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NATURAL ENVIRONMENT RESEARCH COUNCIL

Applied geoscience for our changing Earth

Emerging organic groundwater contaminants and their transformation products

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Emerging organic groundwater contaminants and their transformation products

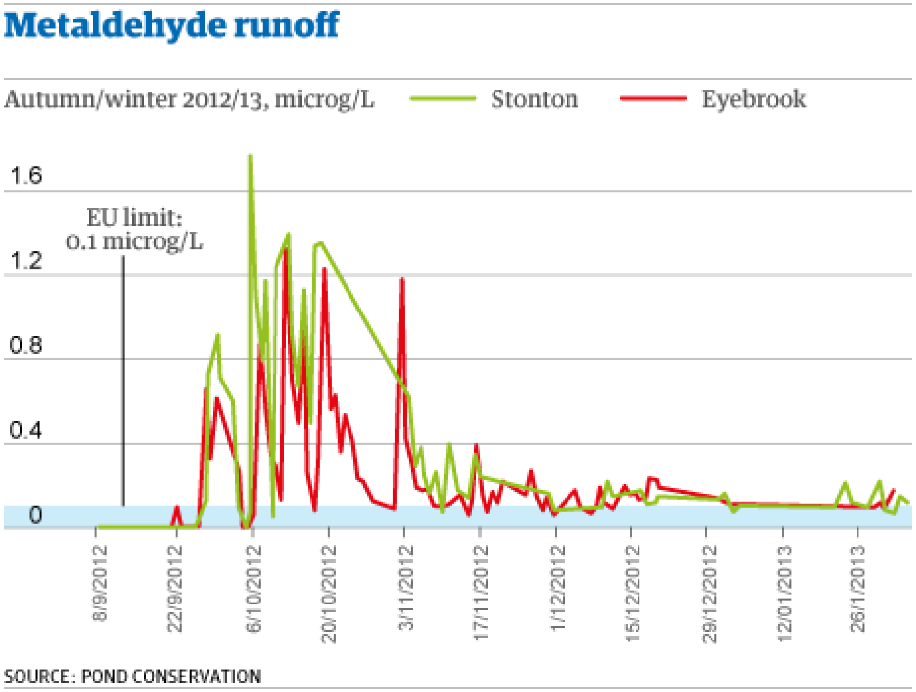
- Definition
- Sources, pathways and receptors
- Examples
- Hydraulic fracturing
- Oxford case study
- Conclusions

http://toxics.usgs.gov/photo_gallery/emercont_page4.html

Emerging contaminants

www.gardenorganic.co.uk

- Anthropogenic organic compounds and their transformation products
- Emerge as result of:
  - Changes in use of manufactured chemicals
  - Advances in analytical techniques
  - Better monitoring



- Many do not have quality standards
- Groundwater is less well characterised than surface water, mainly due to lower concentrations found

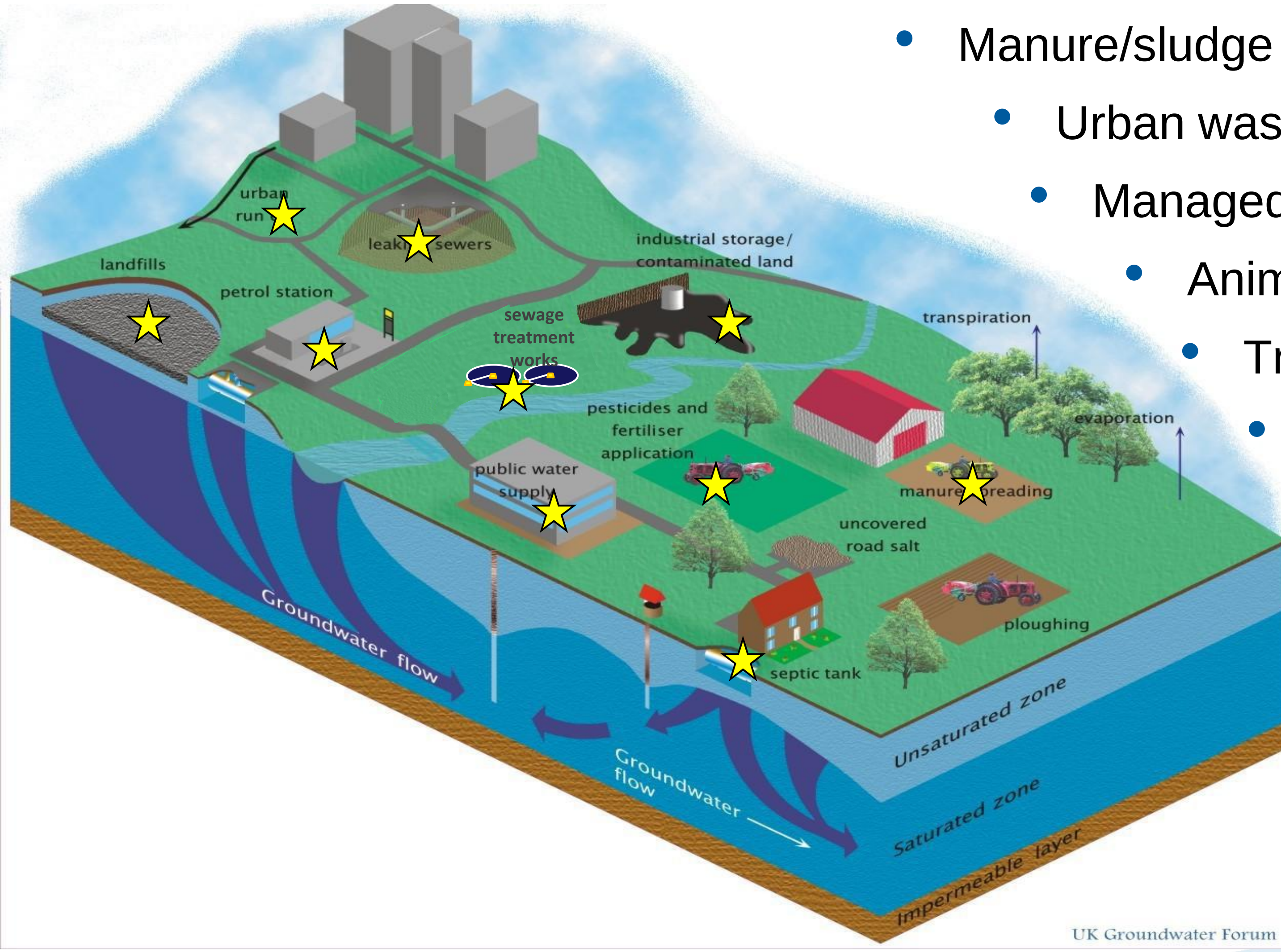
Emerging organic contaminants

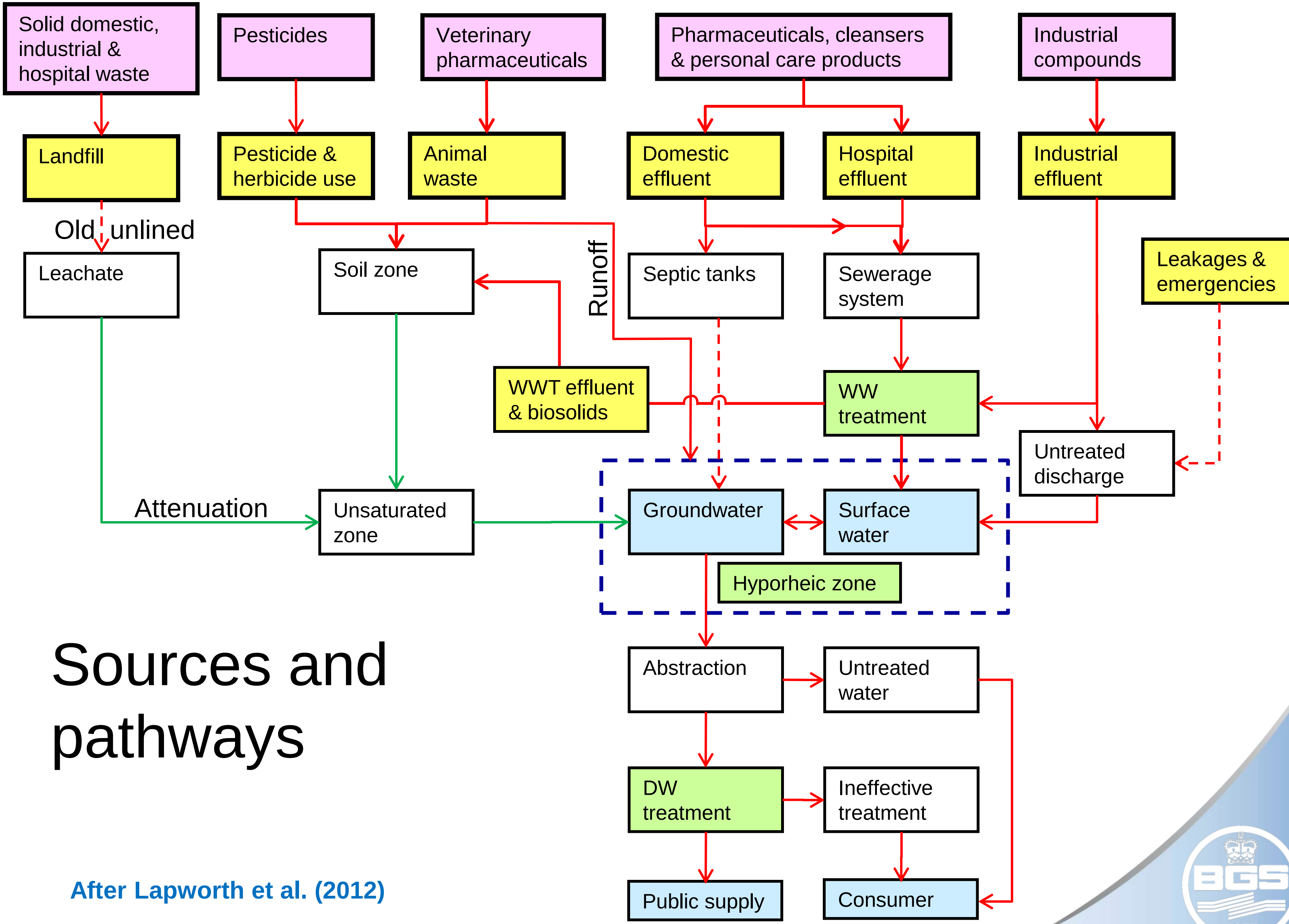
- Pesticides – parent compounds (e.g. metaldehyde), metabolites
- Pharmaceuticals – human, veterinary, illicit
- "Life style" – nicotine, caffeine
- Personal care – DEET, parabens, triclosan, musks, UV filters
- Industrial additives and by-products – dioxanes, bisphenols, MTBE
- Food additives – BHA, 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

