Emerging organic contaminants in groundwater in urban areas

Marianne Stuart, Debbie White, Kat Manamsa, Dan Lapworth, Peter Williams, James Sorensen

Emerging contaminants in water and soil, practical considerations: sampling, analysis and consequences. RSC, Sheffield, 4 March 2015

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

www.gardenorganic.co.uk

- 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

Microorganic 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
- 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
- For pesticides:
  - Desethyl, desisopropyl - 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
- May have long arrival time due to thick unsaturated zone or low aquifer permeability

Stuart & Lapworth (2014)

New Priority Substances

- 2012 Commission proposal on priority substances (COM(2011)876)
- New priority substances - aclonifen, bifenox, cybutryne, cypermethrin isomers, dichlorvos, dicofol, dioxins*, hexabromocyclododecane*, heptachlor/ heptachlor epoxide*, PFOS*, quinoxyfen*, terbutryne

  *designated as priority hazardous substances
- Supplementary monitoring programmes for new substances to be in place by 2018
- Revised EQS for existing substances – including anthracene, fluoranthene, naphthalene, PBDEs, trifluralin to be included in RBMPs by 2015
- For surface water but also impact of groundwater

Watch lists

Surface water

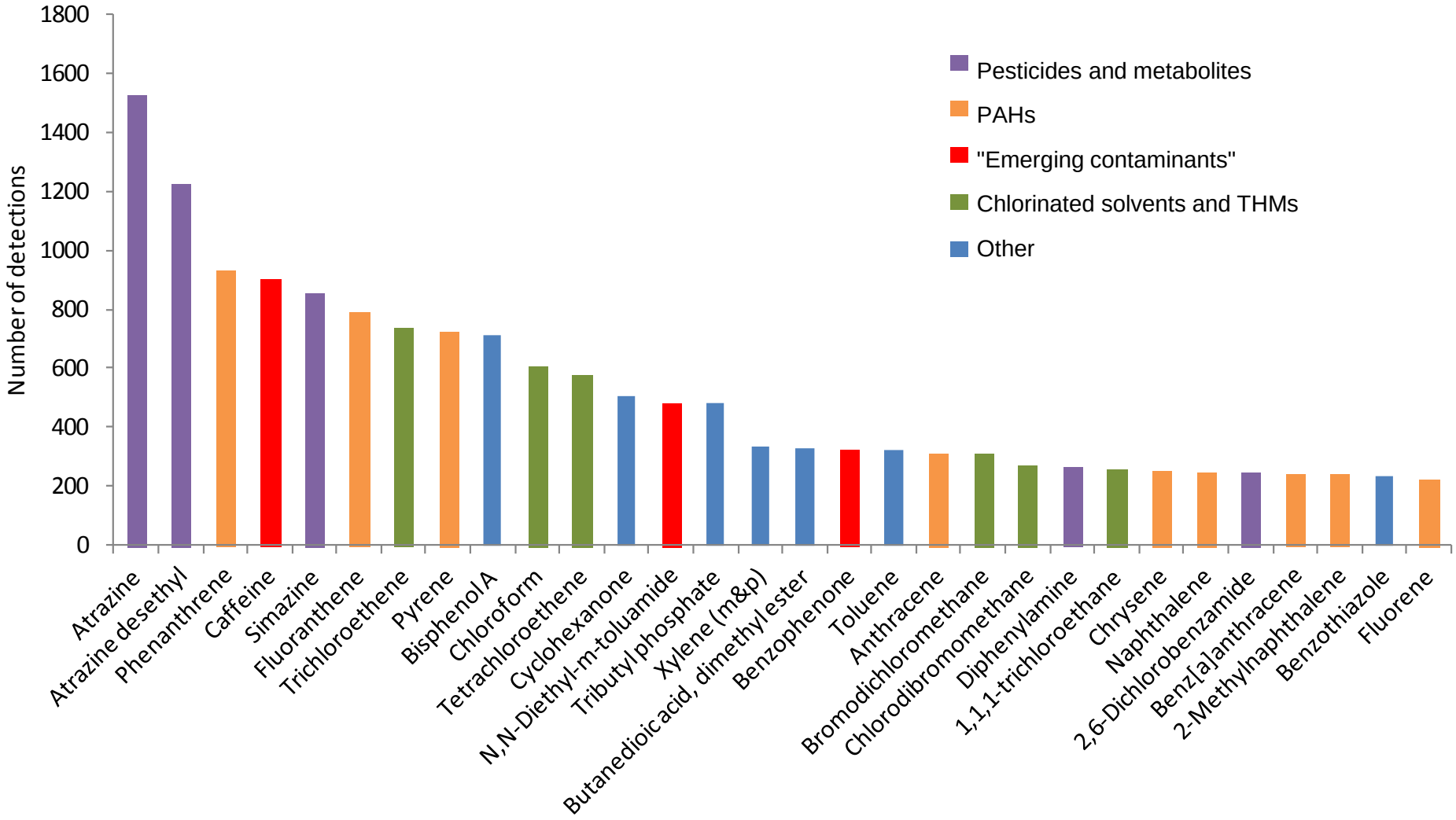
- Priority Substances Directive amendment 2013/39/EU
- Targeted EU-wide monitoring of substances of possible concern to support the prioritisation process in future reviews (10-14 in rolling programme)
- First watch list -17α-ethinylestradiol,17β-estradiol, diclofenac

Groundwater

- Draft COM Directive (Recital 4) amending Annex II of the GWD
- Less developed than surface water
- Increased availability of monitoring data to facilitate identification of substances

