



**British
Geological Survey**

NATURAL ENVIRONMENT RESEARCH COUNCIL



Emerging organic groundwater contaminants and their transformation products

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Thanks to Dan Lapworth and Kat Manamsa

Degradation and Toxicity of Organic Contaminants in the Ground

Emerging organic groundwater contaminants and their transformation products

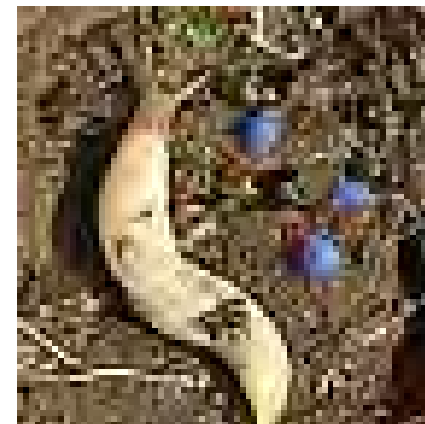
- Definition
- Sources, pathways and receptors
- Examples
- Hydraulic fracturing
- Oxford case study
- Conclusions



http://toxics.usgs.gov/photo_gallery/emergcont_page4.html

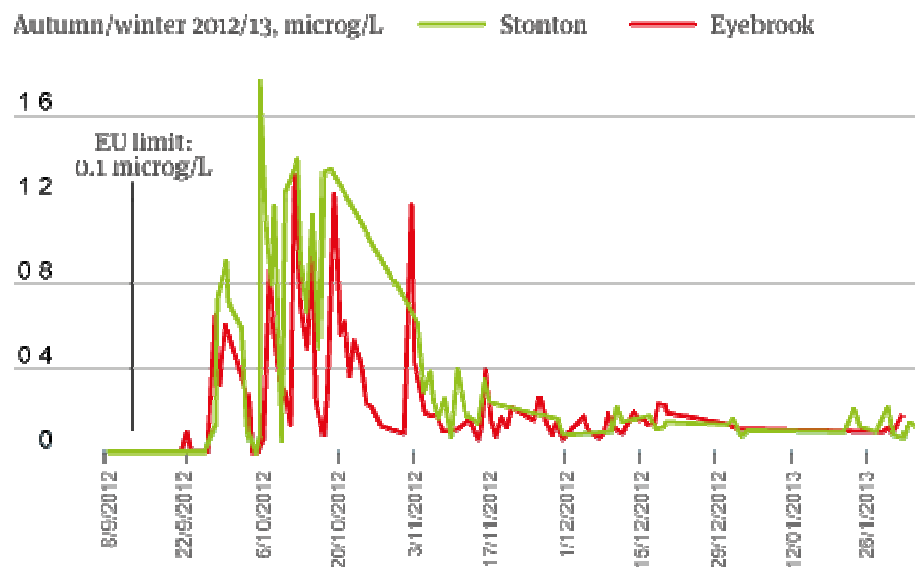
Emerging contaminants

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



www.gardenorganic.co.uk

Metaldehyde runoff



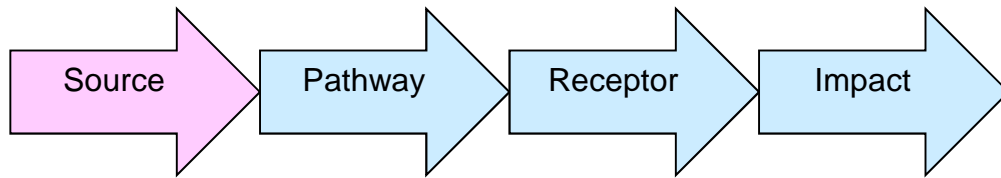
SOURCE: POND CONSERVATION

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

Emerging organic contaminants

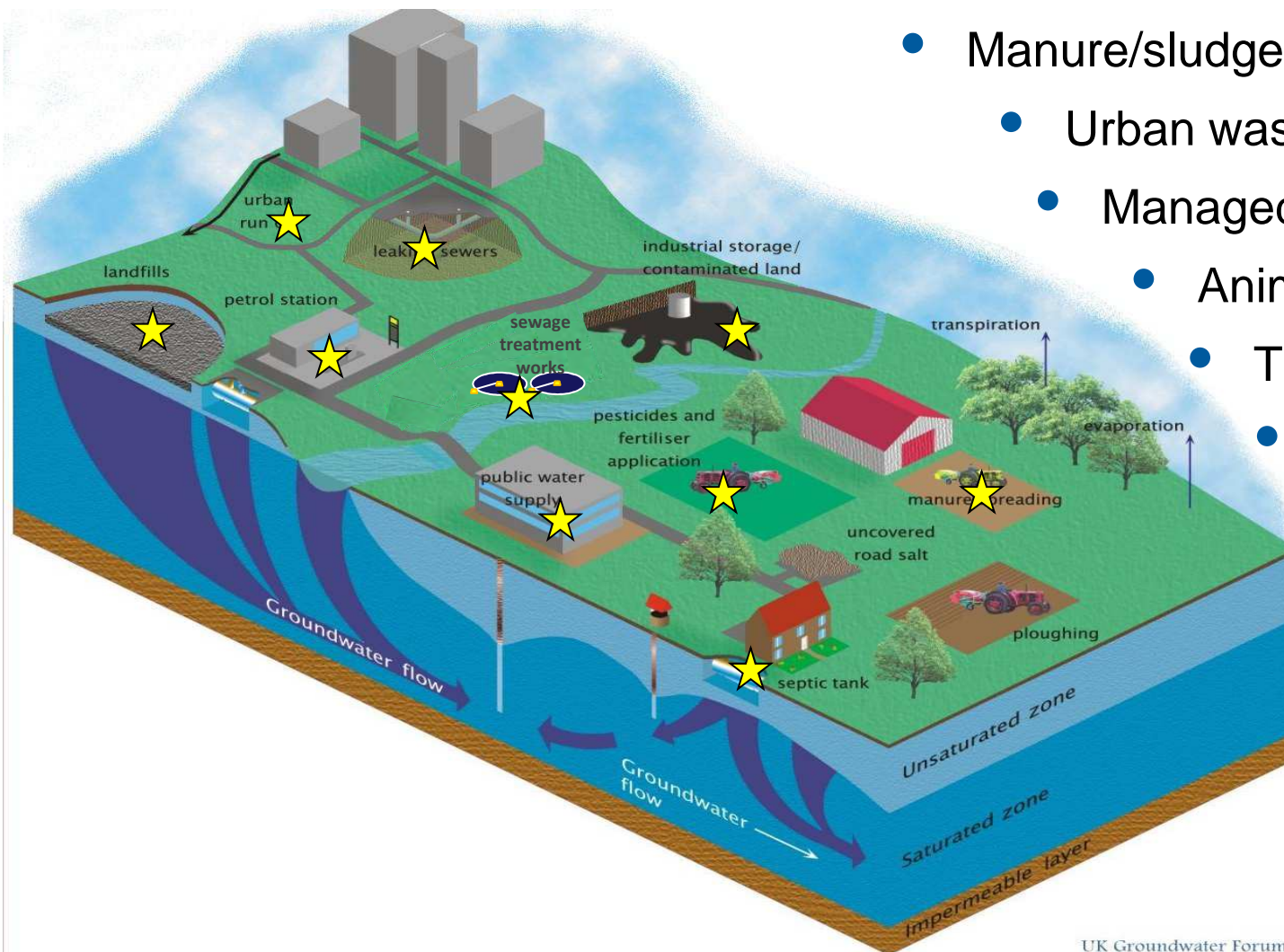
- Pesticides – parent compounds (e.g. metaldehyde), metabolites
- Pharmaceuticals – human, veterinary, illicit
- “Life style” – nicotine, caffeine
- Personal care – DEET, parabens, triclosan, musks, UV filters
- Industrial additives and by-products – dioxanes, bisphenols, MTBE
- Food additives – BHA,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