Source → Pathway → Receptor → Impact

Sources of ECs in groundwater

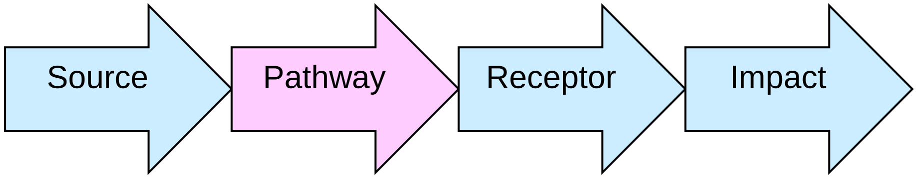
- Treated wastewater discharge to surface water
- Manure/sludge application to soil
- Urban waste water drainage
- Managed aquifer recharge
- Animal waste lagoons
- Transport networks
- Water treatment
- Septic tanks
- Landfill





Sources and pathways

After Lapworth et al. (2012)

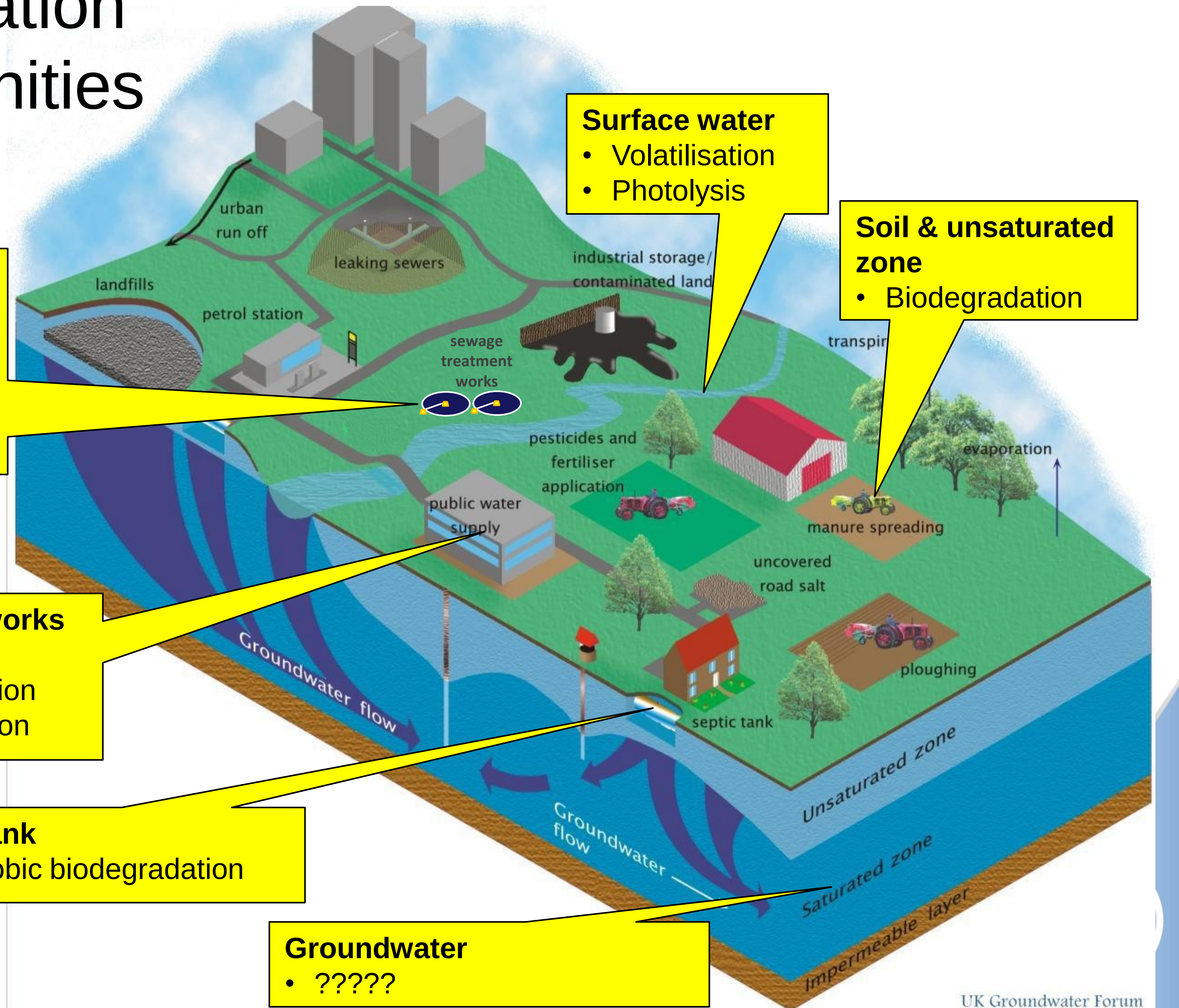


Processes controlling subsurface migration

- Hydraulic regimes and flow-paths − flow, depth to water table, thickness and nature of superficial cover
- Physical and chemical properties of the subsurface media − surface area and charge, organic matter content
- Microbiological processes − population dynamics, factors limiting biological growth
- Redox and other aqueous chemical factors − pH and ionic strength
- Intrinsic molecular properties of the compounds − K_{ow} and D_{ow}
- Potential for colloid facilitated transport

Stuart & Lapworth et al. (2014)

Degradation opportunities



Surface water
- Volatilisation
- Photolysis

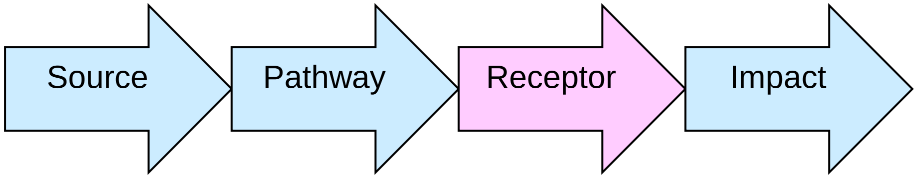
Soil & unsaturated zone
- Biodegradation

Sewage treatment works
- Settling
- Coagulation
- Anaerobic biodegradation

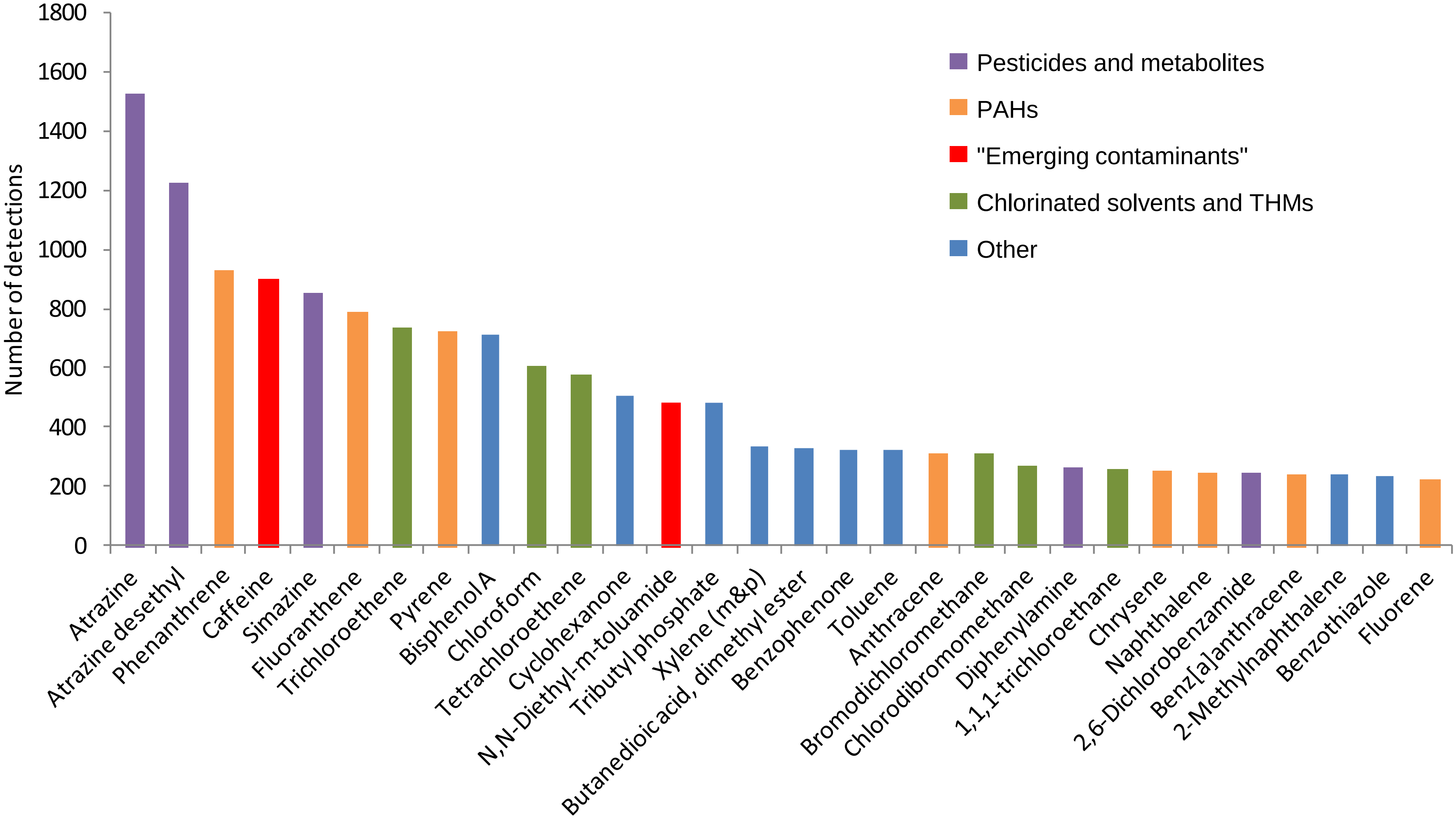
Water treatment works
- GAC
- Enhanced oxidation
- Membrane filtration

Septic tank
- Anaerobic biodegradation

Groundwater
- ?????



