British Geological Survey
NATURAL ENVIRONMENT RESEARCH COUNCIL

Gateway to the Earth

Emerging Contaminants in Groundwater

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IAH 2016 Montpellier, Keynote Lecture, Tuesday 27th September

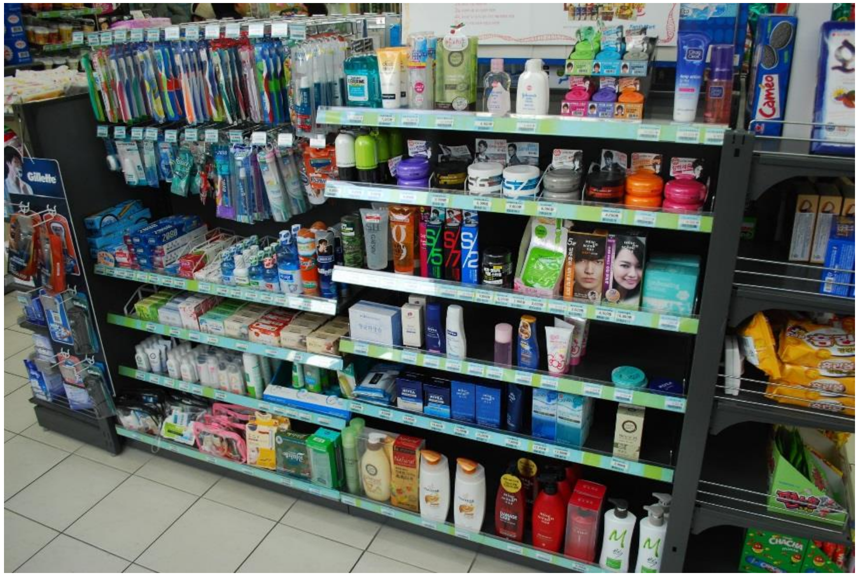
‘Groundwater EC Research Network’

- BGS team: Marianne Stuart; Debbie White, Katya Manamsa; Emily Crane; Rachel Bell; James Sorensen; Rob Ward…..
- Environment Agency: Wayne Civil; Alwyn Hart; Tim Besien
- BRGM: Nicole Baran; Benjamin Lopez
- Birmingham University: Mike Rivett
- University of Zambia: Daniel Nkhuwa
- IIT Kharagpur: Prerona Das; Sahid Jamal; Abhijit Mukherjee

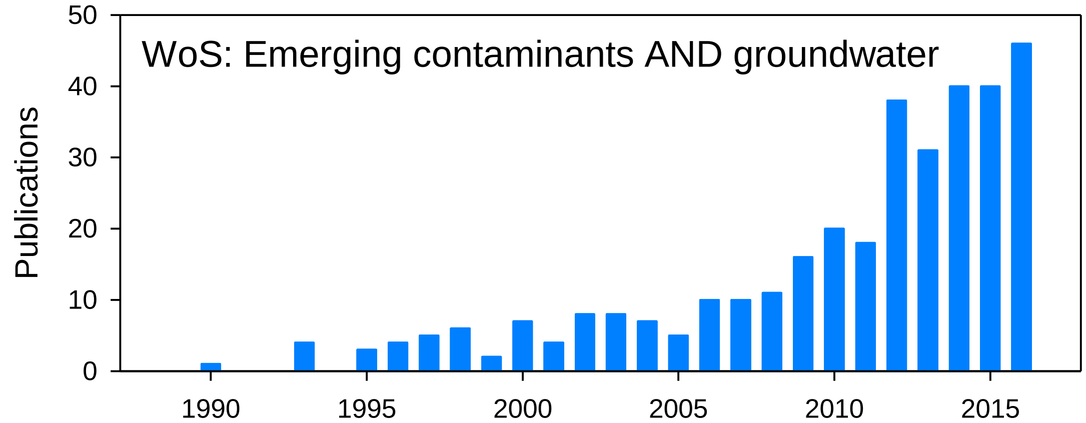
9 peer reviewed journal articles and 2 book chapters since 2012

>600 citations since 2012

Contaminants of Emerging Concern



- New chemical & biological contaminants
- Shift in thinking required from traditional contaminants
- Different dispersal routes in the environment
- Products of interaction between chemosphere and biosphere



Source: www.contaminantsummit.com

Emerging contaminants

- Potentially toxic substances (aquatic ecology, human)
  - Newly developed substances
  - Newly categorised substances (past e.g. endocrine disruptors)
  - Newly discovered in groundwater due to analytical developments – broader screening tools, better detection
  - Subtle distinction between emerging and “newly” emerging contaminants: evidence base, level of regulation/monitoring
- Past/early examples:
  - Pb from fuel additives
  - Endocrine disruptors in rivers (1960s[1] and 1970s[2])
  - Pesticides (e.g. DDT and metaldehyde)

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

Emerging organic contaminants

www.gardenorganic.co.uk

- 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: lower concentrations, greater protection
- 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

Groups of potential emerging contaminants

- Pesticides – metabolites
- Pharmaceuticals – human, veterinary, antibiotics
- “Life style” – nicotine, caffeine, artificial sweeteners
- Personal care – DEET, musks, UV filters
- Industrial additives and by-products – dioxane, phthalates,
- Wastewater treatment by-products – THM, NDMA
- Flame/fire retardants – PBDE, alkyl phosphates
- Surfactants – PFOS & PFOA, alkyl phenols
- Hormones and sterols
- Ionic liquids
- Nanomaterials

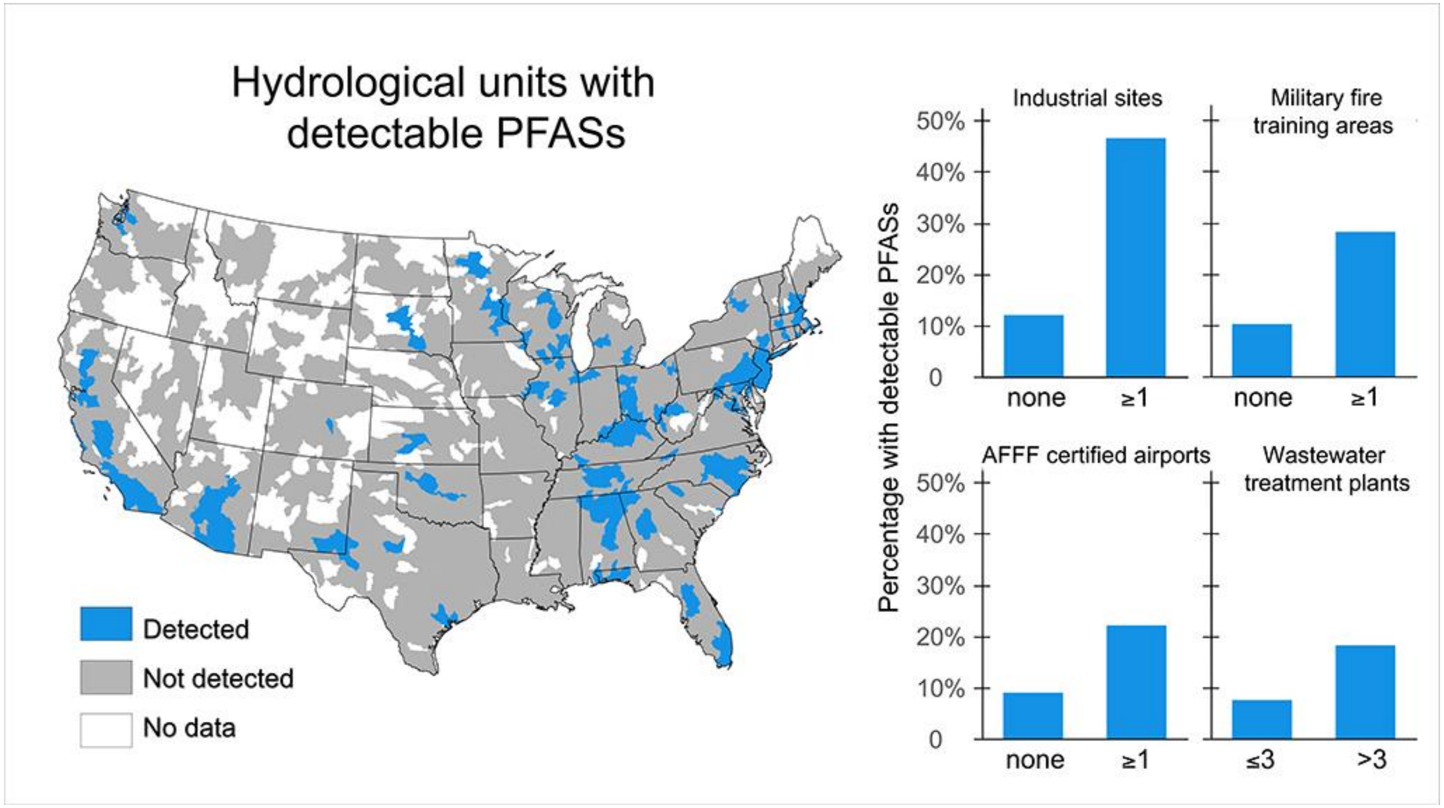
Past example: metaldehyde

- 2007 Bristol Water first 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 a significant proportion of failures in drinking water standards in UK (2009) onwards
- Guardian 2013: ‘Slug poison found in one in eight of England’s drinking water sources’

Get Pelletwise!

