



# Emerging organic contaminants in groundwater in urban areas

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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 often less well characterised than surface water, mainly due to lower concentrations
- Some ecotoxicity data available
- 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



[www.gardenorganic.co.uk](http://www.gardenorganic.co.uk)



# 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 (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
- For pesticides:
  - Desethyl, desisopropyl - atrazine
  - 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

# 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

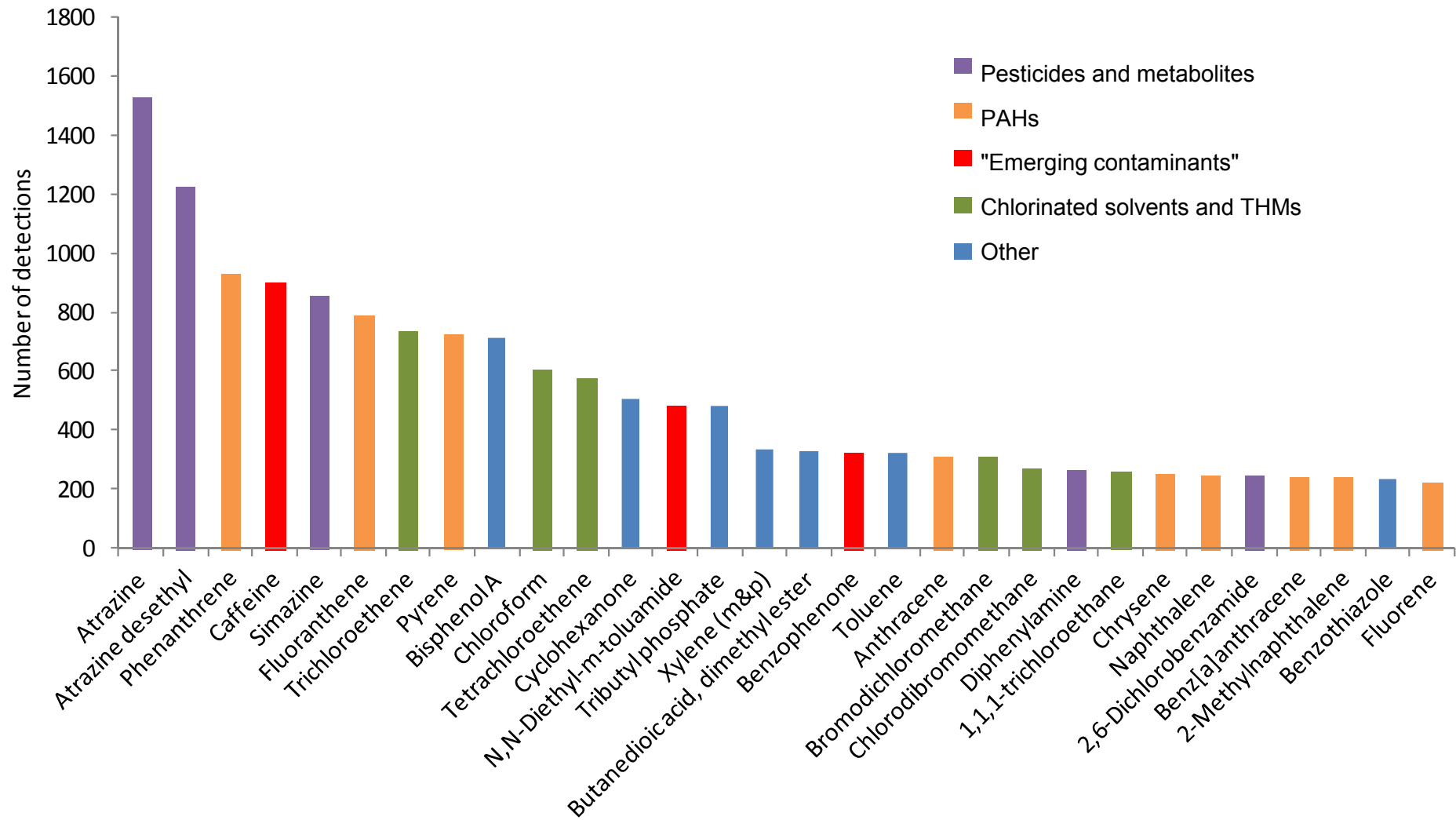
- Priority Substances Directive amendment 2013/39/EU
- Targeted EU-wide monitoring of substances of possible concern to support the prioritisation process in future reviews (10-14 in rolling programme)
- First watch list -  $17\alpha$ -ethinylestradiol,  $17\beta$ -estradiol, diclofenac

