-level piezometers
  - Measure water levels
  - Collect discrete samples at different depths
- Pump (peristaltic) or depth sampler made from inert materials
- Sherwood Sandstone
  - Doncaster & Nottingham
  - Microbial indicators were found to depths 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, Science of the Total Environment, 562, 962-973

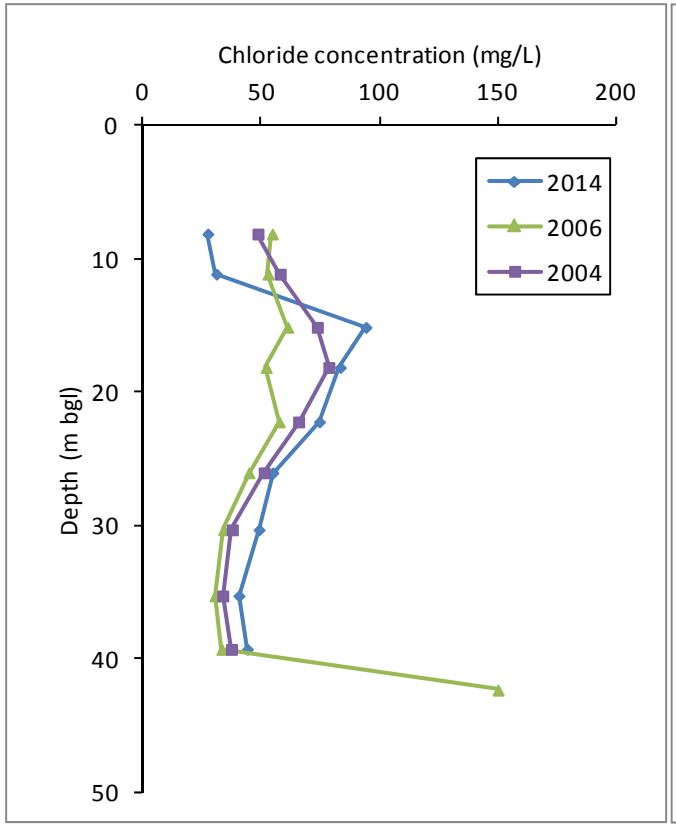
Doncaster B and MO profiles

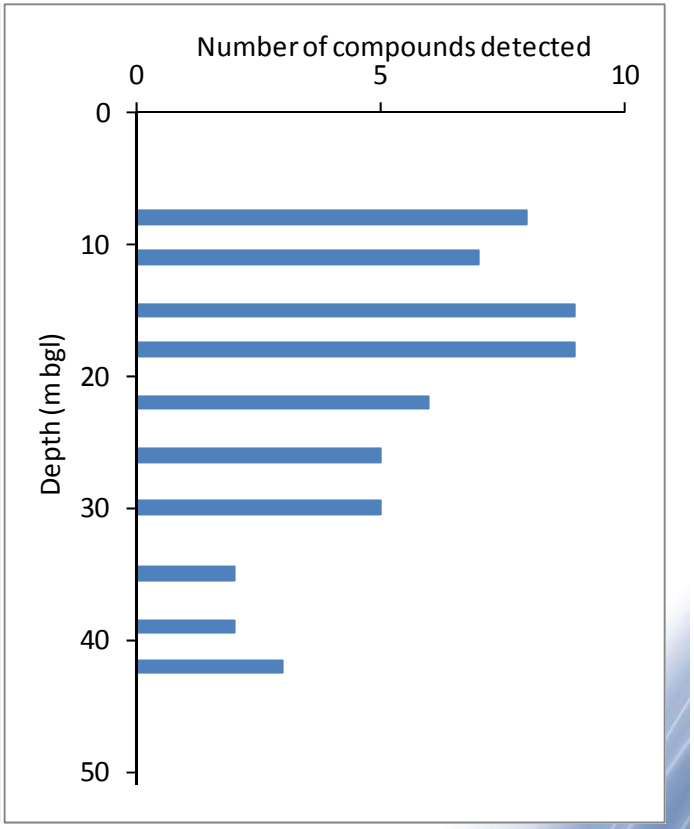
- Boron historical wastewater indicator
- Concentrations have declined with time
- MOs show similar shape
- Penetration to 50 m
- More compounds during high water levels in July