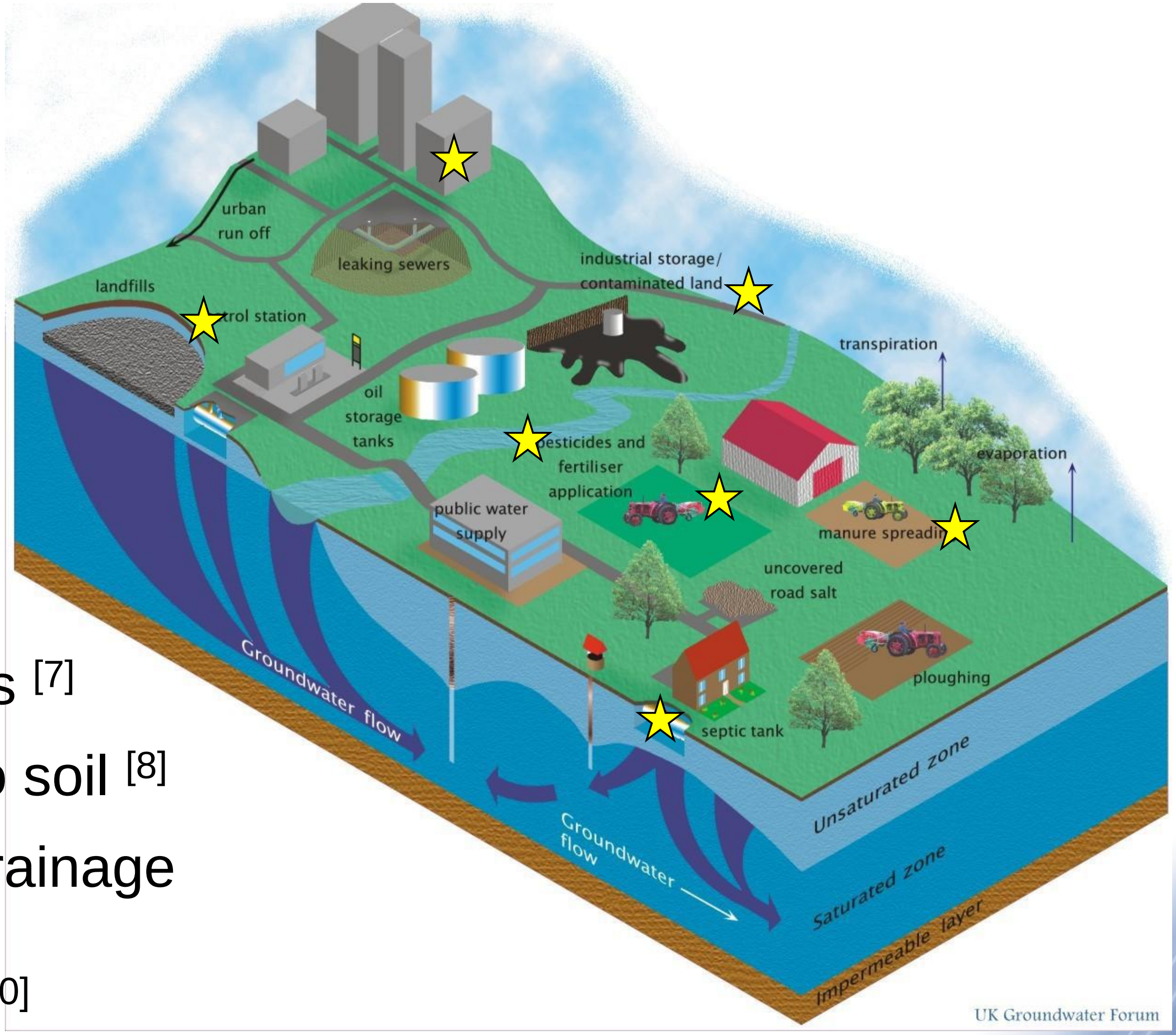
[4] Hall (2010)

August 2016: Unsafe levels of PFAS detected in drinking water for 6 million Americans



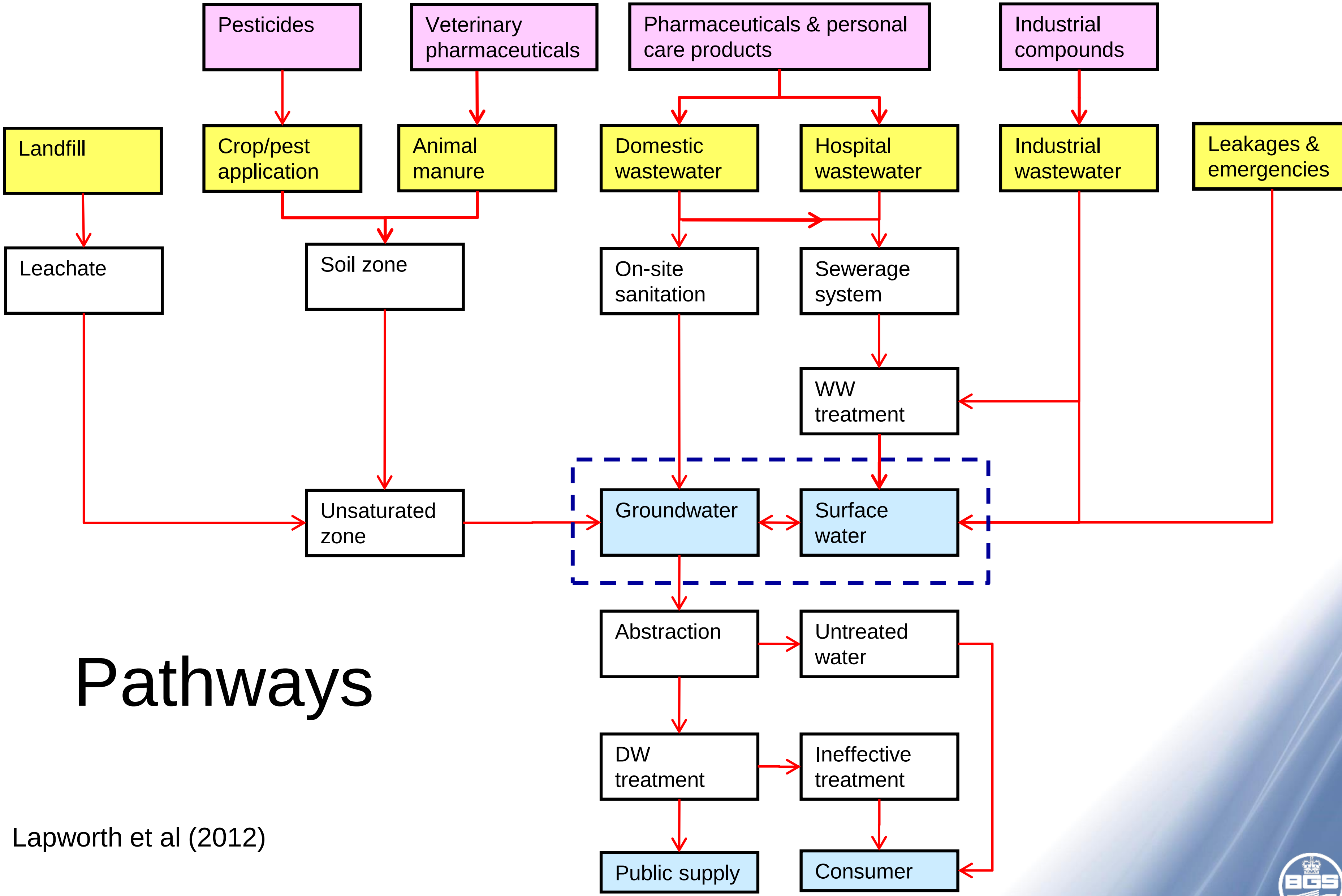
Hu et al (2016) ES&T

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]

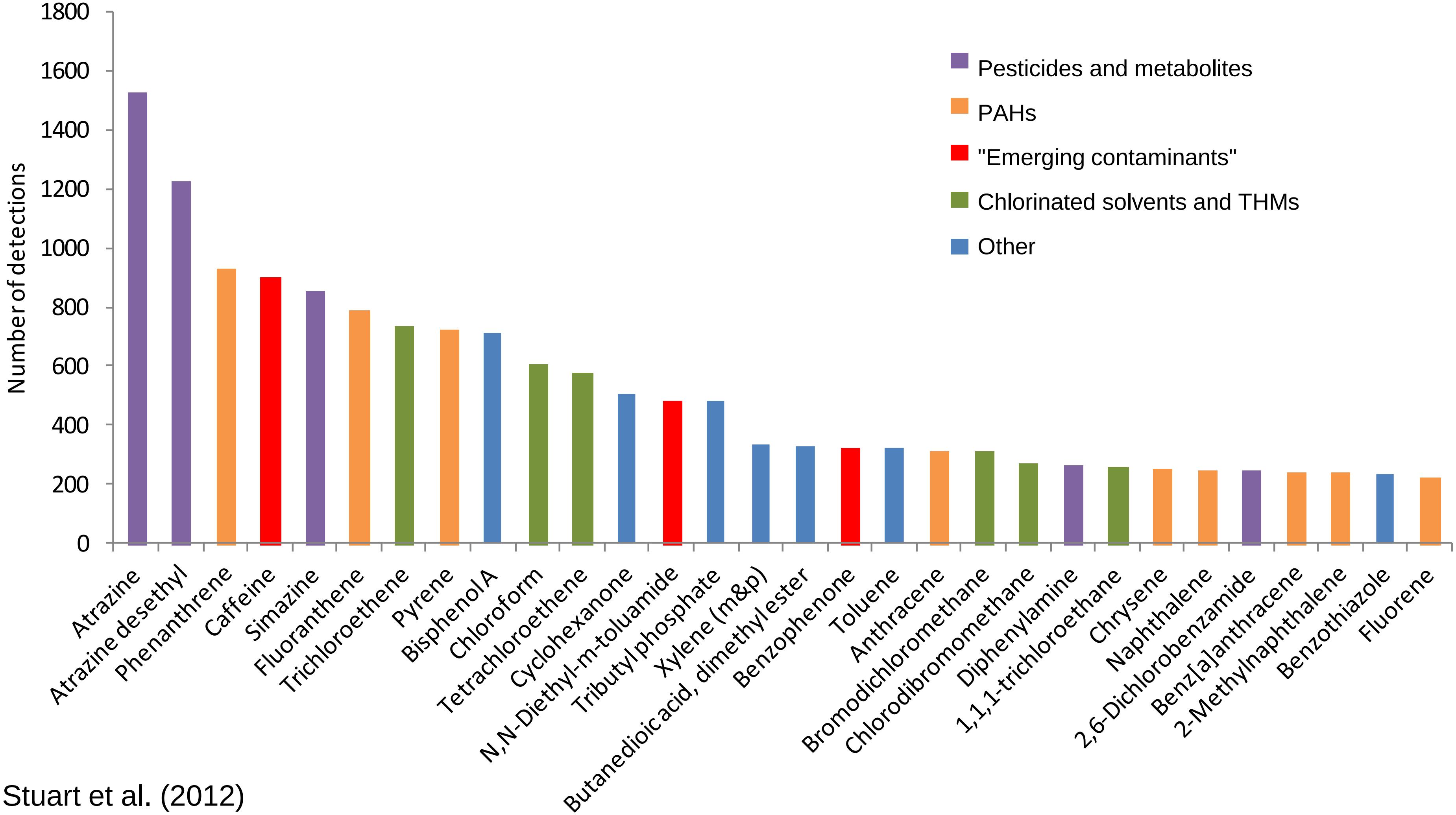
[5] Swartz et al., 2006, [6] Carrara et al., 2007, [7] Watanabe et al., 2010, [8] Buerge et al., 2011, [9] Nakada et al., 2008, [10] Stuart et al, 2011, [11] Buszkaet al, 2009