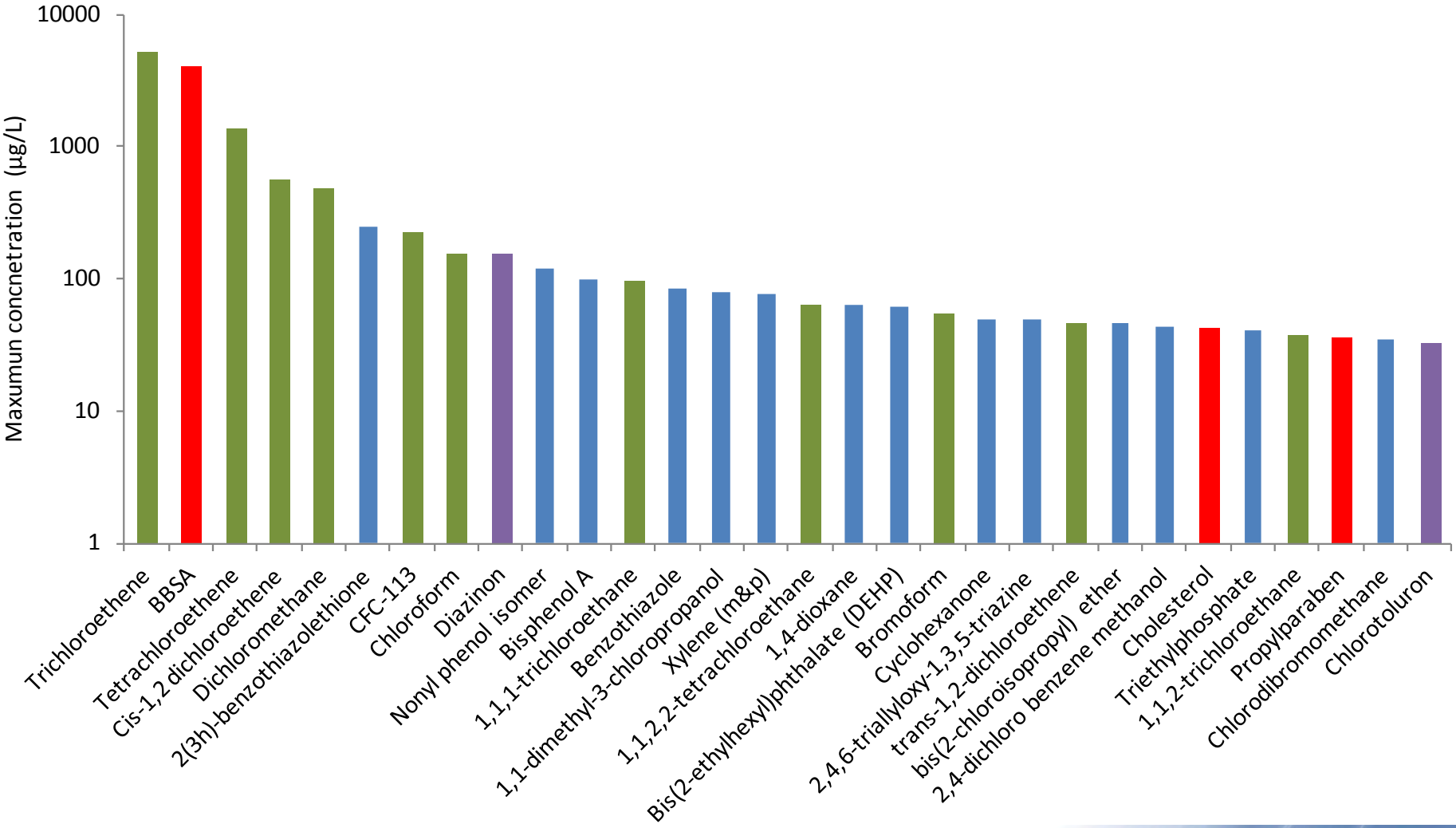
Top 30 microorganics in Environment Agency groundwater screening data 1993-2012

By frequency of detection

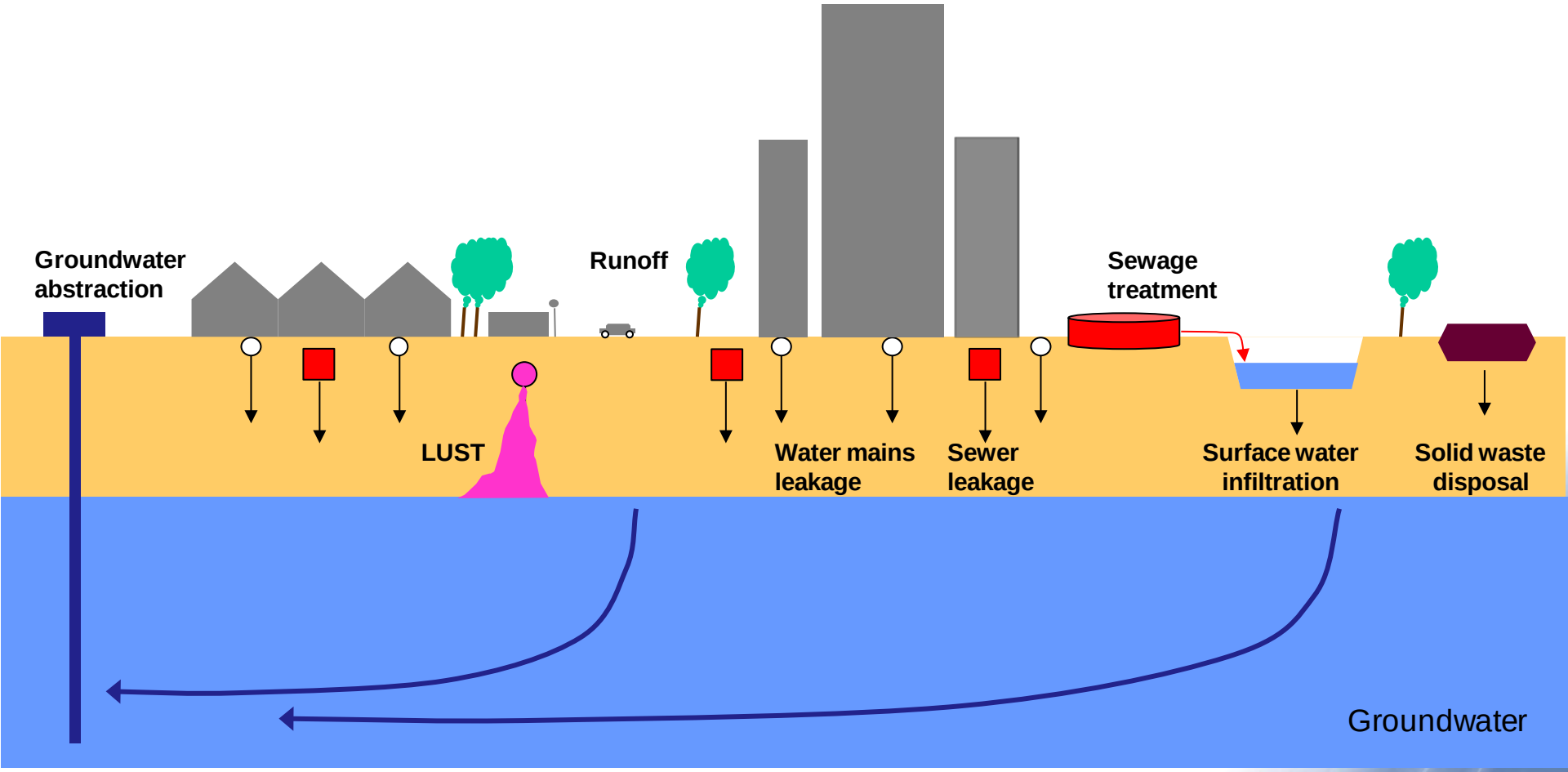


Top 30 microorganics in Environment Agency groundwater screening data 1993-2012

by maximum concentration



Sources of ECs in urban groundwater



Microorganics in urban areas

- Potential sources
  - Sewer leakage
  - Industrial effluent leakage
  - Road runoff
  - Old landfills
  - Green space, and road and railway track maintenance
  - Groundwater/surface water interaction
- Types of compounds anticipated
  - Pharmaceuticals and personal care products (PCP)
  - Household compounds
  - Industrial compounds
  - Amenity pesticides
  - PAH