## Groundwater

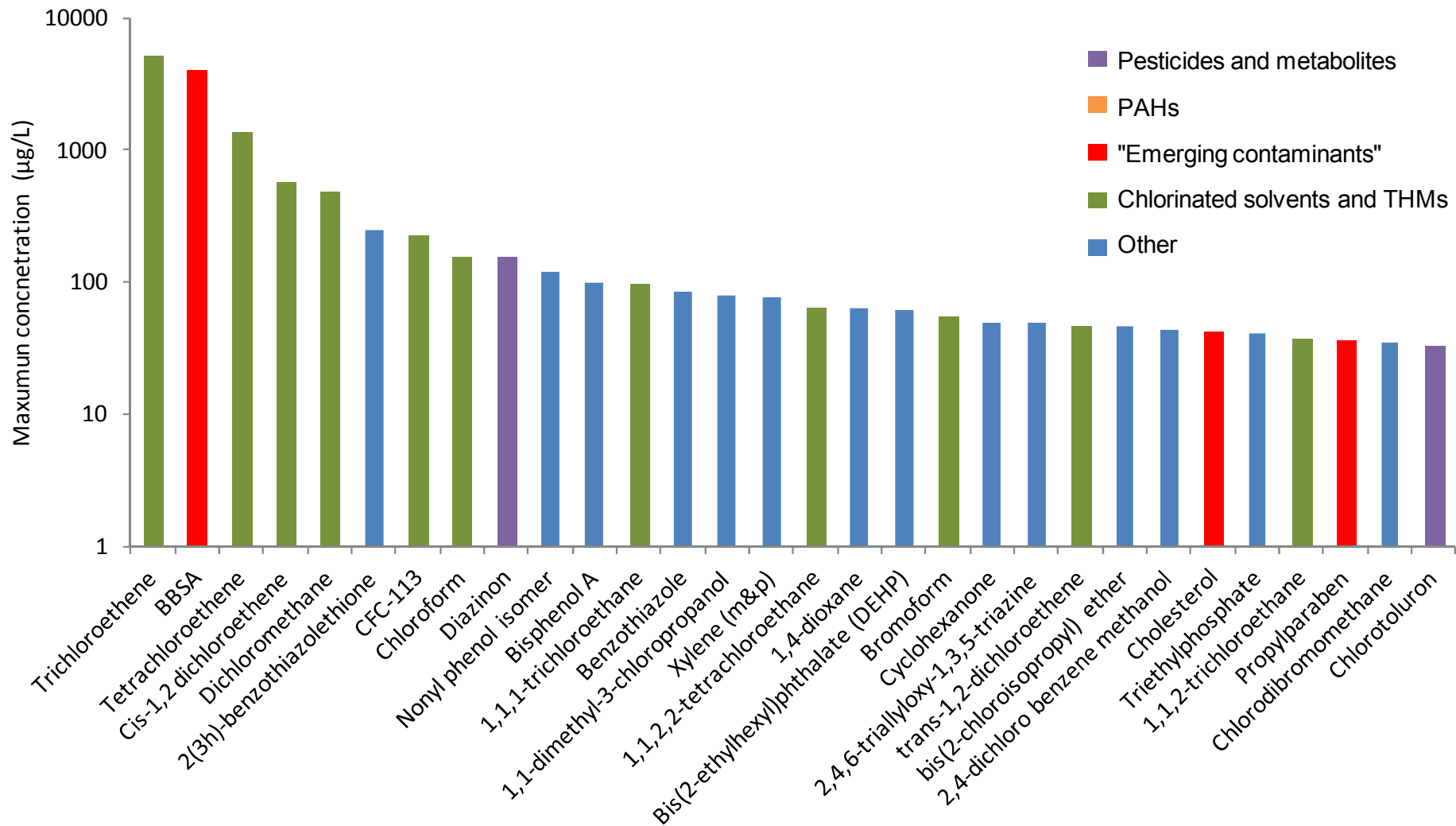
- Draft COM Directive (Recital 4) amending Annex II of the GWD
- Less developed than surface water
- Increased availability of monitoring data to facilitate identification of substances