Pathways

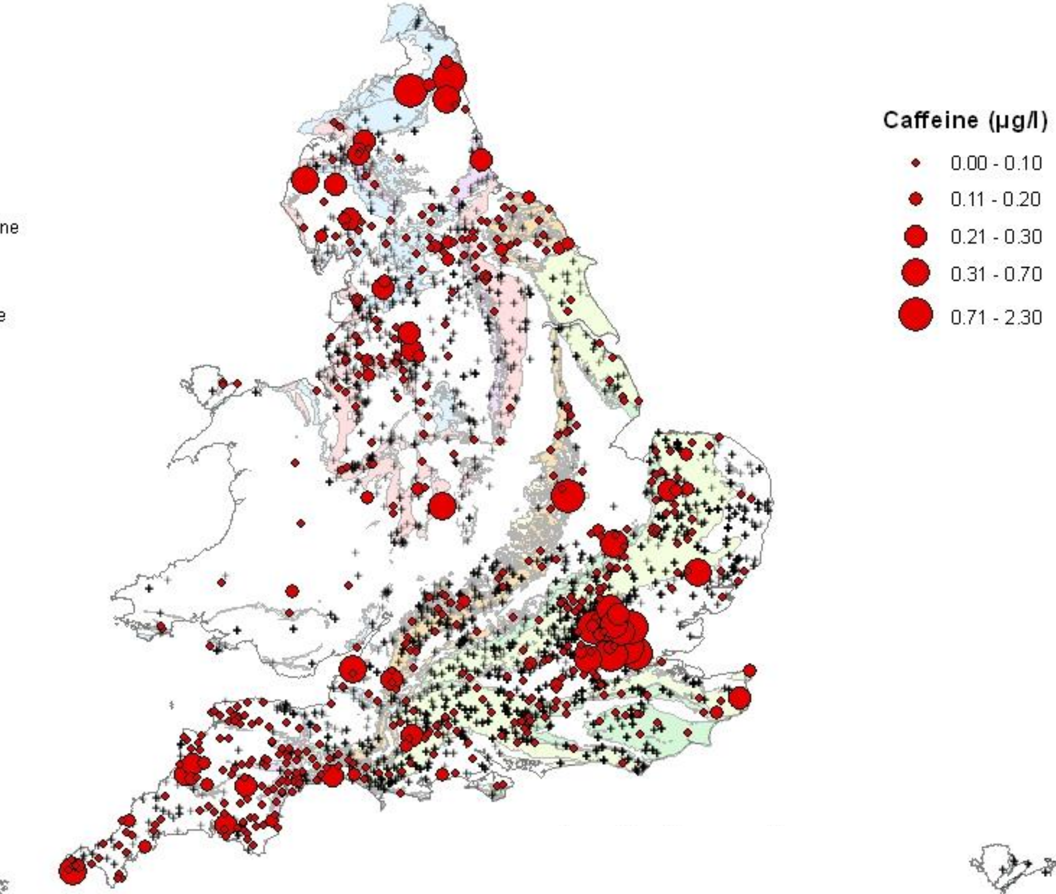
Lapworth et al (2012)

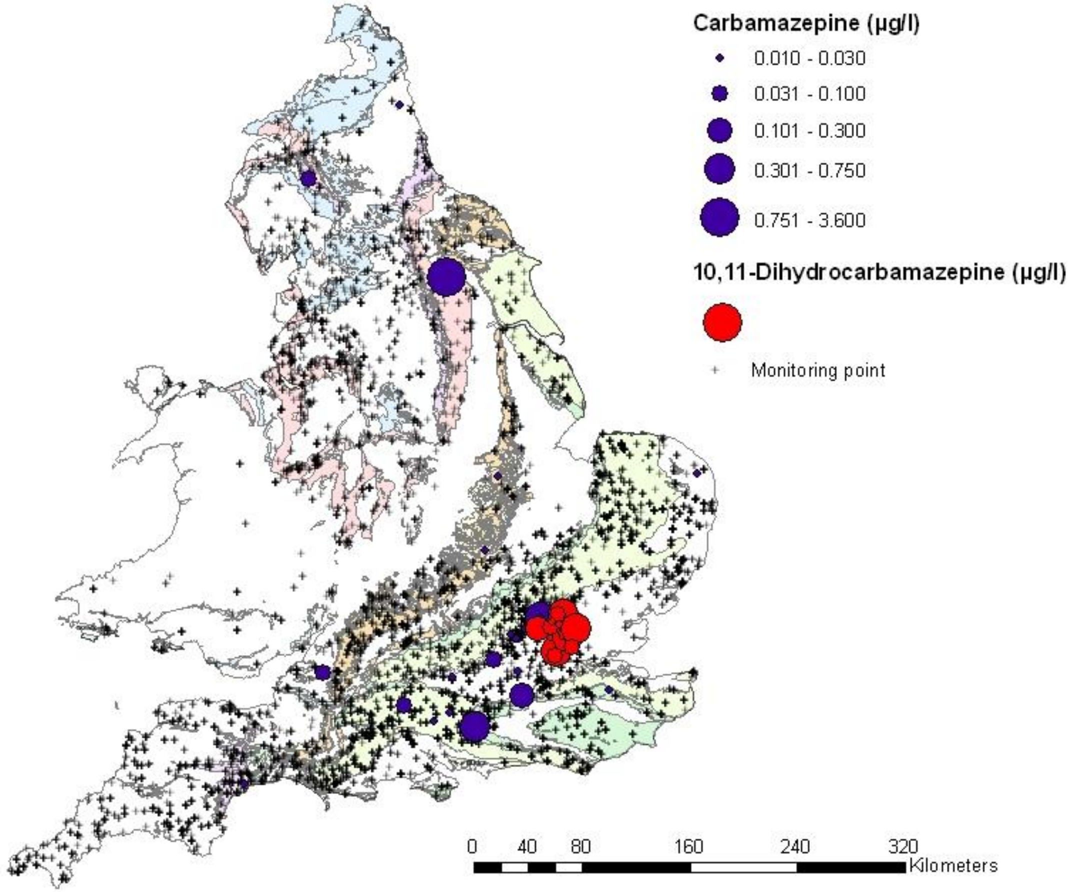
Occurrence: Top 30 microorganics in groundwater in England & Wales 1993-2012
- Environment Agency screening data



Stuart et al. (2012)

Caffeine & carbamazepine





Global review of occurrence in groundwater

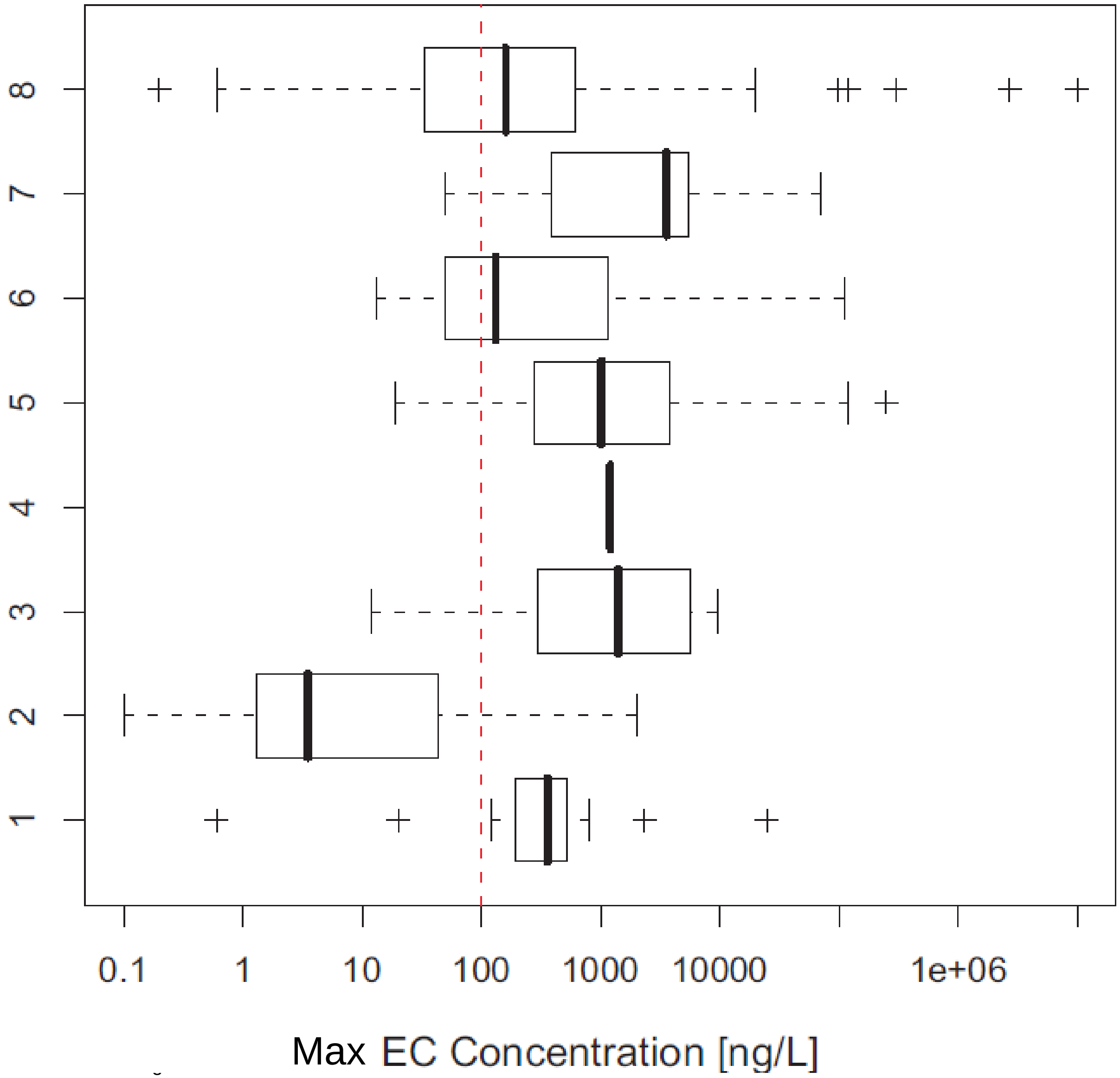
- Looked at pharmaceuticals, personal care products, lifestyle products and some industrial compounds (non-regulated compounds)
- Groundwater EC occurrence from 14 countries reviewed
  - >70 published studies (reconnaissance and targeted)
  - >180 individual EC compounds
  - 23 compounds reported in ≥ 4 separate studies
  - 2 known endocrine disruptors, 6 other potential

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

Compounds	Group	Freq. %	Average	Highest
Carbamazepine	Anti-epileptic	21	5.3	100
Sulfamethoxazole	Antibiotic	14	0.25	1.1
Ibuprofen	Anti-inflammatory	13	1.5	12
Caffeine	Lifestyle	12	9.7	110
Diclofenac	Anti-inflammatory	10	0.12	0.59

Lapworth et al (2012)