Nottingham Cl and MO profiles

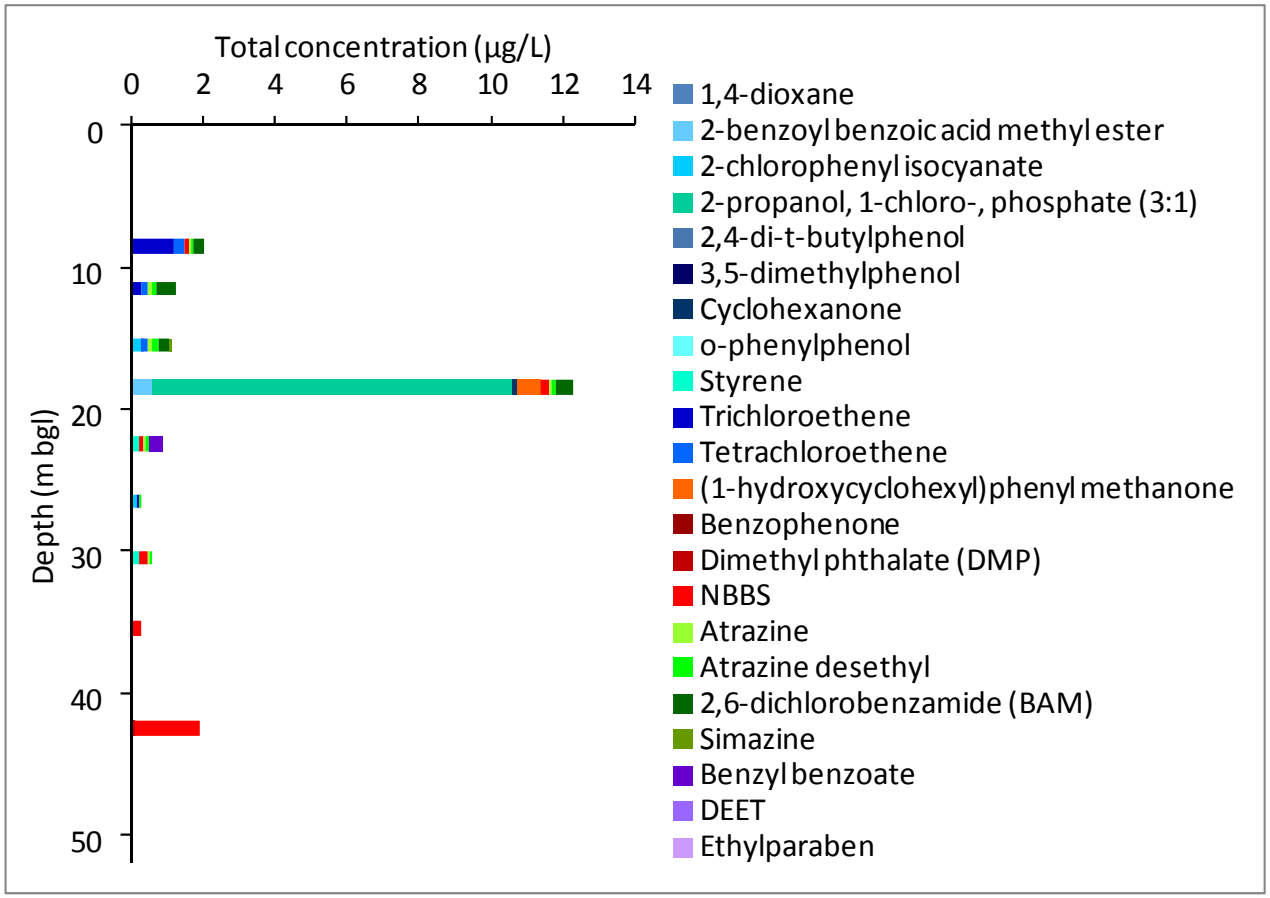
- Chloride profile similar over 10 years
- Possible evidence of Cl at depth
- ECs again show similar shape





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

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