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

## By frequency of detection



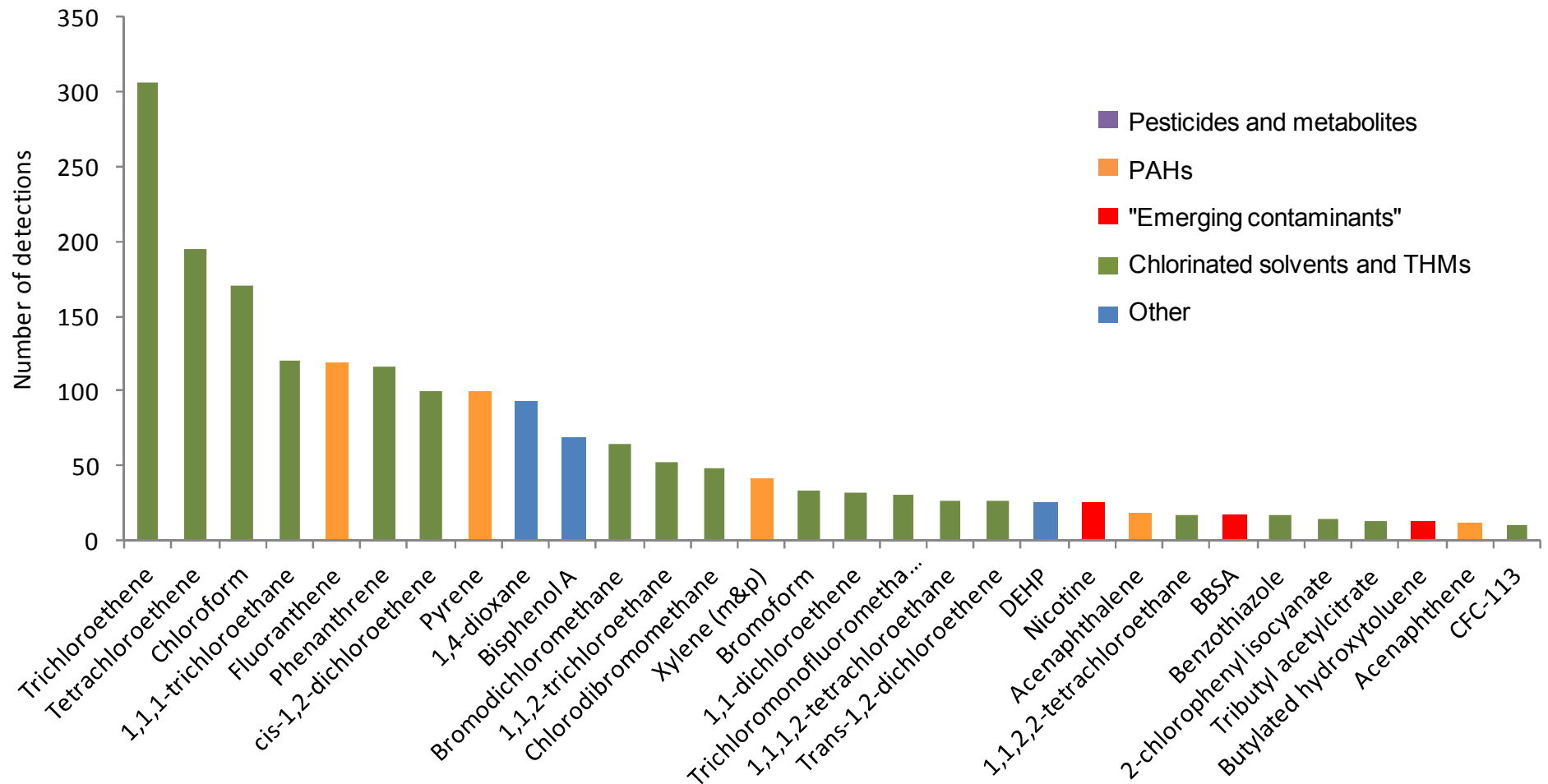
# Top 30 microorganics in Environment Agency groundwater screening data 1993-2012 by maximum concentration