Collecting groundwater samples for microorganics (MOs)

- Boreholes or multi-level piezometers
  - Measure water levels
  - Collect discrete samples at different depths
- Pump (peristaltic) or depth sampler made from inert materials
  - Ptfe
  - Stainless steel
- Cleaned inert sample containers
- Trained sample collection staff
  - These are not generally made from inert materials
  - Care in using PCPs, DEET or gloves
- Specialised laboratory
  - We have used the Environment Agency NLS

Characterised urban sites on the Sherwood Sandstone

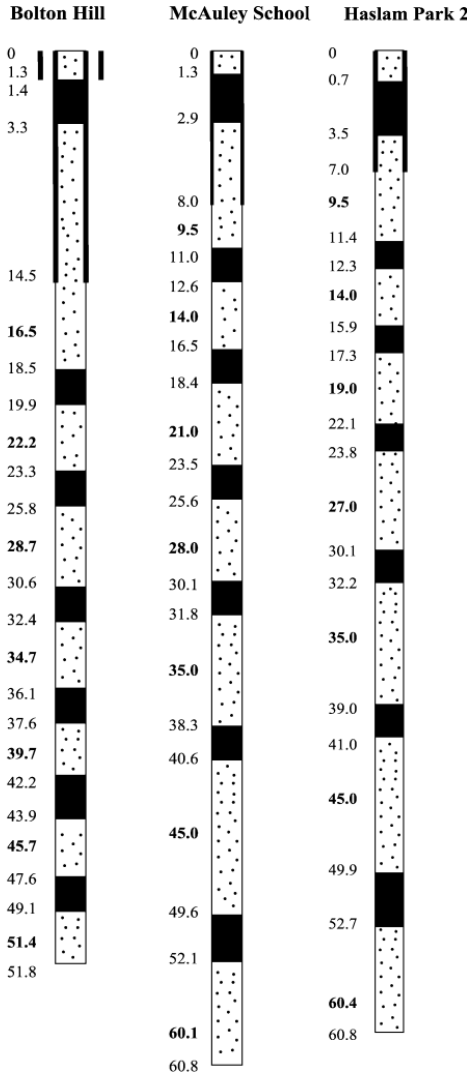
Doncaster

- 3 multilevel sites in suburbs – AISUWRS
- 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

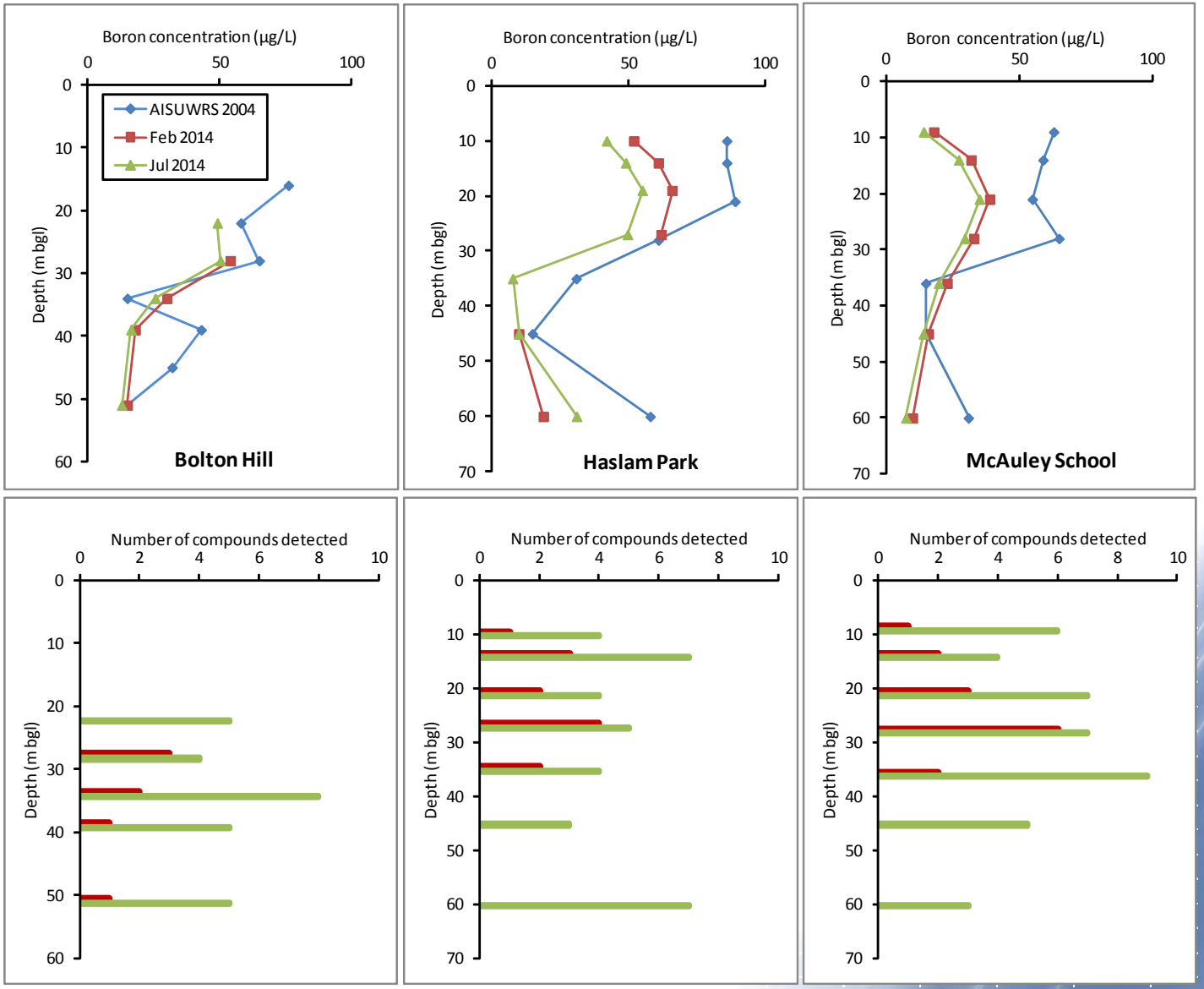
- Multilevel sampler in area close to leaking sewage source
- Assessed range of “marker” species including B, THMs & d-limonene
- Sewage derived bacteria and viruses found to significant depths

