

Review of risk from potential emerging contaminants in UK groundwater

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Abstract

This paper provides a review of the types of emerging organic groundwater contaminants (EGCs) which are beginning to be found in the UK. EGCs are compounds being found in groundwater that were previously not detectable or known to be significant and can come from agricultural, urban and rural point sources. EGCs include nanomaterials, pesticides, pharmaceuticals, industrial compounds, personal care products, fragrances, water treatment by-products, flame retardants and surfactants, as well as caffeine and nicotine. Many are relatively small polar molecules which may not be effectively removed by drinking water treatment. Data from the UK Environment Agency's groundwater screening programme for organic pollutants found within the 30 most frequently detected compounds a number of EGCs such as pesticide metabolites, caffeine and DEET. Specific determinands frequently detected include pesticides metabolites, pharmaceuticals including carbamazepine and triclosan, nicotine, food additives and alkyl phosphates. This paper discusses the routes by which these compounds enter groundwater, their toxicity and potential risks to drinking water and the environment. It identifies challenges that need to be met to minimise risk to drinking water and ecosystems.

Keywords

Emerging contaminants, groundwater, toxicity, risk assessment, pesticides, metabolites, pharmaceuticals, wastewater treatment

1 Introduction

The term emerging groundwater contaminants (EGCs) is generally used to refer to compounds previously not considered or known to be significant in groundwater in terms of distribution and/or concentration, which are now being more widely detected and which have the potential to cause known or suspected adverse ecological or human health effects. Synthesis of new chemicals or changes in use and disposal of existing chemicals can create new sources of EGCs. These will also include substances that have long been present in the environment but whose presence and significance are only now being elucidated (Daughton, 2004). As analytical techniques improve, previously undetected organic micro-contaminants are being observed in the aqueous environment, e.g. metaldehyde. Richardson and Ternes (2011) review recent analytical developments in the emerging contaminant context.

EGCs are commonly derived from a variety of municipal, agricultural, and industrial sources and pathways. Many have remained unidentified presumably due to similar reasons to current, well-established problems. For example, Jackson (2004) ascribes the historical lack of recognition of chlorinated solvent contamination and its subsequent emergence to the lack of a technical paradigm explaining the processes of contamination and the identification of adverse effects.

Many EGCs remain unregulated and Kavanaugh (2003) set out the technical and institutional challenges presented by unregulated contaminants. The number of regulated contaminants will continue to grow slowly over the coming decades. In the European context groundwater quality is currently regulated under the Water Framework Directive and the Groundwater Daughter Directive and drinking water under the Drinking Water Directive. Pesticides are also regulated under the Plant Protection and Biocides Directives. Some of these contaminants can have human or ecological health effects and there is a need for better understanding of their fate in environmental systems.

The European Drinking Water Directive sets limits for a small number of organic micropollutants comprising aromatic hydrocarbons, chlorinated solvents and disinfection by-products (EC, 1998). The Priority Substances Directive establishes a number of Priority Substances, including benzene, octyl and nonyl phenols, specified polyaromatic hydrocarbons (PAH), di(2-ethylhexyl)phthalate and a range of chlorinated hydrocarbons (EC, 2008). Proposed revisions include the emerging contaminants ibuprofen, diclofenac, α -ethinyloestradiol, β -oestradiol and perfluorooctane sulfonate (PFOS) (EC, 2011).

The US EPA have derived statutory guideline values for about 125 contaminants in drinking water of which 31 could be considered to be micro-organic pollutants excluding pesticides. None of these are pharmaceuticals or personal care products (PCP) (US EPA, 2010).

Most emerging contaminant research has focussed on surface waters as these are likely to contain greater concentrations of contaminants from sources such as wastewater treatment works' (WTWs) discharges. Surface water is also easier to monitor than groundwater in some respects. The approach taken in this review is that surface water data can be used to give us an idea of potential future groundwater problems and can provide an early warning.

This paper provides a review of the types of EGCs which are beginning to be found in groundwater of the UK. This is drawn primarily from UK and European studies, supplemented by work from the US. It discusses the routes by which these compounds enter groundwater, including resistance to wastewater treatment, their toxicity and the consequent potential risks posed to drinking water and the environment. This provides the context to a UK groundwater monitoring dataset. Challenges that need to be met to minimise risk are identified.

2 Types of emerging groundwater contaminants

From their sources, physical and chemical characteristics, mobility/behaviour in the aqueous environment and associated hazards the following types of micro-contaminants may be considered to be emerging in groundwater. The world-wide occurrence, sources and fate of a range of EGCs, including pharmaceuticals and personal care compounds in groundwater has been reviewed by Lapworth et al. (submitted).

Much more is known about pesticides in groundwater compared to other compounds, such as pharmaceuticals, which are more poorly characterised. The hazards to human health of some compounds are well documented, but their ability to travel through the aqueous environment is only just being investigated, and environmental persistence is as yet unknown.

2.1 Pesticides

Pesticides have been detected at trace concentrations in UK groundwater for a considerable period. As those compounds which pose the greatest threat to the environment are gradually withdrawn, e.g. atrazine in 1993, the compounds which are substituted can in turn lead to problems, e.g. diuron which is itself now banned. A number of compounds have recently

caused problems as analytical methods have improved, for example metaldehyde (Bristol Water, 30/1/2009; Environment Agency, Jan 2010; Water UK, 2009). Attention has now also turned to pesticide metabolites, also termed degradates and reaction products (Kolpin et al., 1998). By their nature these compounds are biologically active and many may be toxic and such data forms part of the pesticide registration process. Studies have shown that pesticide metabolites are often detected in groundwater at higher concentrations compared to parent compounds from both agricultural and amenity use (Kolpin et al., 2004; Lapworth and Goody, 2006).

2.2 Pharmaceuticals

The presence of pharmaceutical chemicals in the aquatic environment has long been recognised as a concern (Richardson and Bowron, 1985). The primary routes for pharmaceuticals into the environment are through human excretion, disposal of unused products and through agricultural usage (Poynton and Vulpe, 2009). A wide range of pharmaceutical products have been detected in surface and groundwater, associated with wastewater disposal (Barnes et al., 2008; Miller and Meek, 2006; Nikolaou et al., 2007; Pérez and Barceló, 2007; Ternes and Hirsch, 2000; Vulliet and Cren-Olivé, 2011; Watkinson et al., 2009). These have included:

- veterinary and human antibiotics: e.g. ciprofloxacin, erythromycin, lincomycin, sulfamethoxazole, tetracycline
- other prescription drugs: codeine, salbutamol, carbamazepine
- non prescription drugs: acetaminophen (paracetamol), ibuprofen, salicylic acid
- iodinated X-ray contrast media: iopromide, iopamidol

Other potential threats to surface water which have been identified are tamiflu and chemotherapy drugs, such as 5-fluorouracil, ifosfamide or cyclophosphamide (Buerge et al., 2006; Johnson et al., 2008; Moldovan, 2006; Singer et al., 2007) and illicit drugs such as cocaine and amphetamines (Kasprzyk-Hordern et al., 2008; Zuccato et al., 2008).

2.3 “Life-style compounds”

Caffeine and nicotine, and the nicotine metabolite cotinine, are widely detected in groundwater impacted by sewage effluent (Godfrey et al., 2007; Seiler et al., 1999; Teijon et al., 2010). Van Stempvoort et al. (2011) found high concentrations of the artificial sweeteners

acesulfame, saccharine, cyclamate and sucralose in groundwater impacted by sewage infiltration ponds and Buerge et al. (2009) showed acesulfame to be widely detected in the aquatic environment due to its use, mobility and persistence.

2.4 Personal care

Personal care compounds are commonly transmitted to the aqueous environment through WTWs. These have included:

- DEET – N,N-diethyl-meta-toluamide, the most common active ingredient in insect repellents
- parabens – alkyl esters of p-hydroxybenzoic acid, used since the 1930s as bacteriostatic and fungistatic agents in drugs, cosmetics, and foods
- bactericide and antifungal agents – triclosan is widely used in household products, such as toothpaste, soap and anti-microbial sprays
- polycyclic musks – tonalide and galaxolide are used as fragrances in a wide range of washing and cleaning agents and personal care products
- UV filters/sunscreen – organic filters include the benzophenones and methoxycinnamates

Lindström et al. (2002) detected triclosan and its metabolite methyl triclosan in surface water in Switzerland and considered the metabolite to be persistent.

Tonalide (AHTN), galaxolide (HHCB) and HHCB-lactone have been detected in WTW effluents (Horii et al., 2007). These compounds have been used as markers for wastewater in surface water (Buerge et al., 2003; Fromme et al., 2001). Heberer (2002a) discusses the results from investigations of synthetic musk concentrations found in sewage, sewage sludge, surface water, aquatic sediment, and biota samples in terms of bioaccumulation, metabolism in fish, and environmental and human risk assessment.