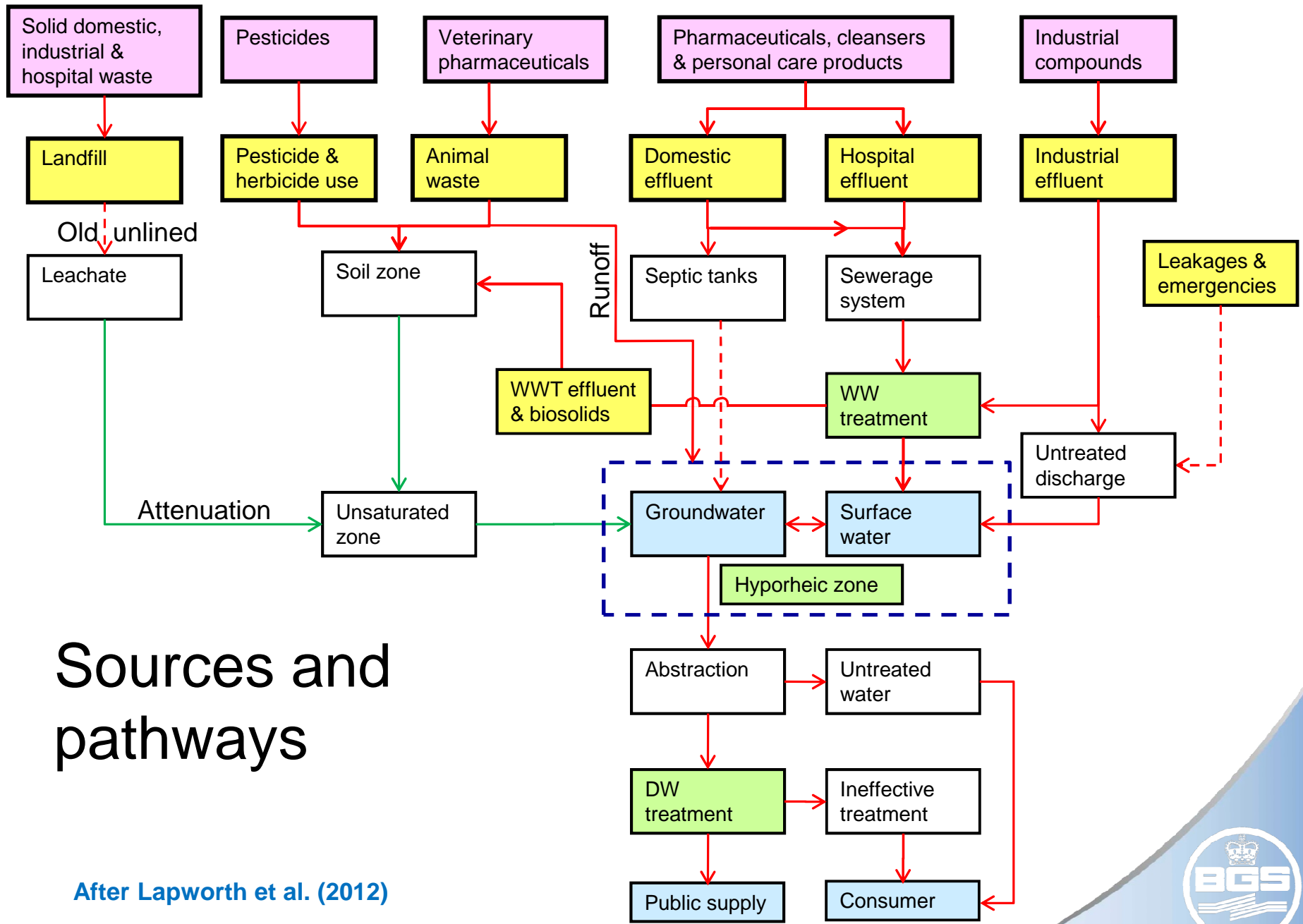




Sources of ECs in groundwater

- 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

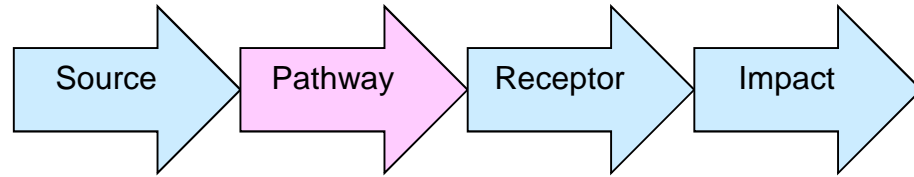




Sources and pathways

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

Degradation opportunities

Sewage treatment works

- Settling
- Coagulation
- Anaerobic biodegradation

Water treatment works

- GAC
- Enhanced oxidation
- Membrane filtration

Septic tank

- Anaerobic biodegradation

Groundwater

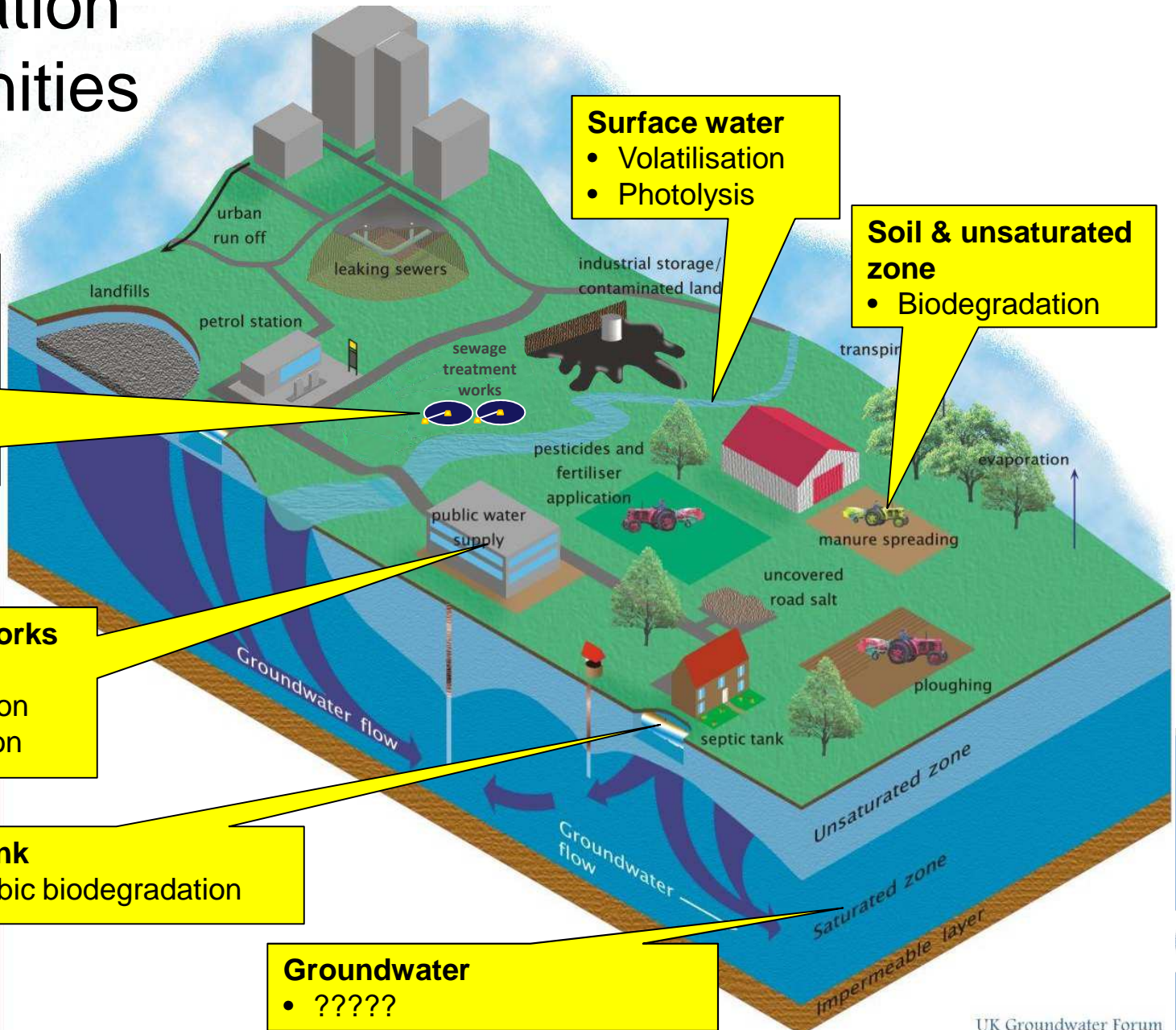
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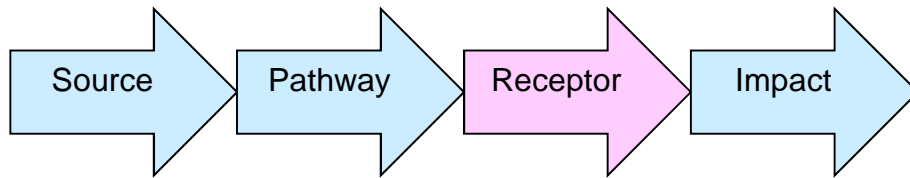
Surface water