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

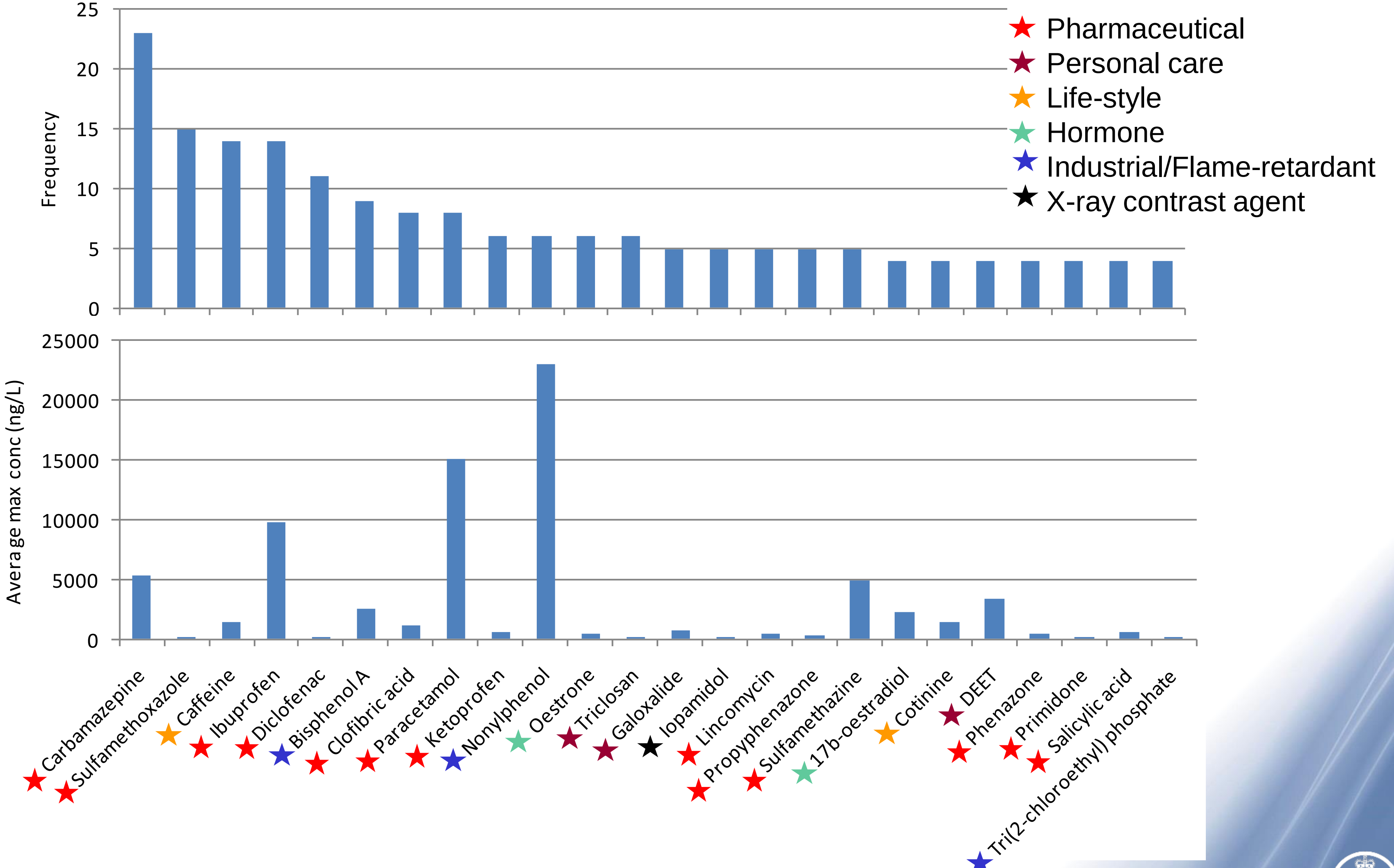
4: Illicit drugs: cocaine (n=1)

3: Food additives and artificial sweeteners

2: Steroids, hormones and metabolites

1: Veterinary antibiotics and hormones

Compounds reported in ≥ 4 separate studies



Recent research focus: Application of EoC tracers in urban areas, examples from Africa, India and UK

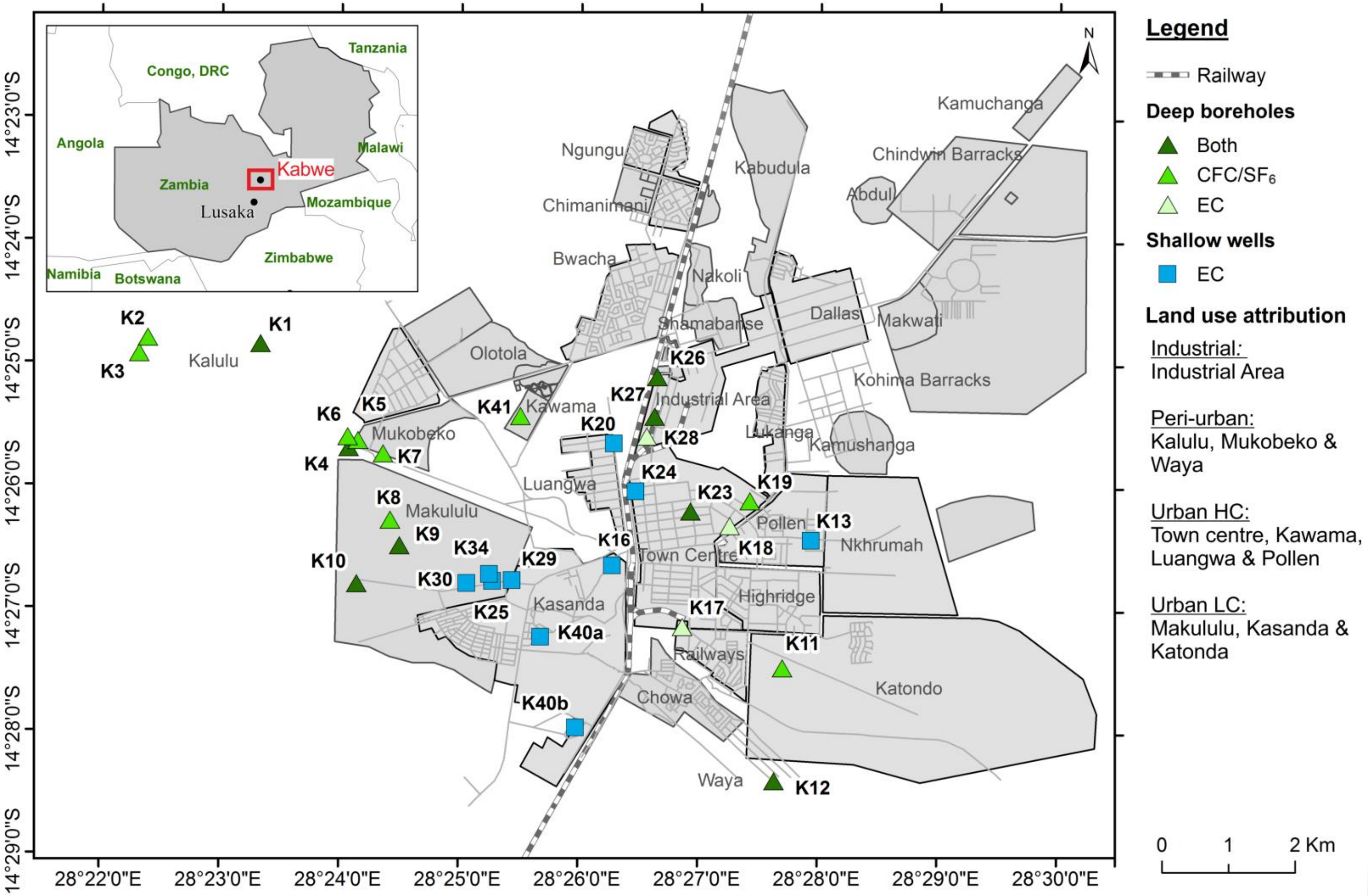
Collecting groundwater samples for microorganics (MOs)

- Boreholes or multi-level piezometers
  - Collect discrete samples at different depths
- Pump (peristaltic) or depth sampler made from inert materials
  - PTFE – *cannot look for PFAS compounds!*
- Cleaned inert sample containers & field blanks
- Trained sample collection staff
  - Care in using PCPs, DEET or gloves
- Analysis
  - SPE isolation in the field
  - Broad screening methods LC-MS-MS & GC-MS-MS

Kabwe, Zambia 2014-15: Tracing shallow groundwater vulnerability

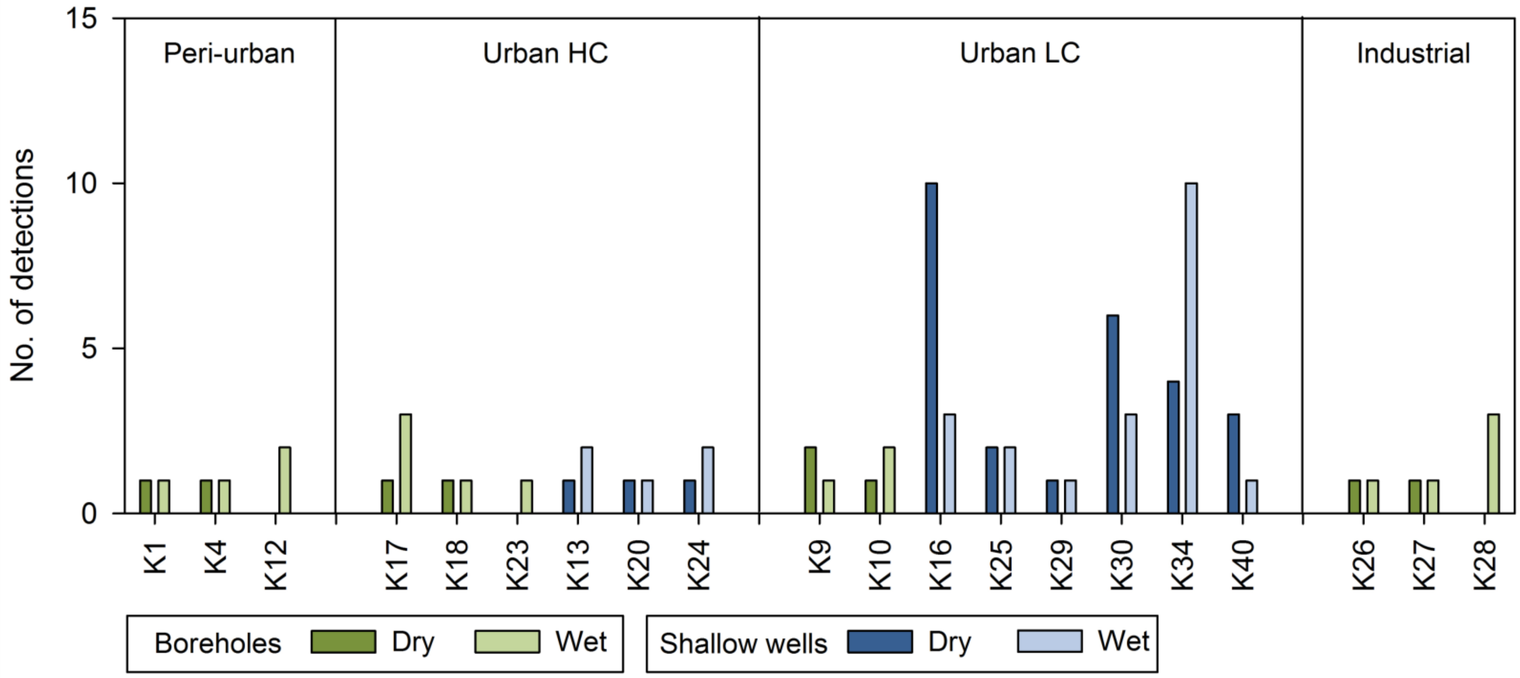
- Former mining town in Zambia with large informal settlements
- Samples from supply wells and boreholes
- Routes to groundwater from poor well completion
- Sources – on-site sanitation