The majority of compounds used as sun screens are lipophilic, conjugated aromatic compounds, but are detected in the aqueous environment (Jeon et al., 2006).

2.5 Industrial additives and by-products

There are a wide range of industrial compounds which can be released to the environment. Many of these have led to well-established problems, such as the chlorinated solvents, petroleum hydrocarbons, including the polyaromatic hydrocarbons and the fuel oxygenate

methyl tertiary-butyl ether, and plasticisers/resins bisphenols, adipates and phthalates (Garrett et al., 1986; Moran et al., 2005; Moran et al., 2006; Verliefde et al., 2007). Most of these industrial compounds are classed as priority pollutants or now have drinking water limits and as such are not emerging contaminants. However, some breakdown products may be regarded as emerging contaminants.

Industrial EGCs may include:

- 1,4-dioxane, a stabiliser used with 1,1,1-trichloroethane which is highly soluble in groundwater, resistant to naturally occurring biodegradation processes., does not readily bind to soils, and readily leaches to groundwater (Abe, 1999). In 2008, testing, sponsored by an independent consumers organization, found 1,4-dioxane in almost half of tested personal-care products.
- Benzotriazole derivatives which are found in pharmaceuticals such as antifungal, antibacterial, and antihelmintic drugs. Benzotriazoles are persistent in the aqueous environment (Giger et al., 2006; Voutsas et al., 2006).
- Dioxins can be produced as a consequence of degradation of other micropollutants e.g. from the antimicrobial additive triclosan (ENDS, 2010; Mezcuca et al., 2004).

2.6 Food additives

Triethyl citrate is used as a food additive to stabilise foams, e.g. egg white, and is also used in pharmaceutical coatings and as a plasticiser. Butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT) are used to prevent fat spoilage in foods. Other food additives include camphor, 1,8-cineole (eucalyptol), citral, citronellal, cis-3-hexenol, heliotropin, hexanoic acid, menthol, phenylethyl alcohol, triacetin, and terpineol. Some of these may be implicated as oxidants or endocrine disruptors (Jobling et al., 1995).

2.7 Water treatment by-products

The trihalomethanes and haloacetic acids are well established by-products of water disinfection (Boorman, 1999). More recent concern has focused on N-nitrosodimethylamine (NDMA) as a drinking water contaminant resulting from reactions occurring during chlorination or via direct industrial contamination. Because of the relatively high concentrations of this the potent carcinogen formed during wastewater chlorination, the intentional and unintentional reuse of municipal wastewater is a particularly important area

(Mitch et al., 2003). Richardson (2003) found that the change from disinfection with chlorine to ozone and chloramines can increase levels of other potentially toxic by-products, e.g. bromo- and iodo- THMs and brominated MX (3-chloro-4-dichloromethyl)-5-hydroxy-2(5H)-furanone). Other by products of water treatment can include polyacrylamide and epichlorohydrin.

2.8 Flame/fire retardants

Polybrominated diphenyl ether flame retardants are extensively used in resins for household and industrial use (Rahman et al., 2001) and may enter the environment via waste disposal to landfill and incineration. Phosphate-based retardants such tris-(2-chloroethyl) phosphate (TRCP) appear to work by forming a non-flammable barrier (Weil et al., 1996) are used in industrial and consumer products.

2.9 Surfactants

The priority pollutants octyl- and nonyl-phenol (OP and NP) are used in the production of alkyl phenol ethoxylates (APEs) which are used in the manufacture of surfactants. Both the parent ethoxylates and their metabolites, alkyl phenols and carboxylic degradation products, persist in the aquatic environment (Montgomery-Brown and Reinhard, 2003; Soares et al., 2008).

Perfluorinated sulfonates and carboxylic acids including perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) have been used for over 50 years in food packaging and cookware coatings, paints and surfactants cosmetics and fire-fighting foams with consequent entry to the environment by run-off from sites of major fires (e.g. Buncefield, UK). They are found in WTW effluents and surface water and are very persistent in the environment (Ahrens et al., 2009; Poynton and Vulpe, 2009). Harada et al. (2003) showed PFOS to be present in sewage effluent in Japan and it has been detected in surface water in Japan (Harada et al., 2003; Saito et al., 2003).

Siloxanes are used in many personal care products and industrial coatings and there is concern about potential toxicity and transport into the environment (Richardson, 2007).

2.10 Hormones and sterols

Sex hormones include androgens, such as androstenedione and testosterone, and oestrogens such as oestrone, oestriol, 17 α - and 17 β -oestradiol, and progesterone. There are also synthetic

androgens such as oxandrolone, nandrolone and more importantly synthetic oestrogens (xenoestrogens) such as 17 α -ethinyl oestradiol and diethylstilbestrol, used as contraceptives. Some of these compounds are commonly present in wastewater and WTW effluent (Johnson et al., 2000; Standley et al., 2008; Vulliet and Cren-Olivé, 2011).

A related group of compounds are cholesterol and its metabolite 5 β -coprostanol, and the plant sterols stigmasterol, stigmastanol and β -sitosterol. Plant sterols (phyto-oestrogens) are ingested in edible plants and excreted to wastewater, which may be the largest source of these compounds in the environment (Liu et al., 2010).

2.11 Ionic liquids

Ionic liquids are salts with low melting point which are being considered as 'green' replacements for industrial volatile compounds (Thi et al., 2010; Richardson and Ternes, 2011). These compounds include nitrocyclic rings (e.g. pyridinium, pyrrolidinium, morpholinium moieties) and quaternary ammonium salts. Ionic liquids are not yet widely used but current formulations have significant water solubility and are likely to be toxic and poorly degradable (Thi et al., 2010).

3 Sources, pathways and receptors

3.1 Concepts

Significant risks to human health may result from exposure to non-pathogenic, toxic contaminants that are often globally ubiquitous in waters from which drinking water is derived. The transport of contaminants in the aqueous environment can be described by a source-pathway-receptor model, which considers:

- the source of the contaminant, e.g. sewage sludge spread on to agricultural land
- the pathway by which it travels from the source, e.g. fracture flow through an aquifer
- the receptor, e.g. a consumer drinking tap water

Sources of contaminants to surface waters, groundwater, sediments, and drinking water are varied and include pesticide applications to agricultural land, horticulture, parks, gardens, golf courses, urban infrastructure, and the transport network, discharges or leaks of domestic, hospital or industrial wastewater containing pharmaceutical or personal care compounds,

sewage sludge application to land, pharmaceuticals and pesticides used to treat animals present in manure stores or applied to agricultural land and solid waste disposal.

Point-source pollution originates from discrete sources whose inputs into aquatic systems can often be defined in a spatially explicit manner. Examples of point-source pollution include industrial effluents (pulp and paper mills, steel plants, food processing plants), municipal WTWs and combined sewage-storm-water overflows, animal waste lagoons, resource extraction (mining), and land disposal sites (landfill sites, industrial impoundments).

Non-point-source pollution, in contrast, originates from poorly defined, diffuse sources that typically occur over broad geographical scales. Examples of non-point-source pollution include agricultural runoff (pesticides, pathogens, and fertilizers), storm-water and urban runoff, and atmospheric deposition (wet and dry deposition of persistent organic pollutants) (Bedding et al., 1982; Ritter et al., 2002). About 70% of land area in the UK is used for agricultural purposes and about 6% is urban.

3.2 Source terms

Potential source terms include wastewater, derived from domestic, industrial, or hospital premises and waste disposal sites (Bester et al., 2008; Heberer and Feldmann, 2005; Stangroom et al., 1998). The presence of persistent organic pollutants in wastewater, such as polyaromatic hydrocarbons, polychlorinated biphenyls, alkyl phenols, dioxins and furans, chlorinated solvents and benzene derivatives, has been long established (BGS et al., 1998; Rudel et al., 1998, among many others).

The primary sources of pharmaceuticals in the environment are human excretion and disposal of unused products. Hospital waste water forms an important source for a range of EGCs including disinfectants and musks, as well as rare earth elements, heavy metals, and iodised contrast media (Putschew et al., 2000; Sacher et al., 2001; Ternes and Hirsch, 2000; Verlicchi et al., 2010; Watkinson et al., 2009). There are a large number of studies of WTW effluent and septic tanks (Clara et al., 2004; Drewes et al., 2003; Gasser et al., 2010; Glassmeyer et al., 2008; Heberer et al., 1997; Kreuzinger et al., 2004), of raw sewage (Sodré et al., 2009) and of artificial recharge using treated effluent (Cordy et al., 2004; Díaz-Cruz and Barceló, 2008). Manufacturing sites may also contribute (Larsson, 2008; Larsson et al., 2007). There are about 9000 WTWs in the UK serving 95% of the population (Water UK, 2006).