- Volatilisation
- Photolysis

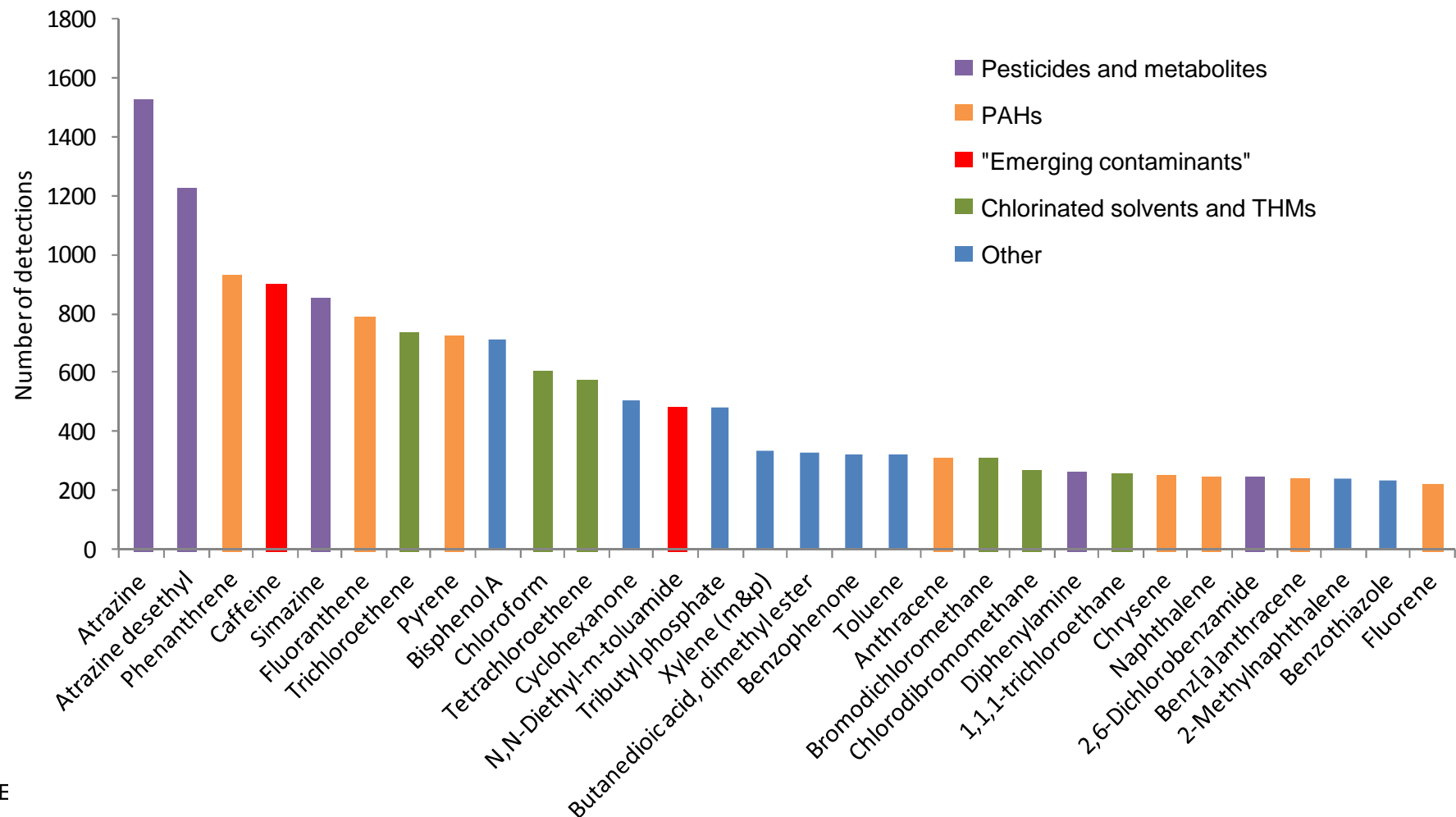
Soil & unsaturated zone

- Biodegradation





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



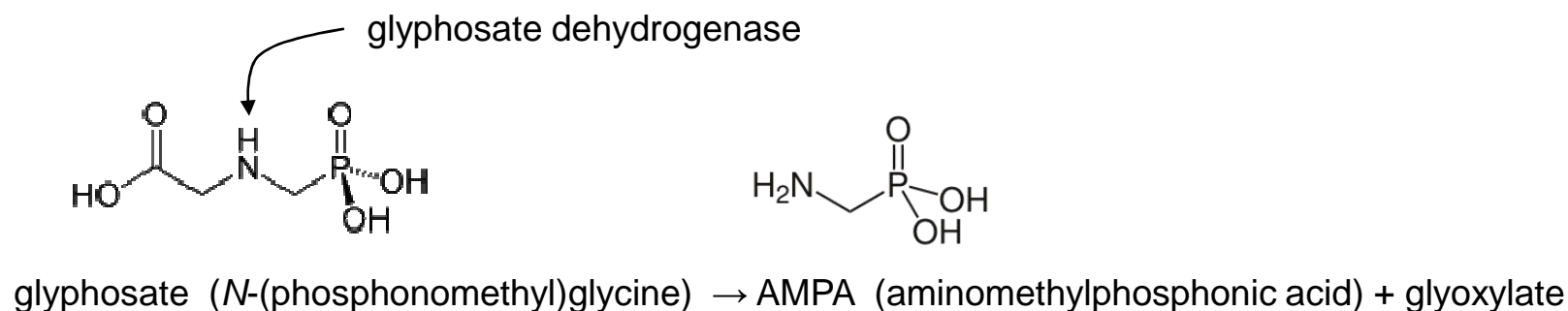
Regulatory framework

- 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

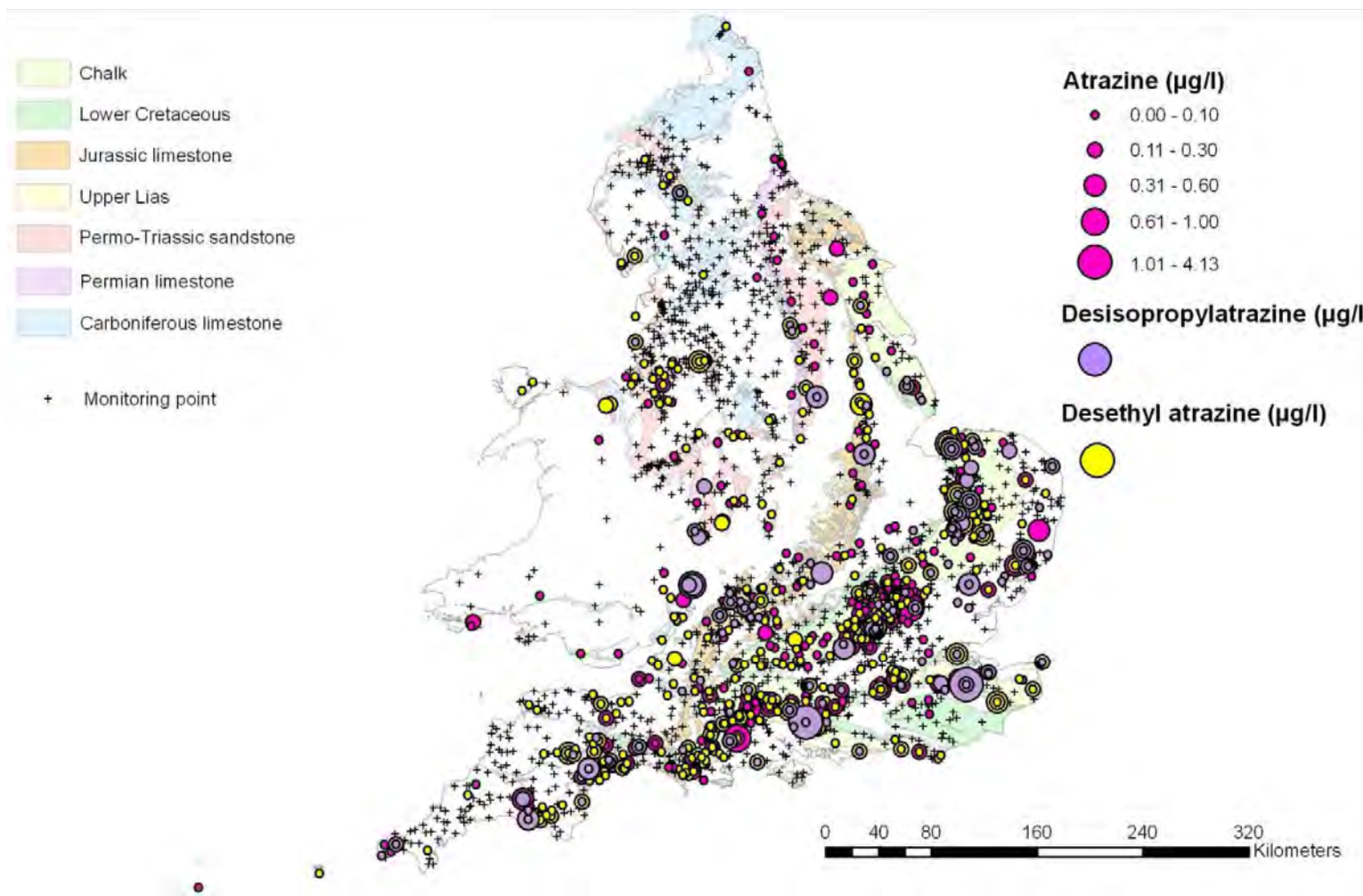


- TPs often more mobile and persistent than their parents and found more frequently or at higher concentrations – BAM from diclobenil, AMPA from glyphosate
- TPs often more polar than their parent and more difficult to analyse for
- Some formed as TPs of other pesticides – carbendazim from benomyl



BAM - 2,6-dichlorobenzamide

Atrazine and its metabolites in groundwater



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

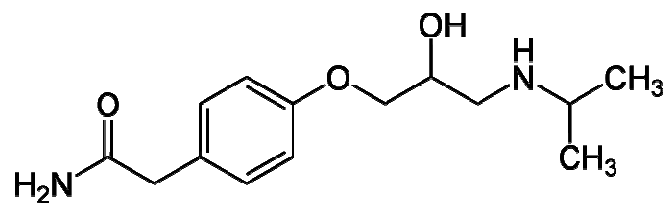
Pharmaceuticals



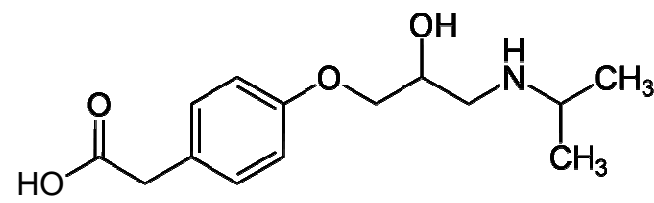
- Next most frequently reported group after pesticides
- Most common are:
 - Analgesics (paracetamol>ibuprofen>phenazone>propyphenazone>salicylic acid)
 - Anti-inflammatories (ibuprofen>ketoprofen>diclofenac)
 - Antibiotics (triclosan>sulfamethoxazole>lincomycin>erythromycin)
 - Anti-epileptics (carbamazepine)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