Sampling multilevel piezometers in Doncaster



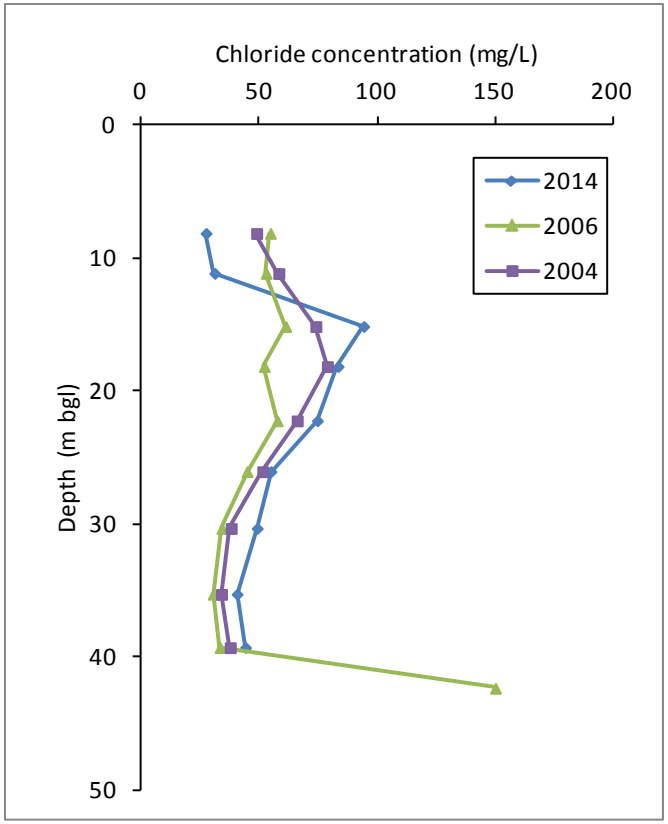
Doncaster B and MO profiles

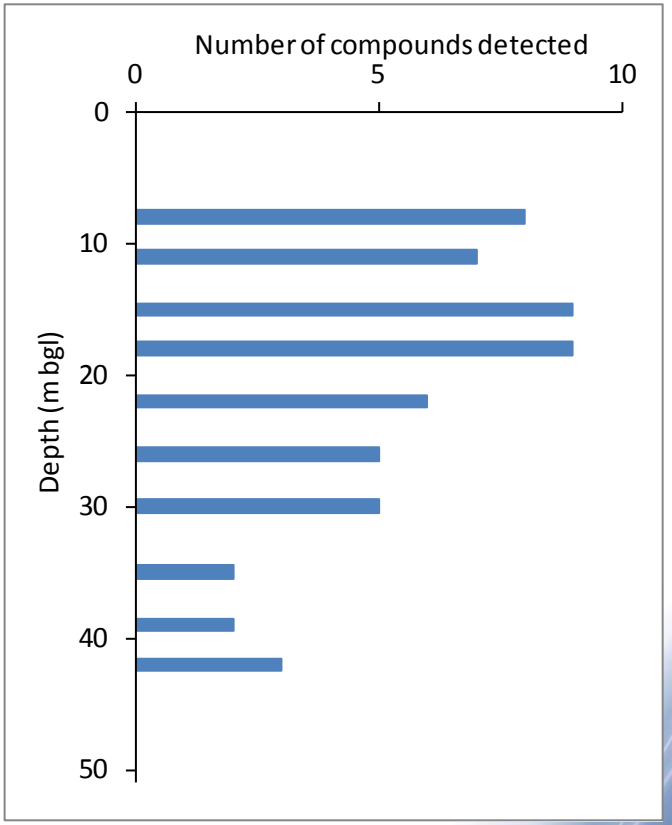
- Boron historical wastewater indicator
- Concentrations have declined with time
- MOs show similar shape
- Penetration to 50 m
- More compounds during high water levels in July



Nottingham Cl and MO profiles

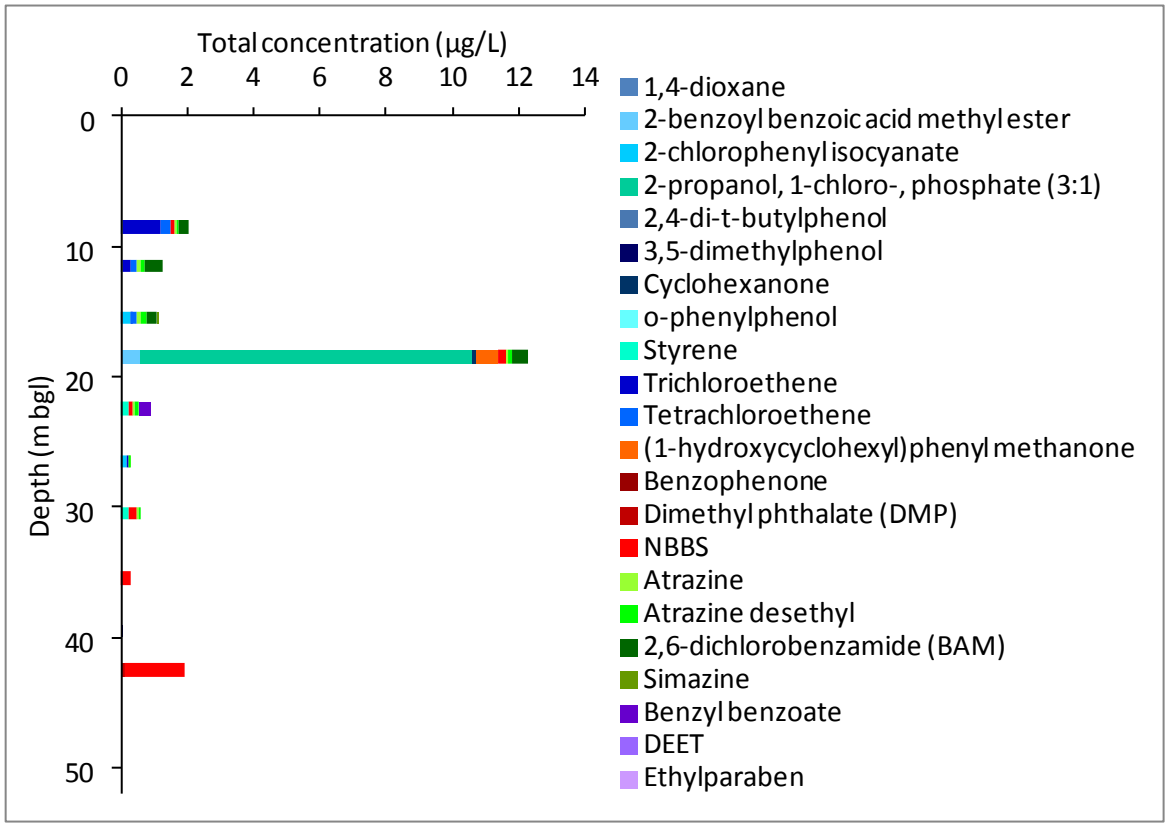
- Chloride profile similar over 10 years
- Possible evidence of Cl at depth
- ECs again show similar shape