Kabwe, sample sites, n=20



Kabwe

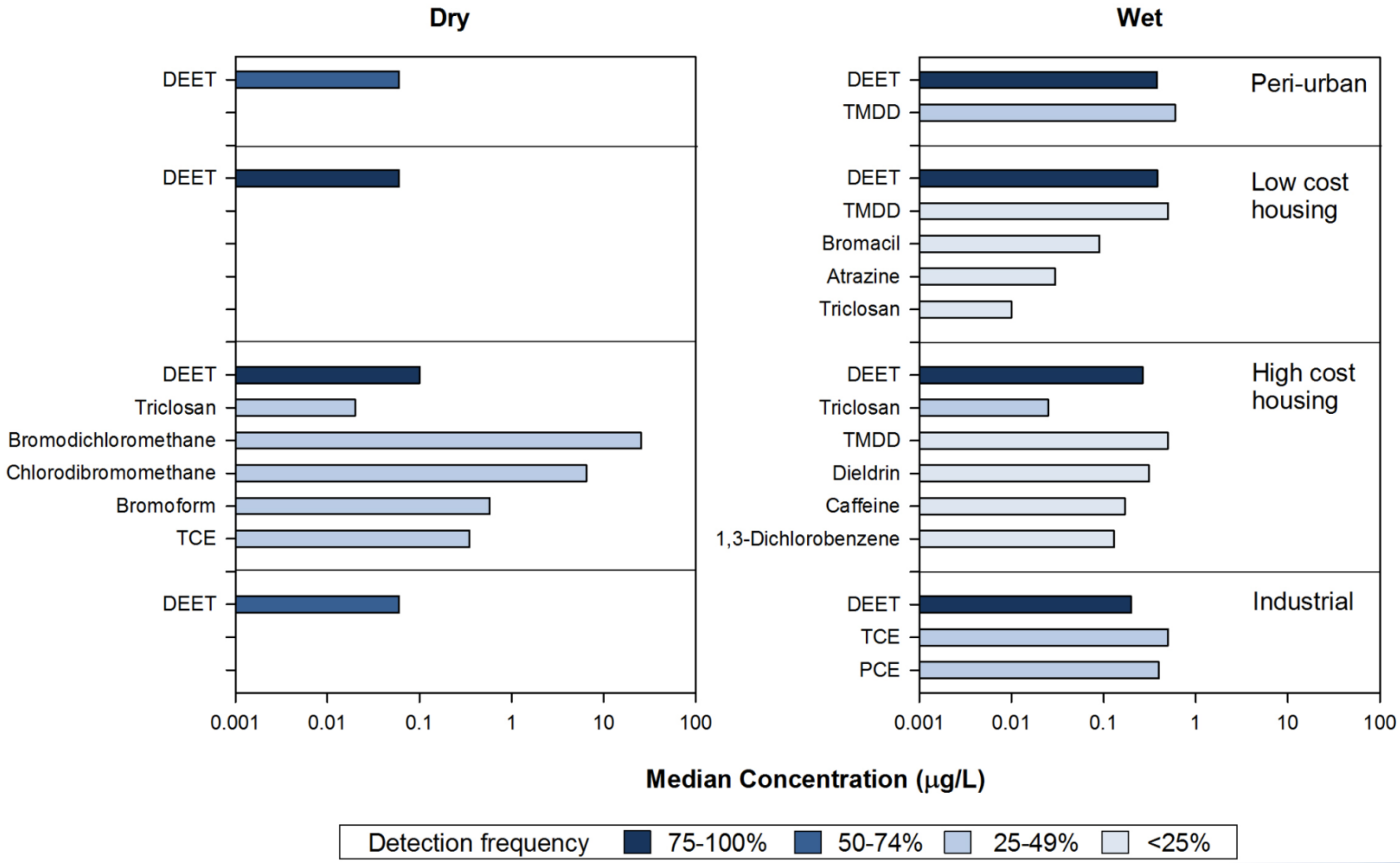
- Microorganics in groundwater most frequent in:
  - Wells
  - Low cost housing areas
  - Generally in the wet season



Sorensen et al (2015)

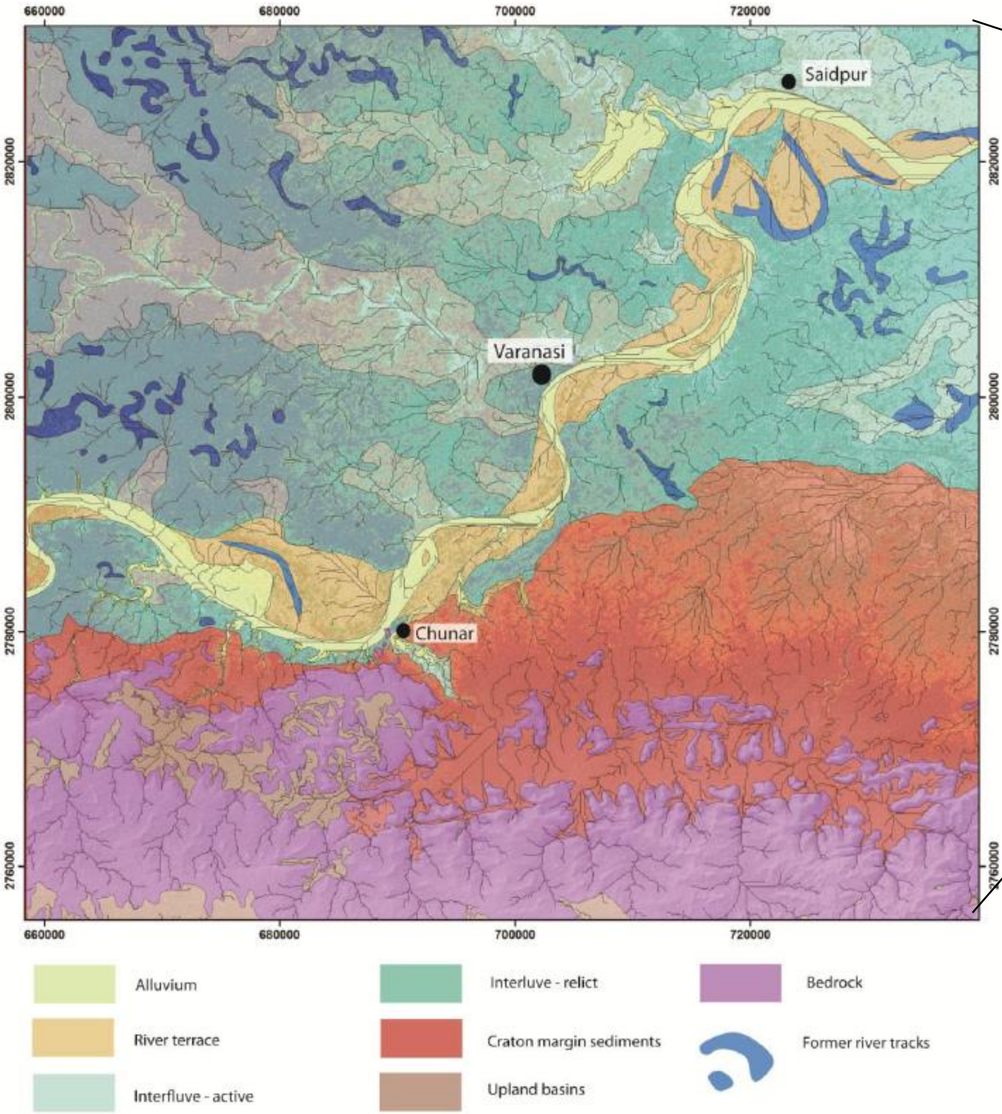
Kabwe, key compounds

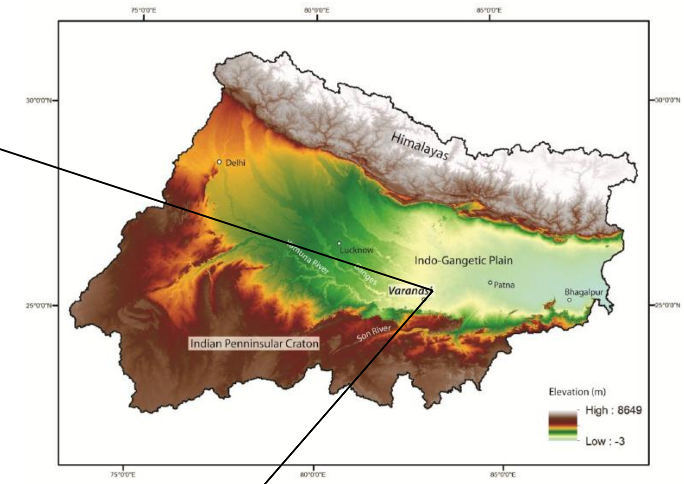
- DEET was ubiquitous and higher in wet season

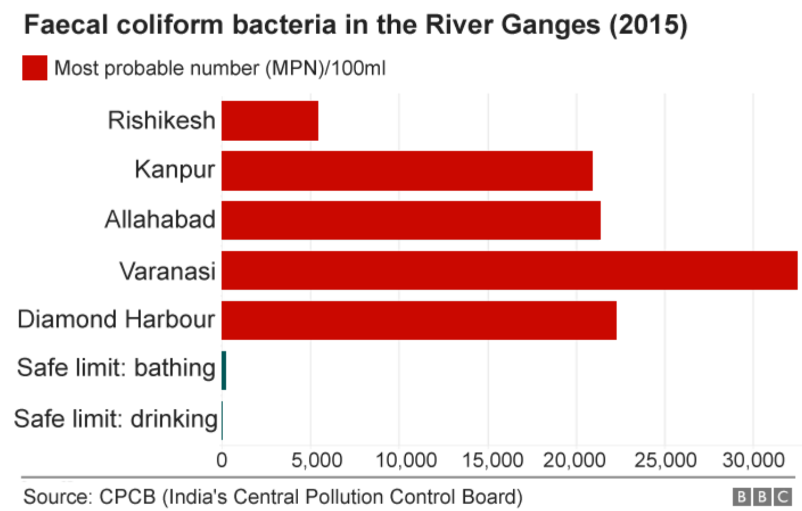


Sorensen et al (2015)