Pharmaceuticals degradation

- Recalcitrant TPs

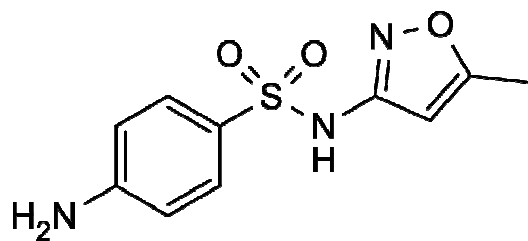


Atenolol

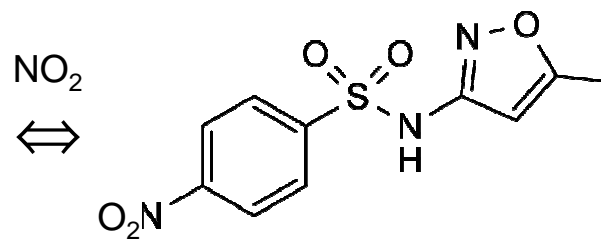


Atenololic acid

- Influenced by redox
 - Phenazones, naproxen, erythromycin only degraded under oxic conditions
- May be deactivated (not degraded) e.g. by nitrite



Sulfamethoxazole

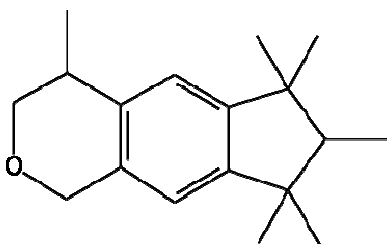


4-nitro-sulfamethoxazole

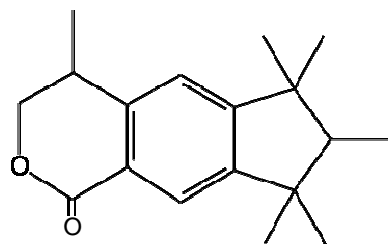
Personal care products



- Skin care products:
 - UV blockers, isopropyl myristate, phenoxy-ethanol, lialial
- 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

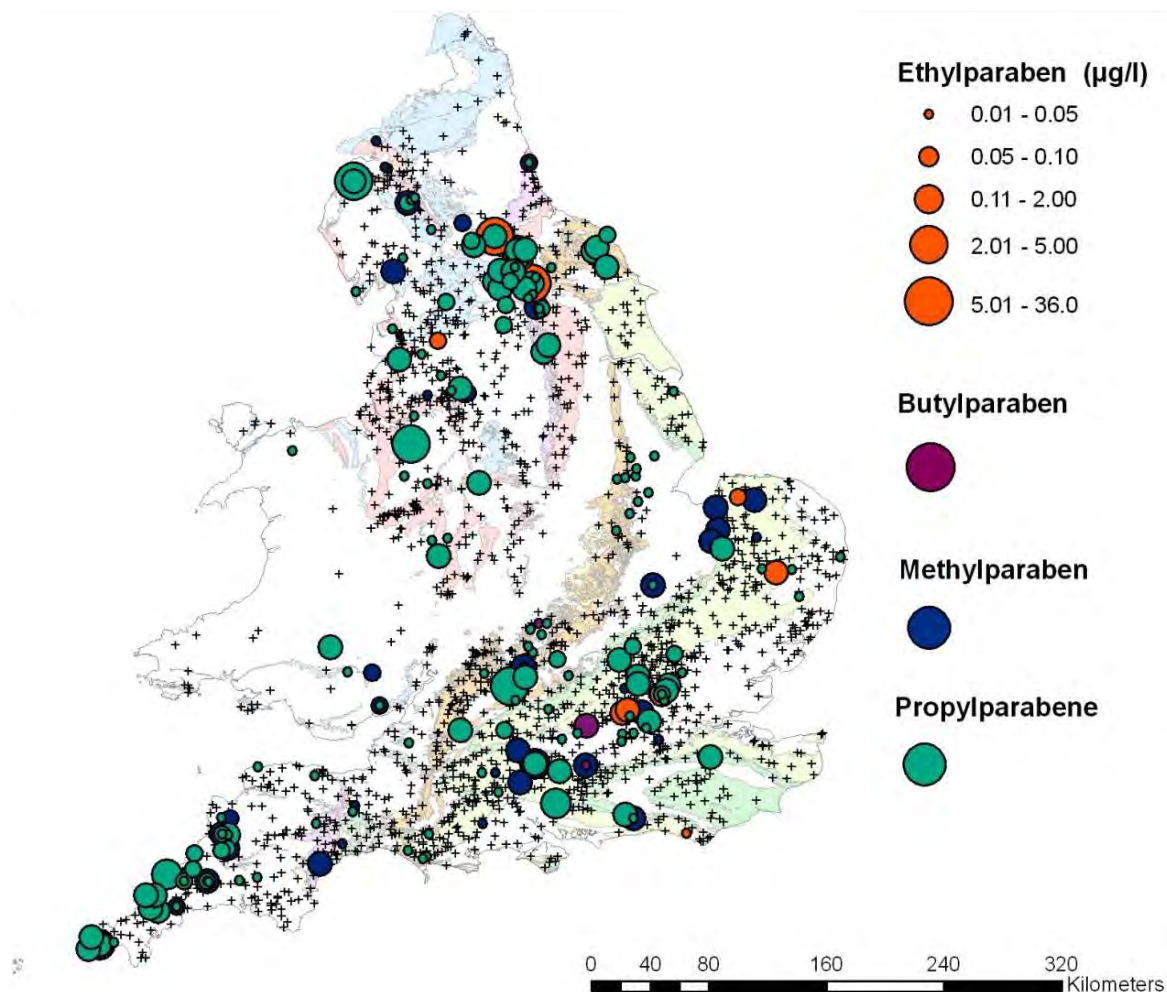
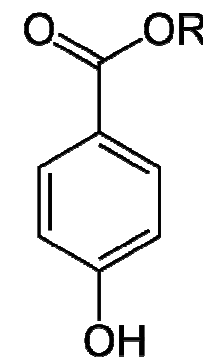


HHCB



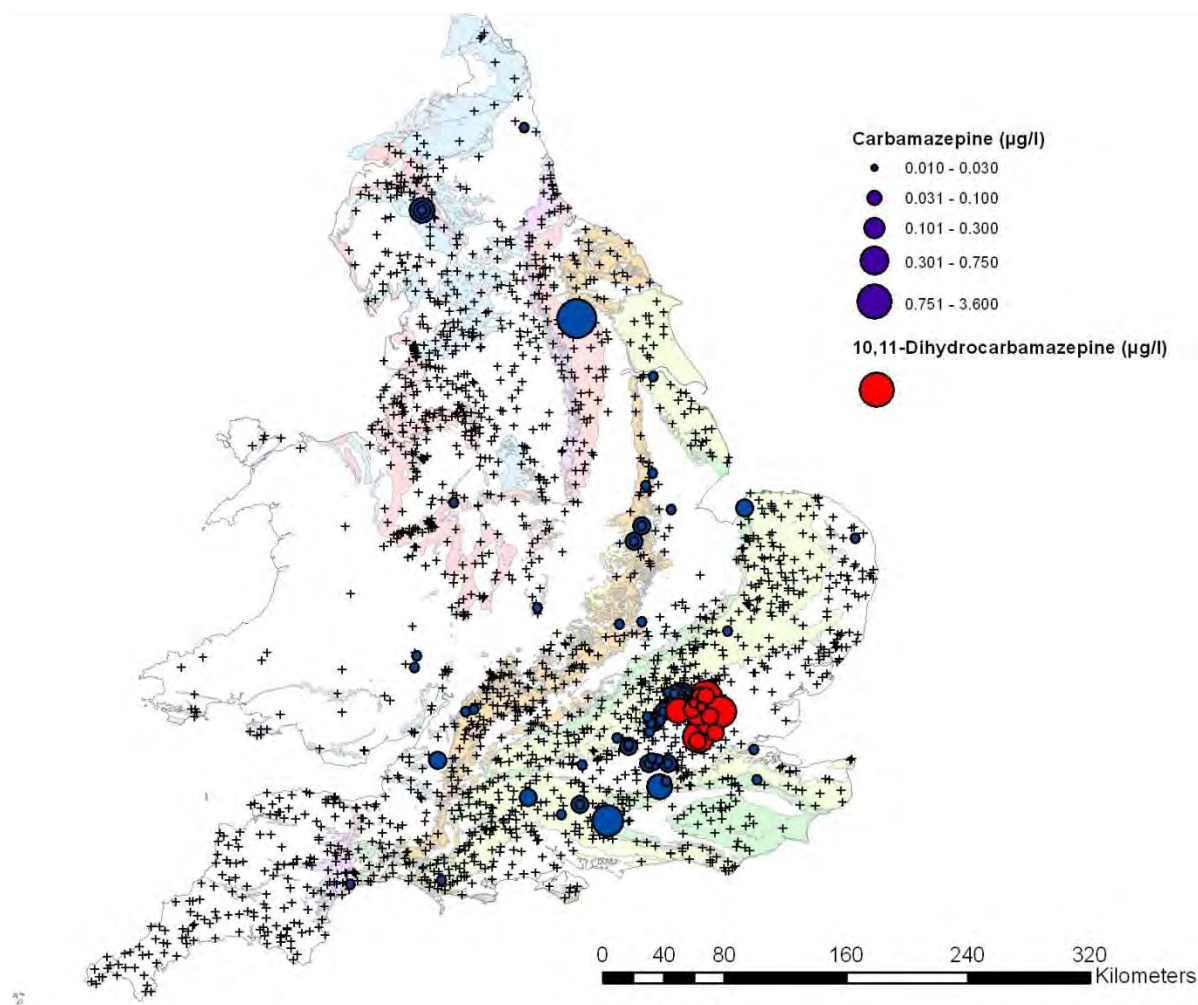
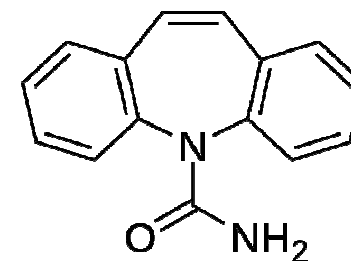
HHCB-lactone from autoxidative formation