The use of veterinary antibiotics in concentrated animal feeding operations is an important source of environmental contamination in the USA and parts of Europe and Asia (Bartelt-Hunt et al., 2010). Veterinary antibiotics have been investigated in various environmental compartments including waste lagoons, groundwater below lagoons, as well as shallow groundwater from areas where animal waste had been applied to fields (Bartelt-Hunt et al., 2010; Hu et al., 2010; Kim et al., 2011; Kolodziej et al., 2004; Sarmah et al., 2006; Watanabe et al., 2010; Watanabe et al., 2008).

Landfill leachates contain large amounts of short and long-chain fatty acids, and can also contain caffeine, nicotine, phenols, sterols, PAH, chlorinated solvents and phthalates (Stuart and Klinck, 1998). The presence of pharmaceuticals in groundwater beneath or downgradient of a landfill has been confirmed by several authors (Ahel and Jelicic, 2001; Ahel et al., 1998; Eckel et al., 1993; Holm et al., 1995). Two recent studies (Barnes et al., 2004; Buszka et al., 2009) investigating the occurrence of groundwater down gradient of landfills detected a range of industrial compounds (detergents, antioxidants, fire retardants, plasticisers) as well as PPCPs (antibiotics, anti-inflammatories, barbiturates) and the caffeine and the nicotine metabolite cotinine.

3.3 Pathways

For many EGCs the pathway from the source to the receptor is very unclear, since there is a paucity of information for most such novel contaminants. The pathway taken by a contaminant through the environment will depend upon its physicochemical properties, such as its solubility in water.

Direct pathways for pharmaceuticals, urban and industrial contaminants to reach groundwater include leaking sewers, discharge of WWT effluent (directly to ground or to surface water which then infiltrates), landfill leachate, leaking storage tanks and other discharges to the ground that bypass the soil zone, such as septic tanks (Figure 1). Pathways to humans and groundwater from human and animal pharmaceuticals are set out by Boxall et al. (2002), Halling-Sørensen et al. (1998) and Jones et al. (2002). Verma et al. (2007) studied the behaviour of a pharmaceutical in surface and wetland waters.

Contaminants applied to the soil surface will migrate through the soil zone, the unsaturated zone and the saturated zone in the well-established way. This may be the route for agricultural pesticides and components of sewage sludge. The potential for organic

contaminants present in sewage sludge to leach following application to agricultural land was highlighted by Wilson et al. (1996), although in this study no problems were found using a screening exercise.

Another important pathway is groundwater-surface water interaction. In many instances treated effluent from industrial premises and sewage works is discharged to surface water. This may then infiltrate to groundwater from losing reaches of rivers.

In this review we have not highlighted the atmospheric transmission route as being significant but there may be mechanisms for non-volatile compounds to be mobilised. For example, Hamscher and Hartung (2008) suggest that dust may be a new route for veterinary compounds to enter the environment.

3.4 Receptors

Groundwater supplies about one third of public water supply in the UK rising to about 80% of public supply in the south and southeast of England. It also provides water for industry and irrigation, baseflow support to surface water and aquatic ecosystem health Under the Water Framework Directive (EC, 2000). Receptors, in terms of chemical status, include the groundwater body itself, drinking water abstractions, associated surface waters and directly dependent ecosystems. In parts of south east England, river baseflow from groundwater can be up to 90% of total flow. Receptors therefore can include human beings drinking tap water, other living creatures such as invertebrates and fish or the environment more widely.

A clear connection between source terms of these contaminants as set out in section 3.2 and groundwater or its receptors is often not well defined enough for significant problems in groundwater to be anticipated. However the risks to such a valuable resource do need to be considered.

4 Risk assessment for pesticides and their metabolites

In order to assess the hazards presented by contaminants, information on usage, persistence, leachability and a robust sensitive analytical method is required. For many pesticides these requirements are fulfilled and an assessment of risk of leaching to groundwater can be made. However, the UK metaldehyde problem was not originally discovered due to lack of an analytical method and was exacerbated by recalcitrance to water treatment. For pesticide

metabolites this information can be sparse, and for other EGCs such as pharmaceuticals it can be lacking.

4.1 Pesticides

Pesticides can be synthetic chemical or natural substances and vary in their use, properties and potential impact on the environment. There are currently around 350 ingredients approved for use in agricultural pesticide products in the UK (BCPC and CABI, 2010). Agriculture and horticulture use nearly 80 per cent of all plant protection pesticides in England and Wales. There has been a trend towards more frequent treatments using complex tank mixes but using less persistent compounds and at an overall lower rate of application. Pesticides are also used to control weeds and pests in gardens and weeds on pavements and along railway lines. Pesticides used for seed dressings and biological pesticides were excluded from this study.

Solubility and K_{ow} can both give an indication of a compound's mobility and likely sorption in water treatment. K_{ow} is commonly expressed as the log of the coefficient. It is used in environmental fate studies and large values (+4 or higher) are regarded as an indicator that a substance may tend to bioaccumulate. Conversely, low values indicate environmental mobility. Table 1 shows UK pesticides with the potential to persist in WTW effluent based on their K_{ow} . They may however, have other properties which are not assessed by this method; bipyridilium compounds such as diquat are cationic and form charge transfer complexes with organic matter (Gevao et al., 2000). Wells (2006) proposes Dow, a pH-dependent coefficient as a better measure of hydrophilicity.

Pesticides most likely to pose a threat include those which remain difficult to analyse at low concentrations and also those in Table 1 which have the potential to persist in drinking water e.g. clopyralid.

4.2 Pesticide metabolites

Once released to the environment, pesticides may be degraded by both abiotic and biotic processes. While parent compounds are assessed in detail in many regulatory schemes, the requirements for the assessment of transformation products are less well developed. The potential issue of pesticide metabolites was highlighted by Kolpin et al. (2004) who found atrazine and metalochlor metabolite concentrations present in groundwaters at concentrations higher than the parent compounds. An initial assessment suggested that as many as 30% of

pesticide metabolites can be more toxic than the parent compound (Sinclair and Boxall, 2003). Often their different properties can make them difficult to detect and quantify.

Sinclair et al. (2010) reported measured metabolite concentrations in groundwater of the UK. These were all from compounds no longer licensed in the UK: DDT, heptachlor and atrazine. They also reported a desk study of impact on UK surface water derived drinking water based on potential to contaminate water for 53 pesticide metabolites based on parent compound usage, formation rates in soil, persistence and mobility, estimated toxicity and/or potential to exhibit pesticidal activity, the estimated efficiency of removal during drinking water treatment as well as during environmental degradation (Sinclair et al., 2010). This included compounds currently licensed and those which have recently been withdrawn, e.g. atrazine and isoproturon. About half of the compounds had been identified during environmental degradation as well as in mammalian toxicity testing of the parent. For five of the metabolites significant concentrations in surface water derived drinking water were predicted by their model. These were aldicarb sulphone (aldicarb metabolite), 3-carbamyl-1,2,4,5-tetrachlorobenzoic acid (chlorothalonil metabolite), cyanazine chloroacid (cyanazine metabolite), desisopropyl atrazine and methomyl (thiodicarb metabolite and also parent compound).

Parsons et al. (2008) carried out an assessment of risk from pesticide metabolites for both the US and the UK. For the UK, 54 pesticides were identified as representing 90% of all pesticide use. A risk index was used derived from an exposure index, depending on usage, fraction formed, water/organic carbon partition coefficient (K_{oc}) and half life (DT_{50}) together with acceptable daily intake. Compounds with the highest risk index were metabolites of cyanazine, followed by those of isoproturon, flufenacet, tebuconazole and dicamba.

Table 2 summarises some European pesticide metabolite studies. Other studies of pesticide metabolites in groundwater, have tended to be in areas where the suite of applications differs from that currently used in the UK (Chang and Liao, 2002; Fava et al., 2005; Giacomazzi and Cochet, 2004; Hancock et al., 2008; Hildebrandt et al., 2007; Kolpin et al., 2004; Montana Dept of Agriculture, 2006).

Worrall et al. (2000) proposed using a probability index for predicting groundwater contamination risk using soil K_{oc} and DT_{50} where points along a diagonal line have a similar estimated leaching probability. A simple assessment for pesticide metabolites for pesticides with UK usage >50,000 ha can be made using this method (Figure 2). Estimates of

persistence, physical properties and leachability data are available from the Footprint website (AERU, 2010) for some metabolites but these are much less comprehensive than for the parent compounds. The line shown is a cut-off between leachers and non-leachers. Values close to the line have been assessed as leachers. Compounds were assessed as non-leachers where $\text{Log } K_{oc} > 4$ and $\text{Log } DT_{50} < 0.5$. Key metabolites are shown in Table 3. This approach takes no account of the activity or toxicity of these metabolites and some of the metabolites may be trivial.

The different approaches indicate that the metabolites of chlorothalonil, cyanazine, diflufenican, flufenacet, iodosulfuron-methyl, metaldehyde, metazachlor and metsulfuron-methyl are likely to pose the greatest risk to drinking water. In many cases these metabolites are derived from parent compounds which have a lesser risk.