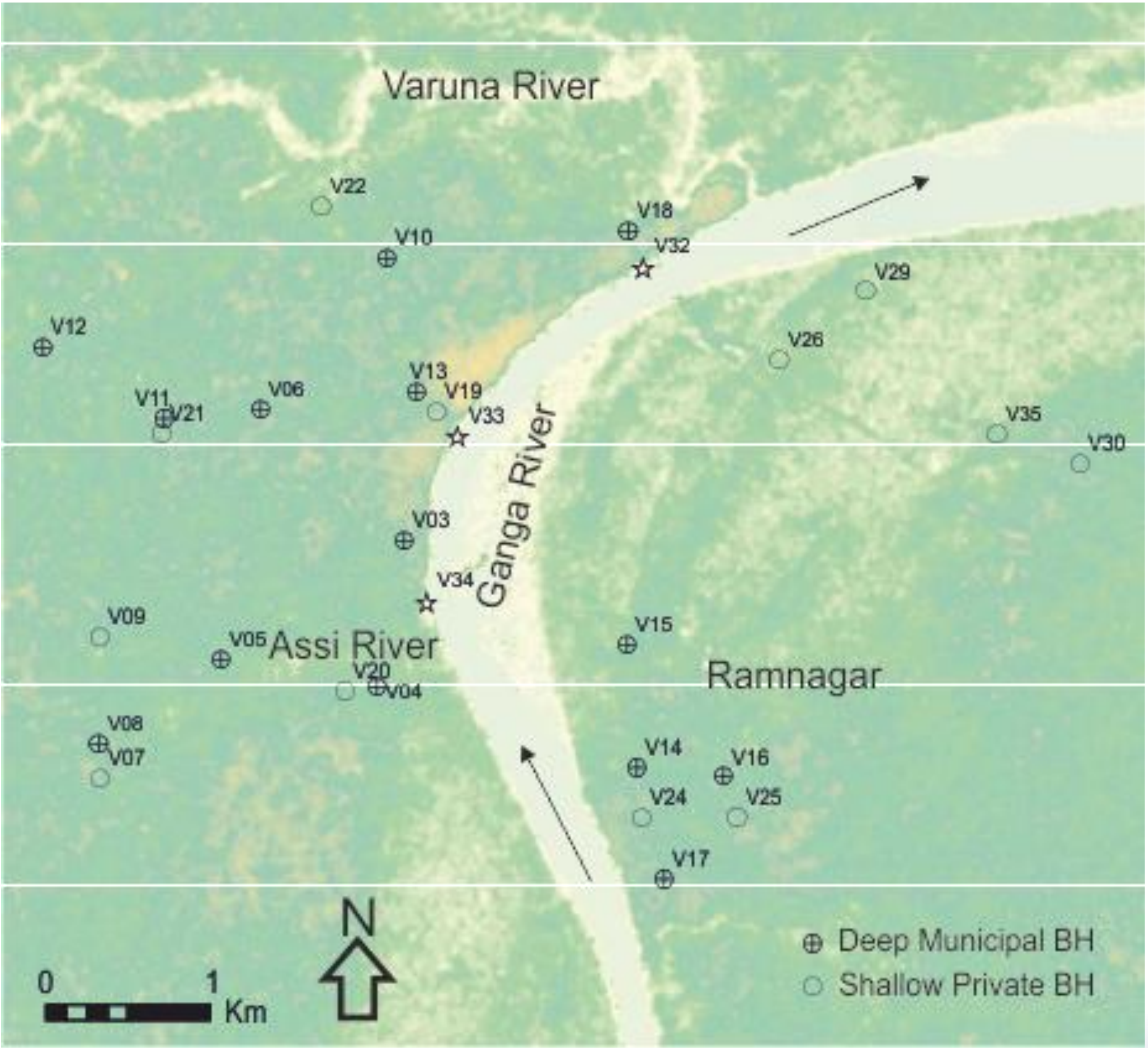
Varanasi, India – 1.4 million



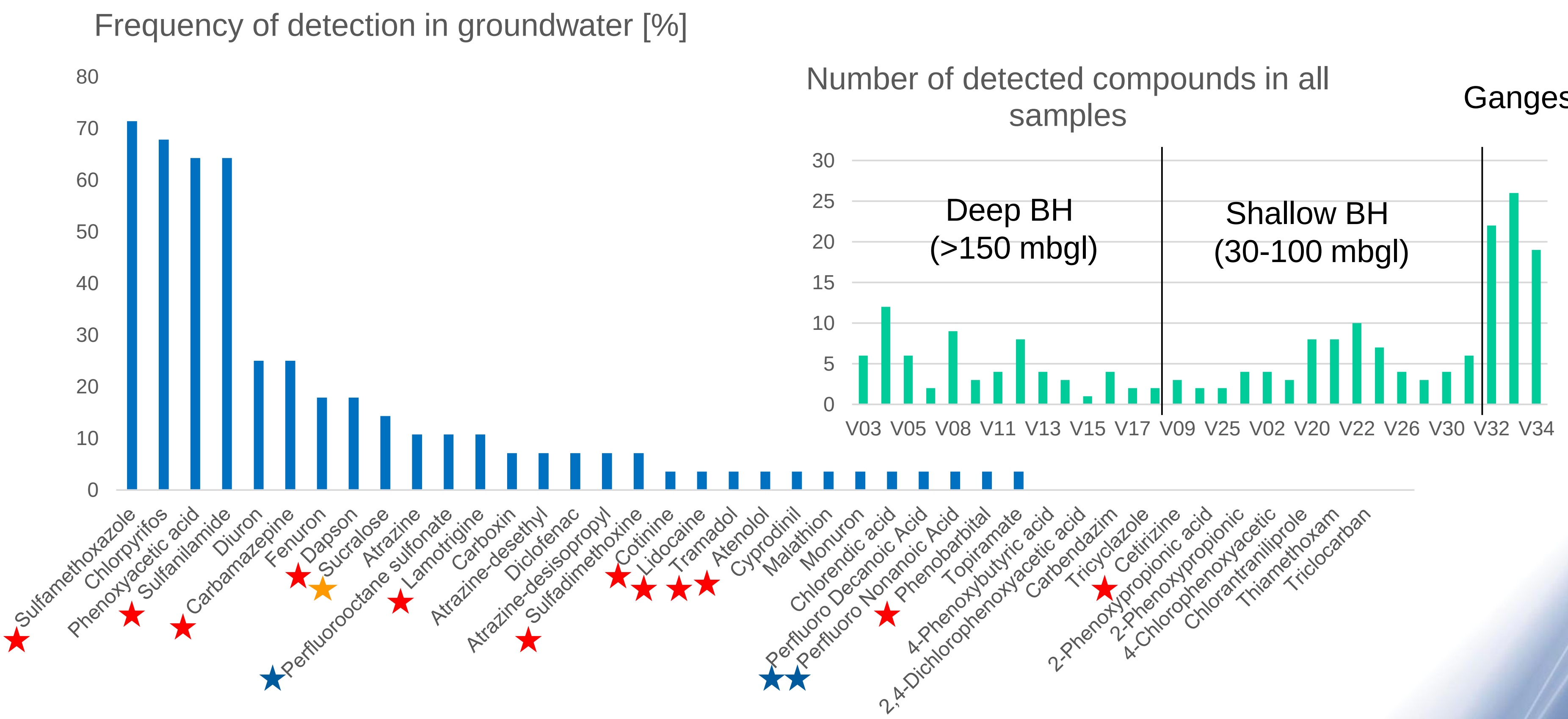




Sampling sites: 31 BHs and 3 River samples



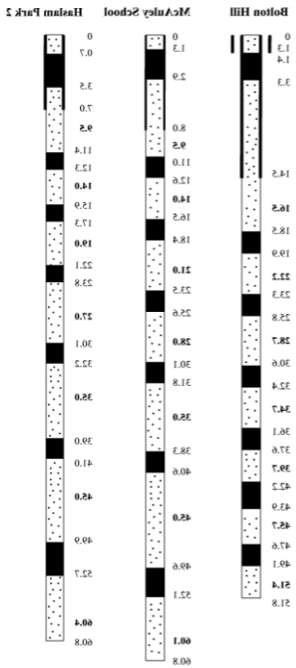
Varanasi: Emerging contaminants in drinking water sources



★ Pharmaceutical
★ PFAS
★ Artificial sweetener

More detail in IAH talk later today: session 5.04 on Emerging Contaminants, 15:00

UK: Urban sites on the Sherwood Sandstone



Doncaster

- 3 multilevel sites in suburbs
- Profiles showed recharge from sewerage typically to depths of about 35 m bgl.
- Microbial indicators were found to depths of 60 m bgl
- Recharge estimates (mm/y) - foul sewer (22), storm water (12), mains water (22) = approx 30-40% of total recharge

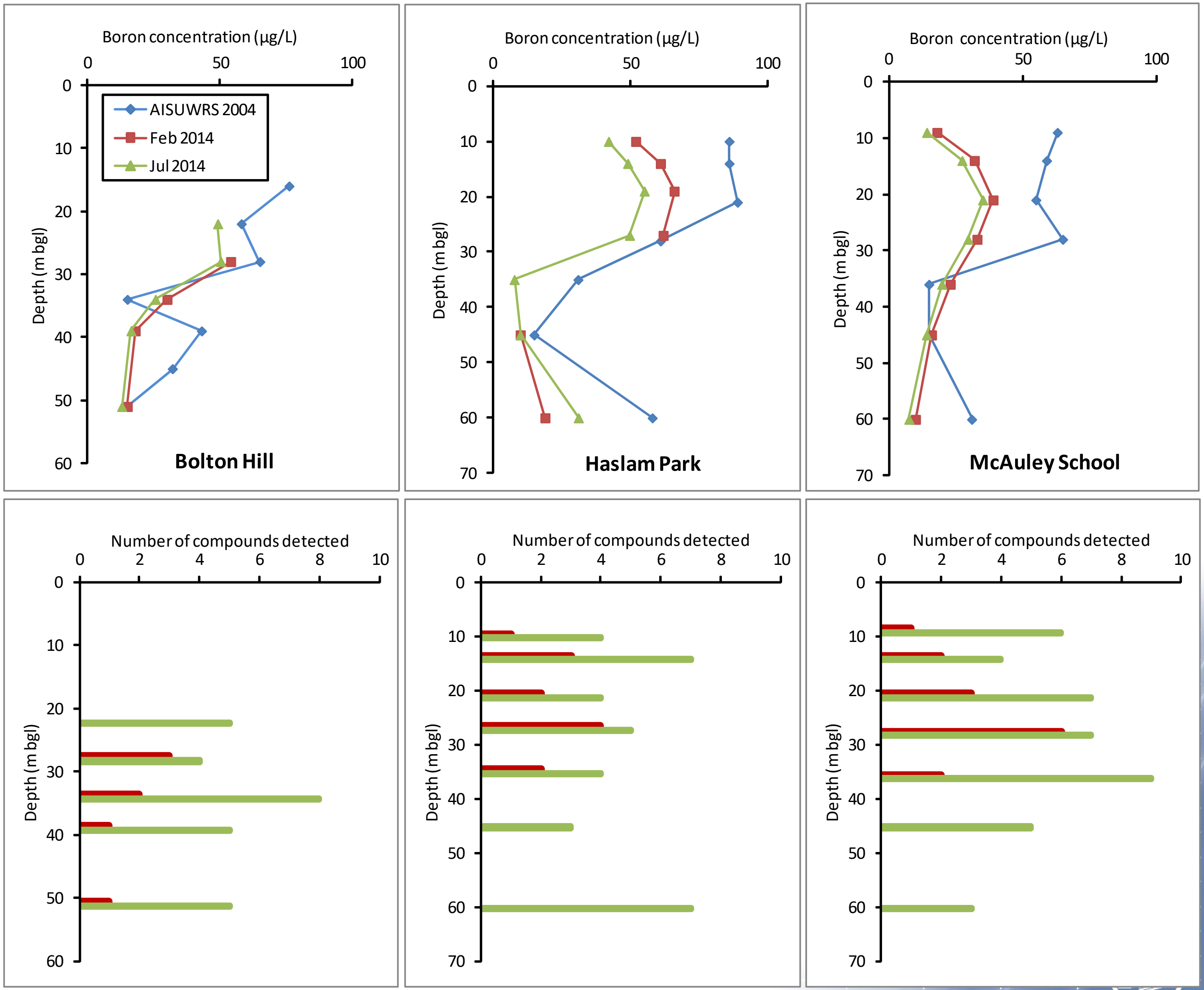
Nottingham

- Multilevel sampler in area close to leaking sewage source
- Assessed range of “marker” species including B, THMs & d-limonene
- Sewage derived bacteria and viruses found to significant depths