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



Drinking water treatment

- Low percentage removed by clarification
- Many ECs not fully removed by combined or free chlorine and can produce undesirable by-products
- GAC or PAC filtration useful for compounds with K_{ow}>3
- Ozonation effective for compounds with double bonds, aromatic structure or heteroatoms such as N or S
- Also other advanced oxidation methods (AOP) e.g. using H_2O_2 or OH radical generated by UV, sensitised processes using semiconductors
- Membrane or nano filtration can be effective for negatively charged compounds

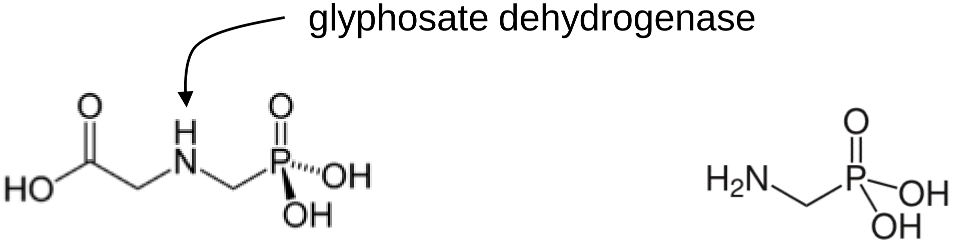
Regulatory framework

- Water Framework Directive (2000/60/EC); Groundwater Daughter Directive (2006/118/EC); Priority Substances Directive (2008/105/EC)
  - Defined 33 Priority Substances + 8 other pollutants
  - Required setting of Threshold Values for all pollutants which put the groundwater body at risk
- **Groundwater (England & Wales) Regulations (2009)**
  - Aim to avoid pollution by preventing the input of Hazardous Substances and limiting the introduction of non-hazardous pollutants to groundwater
- **Environmental Permitting (England & Wales) Regulations (2013)**
  - Replaces parts of above, defines substances, or groups of substances, for which releases are controlled and sets limits.

- Drinking Water Directive (98/83/EC)
- **Water Supply (Water Quality) Regulations, England & Wales (2000)**
  - Pesticides (metabolites), aromatic hydrocarbons, chlorinated solvents and some disinfection by-products are included
  - Many emerging contaminants i.e. pharmaceuticals, “personal care” and “lifestyle” compounds are not covered

Pesticides

- TPs often more mobile and persistent than their parents and found more frequently or at higher concentrations − BAM from diclobenil, AMPA from glyphosate
- TPs often more polar than their parent and more difficult to analyse for
- Some formed as TPs of other pesticides − carbendazim from benomyl

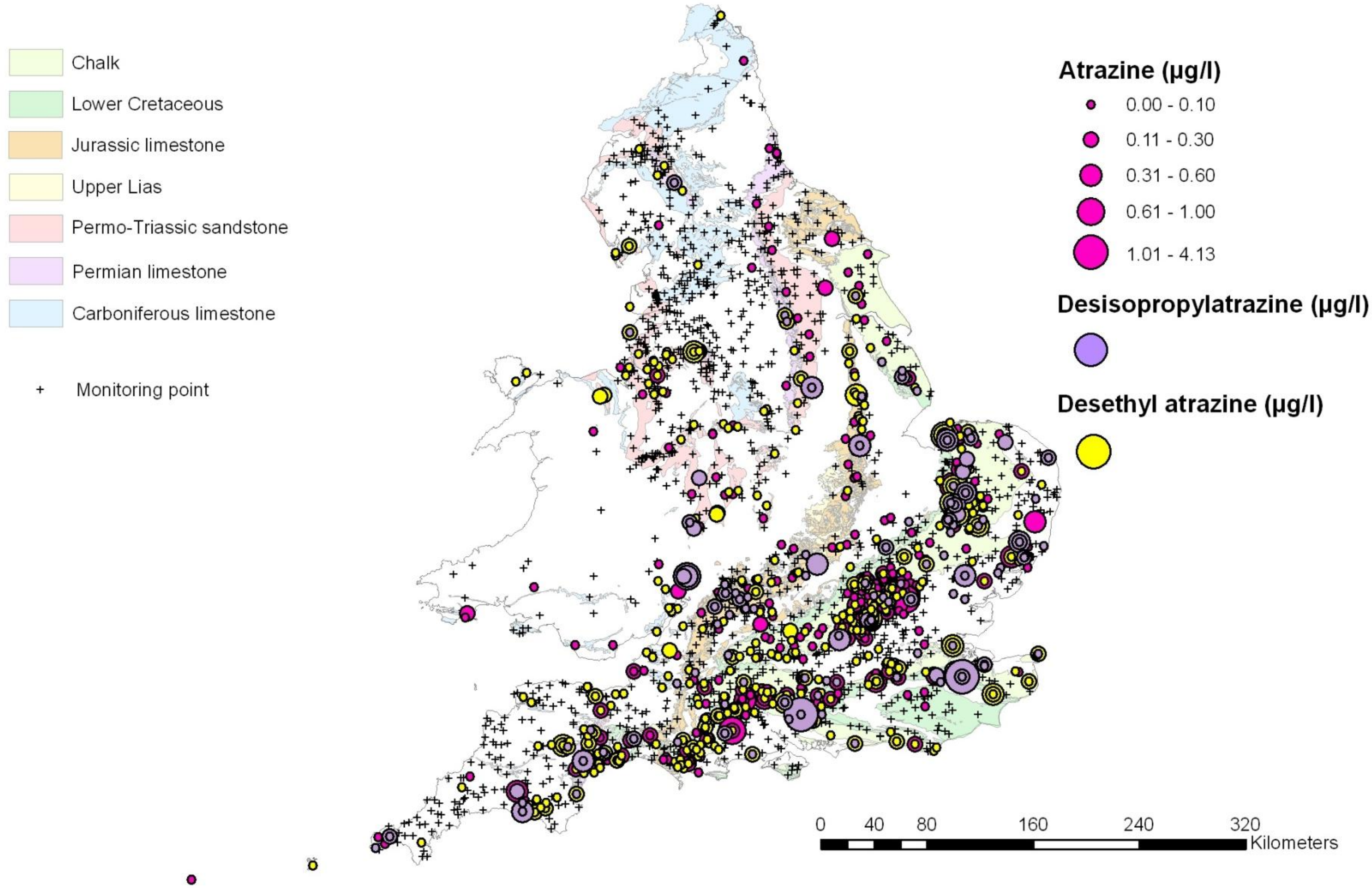


glyphosate (*N*-(phosphonomethyl)glycine) → AMPA (aminomethylphosphonic acid) + glyoxylate

BAM - 2,6-dichlorobenzamide

Holtze et al. (2008); Kolpin et al. (2000)

Atrazine and its metabolites in groundwater



Environment Agency monitoring 1993 -2012
using semi-quantitative GCMS scanning

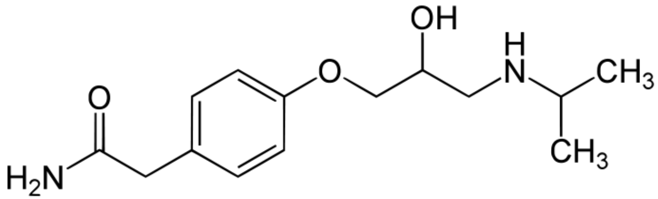
Pharmaceuticals

- Next most frequently reported group after pesticides
- Most common are:
  - Analgesics (paracetamol>ibuprofen>phenazone>propyphenazone>salicylic acid)
  - Anti-inflammatories (ibuprofen>ketoprofen>diclofenac)
  - Antibiotics (triclosan>sulfamethoxazole>lincomycin>erythromycin)
  - Anti-epileptics (carbamazepine)
  - Barbiturates (primidone)
  - Lipid regulators (fenofibrate, clofibrate)
  - Insecticides (DEET)
  - X-ray contrasting agents (iopamidol)
  - Veterinary medicines (sulfamethazine, monensin, tylosin)
- TPs
  - Clofibric acid from clofibrate
  - 4-hydroxypropanolol from propanolol (β-blocker)

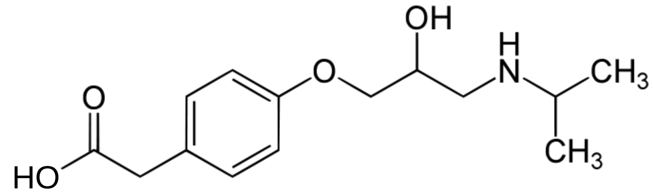
Lapworth et al. (2012); Barnes et al. (2004, 2008); Watanabe et al. (2010); Scheytt et al (2007); López-Serna (2013)

Pharmaceuticals degradation

- Recalcitrant TPs



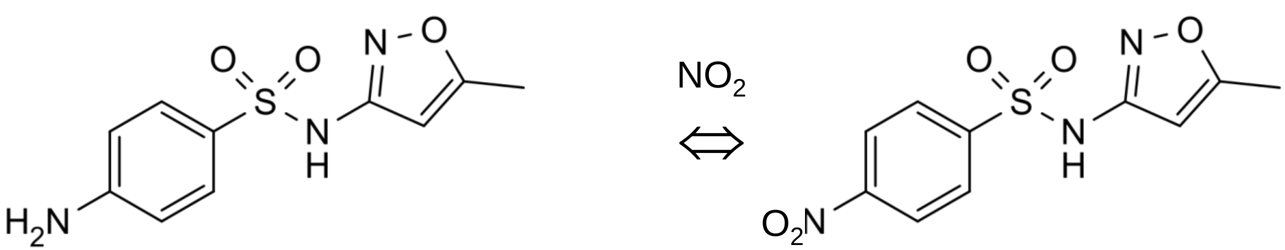
Atenolol



Atenololic acid

- Influenced by redox
  - Phenazones, naproxen, erythromycin only degraded under oxic conditions

- May be deactivated (not degraded) e.g. by nitrite



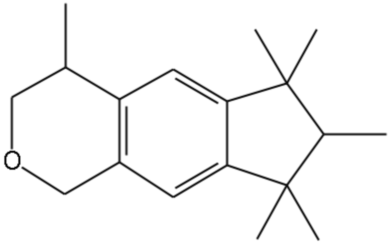
Sulfamethoxazole

4-nitro-sulfamethoxazole

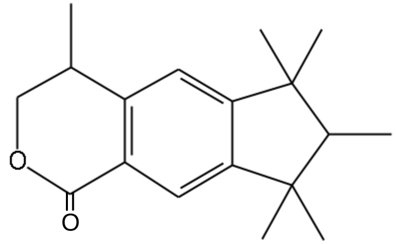
Barbieri et al (2012a,b): Massmann et al. (2008)

Personal care products

- Skin care products:
  - UV blockers, isopropyl myristate, phenoxy-ethanol, lilial
- Parabens and triclosan
- Polycyclic musks
  - Galaxolide (HHCB), tonalide (AHTN), celestolide (ADBI) and phantolide (AHDI), and the nitro musks (musk xylene and musk ketone)
  - Musks are degraded to more polar compounds in water treatment and in the soil
  - HHCB-lactone, 2-amino-musk ketone, 4-amino musk ketone, 2-amino-musk xylene in effluents