Glyphosate is now the most widely used herbicide in the world, with dramatic increases in agricultural use since the introduction of glyphosate resistant crops. Microbial degradation produces amino methyl phosphonic acid (AMPA) (Kolpin et al., 2000) and it has been anticipated that AMPA may be problematic. The high water solubility of both the parent and the metabolite has meant that their analysis has been difficult. Kolpin (2006) showed AMPA to be detected in wastewater-impacted surface waters about four times as frequently as the glyphosate parent. Although AMPA has a DT_{50} of about 151 days and is therefore persistent it also has a relatively high K_{oc} of 8087 mL/g and would not be classified as vulnerable to leaching by the simple method described above. Similarly for parent compounds which have non-agricultural applications, there will be routes to groundwater which would not be identified, such as routes which bypass the soil zone.

5 Risk assessment for other emerging contaminants

These include pharmaceuticals, personal care products, lifestyle compounds, and industrial compounds. Many of this group of compounds cannot as yet be assessed in the same way due to a lack of persistence data since the majority of studies have been directed at water treatment. There is a scarcity of data on human health effects at environmental levels, effects on aquatic organisms, and other harmful effects and therefore it is difficult to predict which health effects they may have on humans, terrestrial and aquatic organisms, and ecosystems. Studies often use a mixture of physical properties, degradation rates and monitoring case studies to reach an assessment. Many of these compounds are considered to be persistent in

the aqueous environment. However, it is characteristic of some contaminants that they do not need to be persistent to cause negative effects since their high transformation/removal rates is compensated by their continuous introduction into the environment (EUGRIS, 2011).

5.1 Attenuation in treatment works

The effective operation of WTWs plays an important role in minimising the release of xenobiotic compounds into the aquatic environment (Byrns, 2001). A feature of some emerging contaminants is their recalcitrance to sewage treatment (Heberer, 2002b) or drinking water treatment which allows them to pass through into the treated water (Zwiener, 2007).

5.1.1 Wastewater treatment

The first concerns regarding the potential adverse effects of pharmaceuticals in wastewater were expressed in the 1960s following a study of oestrogenic hormones in activated sludge (Stumm-Zollinger and Fair, 1965). A review of implications for the US water industry is provided by Snyder et al. (2003) starting from an analytical perspective.

Joss et al. (2006) showed that efficiency of elimination of micro-organics depends on the relative rate of degradation and retention times in the plant. Maurer et al. (2007) showed that β -blockers were incompletely removed in WTW due to both to limited sorption and degradation rates similar to the retention time. Many pharmaceuticals which pass through treatment may not be in the fully dissolved state and are often as glucuronaric acid or sulphate conjugates which enhances their polarity before excretion, and makes them harder to remove, but which can be cleaved during treatment to release further active ingredient (Ternes et al., 2004).

Rosal et al. (2010) report a survey of over 70 individual pollutants in a WTW effluent using biological treatment followed by ozonation where several important groups of pharmaceuticals had typical removal efficiencies of <20%. Ashton et al. (2004) suggested that most WTWs in England and Wales are likely to be routinely discharging small quantities (ng/L) of pharmaceuticals. A number of other studies have similar findings (Carballa et al., 2004). A study in Sweden found diclofenac at higher concentrations in the effluent than in the influent (Zorita et al., 2009).

The oestrogenic effects of WTW effluent ascribed to ethinyl oestradiol and alkyl phenols have been recognised for two decades (Montagnani et al., 1996; Purdom et al., 1994). Rutishauser et al. (2004) showed that in-vitro tests were able to detect oestrogenic effects in effluents from these compounds and bisphenol A. An assessment of oestrogen removal efficiency for WTW in the UK (Johnson et al., 2007b) showed simple biological plants to be poor with only about 30% removal. Johnson and Williams (2004) were able to estimate the amount likely to be discharged using predictions of excretion fate and behaviour in the wastewater treatment system.

Degradation of APEs in WTWs generates more persistent shorter-chain APEs and alkyl phenols such as NP, OP and alkylphenol mono- to tri-ethoxylates (Ying et al., 2002). The physicochemical properties of APE metabolites indicate that they will have a significant load in sediments and sludges. APE removal can be enhanced by GAC filtration, UV treatment or ozonolysis but these techniques do not resolve accumulation in sludge (Soares et al., 2008).

Horii et al. (2007) showed that removal efficiencies for synthetic musks by WTWs ranged from 72% to 98% but concentrations of the galaxolide metabolite HHCb-lactone increased during treatment. Flame retardants may be present in effluent from WTWs accepting landfill leachate (Rahman et al., 2001). This may also be a route for other industrial compounds.

Byrns (2001) showed that the effect of some operating parameters has an important influence upon the concentration of xenobiotics released in the sludges and final effluent. This may have significance for a wide range of ecotoxic compounds and in particular the class of compounds increasingly recognised as having the potential to disrupt endocrine activity in some aquatic invertebrates.

5.1.2 Drinking water treatment

For drinking water the main types of treatment processes relevant to micro-organics are: clarification/coagulation, granulated or powdered activated carbon (GAC or PAC) sorption, oxidation using ozone or chlorine and membrane filtration. In order to assess removal it is critical to understand their size distribution and particulate and colloidal association of micro contaminants in raw drinking water (Snyder et al., 2003).

Filtration using GAC has been widely used to remove organic micropollutants from drinking water and is effective in removing emerging contaminants provided that it is correctly managed. Removal may be up to 90% for refractory compounds (Schäfer et al., 2002). Its

effectiveness is greatly reduced by the presence of natural organic matter which competes for binding sites, or particulates which block the pore spaces (Bolong et al., 2009; Snyder et al., 2007). PAC is more efficient since it is fed as a new product and is not recycled through the treatment process whereas GAC can have a greater absorption capacity, particularly if steam treated, but needs regular replacement (Snyder et al., 2007). However, small and/or very polar molecules can be difficult to remove by this method.

Membrane filtration, either by nanofiltration or reverse osmosis, has considerable potential to remove a wide range of emerging contaminants (Nghiem et al., 2005a; Nghiem et al., 2005b; Snyder et al., 2007). Membrane filtration can provide good removal except for lower molecular weight uncharged compounds (Snyder et al., 2007). Verliefde et al. (2007) assessed the application of nanofiltration to priority pollutant removal from water sources. Nanofiltration was particularly effective for negatively charged compounds (Zwiener, 2007). Membrane cleaning requires careful management (Nghiem and Schäfer, 2006).

Chlorine and chlorine dioxide have been shown to be ineffective and also produced undesirable by-products (Zwiener, 2007). Chlorine dioxide is anticipated to react particularly with compounds containing phenolic amino and thio functions (Snyder et al., 2003). In a study of 98 organic micro-compounds, Gibs et al. (2007) showed that 50% were not substantially degraded by combined and free chlorine.

Reactions with ozone are reviewed by Snyder et al. (2003). Advanced oxidation, which uses a combination of ozone with other oxidation agents such as UV radiation, hydrogen peroxide or TiO₂, generates reactive intermediates and includes electrochemical mineralisation and solar photocatalysis (Comninellis et al., 2008). This is limited by the radical scavenging capacity of the matrix and can be expensive (Petrović et al., 2003).

Ternes et al. (2002) investigated the elimination of selected pharmaceuticals (bezafibrate, clofibrac acid, carbamazepine, diclofenac) during drinking water treatment processes at laboratory and pilot scale and in real waterworks. No significant removal of pharmaceuticals was observed in batch experiments with sand filtration under natural aerobic and anoxic conditions, thus indicating low sorption properties and high persistence with non-adapted microorganisms. Flocculation using iron(III) chloride in lab-scale experiments and investigations in waterworks exhibited no significant elimination. However, ozonation was in some cases very effective in eliminating the polar compounds diclofenac and carbamazepine

and reducing bezafibrate. Except for clofibrac acid, GAC in pilot-scale experiments and waterworks provided a major elimination of the pharmaceuticals under investigation.

Westerhoff et al. (2005) reviewed the effectiveness of a range of drinking water treatment processes for emerging contaminants on the laboratory scale. Aluminium sulphate and ferric chloride coagulants or chemical lime softening removed <25% of most emerging contaminants (ECs). PAC effectiveness was variable, from 10 to 90% depending on compound polarity (K_{ow}). Ozone oxidized steroids containing phenolic moieties (oestradiol, ethinyloestradiol, or oestrone) more efficiently than those without aromatic or phenolic moieties (androstenedione, progesterone, and testosterone). EC reactivity with oxidants were separated into three general groups: (1) compounds easily oxidized (>80% reacted) by chlorine are always oxidized at least as efficiently by ozone; (2) 6 of the 60 compounds (TCEP, BHC, chlordane, dieldrin, heptachlor epoxide, musk ketone) were poorly oxidized (<20% reacted) by chlorine or ozone; (3) compounds (24 of 60) reacting preferentially (higher removals) with ozone rather than chlorine.