Doncaster B and emerging contaminant profiles

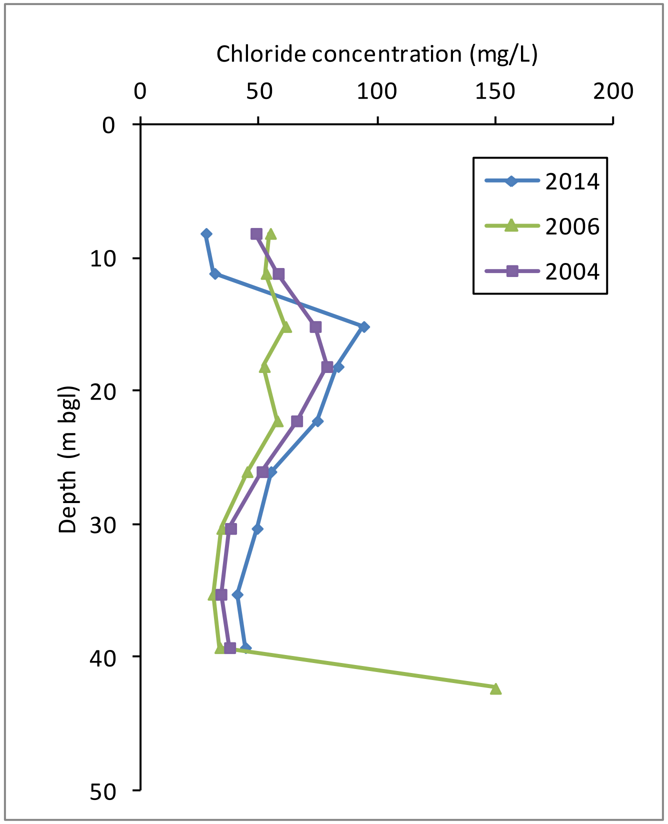
- Boron historical wastewater indicator
- Concentrations have declined with time
- MOs show similar shape
- Penetration to 50 m
- More compounds during high water levels in July

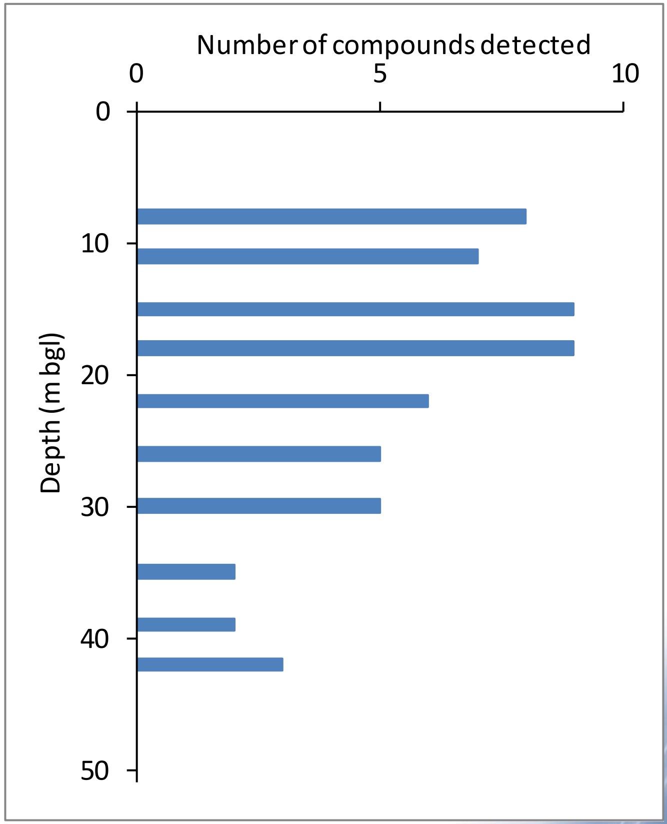
White et al (2016)



Nottingham Cl and MO profiles

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

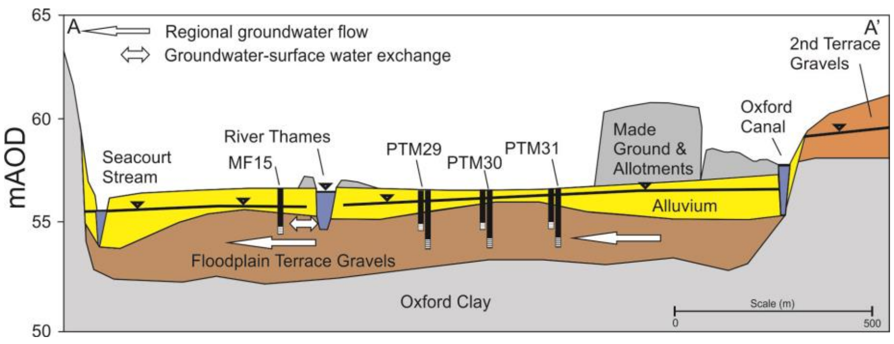


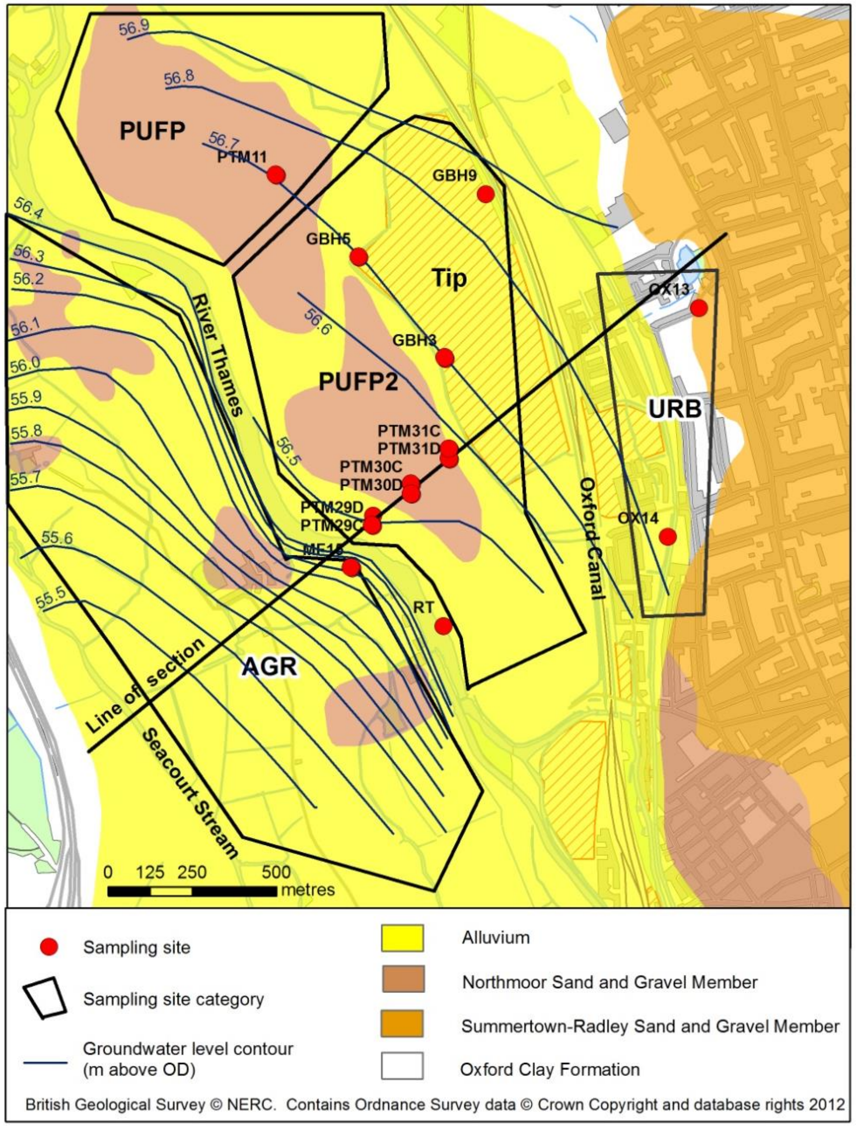


From MSc project work undertaken by BGS jointly with Stephanie Allcock and Nicola Moorhead and Mike Rivett (Birmingham University)