Parabens in groundwater



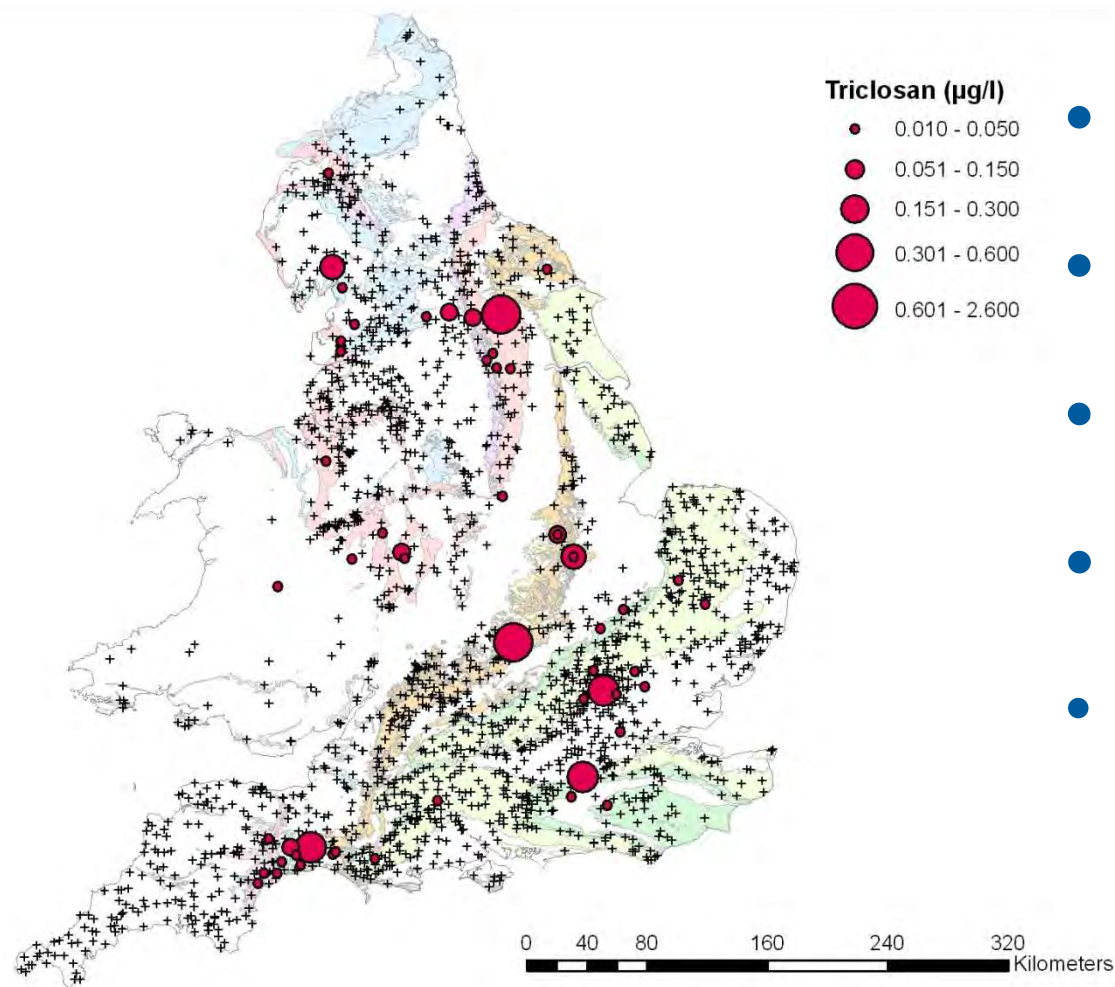
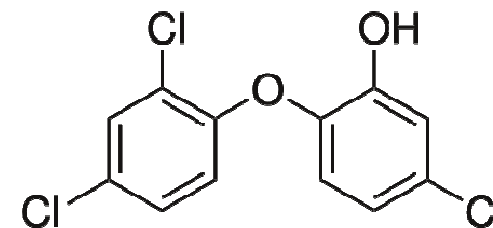
- Bactericidal and fungicidal properties
- Widely used
- But potential links with cancer and endocrine disruption
- Environment Agency monitoring 1993 -2012 using semi-quantitative GCMS scanning

Carbamazepine in groundwater



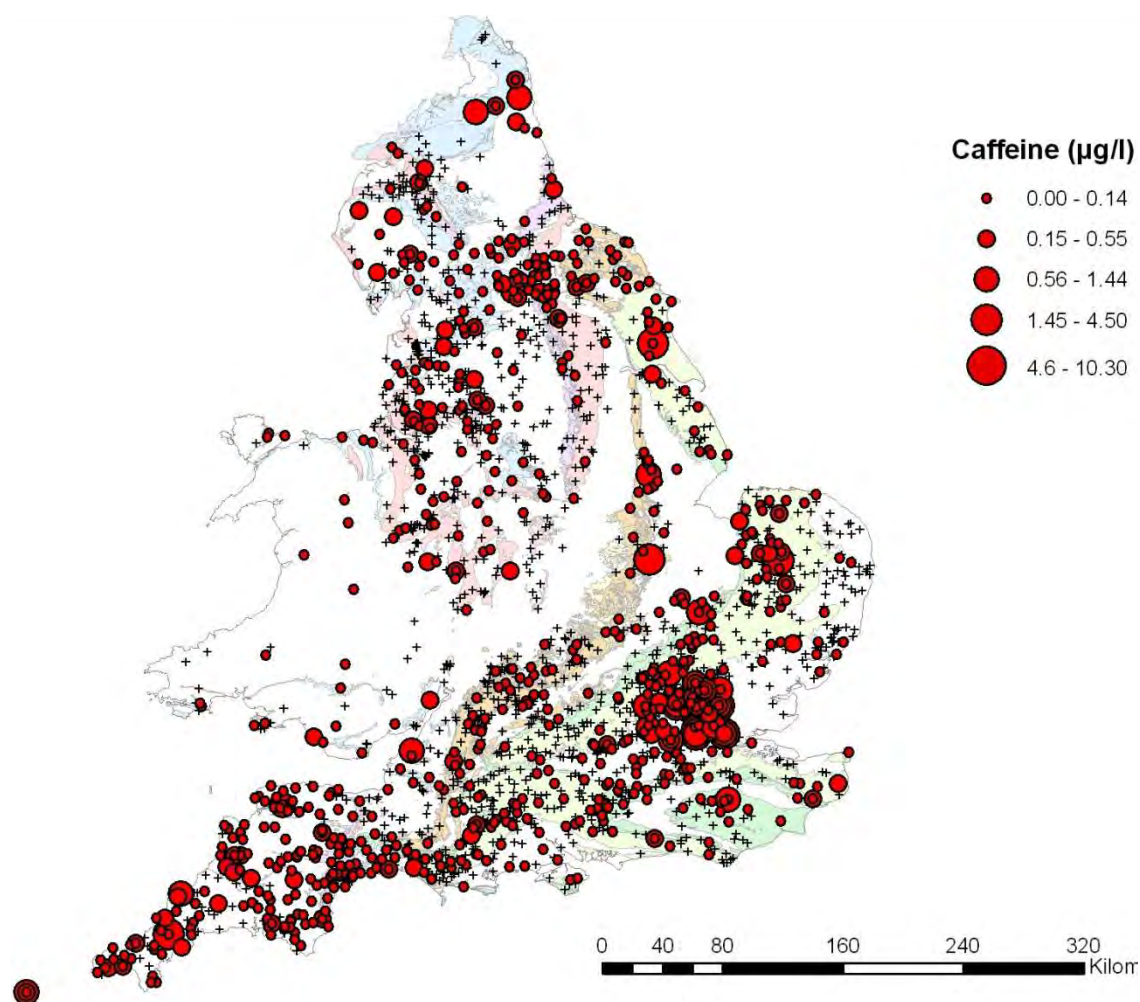
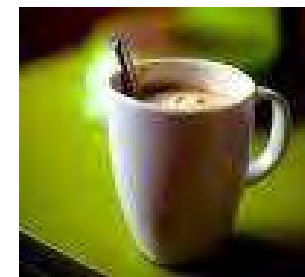
- Used to treat epilepsy and bipolar disorder
- Possible biotransformation product
- Environment Agency monitoring 1993 -2012 using semi-quantitative GCMS scanning

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

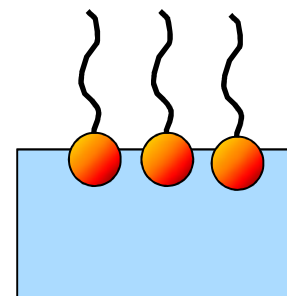
Caffeine and nicotine



- 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

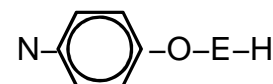
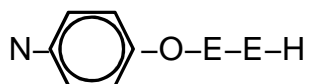
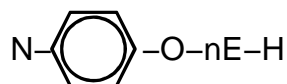
Barnes et al. (2008); Seiler et al. (1999); Swartz et al. (2006)