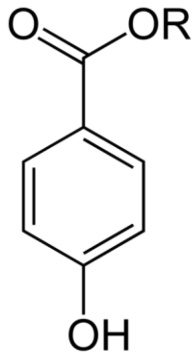
HHCB

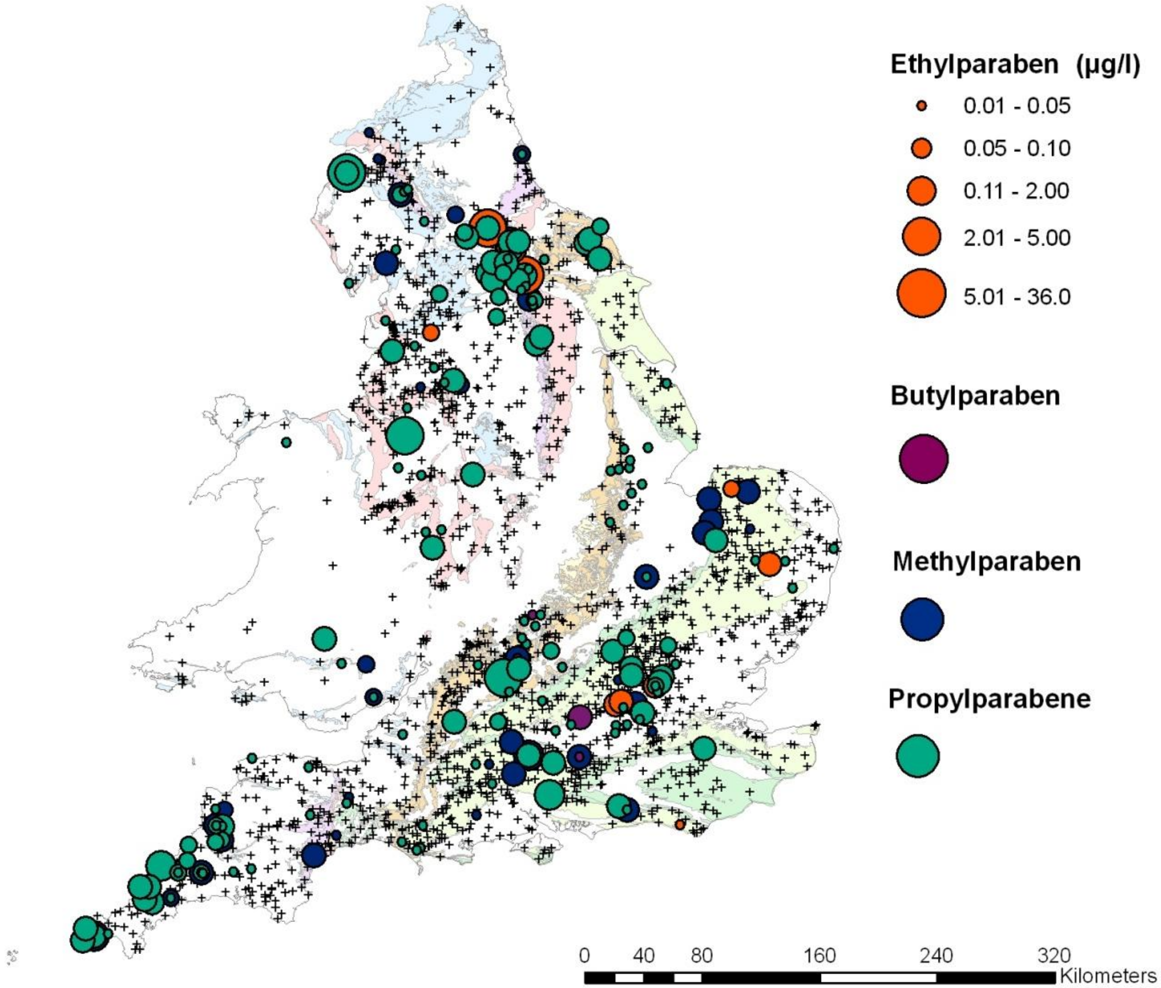


HHCB-lactone from autoxidative formation

Martin et al. (2007), Matamoros et al, (2009)

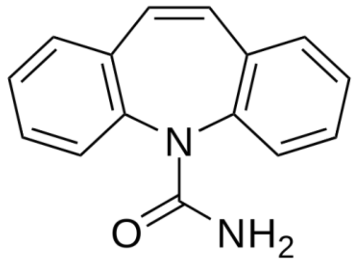
Parabens in groundwater

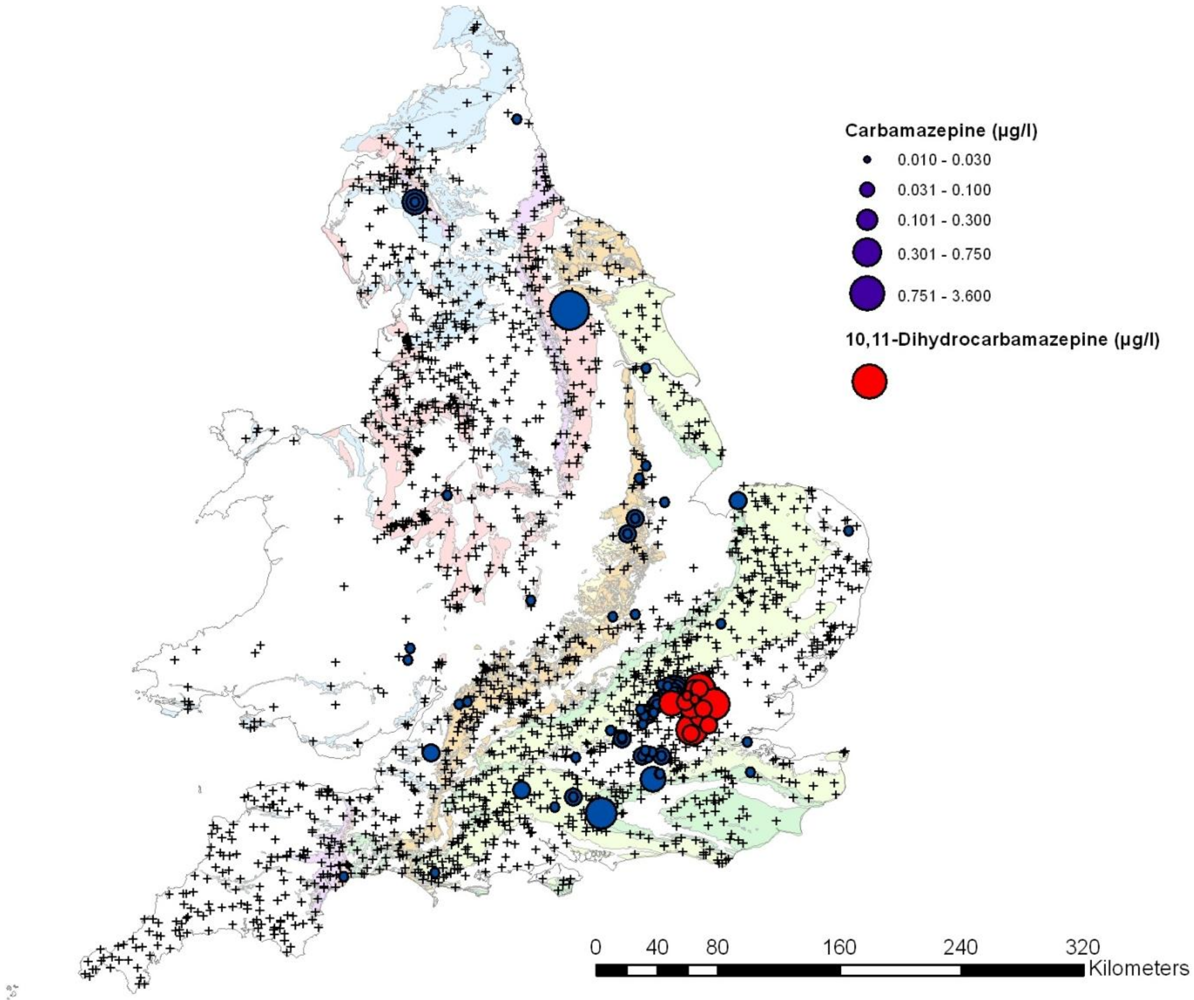




- Bactericidal and fungicidal properties
- Widely used
- But potential links with cancer and endocrine disruption
- Environment Agency monitoring 1993 -2012 using semi-quantitative GCMS scanning