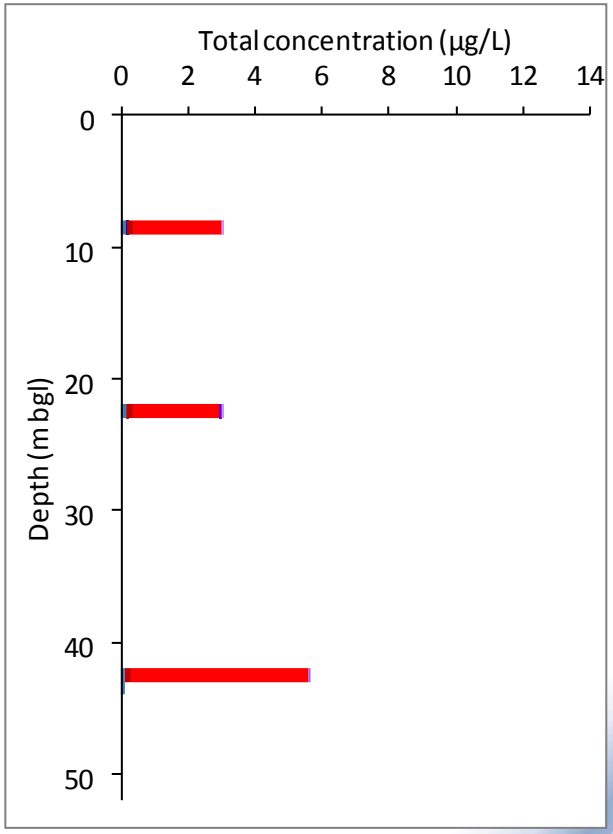




From MSc project work by Stephanie Allcock and Nicola Moorhead

Nottingham MO concentration profile





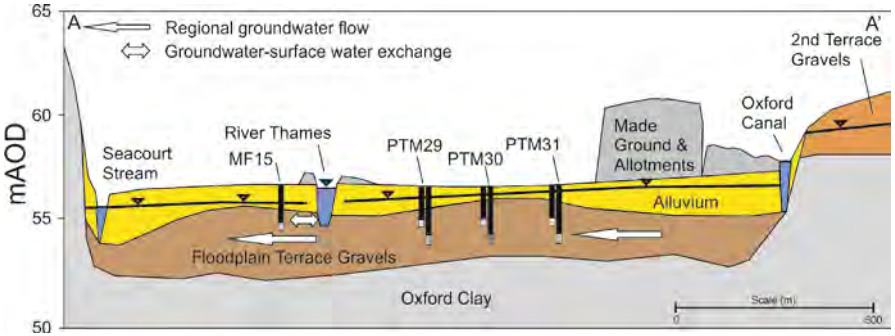
- Left profile shows uncorrected concentrations
- Right profile shows blanks!
- Predominantly industrial compounds and plasticisers