Alkyl phenols and other EDCs



Alkylphenyl ethoxylates and polyethoxylates

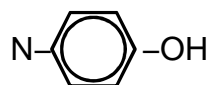
- Both parents and metabolites persistent in groundwater
 - APEOs degraded by progressive shortening of ethoxylate chain to AP2EO and AP1EO
 - And/or transformation by oxidation of ethoxylate chain to AP2EC and AP1EC in aerobic conditions
 - Anaerobic treatment favours AP production
- Degradation more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



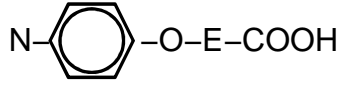
Nonylphenolpolyethoxylate(NPnEO)

Nonylphenoldiethoxylate(NP2EO)

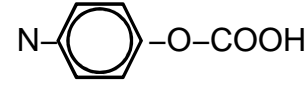
Nonylphenolmonoethoxylate(NP1EO)



Nonyl phenol(NP)



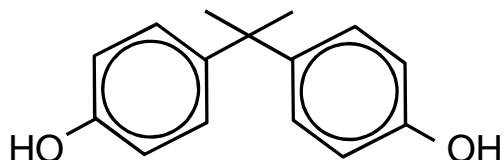
Nonylphenoxyethoxyacetic acid(NP2EC)



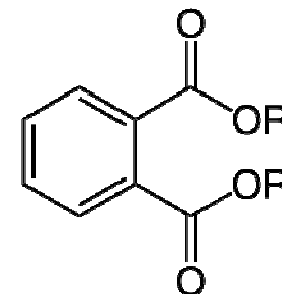
Nonylphenoxyacetic acid(NP1EC)

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 congeners.
 - 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)



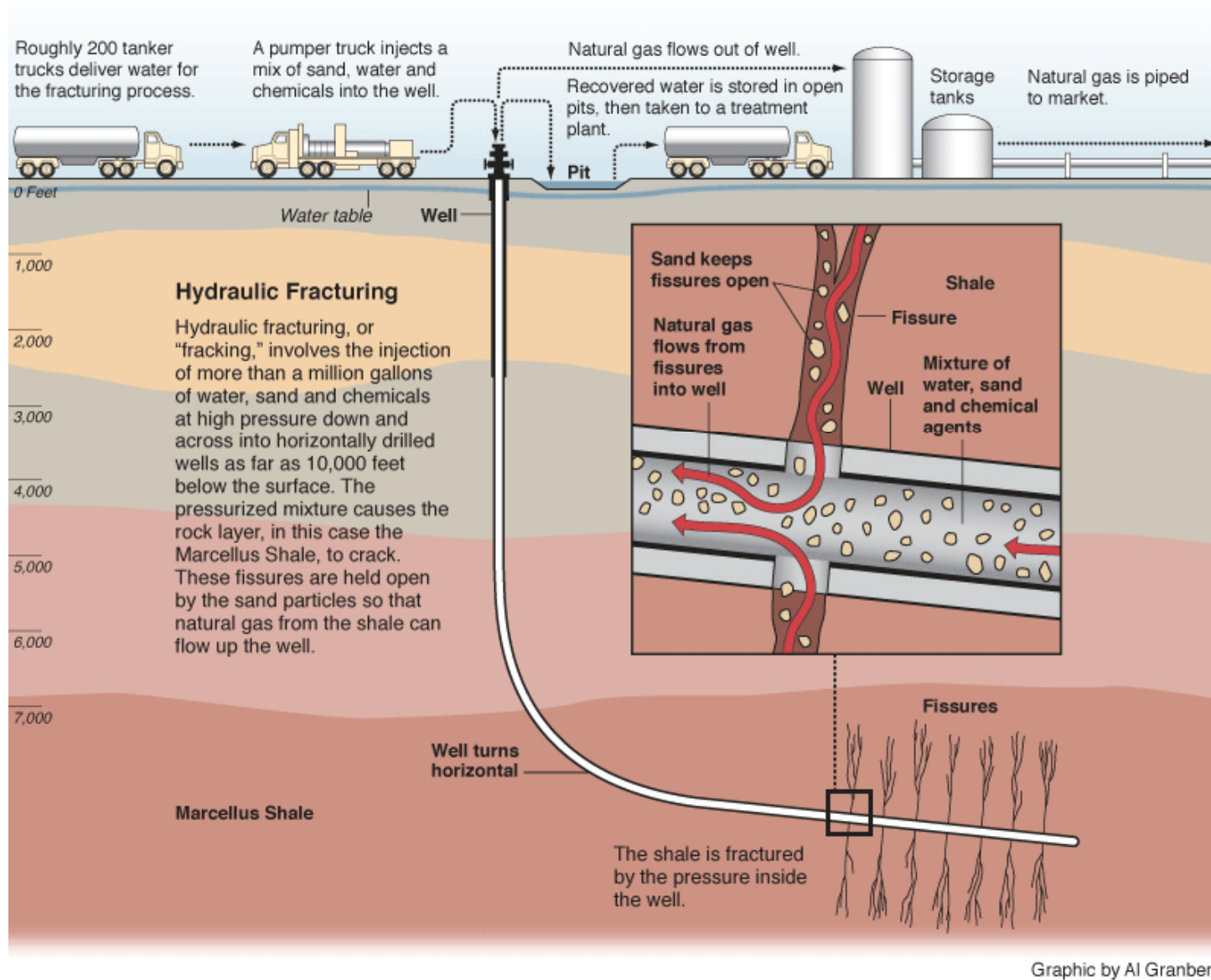
Shale gas

- 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

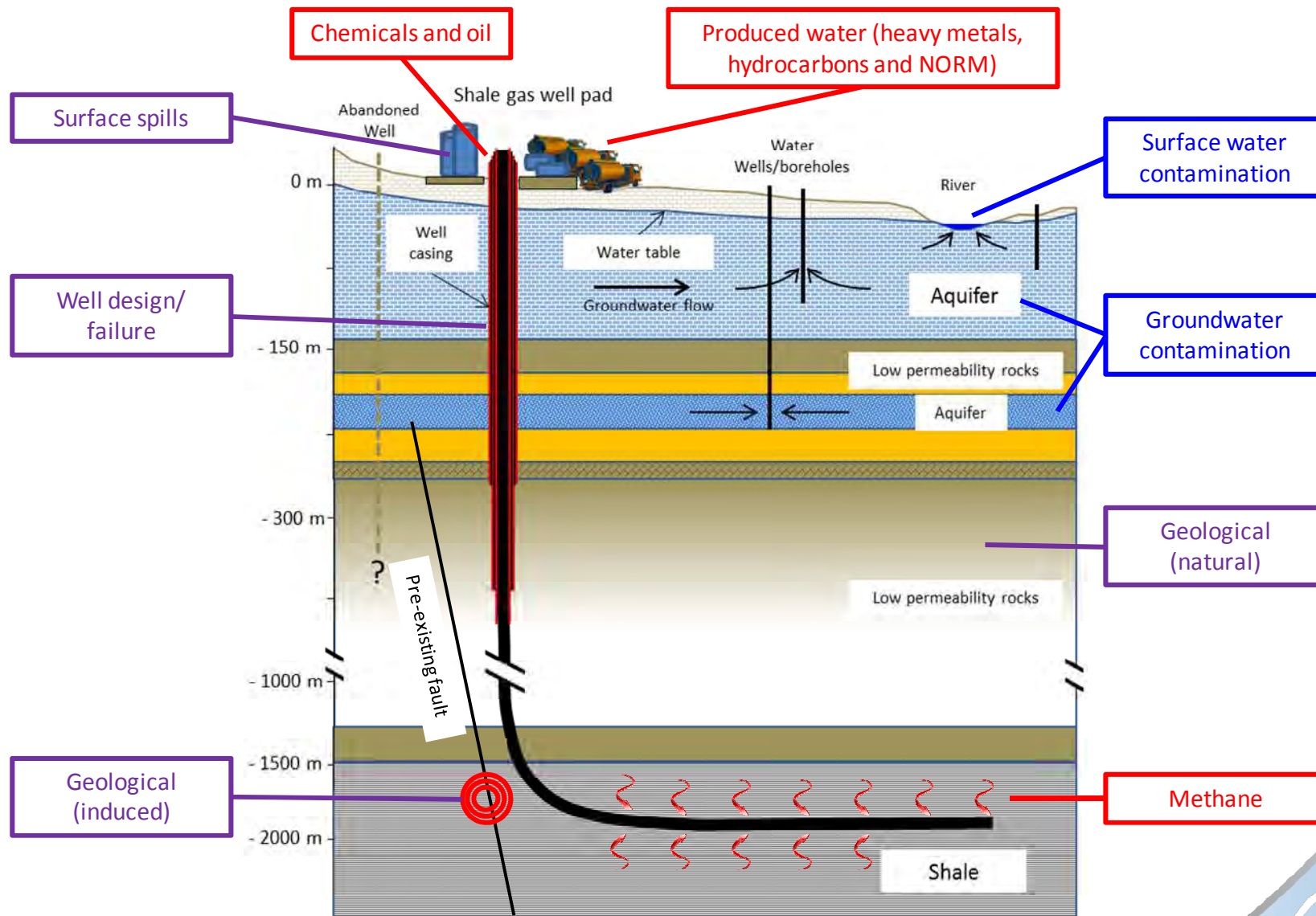
Hydraulic fracturing (fracking) process



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





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” -**

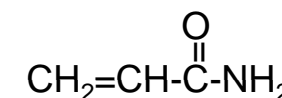
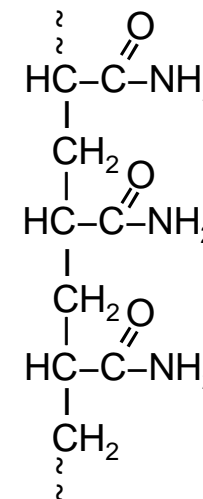
Hydraulic fracturing fluid development