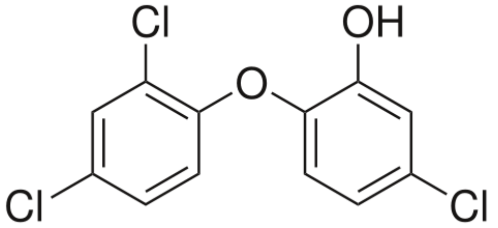
Carbamazepine in groundwater

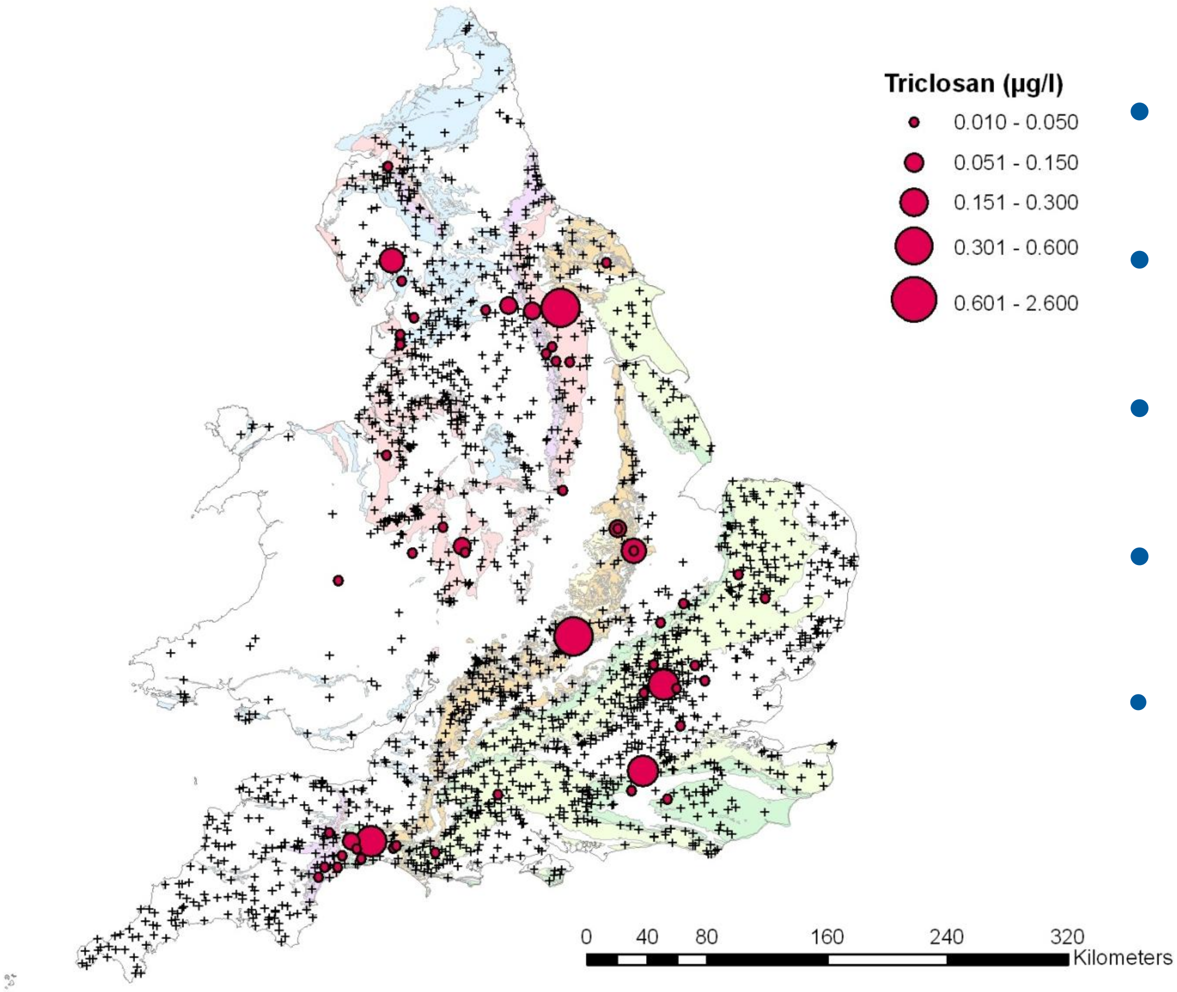




- Used to treat epilepsy and bipolar disorder
- Possible biotransformation product
- Environment Agency monitoring 1993 -2012 using semi-quantitative GCMS scanning

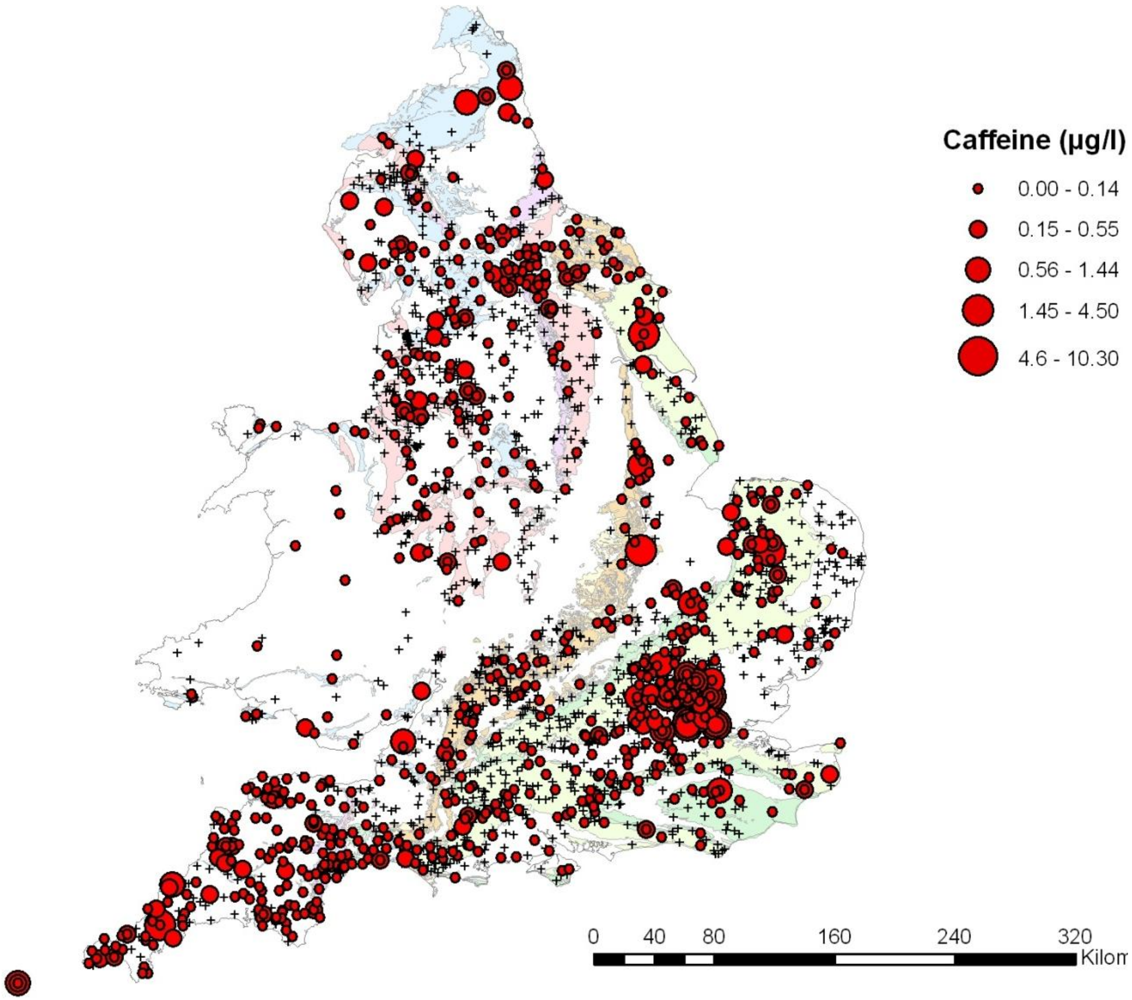
Triclosan in groundwater





- Bactericidal and fungicidal properties
- Used since 1972 especially for hands
- Bacterial resistance concerns
- Reacts with chlorine to dioxin precursor
- Environment Agency monitoring 1993 -2012 using semi-quantitative GCMS scanning

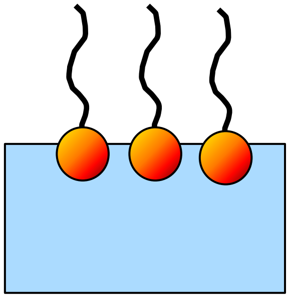
Caffeine and nicotine



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

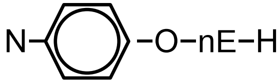
Barnes et al. (2008); Seiler et al. (1999); Swartz et al. (2006)

Alkyl phenols and other EDCs

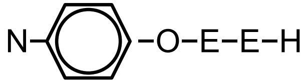


Alkylphenyl ethoxylates and polyethoxylates

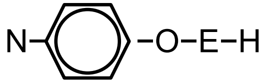
- Both parents and metabolites persistent in groundwater
  - APEOs degraded by progressive shortening of ethoxylate chain to AP2EO and AP1EO
  - And/or transformation by oxidation of ethoxylate chain to AP2EC and AP1EC in aerobic conditions
  - Anaerobic treatment favours AP production
- Degradation more rapid in oxic water



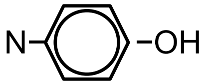
Nonylphenolpolyethoxylate(NPnEO)



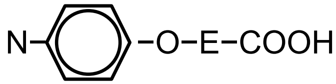
Nonylphenoldiethoxylate(NP2EO)



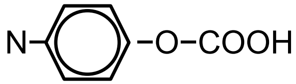
Nonylphenolmonoethoxylate(NP1EO)



Nonyl phenol(NP)

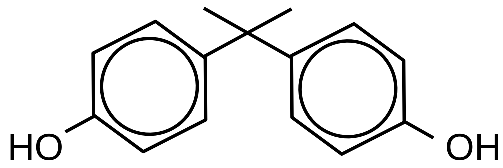


Nonylphenoxyethoxyacetic acid(NP2EC)



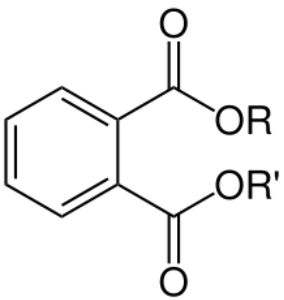
Nonylphenoxyacetic acid(NP1EC)

EDCs



Bisphenols

- Bisphenol A
  - Degraded by hydrolysis at quaternary carbon atom under aerobic conditions
  - Both single and double ring derivatives possible
  - Only parent usually recorded in gw
  - Few detects of diglycidal ether
- Bisphenol F - 2,2’-bisphenol F detected



Phthalates

- Widely detected in groundwater - subject to sampling artefacts
- Persistent under anaerobic conditions
- Dealkylated metabolites anticipated
- DEP can be lost but DEHP, DBP etc can penetrate to depth

Refs

Brominated and fluorinated compounds

PBDE & PDB

- Flame retardants - polybrominated diphenyl ether and polybrominated biphenyl cogeners.
  - Abiotic PDBE degradation dominated by photolysis
  - Microbially mediated PDBE debromination not always demonstrated
  - Concern that lower de-brominated PBDEs more toxic than parent

PFOS and PFOA

- Perfluoroalkane sulfonates and perfluoroalkanoic acids
- Many uses including fire-fighting foams and common household products
  - Widely detected in groundwater
  - PFOS very resistant to degradation