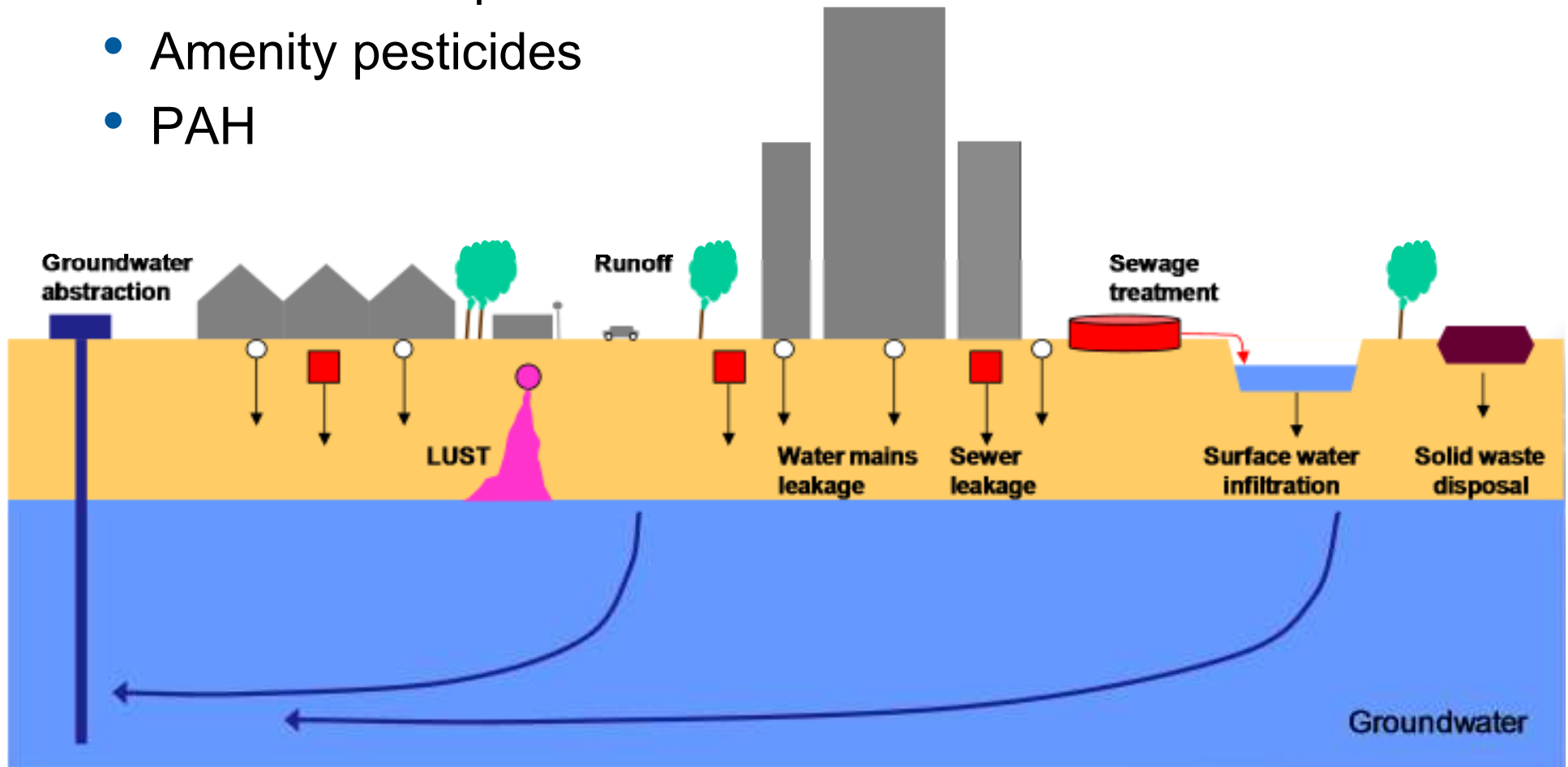
# Top 30 microorganics in Environment Agency groundwater screening data 1993-2012

## By frequency of detection in urban/industrial areas



# ECs in urban groundwater

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



# Sources of microorganics in samples from urban areas

- Sewer leakage and other wastewater
  - PCPs, caffeine and surfactants
- Other sources
  - Industrial discharges
  - Possible amenity pesticide use in UK
  - Petroleum compounds
  - Road run off
- The sampling process
  - Infrastructure - plastic piezometers
  - The sampler – pump components, plastic gloves, sunscreen, insect repellent, PCPs
  - Collect meaningful blanks – use same container as samples