In an overall assessment for 113 organic micro-compounds Stackelburg et al. (2007), 15% of the loading was removed by clarification, 32% by hypochlorite disinfection and 53% by GAC filtration. Compounds most frequently detected in finished water were carbamazepine, DEET, cotinine, tonalide, caffeine and camphor.

The efficacy of drinking water treatment for pharmaceuticals was evaluated for GAC, oxidation and membrane filtration by Zweiner (2007). A good correlation was found between the percentage removal by activated carbon and the octanol/water partition coefficient (K_{ow}) for many compounds with $\log K_{ow} > 3$. High rates of removal by ozonation are usually observed for compounds with double bonds, aromatic structure or heteroatoms, and this was the case for diclofenac, carbamazepine and sulfamethoxazole (Zwiener, 2007). Lower rates were observed for clofibrac acid and ibuprofen which do not have reactive sites. These types of compounds are more readily degraded by advanced oxidation using, for example, the OH radical.

Escher et al. (2009) assessed the efficiency of removal of toxicological activity by ozonation after secondary treatment using bioassays and compared that with removal using GAC. Escher et al. (2006) estimated the removal efficiency of pharmaceuticals and hormones in separated urine using both bioassays and chemical analysis. This approach was extended to

the ecotoxicological effects of polar micro-organics in effluent and receiving surface waters (Escher et al., 2008).

In conclusion we can assume that there is potential for some EGCs to pass through drinking water treatment plants. Many such plants which treat groundwater may not have treatment which would remove these types of compounds as groundwater has a lower organic loading than surface water.

5.2 Attenuation in the environment

Physicochemical properties such as K_{ow} are available for many of urban and industrial organic micropollutants from the SRC database (SRC, 2010). As a first pass estimate of recalcitrance to water treatment, of the compounds listed by Gibs et al. (2007), Stackelberg et al. (2007) and Glassmeyer et al. (2008), only 19 had a K_{ow} of <1.

Zweiner (2007) describes the processes which reduce the concentrations of pharmaceuticals in treated sewage effluent in the aqueous environment as biodegradation, sorption, photolysis and oxidation successively in surface water, bank filtration and drinking water treatment. Most degradation studies have been directed at degradation in surface water (Pal et al., 2010). Pal et al. (2010) also collated physicochemical properties reported in the literature for 14 pharmaceuticals demonstrating their wide range. In general amines have higher sorption coefficients than carboxylic acids and neutral pharmaceuticals (Yamamoto et al., 2009). Lai et al. (2000) showed that synthetic oestrogens were more readily removed from the aqueous phase in rivers and estuaries than natural compounds due to their higher K_{ow} . Sorption was to both organic carbon and iron oxides in sediments.

Oppel et al. (2004) studied the leaching behaviour of 6 selected pharmaceuticals in different soils to simulate soil application. The results indicated that the leaching potential was low for diazepam, ibuprofen, ivermectin and carbamazepine, but clofibric acid and iopromide were very mobile under the experimental conditions.

Drewes et al. (2003) showed that caffeine, gemfibrozil and many analgesics were removed from recharged treated effluent during groundwater recharge within six months, whereas carbamazepine and primidone persisted for up to 8 years. For a group of 8 pharmaceuticals Lam et al. (2004) showed that photolysis was much more significant than hydrolysis. Jürgens et al. (2002) measured the degradation of oestradiol and ethinyl oestradiol in English rivers and estimated a half-life of 10 days or less. Synthetic musks are assessed as being non-

degradable with sorption and sedimentation being minor processes. Tonalide can be removed from surface water by direct photolysis but galaxolide shows negligible photochemical degradation (Buerge et al., 2003).

Jones et al. (2002) made an environmental assessment for the 25 most-used prescription pharmaceuticals in the UK based on usage, removal in treatment works based on sorption and dilution. Degradation was modelled due to lack of data and was predicted to be very limited for most compounds. Jones et al. (2005) assessed the potential for pharmaceuticals to enter the aqueous environment, reviewed the levels reported in drinking water world-wide and assessed the implications.

Lindström et al. (2002) detected triclosan and its metabolite methyl triclosan in surface water in Switzerland and considered the metabolite to be persistent.

Löffler et al. (2005) studied four ¹⁴C-labelled pharmaceuticals (diazepam, ibuprofen, iopromide, and acetaminophen) as well as six non-labelled compounds (carbamazepine, clofibric acid, 10,11-dihydroxycarbamazepine, 2-hydroxyibuprofen, ivermectin, and oxazepam) in batch studies of water/sediment. Ibuprofen, 2-hydroxyibuprofen, and paracetamol displayed a low persistence with DT₅₀ values in the water/sediment system less <20 d and paracetamol was rapidly attenuated due to the extensive formation of bound residues. A moderate persistence was found for ivermectin, iopromide and oxazepam with DT₅₀ values of <60 d. For diazepam, carbamazepine, 10,11-dihydroxycarbamazepine, and clofibric acid, system DT₉₀ values of >365 days were found. An elevated level of sorption onto the sediment was observed for ivermectin, diazepam, oxazepam, and carbamazepine.

Johnson et al. (2007a) applied an existing GIS model to predict the concentrations of the pharmaceuticals, diclofenac and propranolol, in surface water catchments. The model input parameters included consumption, excretion and fate. Concentrations predicted throughout the catchments were 1 ng/L under low flow except for downstream of small WTW where concentrations of up to 25 ng/L were predicted.

Kavlock et al. (2008) reviews the types of model which can be used to estimate physicochemical properties and degradation mechanisms in the environment, and examples are shown in Table 4.

The fate and transport of emerging contaminants in the aqueous environment remains poorly understood, particularly for groundwater. Established contaminants, such as pesticides, often

have persistence in groundwater of up to an order of magnitude longer than in soils and surface water.

5.3 Toxicity

5.3.1 Lifestyle and personal care products

Pathways to humans will also include direct exposure through ingestion, inhalation or dermal contact and the risk posed by drinking water is likely to be considerably less.

Caffeine and nicotine have been included in a number of studies of pharmaceutical fate (e.g. Debska et al., 2004; Santos et al., 2007; Schwab et al., 2005). Caffeine's effect on the environment is not well understood, but does not appear to give cause for concern to freshwater organisms at currently detected concentrations (Moore et al., 2008). Nicotine has a high toxicity to humans, compared to other alkaloids and neonicotinoid pesticides, such as imidacloprid, are widely used. The toxicity of artificial sweeteners as food additives is reviewed by Grice and Goldsmith (2000) and by Whitehouse et al. (2008).

DEET has been found to inhibit the activity of a central nervous system enzyme, acetylcholinesterase, in both insects and mammals (Corbel et al., 2009). Collated information on DEET in the aquatic environment suggested risk to aquatic biota at observed environmental concentrations is minimal.

The parabens exert a weak oestrogenic activity (Oishi, 2002; Soni et al., 2002) and are capable of producing immunologically mediated, immediate systemic hypersensitivity reactions (Nagel et al., 1977). Some data on their environmental toxicity is now available (Bazin et al., 2010). Fatta-Kassinos et al. (2010) considered that n-butyl and benzyl parabens should be classified as toxic substances whereas methyl, ethyl and n-propyl parabens are harmful. A synergistic oestrogenic effect was observed when other estrogenic compounds were also present.

Triclosan is degraded to dioxins and is toxic to aquatic bacteria at levels found in the environment (Ricart et al., 2010).

Work on toxicity of musks has mainly assumed a dermal exposure pathway (Ford et al., 2000). They are degraded to more polar metabolites during treatment and in sediments and the soil. Heberer (2002a) discusses the results from investigations of synthetic musk concentrations found in sewage, sewage sludge, surface water, aquatic sediment, and biota

samples in terms of bioaccumulation, metabolism in fish, and environmental and human risk assessment.

Many “lifestyle“ and PCPs which are commonly used may exhibit some toxic effects on humans or the environment.

5.3.2 Industrial compounds

The toxicological effects of many industrial compounds are long established; information is also available for many emerging compounds.

Polybrominated diphenyl ether (PBDE) flame retardants have been found to bioaccumulate and have potential endocrine disrupting properties (Hooper and McDonald, 2000; Meerts et al., 2001; Rahman et al., 2001). Tris-(2-chloroethyl) phosphate (TRCP), which is used in industrial and consumer products, appears to be responsible for brain damage (Matthews et al., 1993). There is relatively little information on PFOS toxicity (Hekster et al., 2003).

Octyl and nonyl phenol have been long established as endocrine disruptors in fish (Petrović et al., 2004; White et al., 1994). The APEs can also be used as pesticide adjuvants. These can therefore be found in groundwater as a result of agricultural activity (Lacorte et al., 2002; Latorre et al., 2003). Thomas et al. (2001) used the toxicological impact of a storm event in an agricultural catchment near Tunbridge Wells to determine that significant components not being measured were present, and used this to identify the surfactant nonylphenol as well as the pesticides diuron, simazine endosulphan sulphate and pendimethalin.