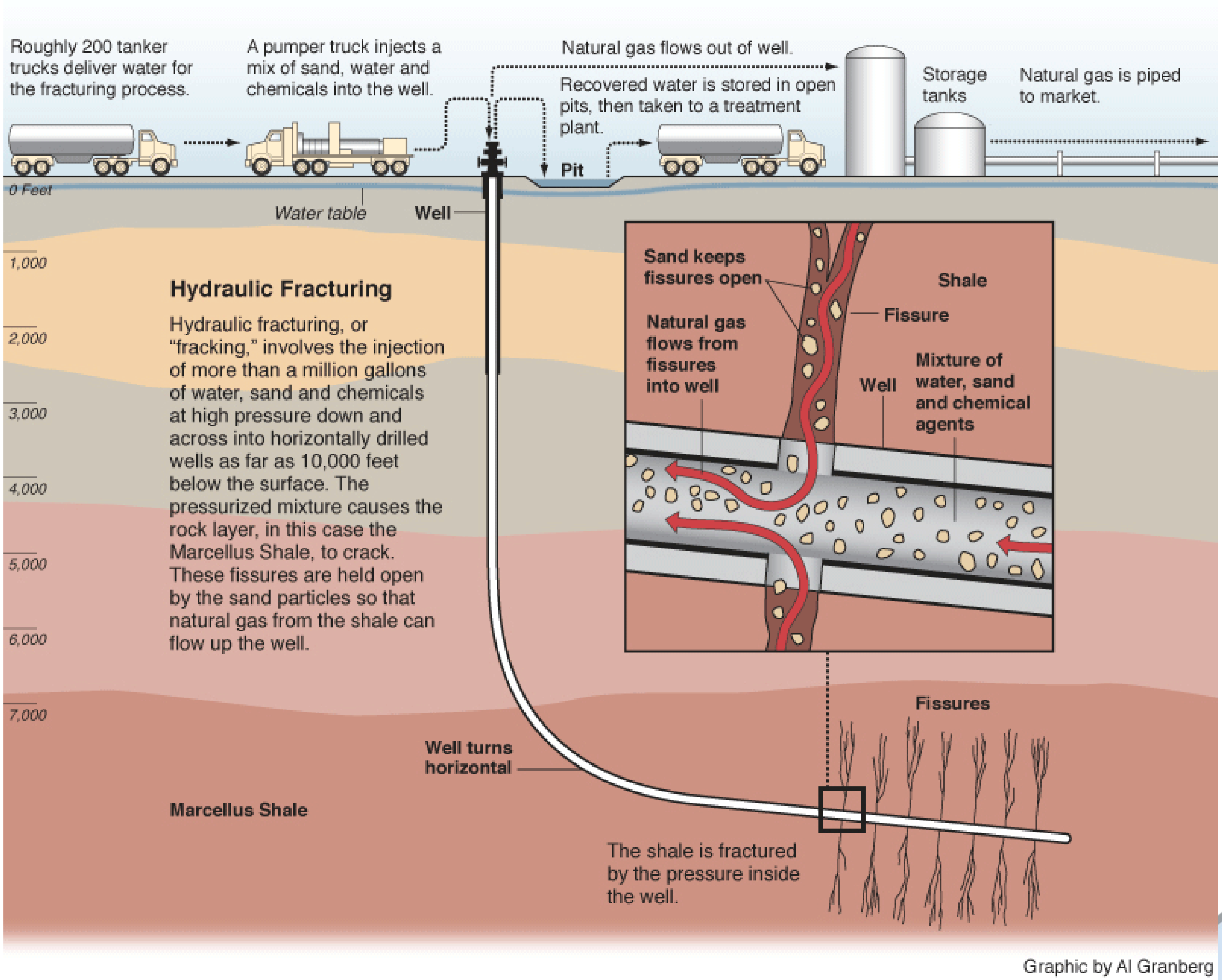
Robrock et al. (2006); Stapleton (2006); Environment Agency (2008)

Shale gas

- Natural gas trapped in fine-grained shales
- Potential across Europe

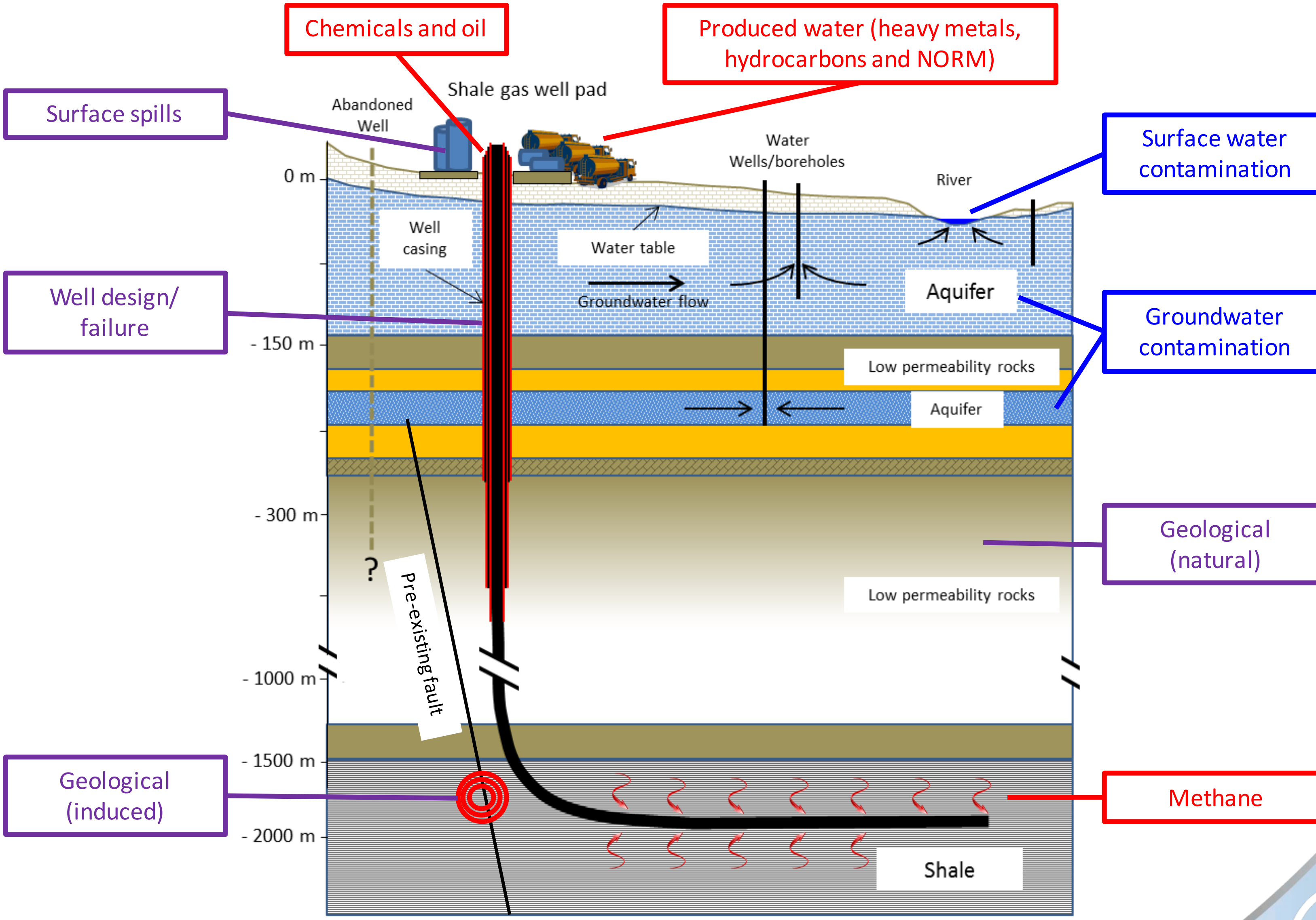
- In UK potential shales include:
  - Lower Carboniferous (Midland Valley of Scotland and Northern England)
  - Jurassic - Lias, Oxford and Kimmeridge Clays (Southern England)
  - Lower Cretaceous may have potential for biogenic gas

Hydraulic fracturing (fracking) process



Potential sources of contamination

- Shale gas
  - Methane and other light hydrocarbons
  - Carbon dioxide, hydrogen sulphide, noble gases
- Fracking fluid
- Flowback / produced water
  - Salinity
  - Heavy metals
  - Naturally occurring radioactive material (NORM)
  - Fracking fluid additives


Chemicals and oil
Produced water (heavy metals, hydrocarbons and NORM)
Surface spills
Abandoned Well
Shale gas well pad
Water Wells/boreholes
River
Surface water contamination
0 m
Well casing
Water table
Groundwater flow
Aquifer
Well design/ failure
Groundwater contamination
- 150 m
Low permeability rocks
Aquifer
- 300 m
Geological (natural)
?
Pre-existing fault
Low permeability rocks
- 1000 m
- 1500 m
Geological (induced)
Methane
- 2000 m
Shale
1835

Hydraulic fracturing fluid

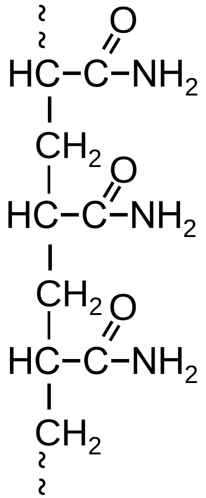
Constituent	Composition (% by vol)	Example	Purpose
Water and sand	99.50	Sand suspension	“Proppant” sand grains hold microfractures open
Acid	0.123	**Hydrochloric acid**	Dissolves minerals and initiates cracks in the rock
Friction reducer	0.088	**Polyacrylamide*** or mineral oil	Minimizes friction between the fluid and the pipe
Surfactant	0.085	Isopropanol	Increases the viscosity of the fracture fluid
Salt	0.060	Potassium chloride	Creates a brine carrier fluid
Gelling agent	0.056	Guar gum or hydroxyethyl cellulose	Thickens water to suspend the sand
Scale inhibitor	0.043	Ethylene glycol	Prevents scale deposits in pipes
pH-adjusting agent	0.011	Sodium or potassium carbonate	Maintains effectiveness of chemical additives
Breaker	0.01	Ammonium persulphate	Allows a delayed breakdown of gel polymer chains
Crosslinker	0.007	Borate salts	Maintains fluid viscosity as temperature increases
Iron control	0.004	Citric acid	Prevents precipitation of metal oxides
Corrosion inhibitor	0.002	n,n-dimethyl formamide	Prevents pipe corrosion
Biocide	0.001	**Glutaraldehyde***	Minimizes growth of bacteria that produce corrosive and toxic by-products
Oxygen scavenger	-	Ammonium bisulphite	Removes oxygen from the water to prevent corrosion

***Used in the UK for shale gas fracking - ENDS Special Report “UK shale gas and the environment” -**

Hydraulic fracturing fluid development

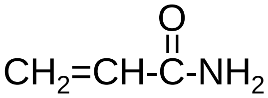
- Historically a wide range of chemicals used in addition to water and proppant
- Fracking fluid and flowback/ produced water can contain:
  - BTEX, phenols, dioxanes, glycols, aldehydes, PAH, phthalates, chlorinated solvents, heterocyclics
- Now move to use less hazardous and simpler mixtures possibly using food and household product constituents:
  - enzymes, ethoxylated sugar-based fatty acid esters, hydrogenated vegetable oils, sulphonated alcohols and polysaccharides

Degradation of fluid additives

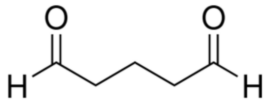


Polyacrylamide

- Originally thought to degrade to acrylamide monomer in soil and groundwater (known neurotoxic) but now no evidence
- Amide nitrogen susceptible and molecular weight progressively reduced
- When 6-7 units long can be degraded by soil microbes under aerobic conditions