# 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

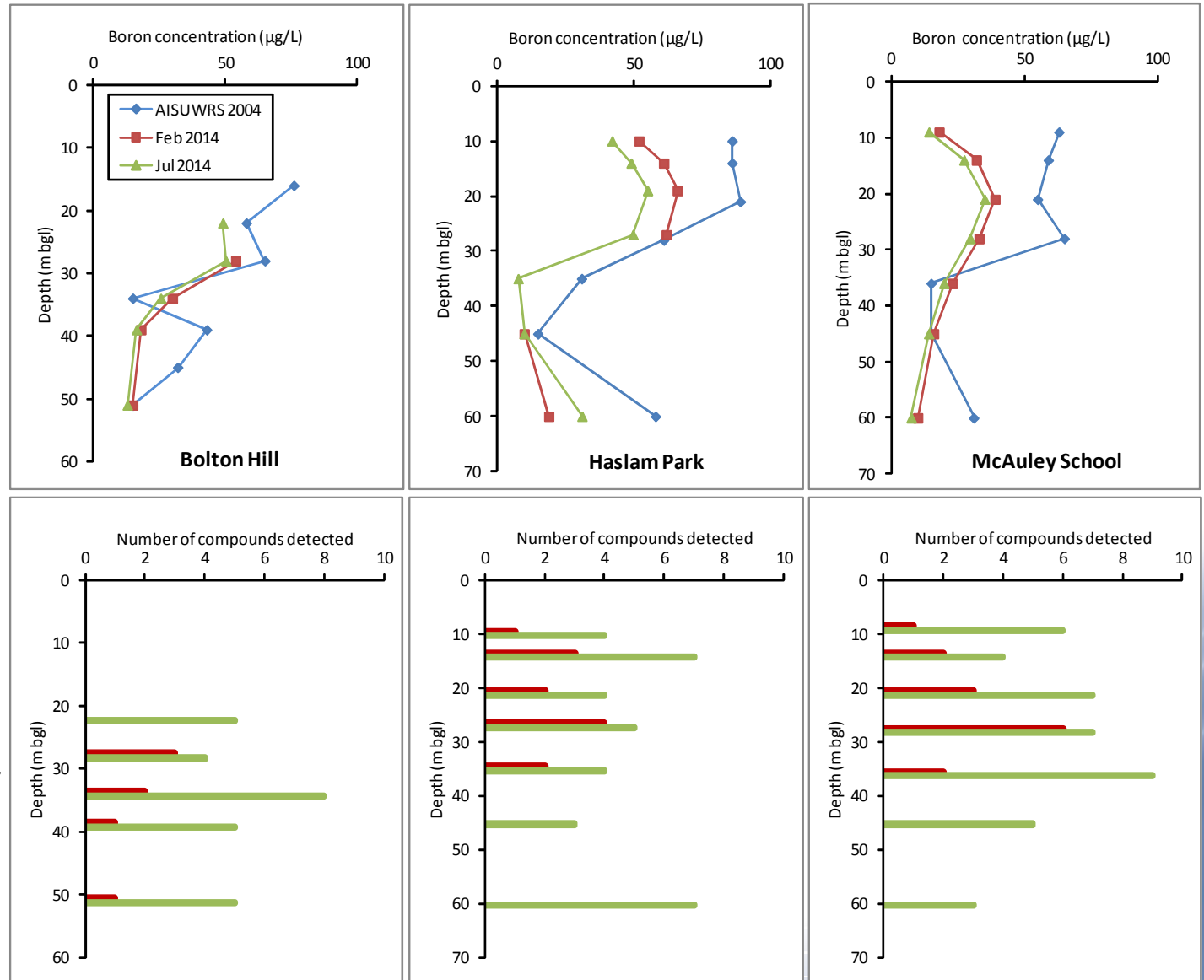
## Nottingham

- 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
- Approach
  - Measure water levels
  - Collect discrete samples at different depths - boreholes or multi-level piezometers