Both the water treatment by products NDMA and acrylamide affect the central nervous system and are carcinogenic (Smith and Oehme, 1991).

Eljarrat and Barceló (2003) attempted to prioritize emerging and persistent organic pollutants in the environment based on their relative toxic potency. These included dioxins and polybrominated compounds.

Carlsson et al. (2006) assessed 27 active ingredients, with 9 being identified as dangerous for the aquatic environment and only oestradiol and ethinyloestradiol considered to have possible aquatic environmental risks.

Farré et al. (2008) review the fate and the ecotoxicology of emerging pollutants, especially focusing on their metabolites and transformation products (TPs) in the aquatic environment,

including pharmaceuticals, hormones, perfluorinated compounds, by-products of drinking-water disinfection, sunscreens or UV filters, benzotriazoles and naphthalenic acids.

Poynton and Vulpe (2009) applied an ecotoxicogenomic approach to assess the potential effects of a range of pharmaceuticals, endocrine disruptors, polybrominated flame retardants, perfluorinated compounds and nanomaterials. DNA-microarrays can be used to understand the effects of single compounds and mixtures, to suggest potential modes of action and predict exposure to pollutants in the environment.

Schriks et al. (2010) derived provisional drinking water values for a selection of emerging contaminants based on toxicological literature data. Where no published values existed these were derived from the ADI or failing this from the LOEC/NOEC. These were compared with occurrence data for surface water of the Rhine and Meuse. This study identified 1,4-dioxane, benzene and NDMA as being found at the highest concentrations relative to the guidelines. PFOS and PFOA were also highlighted. For groundwater the highest concentrations were for the fuel-oxygenate methyl tertiary-butyl ether.

5.4 Synergistic toxic effects

Concern over the potential adverse health effects of groundwater contaminated by a cocktail of contaminants has existed for many years (Germolec et al., 1989). The implications for mixtures of herbicides considered by WHO, who stated in 1987 that not these could not be handled in isolation (WHO, 1987). Carpy et al. (2000) reviewed the possible effects of pesticide mixtures and Relyea (2009) showed how aquatic communities can be dramatically impacted by a cocktail of low concentrations of pesticides. Yang et al. (1989) describe the approaches to evaluating the toxicology of chemical mixtures. Seed et al. (1995) discuss the applicability and validity of the methods for the assessment of risk posed by exposure to environmentally relevant concentrations of chemical mixtures. Borgert et al. (2001) describe a set of criteria to: evaluate the quality of data and interpretations in chemical interaction studies said to reflect the consensus of the literature on interaction analysis which apply to interaction data for drugs, pesticides, industrial chemicals, food additives, and natural products.

In a different approach Eljarrat and Barceló (2003) define a toxic equivalency factor (TEF) which provides a single number that is indicative of the overall toxicity in a mixture of related compounds. They used this for a mixture of dioxin and dioxin analogues.

Pomati et al. (2006; 2008) investigated the effects and interactions of a mixture of commonly used pharmaceuticals, including carbamazepine, ibuprofen and sulfamethoxazole at low concentrations, designed to mimic those found in the environment using in vitro tests on human and zebrafish cells. They concluded that a mixture of drugs at ng/L levels can inhibit cell proliferation by affecting their physiology and morphology and that waterborne pharmaceuticals may have an effect on aquatic life.

Synergy remains an important topic with the complex mixtures of trace organic compounds being released to the environment.

5.5 Risk assessment

In their editorial to the special issue of Water Research ‘Emerging contaminants in water’ Ternes and von Gunten (2010) state that to elucidate the relevance of micropollutants in aquatic systems their (eco)toxicological potential must be addressed. Almost all studies of risk to the aquatic environment have been directed to surface water; risk assessment to humans from consumption of surface water has therefore been used as an analogue for groundwater accepting that groundwater itself may be less at risk from emerging contaminants.

In an early review, Halling-Sørensen et al. (1998) collated concentrations of pharmaceuticals in the environment from human and veterinary use and also assessed their environmental fate and toxicity. They concluded that pharmaceuticals were present in the environment at concentrations similar to other xenobiotics, and highlighted the paucity of information.

The principles of human risk assessment are set out by Lioy (1990) and these are illustrated using a flow diagram relating the source of contaminant to health effects in humans. Risk assessments of pharmaceuticals in the aquatic environment use the comparison of predicted environmental concentration (PEC) and predicted no-effect concentration (PNEC) derived from the Acceptable Daily Intake (ADI). The process for registration of new drugs at the European level requires a risk assessment of the PEC using data on the volume of drug prescribed and the amount of dilution in the wastewater stream (EMEA, 2005). The method assumes “no biodegradation or retention of the drug substance in the WTW”. This approach can also be used to assess existing compounds. Bound and Voulvoulis (2006) used the proportion of the population being treated, the dosage, the amount of wastewater generated

per day and an estimate of dilution to identify candidate compounds for a study of pharmaceuticals in UK rivers.

Stuer-Lauridsen et al. (2000) calculated the PEC using the amount of compound used divided into the amount of wastewater generated both per capita diluted into the environment using a default value of 10, and estimating K_{ow} and DT_{50} from literature values. They found limited ecotoxicity data to be available for calculation of PNEC and showed for the six compounds possible, $PEC/PNEC > 1$ for ibuprofen, paracetamol and acetyl-salicylic acid. Webb (2000) made a similar assessment for drugs used in the UK in 1995. Of the 67 compounds assessed only 7 had $PEC/PNEC > 1$ and only 11 had $PEC/PNEC > 0.1$.

Schwab et al. (2005) and Cunningham et al. (2009) presented human health risk assessments for a range of active pharmaceutical ingredients and/or their metabolites, representing different drug classes, using environmental monitoring data. ADIs were used to estimate PNECs for both drinking water and fish ingestion. The PNECs were compared to measured environmental concentrations (MECs) from the published literature and to maximum PECs generated using the regional assessment models *PhATE*TM (Anderson et al., 2004) for North America and GREAT-ER (Feijtel et al., 1997) for Europe. The model predictions assumed low river flow and no depletion (no metabolism, no removal during wastewater or drinking water treatment, and no instream depletion). Ratios of MECs to PNECs were typically very low and consistent with PEC to PNEC ratios. For all 26 compounds, these low ratios indicate that no appreciable human health risk exists from the presence of trace concentrations in surface water and drinking water.

Straub (2008) reviewed the derivation of PECs, PNECs and MECs for diazepam by both deterministic and probabilistic procedures and the probabilistic safety margin. No significant concern was identified. In contrast, Cooper et al. (2008) ranked drugs by their potential environmental exposure and risk using annual prescriptions dispensed, surface water concentrations, effluent concentration, environmental half life, biological half life, mammal, fish and crustacean toxicity, K_{ow} , solubility and ECOSAR (model used to estimate the aquatic toxicity of industrial chemicals). These were compiled into the PEIAR (Pharmaceuticals in the Environment, Information for Assessing Risk) database (CHBR, 2009). A preliminary assessment indicated that anti-infective, cardiovascular and central nervous system (analgesic, anti-inflammatory and psychotherapeutic) pharmaceuticals had the highest risks.

Toxicological and ecological assessments for pharmaceuticals are summarised by Pal et al. (2010). These used toxicity tests using freshwater invertebrates, fish, mussels and human embryonic cells. The sex hormones were viewed to be of the greatest concern, followed by cardiovascular drugs, antibiotics and antineoplastics (chemotherapy drugs) (Sanderson et al., 2004a). Currently, antibacterial resistance represents the most significant human health hazard, and potentially the largest non-target organism hazard is sex hormones acting as endocrine modulators in wildlife.

In a study which did include groundwater, Schulman et al. (2002) assessed the risk to human health for 4 representative pharmaceuticals: acetylsalicylic acid, clofibrate, cyclophosphamide, and indomethacin which have been detected in aqueous environmental media including WTW effluent, surface water, drinking water, and groundwater. The toxicological and pharmacological nature, exposure assessment, and environmental fate and transport of each pharmaceutical were considered. The overall conclusion was that based on available data there was appreciable risk to humans, as the detected concentrations of each compounds were far below the derived safe limits.

A number of studies have assessed the risk to aquatic organisms using species dependent criteria. Ferrari et al. (2003) calculated PNEC from bioassays for bacteria, algae, microcrustaceans, and fishes to perform an initial risk characterization against both MEC and PEC for carbamazepine, clofibric acid, and diclofenac. Only carbamazepine had a risk quotient >1. Sanderson et al. (2004b) ranked 2986 different pharmaceutical compounds in 51 classes relative to hazard toward algae, daphnids, and fish using a quantitative structure-activity relationship (QSAR) type model. Modifying additives were the most toxic classes. Cardiovascular, gastrointestinal, antiviral, anxiolytic sedatives hypnotics and antipsychotics, corticosteroid, and thyroid pharmaceuticals were the predicted most hazardous therapeutic classes.