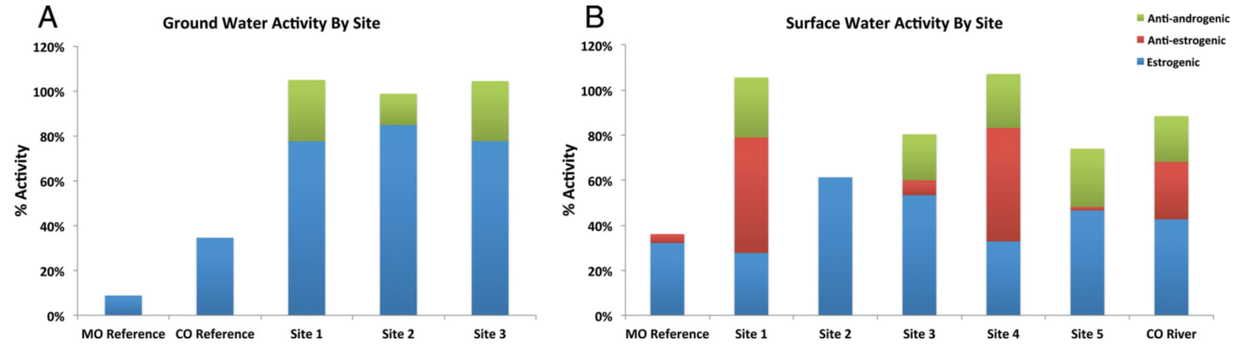
Glutaraldehyde



- Not approved for pesticide use
- Has DT_{50} in soil of a few days
- Metabolites less toxic than parents – aerobic → glutaric acid → carbon dioxide – anaerobic → 1,5-pentadiol

(Langenhoff (2011) - Deltares)

What has actually been found

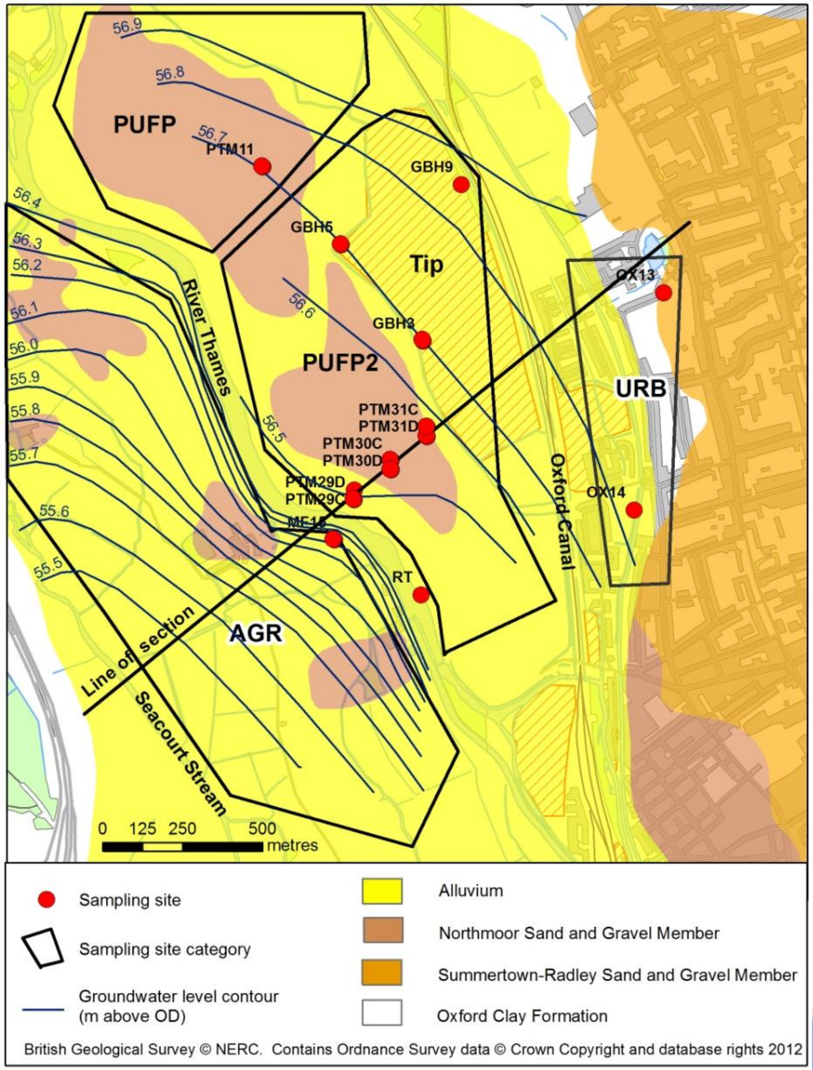


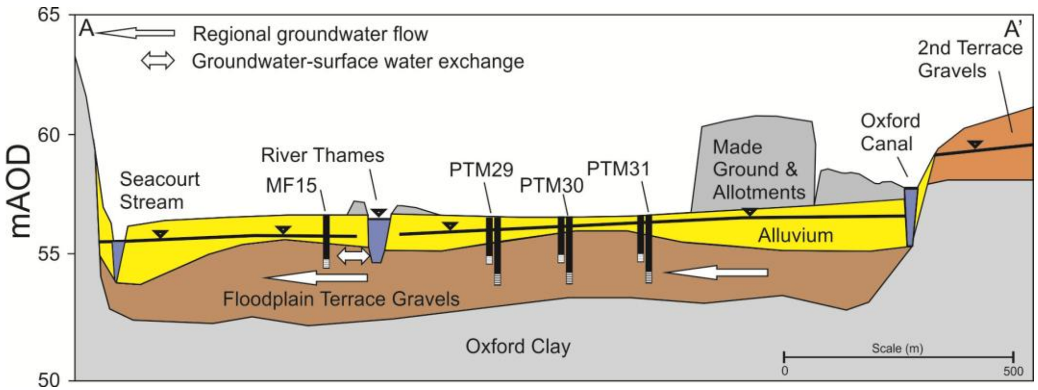
- Measured endocrine disruption in water in densely-drilled area of Colorado catchment
- 89%, 41%, 12%, and 46% of water samples exhibited oestrogenic, anti-oestrogenic, androgenic, and anti-androgenic activities respectively:
  - **Anti-oestrogens** - 2-ethyl-1-hexanol and ethylene glycol greatest, plus ethylene glycol monobutyl ether, 2-ethylhexanol, ethylene glycol, diethanolamine, diethylene glycol methyl ether, sodium tetraborate decahydrate, 1,2-bromo-2-nitropropane-1,3-diol, n,n-dimethyl formamide, cumene, and styrene
  - **Anti-androgens**- n,n-dimethyl formamide, cumene greatest plus 2-ethylhexanol, naphthalene, diethanolamine, sodium tetraborate decahydrate, 1,2- bromo-2-nitropropane-1,3-diol, and cumene.
  - **Oestrogens** – bisphenol A

Kassotis et al 2013

Port Meadow research site

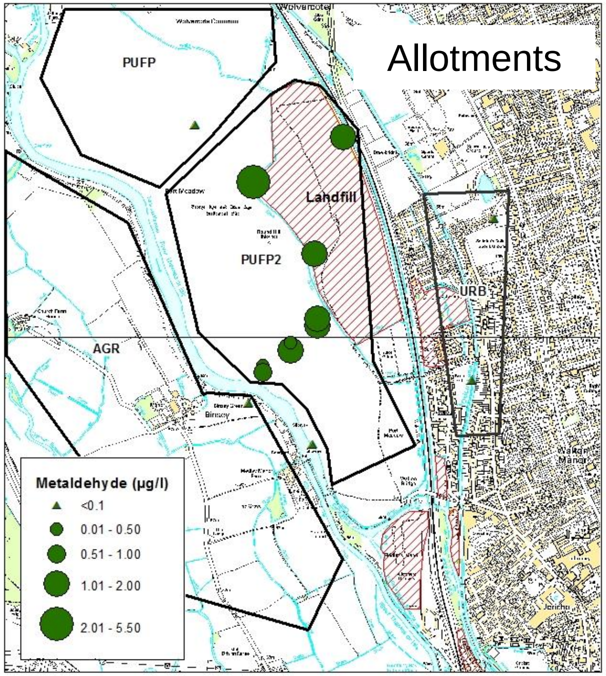
- On Thames floodplain west of Oxford
- Urban area, old landfill, agriculture
- Dynamic environment – shallow fluctuating water table, flood inundation, reversal in gradient
- Implications for attenuation of groundwater pollutants and discharge to rivers