Oxford: Port Meadow

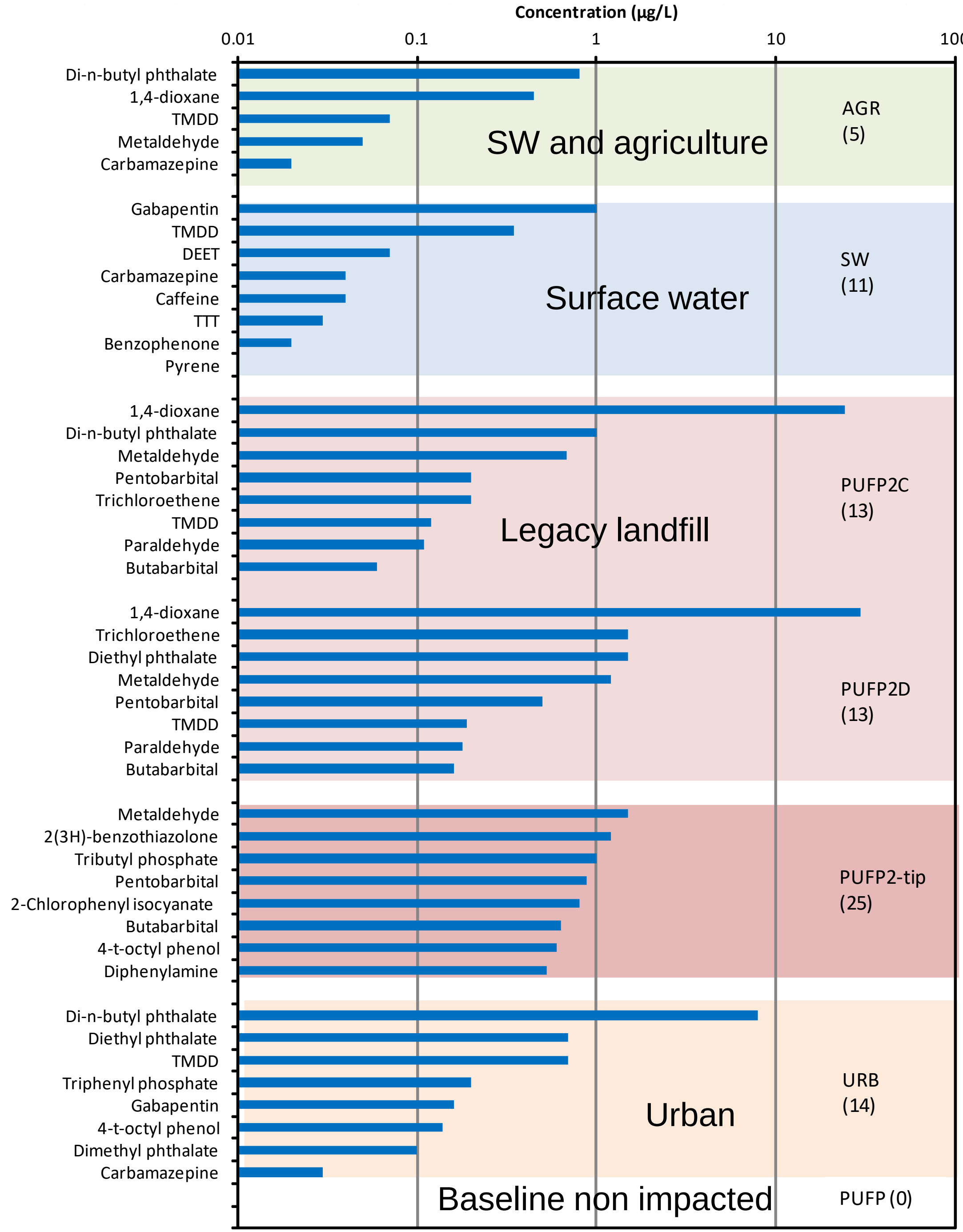
- Thames floodplain gravels
- Areas:
  - Urban
  - Landfill
  - Landfill plume
  - Agricultural
  - Thames





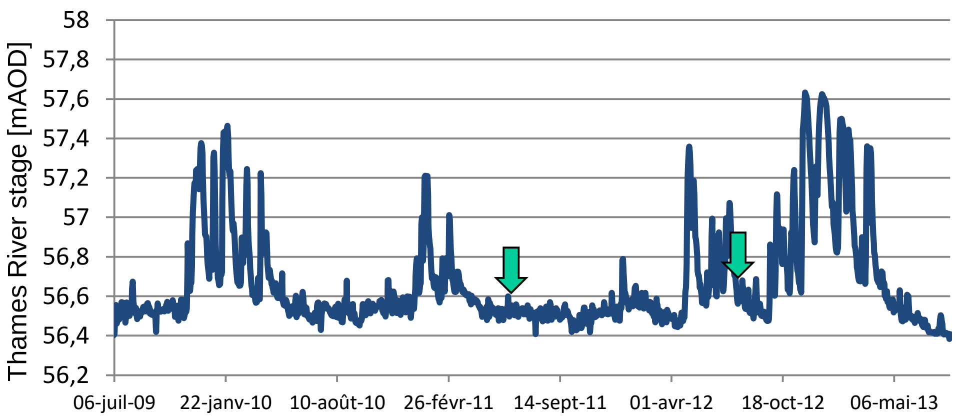
Fingerprinting groundwater

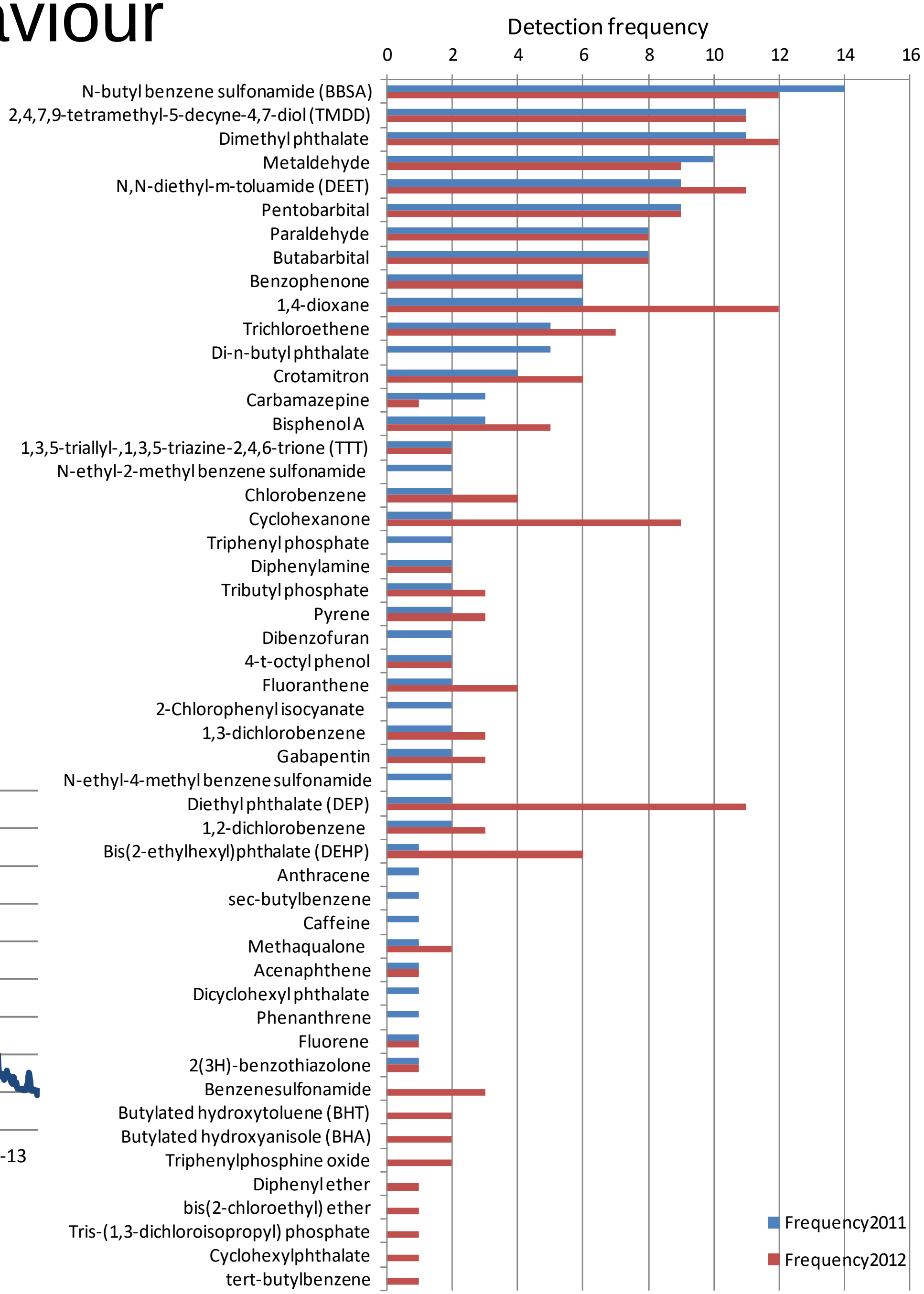
- Concentration and species clearly delineate landuse in the floodplain
- Can be used as tracers for catchment pathways and groundwater/surface water interaction



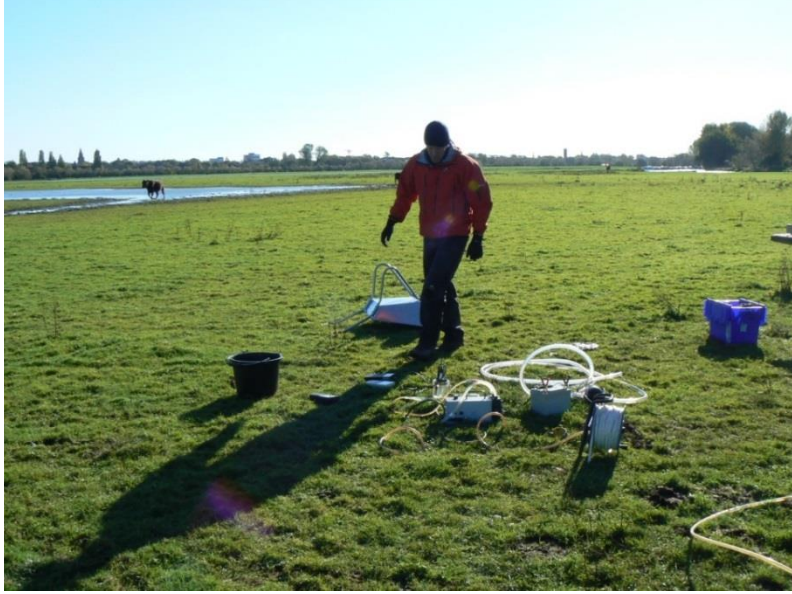
Portmeadow seasonal behaviour

- Two sampling campaigns
- Main compounds show similar detection frequency
- Many with only one detection
- Likely link to antecedent conditions





Groundwater Watch list



Selection of (groups of) substances

↓ ↓

Column I
(Collection of existing monitoring data)

Set up a database for existing monitoring data (agreed format, including meta-data and supporting information, …)
Summary and assessment

↓

Column II
(Exposure assessment)

Use data
Persistence
Mobility
…

↓

Column III Prioritization - Risk assessment
(taking into account toxicity, bioaccumulation, etc.)
(Dynamic) Watch list

Identification of research needs

Source: Groundwater Watch list Working Group concept paper (draft)

Importance of understanding emerging contaminants in urban groundwater

- Important drinking water source globally where an increasing range of compounds are being detected
- Many compounds can be considered low threat to health – often very low concentrations are found in groundwaters but there is a very limited evidence base
- Others are potentially more concerning: microbial resistance; endocrine disruptors, toxic PFAS compounds…
- Urban areas show impact from wastewater sources and environmental load increases with development
- We may see increasing PCPs and industrial chemicals in groundwater as counties develop - most with limited urban waste management.

Summary

- Frequently detected groups of ECs include antimicrobials, pharmaceuticals and PFAS – further research needed
- 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 for EC groundwater contamination globally which warrant further investigation
- Overall there is a poor understanding of the occurrence, transport, fate of ECs, and human and ecological impact of many ECs
- Very useful tracers to understand groundwater flow processes
- 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 EC monitoring and gather evidence, this is facilitated early on by the use broad screening methods