A review by Fent et al. (2006) found that only very little is known about long-term effects of pharmaceuticals to aquatic organisms, in particular with respect to biological targets. For investigated pharmaceuticals the chronic lowest observed effect concentrations (LOEC) in standard laboratory organisms are about two orders of magnitude higher than maximum concentrations in WTW effluents. For diclofenac, the LOEC for fish toxicity was in the range of wastewater concentrations, whereas the LOEC of propranolol and fluoxetine for zooplankton and benthic organisms were near to maximal effluent concentrations.

Kostich and Lazorchak (2008) used a simple approach, prioritising pharmaceuticals using marketing data and predicted concentrations of likely activity in wastewater to evaluate the risk to aquatic organisms using PECs. This approach was extended by comparison with regulatory data (Kostich et al., 2010).

A preliminary risk assessment for a range of PCPs in surface water made by Brausch and Rand (2010), using both environmental fate data and toxicity to aquatic organisms, suggested that only triclosan and triclocarban presented any hazard but this did not take account of endocrine effects.

Overall it is concluded that the sex hormones, PFOS and PFOA, diclofenac, carbamazepine and ibuprofen present the greatest risks to surface water, with possibly benzene and 1,4-dioxane. However the risk assessment approaches available may not be adequate for the groundwater environment where inputs may not be the same and where environmental conditions controlling fate and transport may be very different from the surface.

6 UK and European studies

6.1 Surface water

A possible indication of future groundwater contamination may be given by current surface water issues. It has long been recognised that the pollutant loading to surface waters is both temporally and spatially variable (Haith, 1985; Vega et al., 1998) although the risk and uncertainty can be modelled (Persson and Destouni, 2009).

A summary of published work related to detection of organic micropollutants in UK surface waters is shown in Table 5. This demonstrates that a wide range of pharmaceuticals as well as industrial compounds and pesticides that have been detected. Most of these studies have been associated with the impact of WTWs. It is well established that endocrine disruption in UK rivers is likely and due primarily to natural and synthetic oestrogens in sewage effluents (Johnson et al., 2007b). Mason et al. (1999) showed that point source contamination of surface water from pesticides was more significant than previously recognised.

Loos et al. (2009) report an EU-wide reconnaissance of the occurrence of polar organic persistent pollutants in European river waters. Samples from over 100 rivers from 27 European countries were analysed for 35 compounds, comprising pharmaceuticals, pesticides, PFOS, PFOA, benzotriazoles, hormones and endocrine disrupters. The compounds

detected most frequently and at the highest concentrations were benzotriazole, caffeine, carbamazepine, tolyltriazole and nonyl-phenoxy acetic acid. Only about 10% of the river water samples analysed could be classified as "very clean" in terms of chemical pollution.

6.2 Groundwater

Table 6 summarises European studies of organic micropollutants in groundwater. These confirm the detection of emerging contaminants such as ibuprofen, carbamazepine, diclofenac and sulfamethoxazole.

Loos et al. (2010) report a pan-European reconnaissance for polar persistent organic pollutants in groundwater. In total, 164 individual groundwater samples from 23 European countries were collected and analysed (among others) for 59 selected organic compounds, comprising pharmaceuticals, antibiotics, pesticides (and their metabolites), perfluorinated acids (PFAs), benzotriazoles, hormones, alkylphenolics (endocrine disrupters), caffeine, DEET, and triclosan.

Figure 3 shows the frequency of detection for compounds present in 20% or more of samples and the maximum concentrations detected by Loos et al. (2010). The most relevant compounds in terms of both frequency of detection and maximum concentrations detected were DEET, caffeine, PFOA, atrazine, desethylatrazine, 1H-benzotriazole methylbenzotriazole, desethylterbutylazine, PFOS, simazine, carbamazepine, nonyl-phenoxy acetic acid, bisphenol A, perfluorohexane sulfonate terbutylazine, bentazone, propazine, perfluoroheptanoic acid, 2,4-dinitrophenol, diuron and sulfamethoxazole.

In an investigation into the occurrence of perfluorinated compounds in groundwaters of England and Wales in 2006, perfluorinated compounds were detected in 26% (57 of 219) of groundwater monitoring sites, with detectable concentrations of PFOS found at about 14% of sites (Environment Agency, 2007; Environment Agency, 2008).

Data from the Environment Agency's monitoring programme for organic pollutants presented in this study indicates that within the 30 most frequently detected compounds are a number of emerging contaminants: atrazine metabolites, caffeine and DEET (Figure 4). Specific determinands with multiple detections include pesticides metabolites, pharmaceuticals including carbamazepine, triclosan, nicotine, food additives and alkyl phosphates (Table 7).

This data set is not directly comparable with Loos (2010) since it contains non-polar compounds, fewer pesticides and perfluorinated compounds, has a different limit of detection

and is designed to capture compounds which do not form part of standard monitoring suites. Figure 5 shows the percentage detection for top 15 compounds from this study excluding hydrocarbons, PAH and chlorinated solvents compared with that reported for the same compounds by Loos et al. (2010).

6.3 Comparison of river and groundwater concentrations

These studies allow us to make a comparison between surface and groundwater. Concentrations of some contaminants are much higher in surface than groundwater as might be anticipated. For example, average concentrations of ibuprofen 100 times higher in rivers than groundwater, caffeine 75 times and carbamazepine 21 times. PFOA, ketoprofen, sulfamethoxazole and oestrone are also relatively elevated in river water.

However desethyl atrazine, bisphenol A, 4-octyl phenol are higher in groundwater. Clearly this could be related either to a different source and pathway of entry, but it could of course also be related to their different degradation rate in the subsurface.

These data allow us to begin to identify important sources and routes to groundwater in the UK. The widespread detection of atrazine and its metabolites, and the recent problems with metaldehyde, show that diffuse sources such as agricultural and amenity pesticide use remain important. Pharmaceuticals, personal care products and lifestyle compounds are most likely to be derived from WTWs discharge either to the ground, or from sewer leakage, or through surface water/groundwater interaction. It is possible that some older compounds are the results of leakage from landfills which have received domestic or medical waste. PFOS and PFOA may have been released as the results of incidents such as fires and may both have infiltrated directly to groundwater or via surface water. We might conclude that all of the above routes need to be taken into account.

It is clear that the risks to groundwater and its receptors are real. Loos et al. (2010) report seemingly high concentrations of some compounds, but we as yet have insufficient data to be able to evaluate the significance of these findings. Many groundwater sources do not have treatment which would remove emerging contaminants and their lack of drinking water limits means that they are not currently being monitored. Much more research is needed to demonstrate whether emerging contaminants in river baseflow or groundwater dependent ecosystems are or could potentially have an impact.

7 Challenges in the management of emerging contaminants

7.1 Identifying emerging contaminants

The first challenge will be to identify the chemicals which potentially will become dangerous in the future and minimise the potential threat to groundwater, and to its receptors. To evaluate this threat the scientific community will need to:

- identify possible new groundwater pollutants
- identify possible new sources of such pollutants,
- develop analytical methods to measure these compounds in a variety of matrices (e.g. water, sediment, waste) down to trace levels.
- determine the environmental occurrence of these potential contaminants,
- characterize the sources and source pathways that determine contaminant release to the aqueous environment,
- identify possible new pathways for human exposure from contaminated groundwater, such as vapour intrusion.
- define and quantify processes that determine their transport and fate through the environment, and
- identify potential ecologic effects from exposure to these chemicals or microorganisms

Daughton (2004) raises a number of issues relating to the management of emerging contaminant problems.

- growing questions about pervasiveness and significance of low level effects, and awareness that there may be effects from concentrations below the toxic limit
- issues that may occur from inadequate water infrastructure and decentralised water use
- consequences of water reuse and artificial groundwater recharge
- pollution prevention, early warning programmes, monitoring programmes, use of pollutants as indicators,
- changing consumer behaviour and risk perception, communicating risk, new precautionary principles.

These represent major challenges for both the science community and those with responsibilities for risk assessment and managing pollution.

7.2 Setting appropriate standards

The Water Framework Directive (EC, 2000) and its Groundwater Daughter Directive (EC, 2006) require the setting of threshold values (TVs) for groundwater as part of the assessment of groundwater bodies. TVs have to be set for all pollutants which put the groundwater body at risk of failing to achieve good status. In setting TVs the following criteria must be considered:

- extent of interaction of groundwater and ecosystems,
- toxicology, dispersion tendency, persistence and bioaccumulation potential.

For EGCs the establishment of TVs, if necessary, will be a challenging task and require much better understanding of key properties and their distribution and behaviour in groundwater. As such for individual compounds, this likely to be a lengthy process.

Khadam and Kaluarachchi (2003) set out a multi-criteria decision analysis framework for environmental decision making in subsurface contamination remediation scenarios using probabilistic health risk assessment and economic analysis, in their case for carcinogenic impacts.