- 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

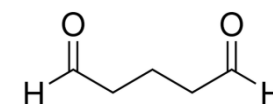
Polyacrylamide

- 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

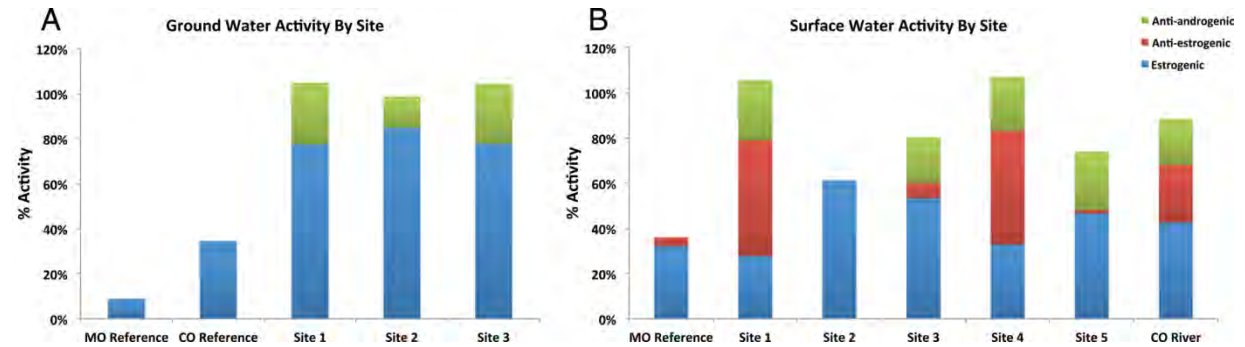


Glutaraldehyde

- 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



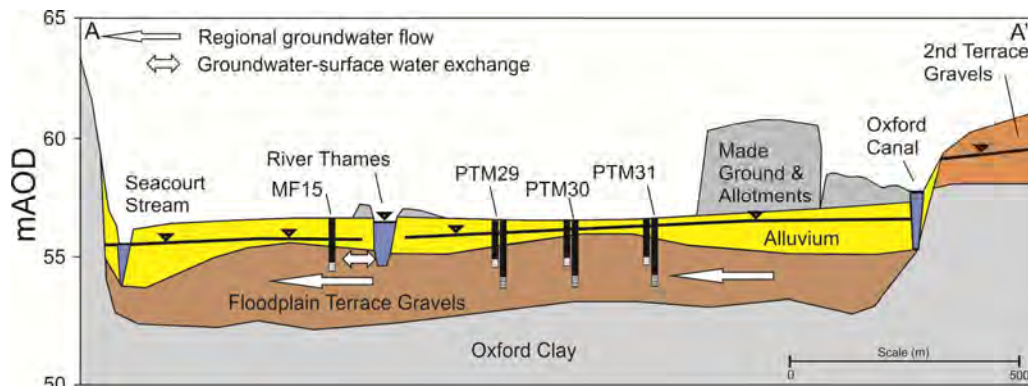
What has actually been found



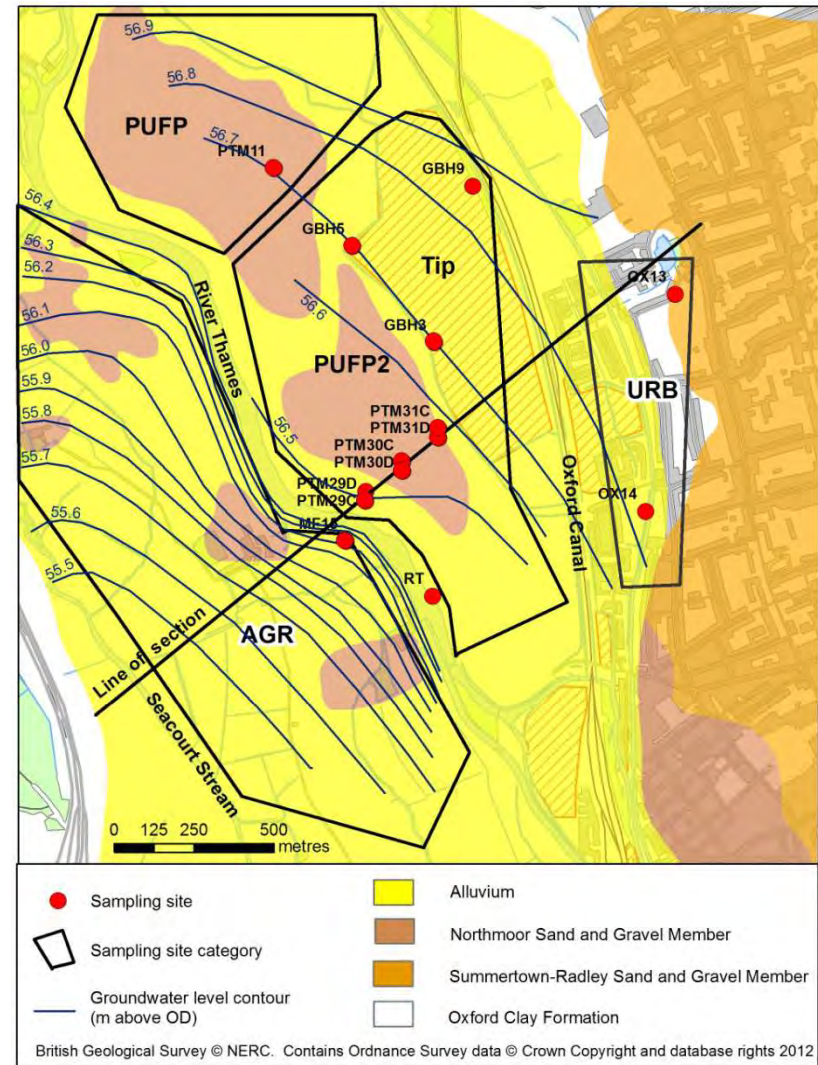
- Measured endocrine disruption in water in densely-drilled area of Colorado catchment
- 89%, 41%, 12%, and 46% of water samples exhibited oestrogenic, anti-oestrogenic, androgenic, and anti-androgenic activities respectively:
 - **Anti-oestrogens** - 2-ethyl-1-hexanol and ethylene glycol greatest, plus 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

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

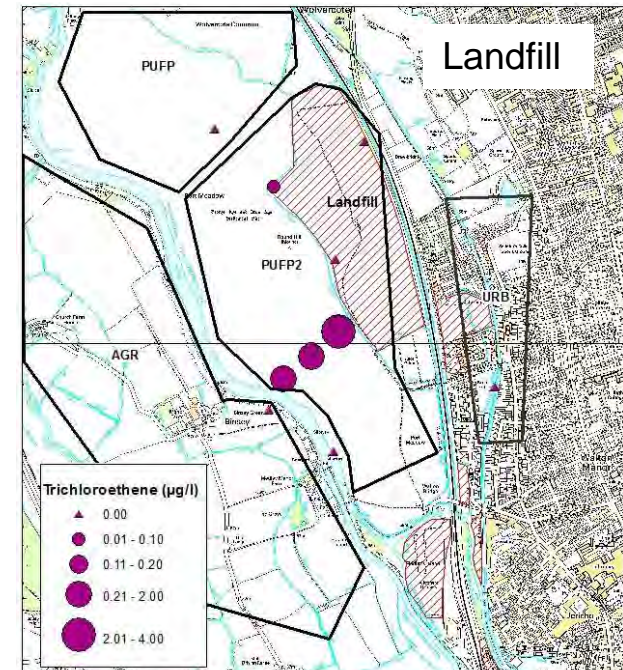
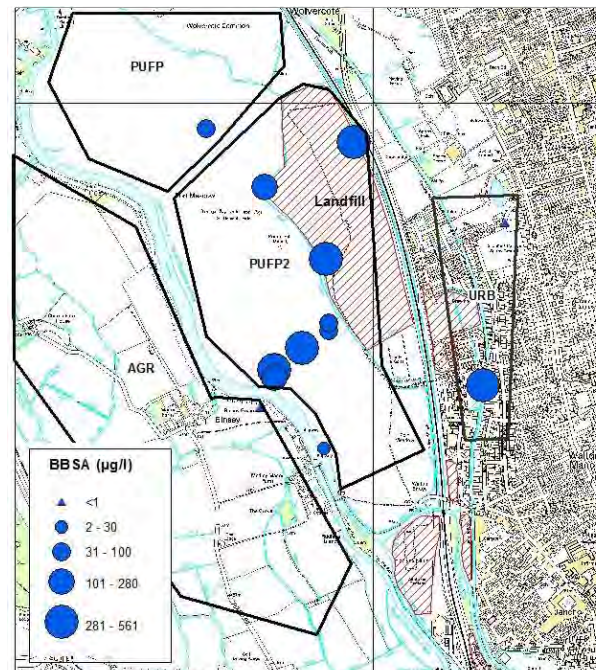
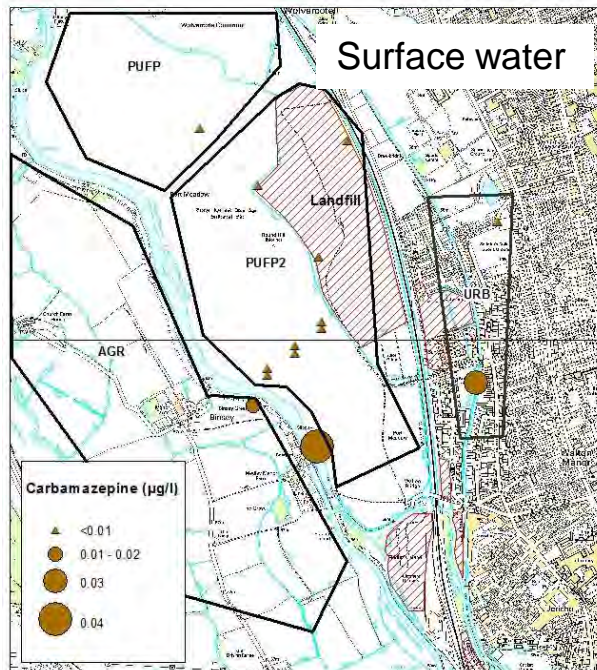
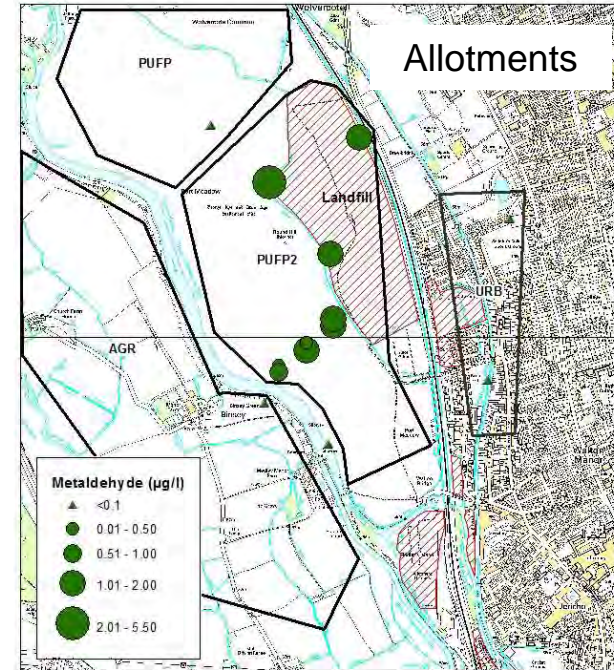