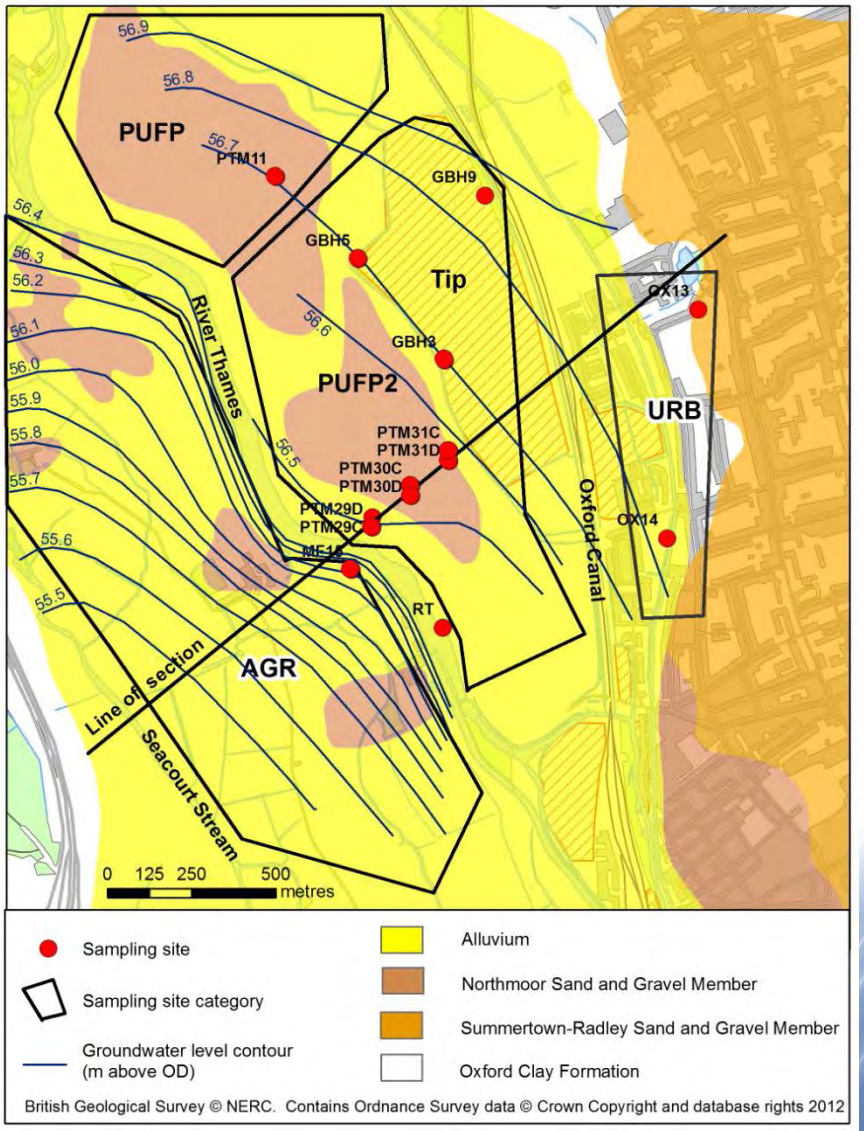
Summary of compounds found

- **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

Oxford Portmeadow

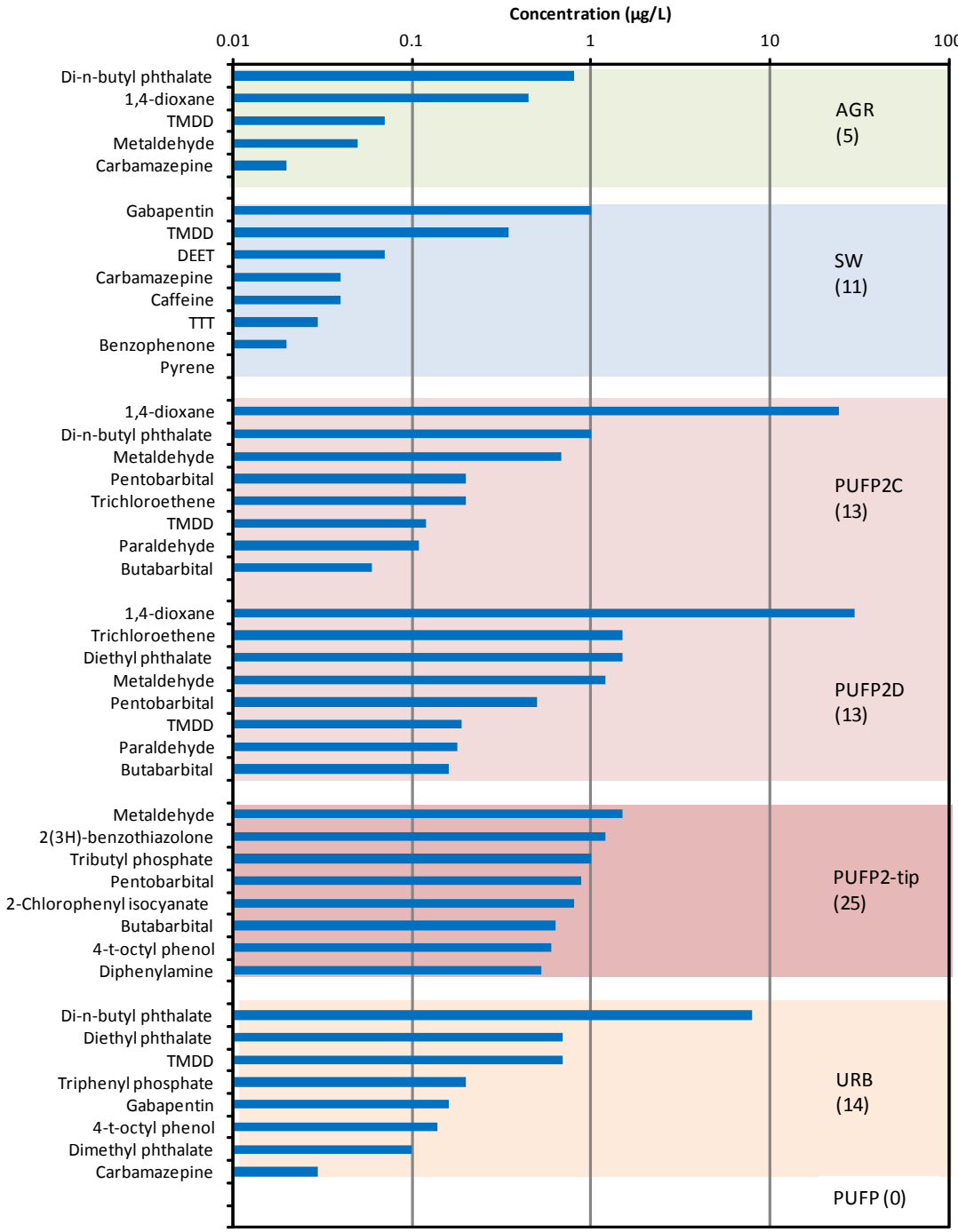
- Contrasting setting on shallow Thames floodplain gravels
- Areas:
  - Urban
  - Landfill
  - Landfill plume
  - Agricultural
  - Thames