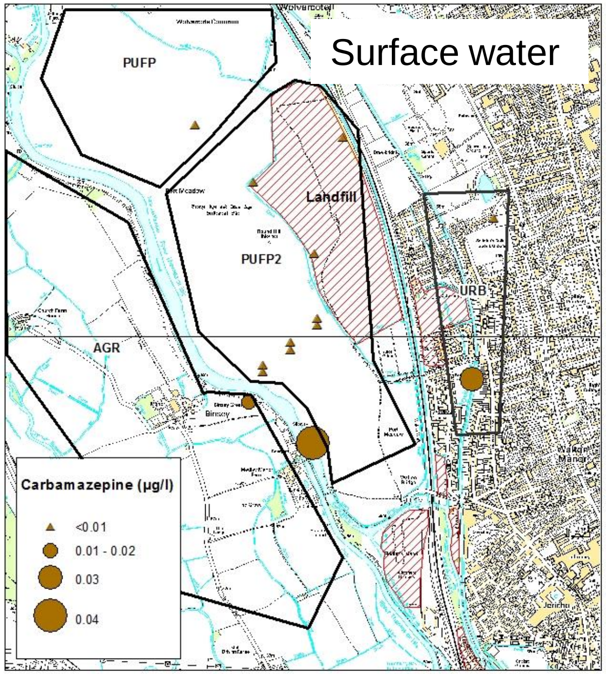


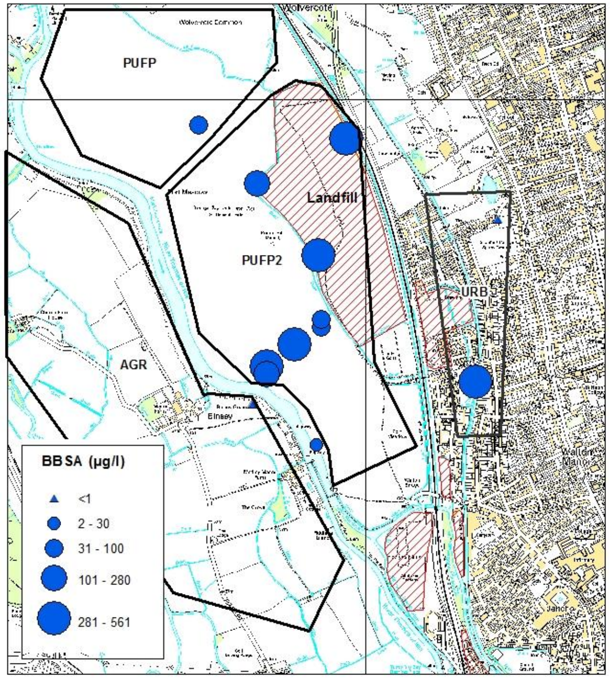


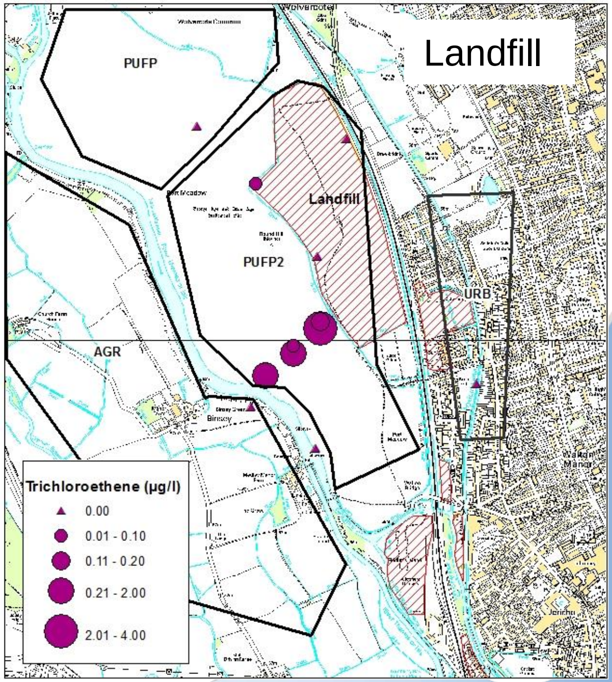
Port Meadow

- Groundwater predominantly reducing inundated areas – nitrate removal
- Impact of landfill leachate plume from NH_4, Cl, HCO_3 etc
- Microorganics fingerprint different types of water

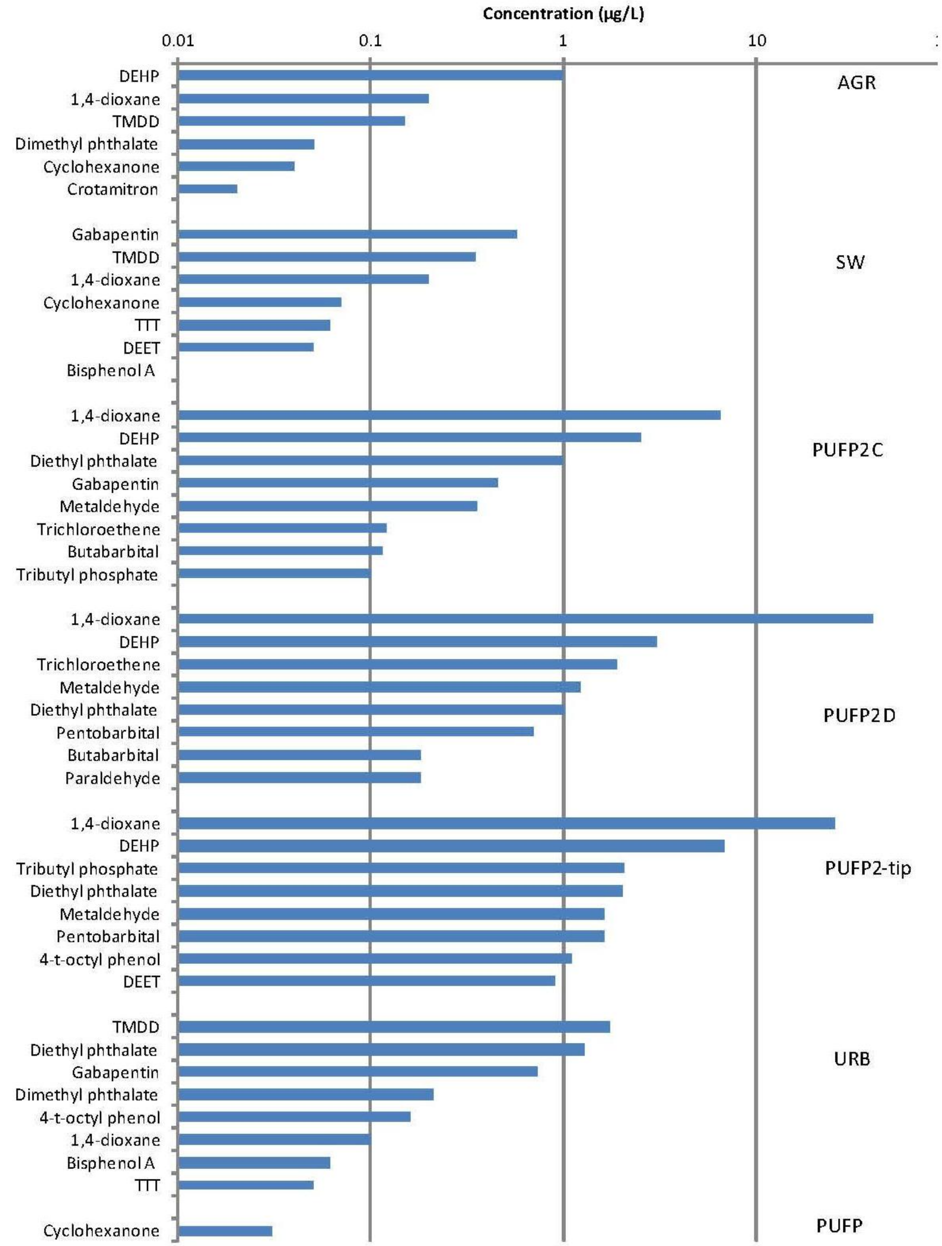








Fingerprinting

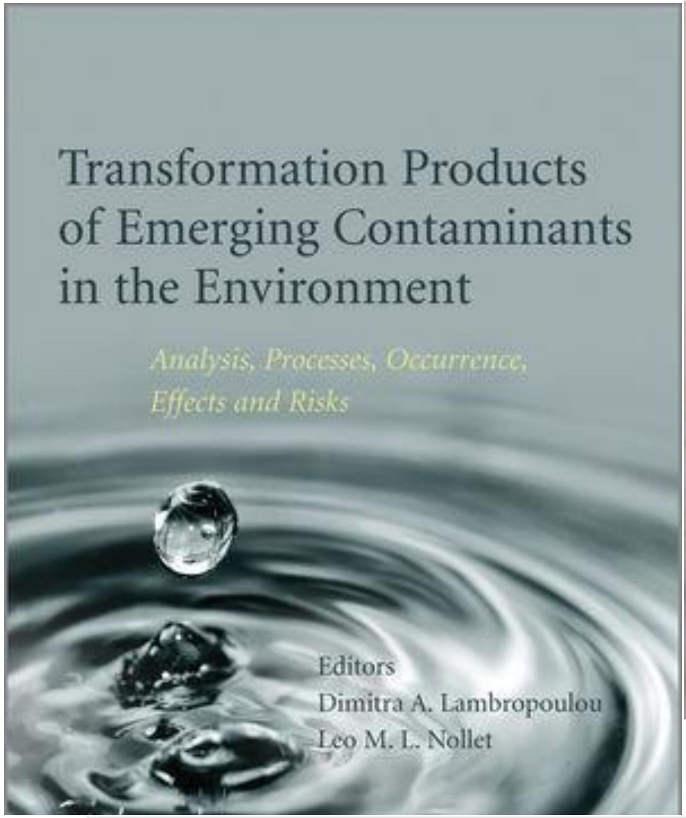


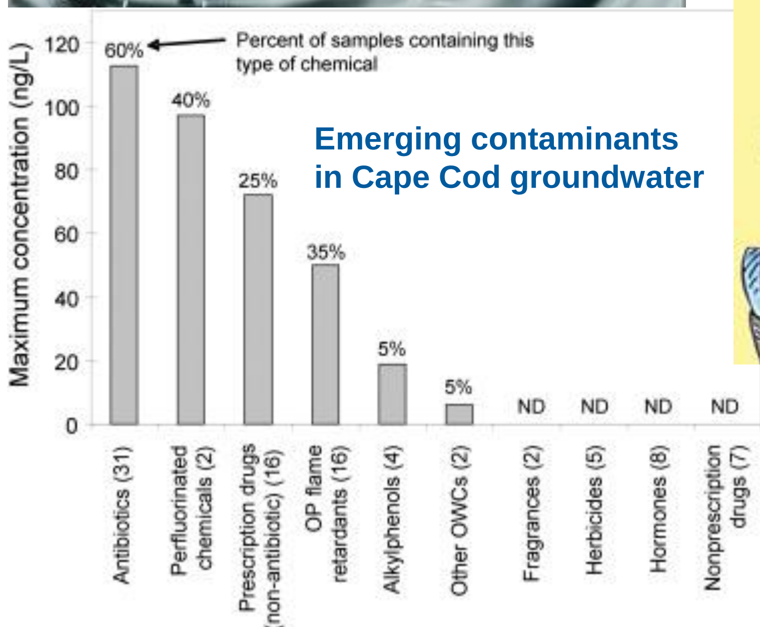
Conclusions 1

- Many different sources and pathways into groundwater: wastewater, biosolids from water treatment and animal wastes are important
- Hydraulic fracturing potentially adds to these
- Frequently detected groups of ECs include antibiotics, lifestyle compounds, pharmaceuticals and preservatives
- Opportunities for formation of TPs: likely to be greatest in the soil and unsaturated zone
- TPs can be found at concentrations higher than the parent and may be more mobile or polar, and more toxic
- There are hot-spots of ECs groundwater contamination in several parts of the UK which warrant further investigation
- Although mostly detected in low ng/L concentrations in groundwater there are many examples where high concentrations have been found

Conclusions 2

- Overall for ECs in groundwater there is a poor understanding of:
  - Occurrence
  - Fate and transport (particularly in the unsaturated zone)
  - Human and ecological risk
- Although many ECs are not regulated the number of regulated contaminants will continue to grow over the coming decades - a real challenge for industry, utilities and regulators
- Ongoing need to prioritise ECs, cannot look for everything everywhere
- Potential for use as novel environmental tracers (e.g. pharmaceuticals, sweeteners)





Emerging contaminants in Cape Cod groundwater