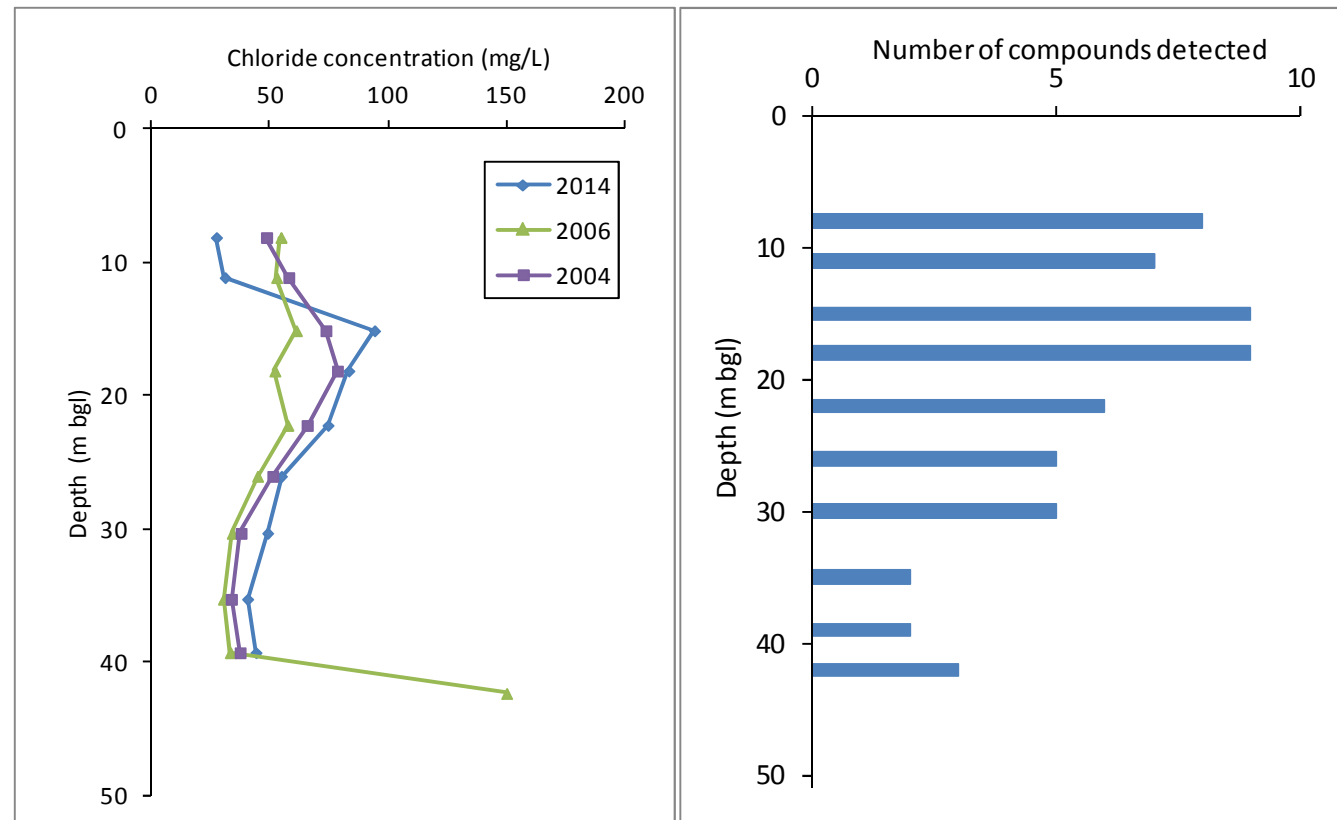
# Doncaster B and MO profiles

- 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



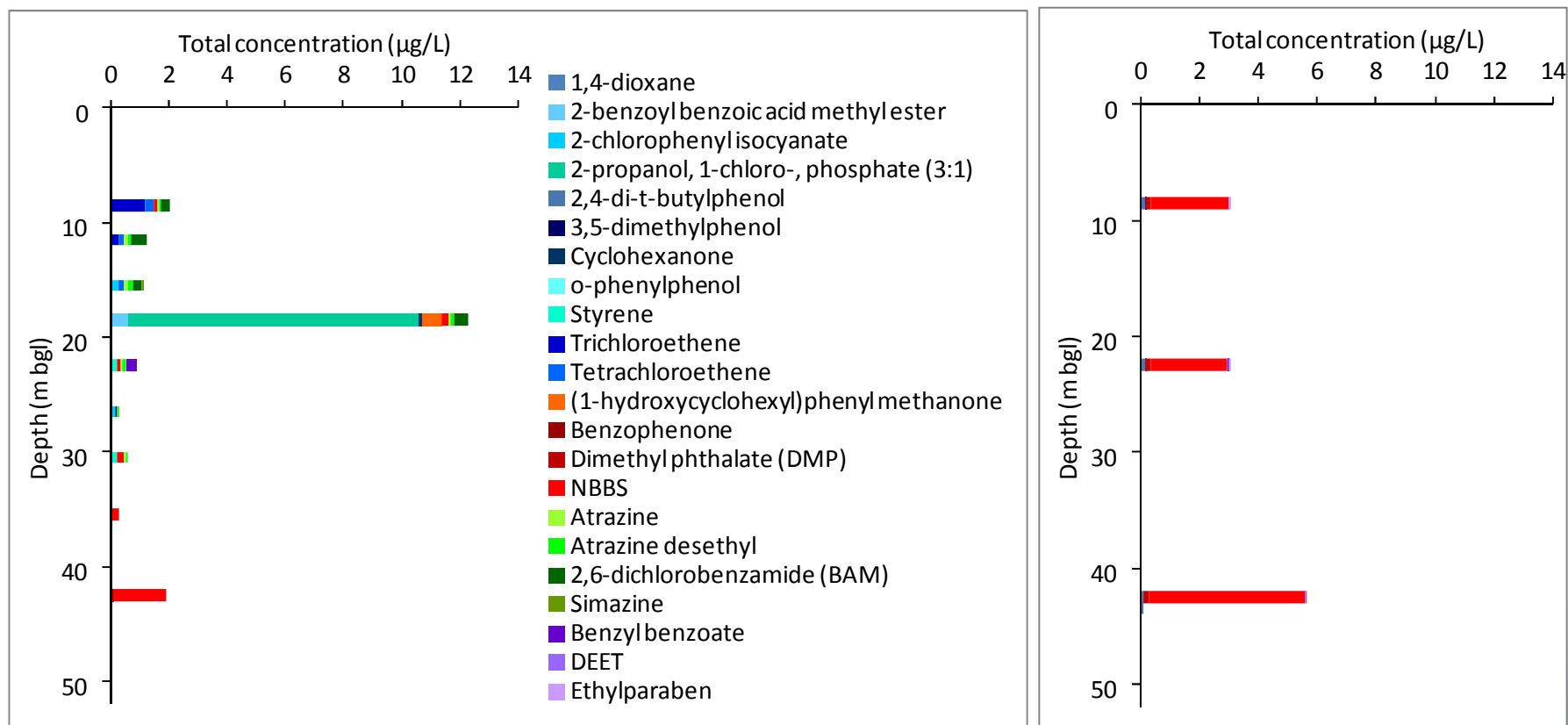
