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 diclofenil
  • 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

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
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

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

<table>
<thead>
<tr>
<th>Type</th>
<th>Reference</th>
<th>Exposure</th>
<th>Toxicity</th>
<th>Other</th>
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<tr>
<td></td>
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<td>Chemical properties</td>
<td>Consumption/use</td>
<td>Fate in humans</td>
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<td>Domestic</td>
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<td>OWC</td>
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<td>Storm water priority pollutants</td>
<td>Eriksson 2007</td>
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</tbody>
</table>

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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**

- 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

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
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

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, 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**
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