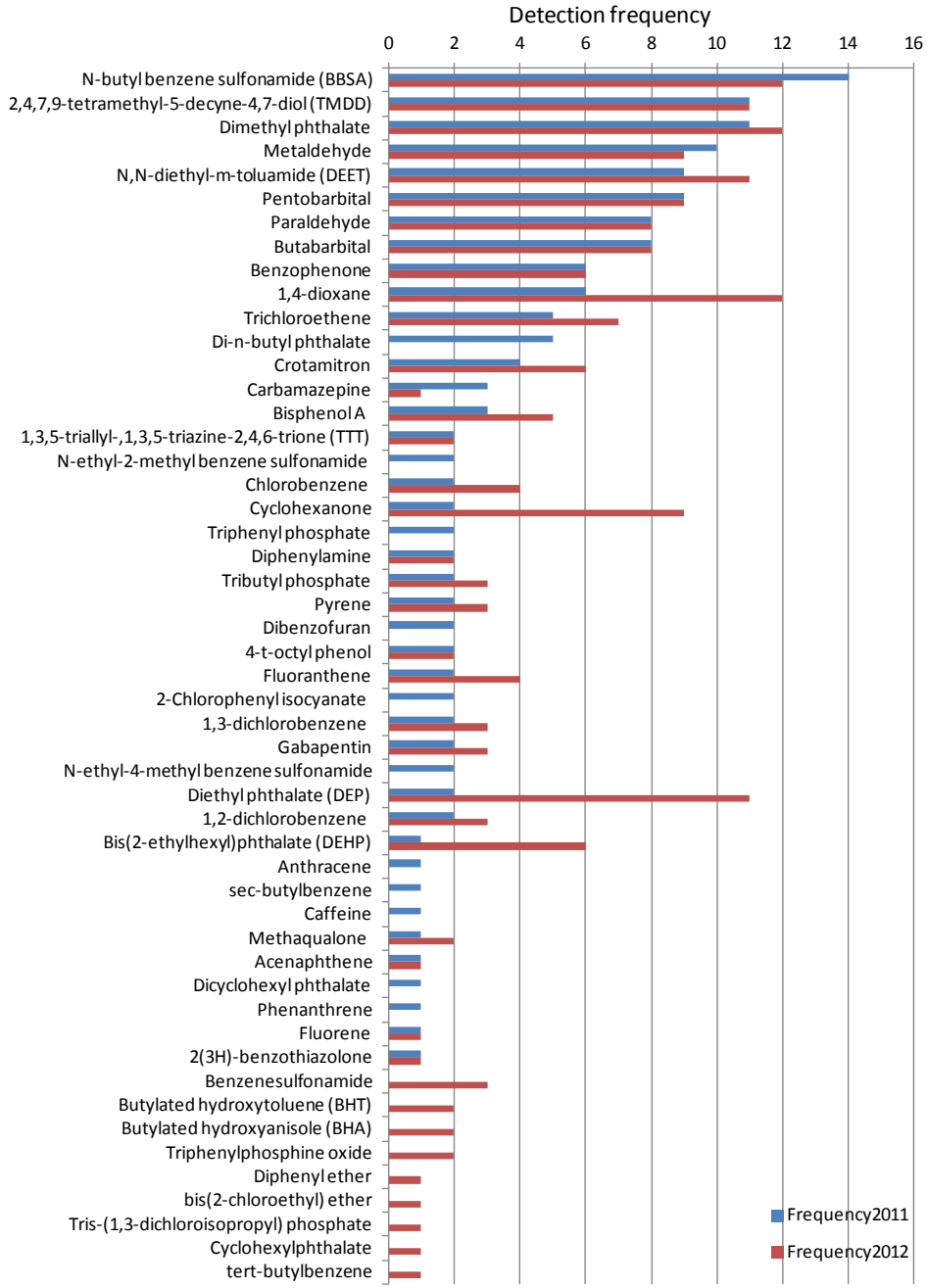
Fingerprinting groundwater

- 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

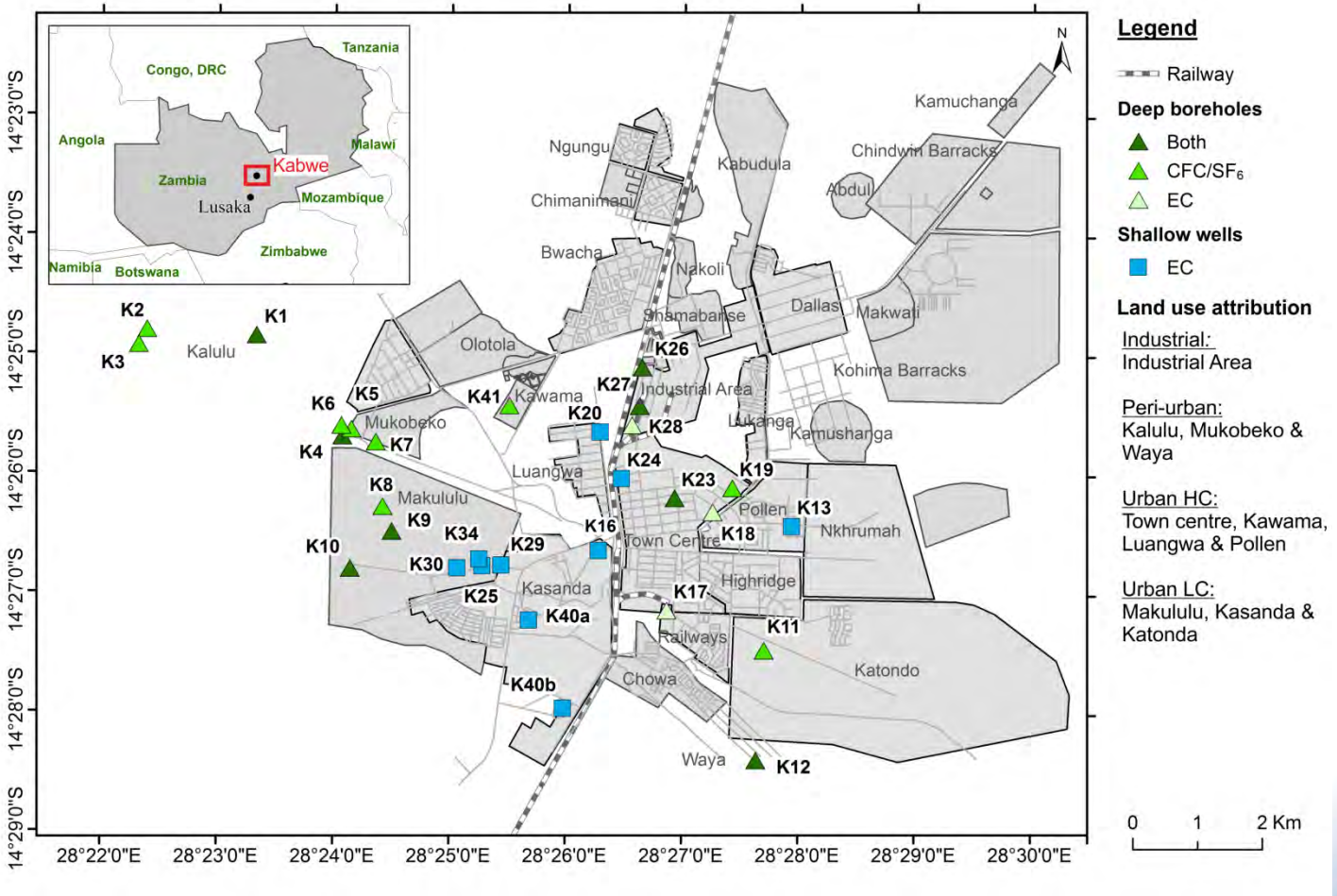
- Two sampling campaigns
- Major compounds similar detection frquency
- Many with only one detection