# Nottingham CI and MO profiles

- 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

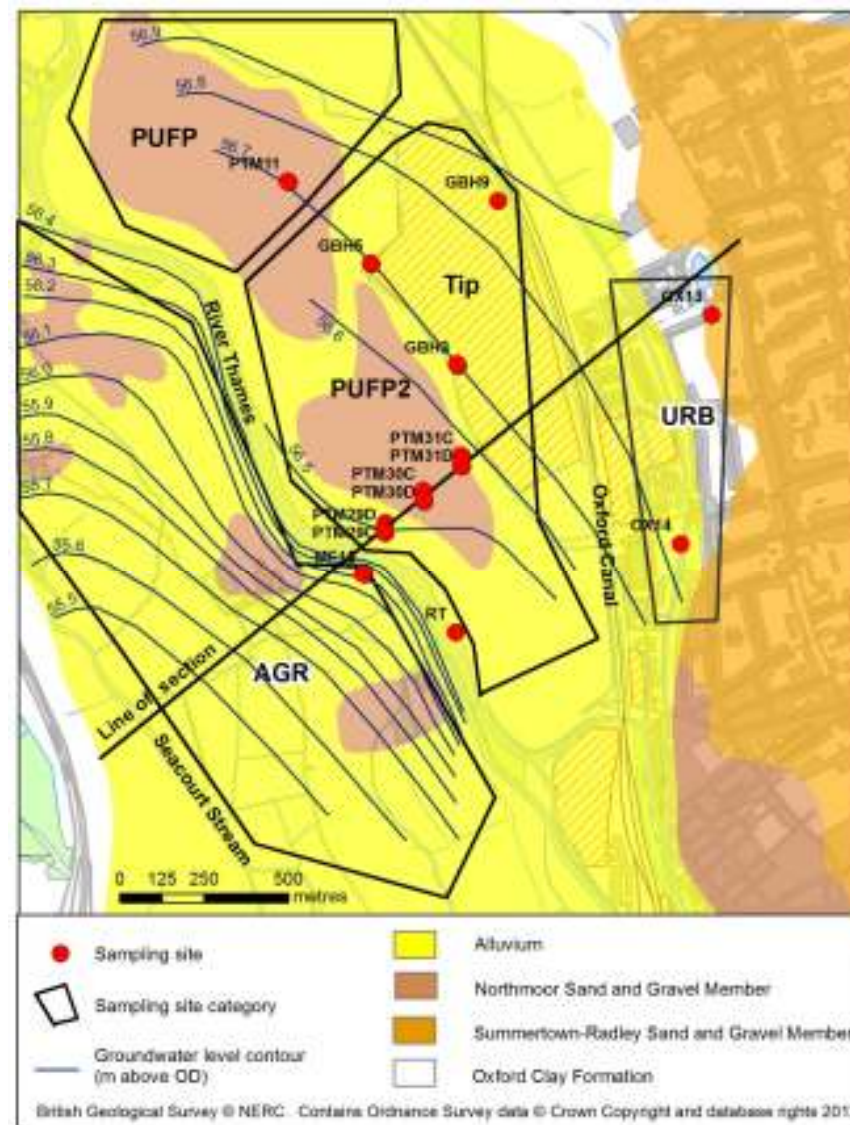
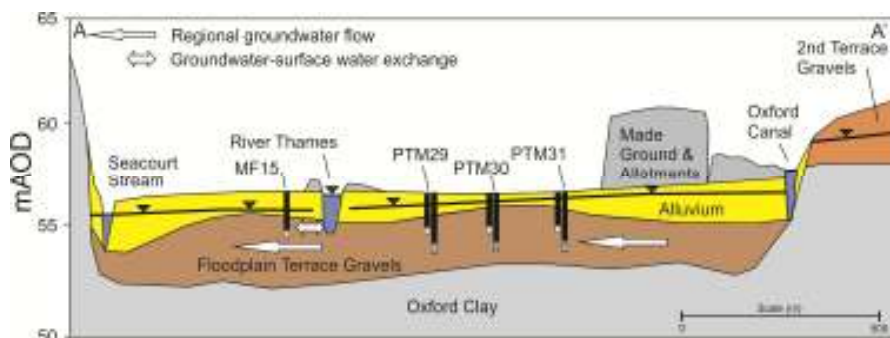
# Summary of compounds found