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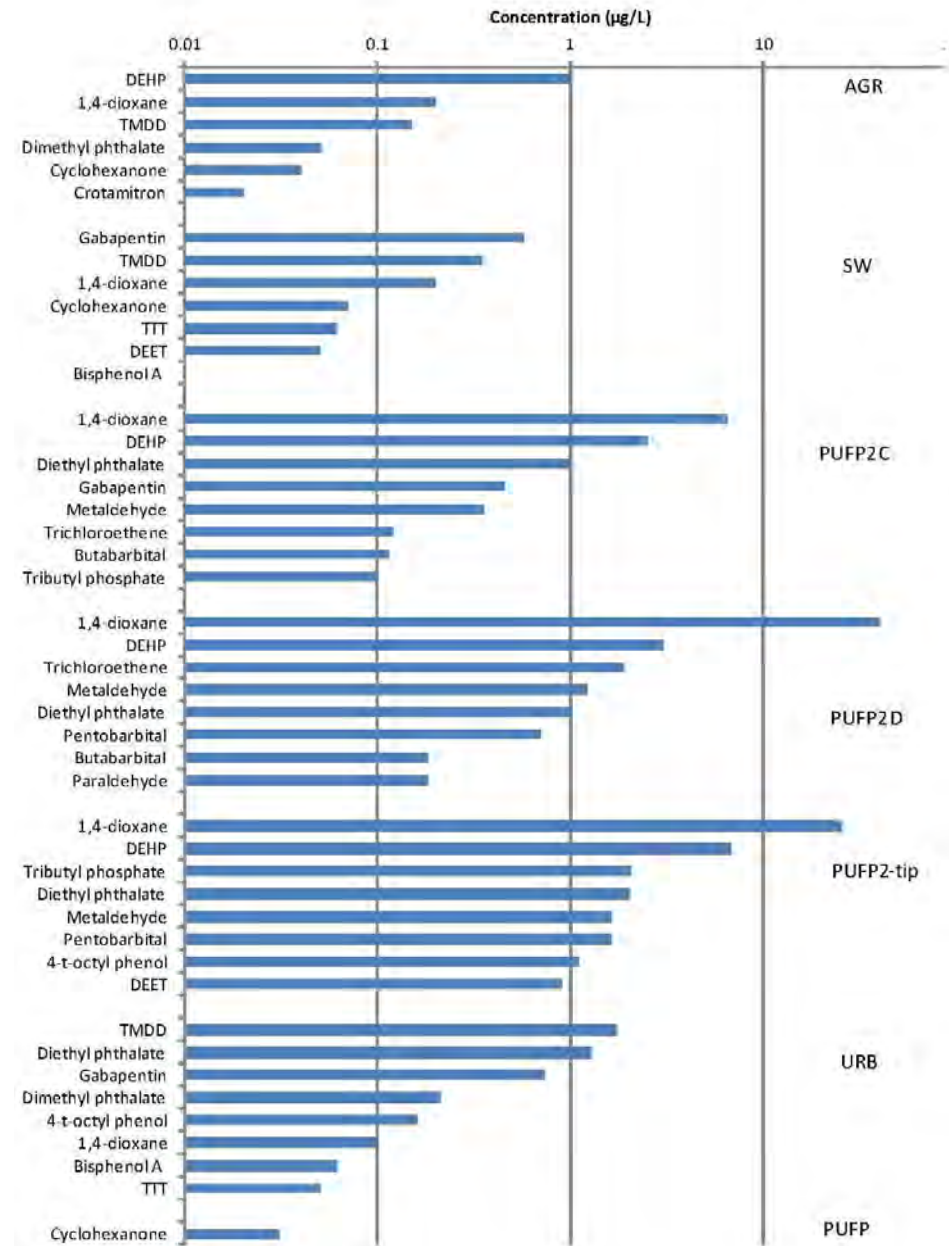


Port Meadow

- 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)

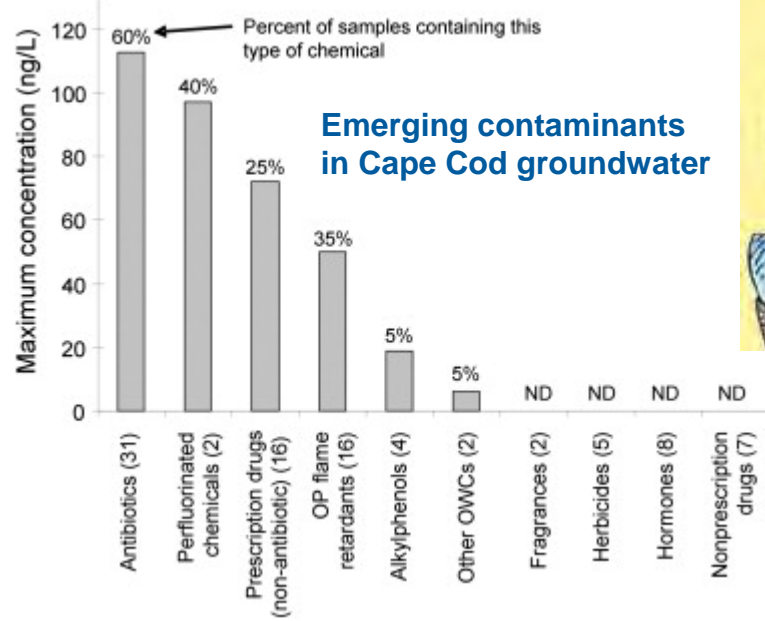


Transformation Products of Emerging Contaminants in the Environment

Analysis, Exposure, Ecotoxicity Effects and Risks




Editors
Dimitra A. Lambropoulou
Leo M. L. Nollet



H₂O Seminar Series

The "H₂O seminar series" is to promote the exchange of ideas, knowledge, and experiences amongst the water professionals in Singapore.

Emerging Contaminants: Implications for Water Sustainability

SPEAKER

PROFESSOR SHANE A. SNYDER
 Ph.D.
 Professor and Co-Director
 Arizona Laboratory for Emerging Contaminants
 University of Arizona, USA
 Visiting Professor, National University of Singapore (NUS).

24 JULY 2013, 3.00PM
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Seats are limited so please register by 18th July 2013 with Ms Nuraini Osman at 68852534 or Nuraini_Osman@pub.gov.sg

SYNOPSIS
 The availability of safe freshwater is diminishing at an alarming rate globally. Increasing human population is stressing water supplies and contributing to water pollution. Population density increases and climate changes including epic droughts in certain parts of the world have led to the utilization of non-conventional water resources. Modern analytical technology has permitted the discovery that minute concentrations of contaminants of distinctly human origin occur in the water cycle. Many of these so-called "contaminants of emerging concern" have been, and will continue to be, detected in potable water supplies. Without question, the propensity for the contamination of fresh water will rise as human population continues to grow. Water treatment technology also continues to evolve. Advanced water treatment processes can provide effective and efficient contaminant removal. In this presentation, Professor Snyder will share on the history, current status, and future implications that the detection of endocrine disruptors and pharmaceuticals will have on water and energy sustainability, with a particular emphasis on water treatment technologies.

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