Kabwe, Zambia

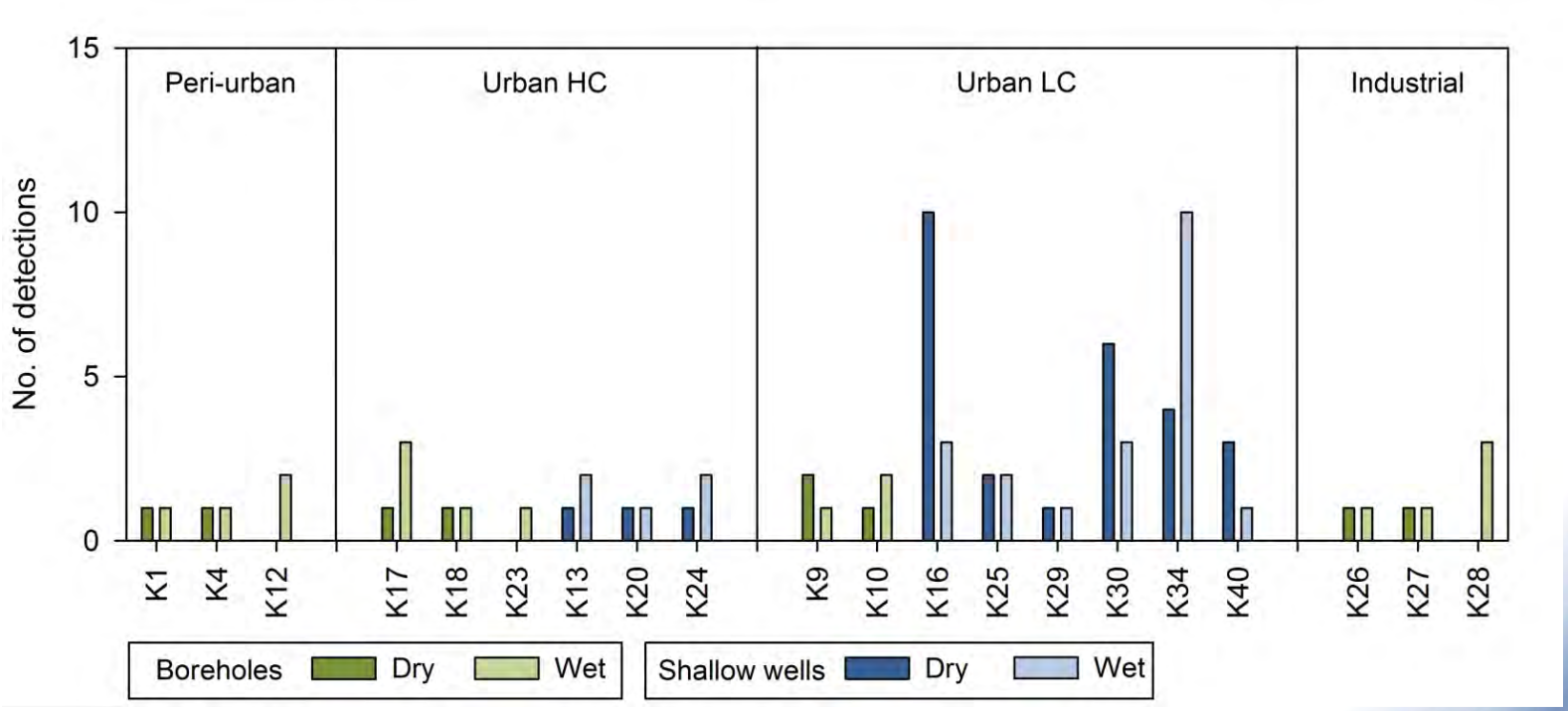
- Shallow aquifer in weathered basement
- Samples from supply wells and boreholes
- Routes to groundwater from poor well completion
- Sources – on-site sanitation

Kabwe, sample sites



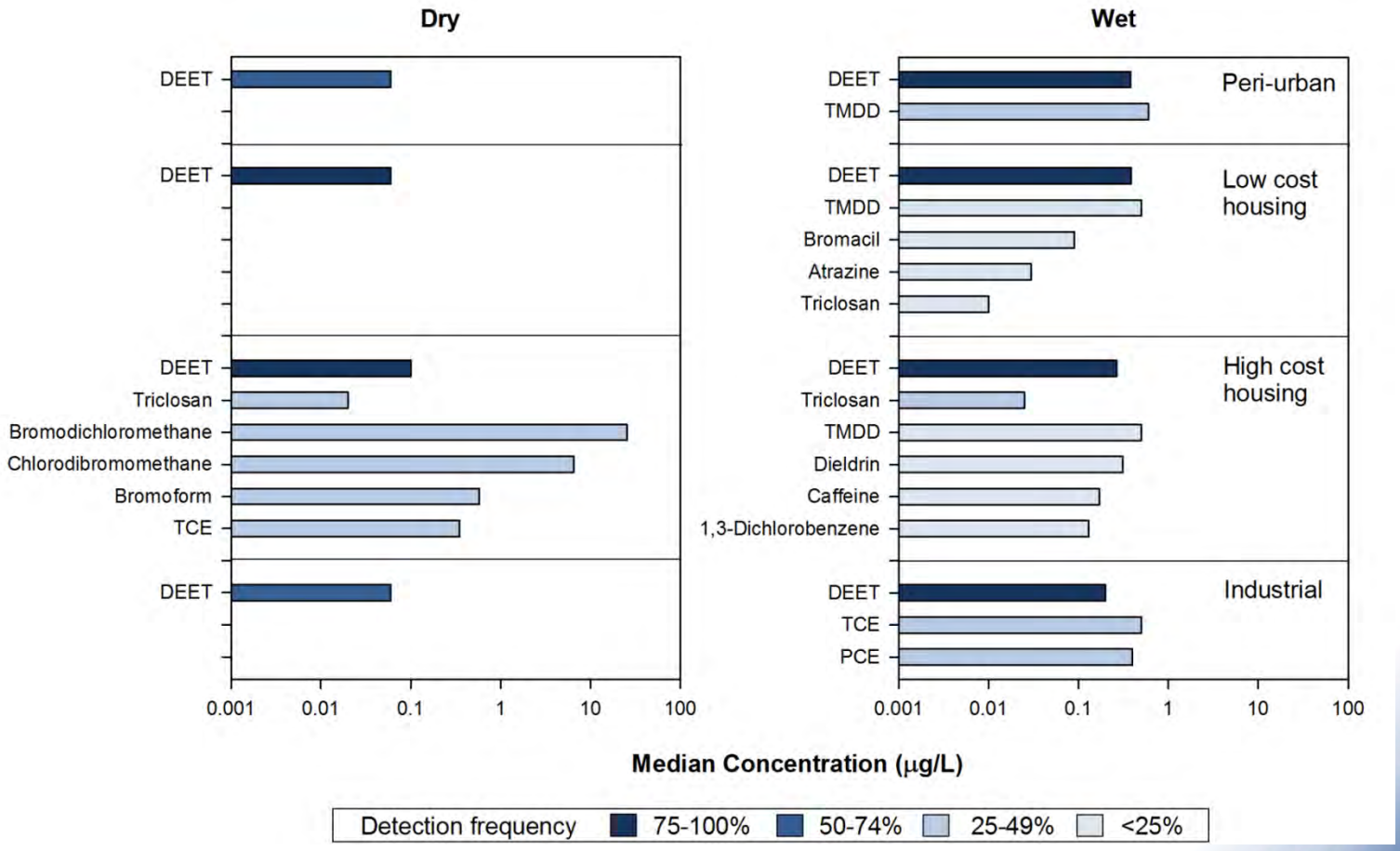
Kabwe

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



Kabwe, key compounds

- PCPs and THMs in dry season in high cost housing only



Sources of microorganics in urban areas

- The sampling process
  - Always be aware of composition of infrastructure i.e. plastic piezometers
  - The sampler
  - Collect meaningful blanks
- Sewer leakage and other wastewater
  - PCPs, caffeine and surfactants
- Other sources
  - Industrial discharges
  - Possible amenity pesticide use in UK
  - Petroleum compounds
  - Road run off

Are emerging contaminants in groundwater important?

- An increasing range of compounds is being detected
- Some are probably no threat to drinking water at such µg/L concentrations, e.g. caffeine
- Others may prove to be in the future
- Urban areas show impact of sewage and industrial wastewater
- We may see increasing PCPs and industrial chemicals as counties develop.
- There is little information on their impact on other groundwater receptors in the environment