- **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, octabenzene
- **PCPs (4):** benzyl benzoate, DEET, ethyl paraben, octocrylene
- **Pesticides (4):** atrazine, BAM, desethyl atrazine, simazine
- **Petroleum-related (3):** indane, indene, naphthalene
- Nottingham, Doncaster, Both



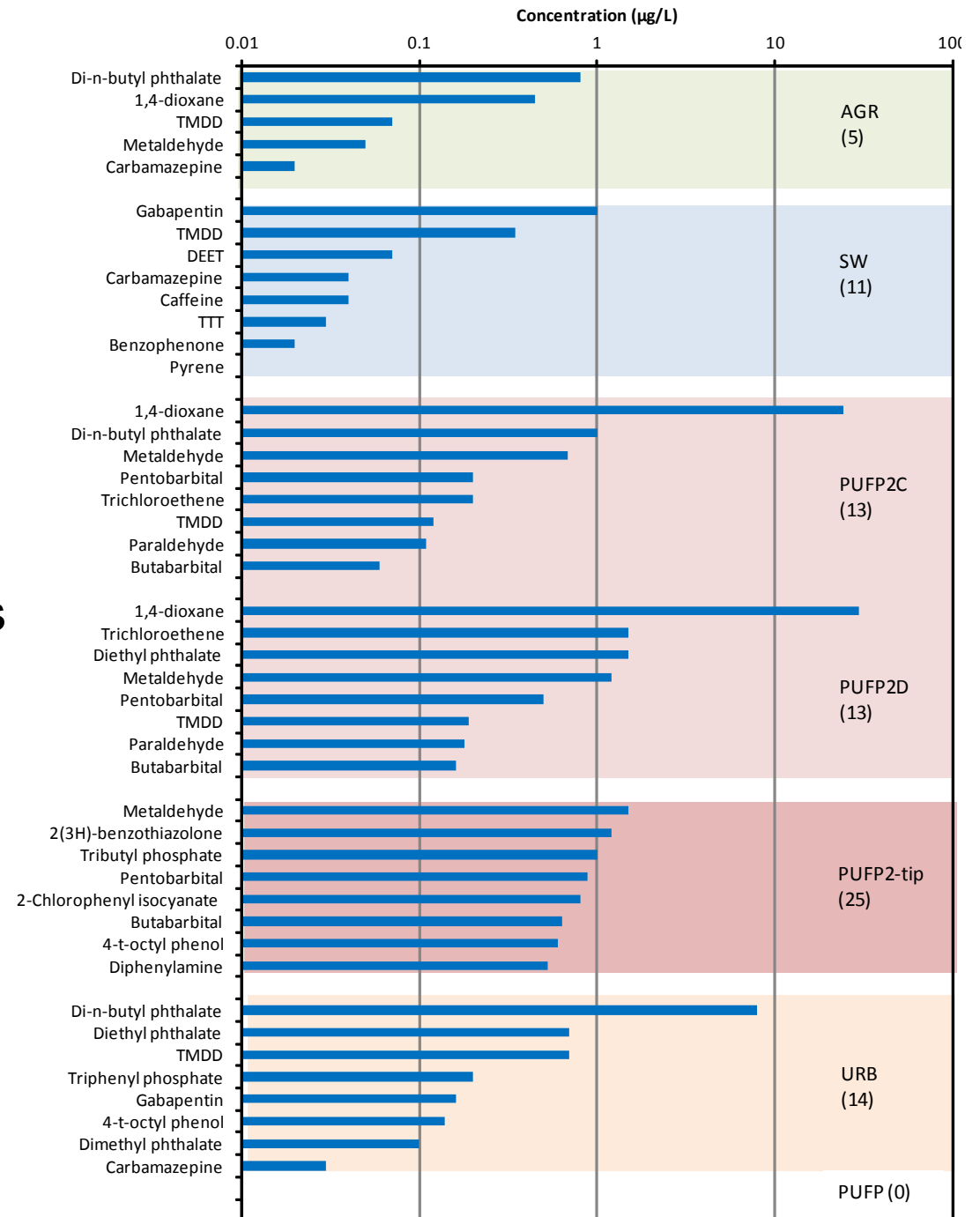
# Oxford Portmeadow

- 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



# Are emerging contaminants in groundwater important?

- An increasing range of compounds is being detected
- Some are probably no threat to drinking water at such  $\mu\text{g/L}$  concentrations, e.g. caffeine
- Others may prove to be in the future
- Urban areas show impact of sewage and industrial wastewater
- There is little information on their impact on other groundwater receptors in the environment