The methodology uses the trade-off between:

- population risk and individual risk by establishing a risk index
- the residual risk and the cost of risk reduction by using cost per life saved as a criterion
- cost-effectiveness as a justification for remediation.

Three approaches to ranking the criteria for decision-making were explored: structured explicit decision analysis, a heuristic approach and fuzzy logic. The results showed the importance of using an integrated approach for decision-making considering both costs and risks.

A similar approach could be developed for establishing what levels of discharge controls and drinking water treatment would be appropriate to achieve an acceptable water quality at a realistic cost. An adaptation of the flowchart developed by Khadam and Kaluarachchi (2003) is shown in Figure 6. The pathway here could either be entry to the environment or migration in groundwater.

7.3 Reducing inputs

There are a number of different areas which need to be tackled to reduce the overall input of emerging contaminants to groundwater. These include better handling and use, minimising waste product, correct disposal, reducing discharge to surface or groundwater and improved drinking water treatment.

For example Kümmerer (2008) and Eckstein and Sherk (2011) set out a number of strategies for reducing PPCP and veterinary medicines in water resources through better control of the source term and minimising wastes, in addition to improved monitoring and regulating compounds entering water. These include:

- product design – maintenance of effectiveness despite reduced dosage
- delivery – more precise targeting and dosing, better delivery routes (e.g. transdermal), completion of course to reduce disposal
- marketing – guidance on disposal, broader range of package size, advertising
- publication of environmental risk assessment data
- dispensing – expiry date, pharmacy inventories, database of both prescription and non-prescription drugs, reduction in availability of non-prescription drugs
- restrictive prescription, and improvement in hygiene for farm animals
- disposal/recycling – effective guidance, reverse distribution (take back programmes), recovery from wastewater
- reduction of input by broken sewage/piping
- separation of waste and rainwater to minimise necessary treatment
- alternative products – improved nutrition, probiotic products
- demonstration of economic benefits of usage reduction by health insurers

A major challenge in wastewater and drinking treatment is to improve existing processes and to design new ones to remove a large number of very different micropollutants in a range of matrices (Schwarzenbach et al., 2006). Future water treatments will require the development of more compact and efficient technologies. Existing strategies that predict relative removals of herbicides, pesticides, and other organic pollutants by activated carbon or oxidation can be directly applied for the removal of many ECs, but these strategies need to be modified to account for recalcitrant species (Westerhoff et al., 2005). Advanced oxidation and solar photocatalysis have the potential for further development (Comninellis, 2008; Robert and Malato, 2002).

7.4 Improved monitoring

Techniques need to be sought to enable the wide range of potential new and existing contaminants to be detected in groundwater and surface water. These could include assays where the toxicological activity of the contaminant loading is measured rather than the identity of individual compounds.

Targeted bioassays can be effective in assessing overall toxicological activity in effluents and surface water. Muller et al. (2007) have shown that combined passive sampling and a series of bioassays was effective in monitoring polar organics in effluents.

Rodriguez-Mozaz et al. (2007) set out the advantages of using biosensors. These depend on recognition of antibodies, molecular sensors or DNA, or inference on enzyme functioning. These can be applied to pharmaceuticals and endocrine disruptors and have been applied to bisphenol A, oestrone, nonyl phenol, diethylstilbestrol, sulfamethazine, and tetracycline. Jardim et al. (in press) found that a yeast bioassay using a bioluminescent reported was more effective for monitoring for endocrine disruptors than analysis for the individual components. Bioassays can be sensitive, highly selective for compounds or activity, readily automatable and represent a cheap and fast way of screening for emerging contaminants.

Biosensors are only one example of possible alternative approaches to monitoring EGCs in groundwater. Others which have been suggested are passive samplers (Alvarez et al., 2004; Stuer-Lauridsen, 2005; Vrana et al., 2001), although there are obvious difficulties/complexities in applying these cumulative sampling methods within a regulatory framework.

8 Conclusions

1. A wide range of organic micropollutants is now being detected in the aqueous environment world-wide. These include nanomaterials, pesticides, pharmaceuticals, industrial additives and by-products, personal care products and fragrances, water treatment by products, flame/fire retardants and surfactants, as well as caffeine and nicotine metabolites and hormones. Many of the compounds are relatively small and/or polar molecules which can often not be effectively removed by conventional drinking water treatment using activated carbon. Many of these compounds are also toxic or are classed as endocrine disruptors.

2. In order to assess the hazards presented by such compounds information on usage, persistence in soil and water, leachability and a robust and suitably sensitive analytical method is required. For many pesticides the above requirements are fulfilled and an assessment of risk of leaching to groundwater can be made. However, for pesticide metabolites this information can be sparse and for many emerging contaminants fate and transport data in the subsurface can be completely lacking with the majority of persistence studies directed at water treatment. A clear connection between source terms of these contaminants and groundwater-related receptors is often not well-defined to anticipate significant problems in groundwater. For compounds with no regulatory limit in groundwater, risk assessments are generally made using a toxicological approach based on estimates of PEC and PNEC. Synergistic effects from mixtures of contaminants cannot yet be fully evaluated.
3. A range of organic micropollutants from urban settings have been detected in European groundwater and surface water. Commonly detected compounds include: bisphenol A, caffeine, carbamazepine, DEET, galaxolide, ibuprofen, iopamidol, phthalates, phenyl ethoxylates, and sulfamethoxazole. Data presented in this study from the England and Wales Environment Agency's monitoring programme for organic micropollutants indicates that within the 30 most frequently detected compounds are a number of emerging contaminants such as pesticide metabolites, caffeine and DEET. Specific determinands with multiple detections include pesticides metabolites, pharmaceuticals including carbamazepine and triclosan, nicotine, food additives and alkyl phosphates.
4. Concentrations of some contaminants, such as ibuprofen and caffeine, are much higher in surface than groundwater but there are others, such as desethyl atrazine, which are higher in groundwater. This relates to different sources and pathways of entry, but it could of course also be related to different degradation rate in the subsurface. These data allow us to begin to identify important sources of emerging contaminants in groundwater in the UK; these include both diffuse sources and wastewater discharges.
5. It is clear that the risks to groundwater and its receptors are real. Many groundwater sources do not have treatment which would remove emerging contaminants and their lack of drinking water limits means that they are not currently being monitored. Much more research is needed to demonstrate whether emerging contaminants in river

baseflow or groundwater dependent ecosystems are or could potentially have an impact.

6. Regulation of these compounds in groundwater and the wider environment will be a challenging task and require much better understanding of key contaminant properties and their distribution and behaviour in groundwater. The challenges include identifying new emerging compounds, setting appropriate standards, developing strategies to reducing inputs to the aqueous environment and applying novel monitoring methods.

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Table 1 Pesticides used in the UK over more than 50,000 ha in 2008 with octanol/water partition coefficients lower than metaldehyde

Compound	Log K _{ow}
Diquat	-4.6
Mepiquat chloride	-3.55
Chlormequat chloride	-3.47
Glyphosate	-3.2
Prohexadione-calcium	-2.9
Clopyralid	-2.63
Picloram	-1.92
Dicamba	-1.88
Metsulfuron-methyl	-1.7
Thifensulfuron-methyl	-1.7
Amidosulfuron	-1.56
Quinmerac	-1.41
Propamocarb hydrochloride	-1.3
Florasulam	-1.22
Imazaquin	-1.09
2,4-D	-0.83
MCPA	-0.81
Mesosulfuron-methyl	-0.48
Trinexapac-ethyl	-0.29
MCPP-P	0.02
Metaldehyde	0.12

Table 2 Summaries of selected studies finding pesticide metabolites in groundwater

Area	Pesticides detected	Metabolites detected	Process	Ref erence
Hesse, Germany	Chloridazon	desphenyl-chloridazon	Parent and metabolite in STW effluent, surface water and groundwater	Buttiglieri et al. (2009)
Rome province, Italy	2,4-D, bentazone, MCPA,	8-hydroxybentazone	Survey	Laganà et al. (2002)
Lincolnshire, UK	MCPP (chiral mixture)	4-chloro-2-methylphenol	Change in enantiomeric ratio during degradation	Williams et al. (2003)
Kent, UK	Diuron, Atrazine, Simazine	DCPMU, DCPU, DCA	Research project	Lapworth and Goody (2006)
Denmark	Atrazine, bentazone, dichlorprop, MCPA, MCPP, simazine	2,6-dichlorobenzamide (dichlobenil) deethylatrazine, deisopropylatrazine, hydroxyatrazine, ethylenethiurea (mancozeb), desamino-diketo- metribuzin, diketo- metribuzin,	National monitoring programme	Jacobsen et al. (2005)
Denmark	Metribuzin	desamino-diketo- metribuzin, diketo- metribuzin	Research project	Kjaer et al.(2005)
Norway	27 including bentazone, clopyralid, dichlorprop, dimethoate, isoproturon, linuron, mecoprop, metalaxyl, metribuzin, propachlor, terbutylazine	desethyl atrazine, 2,6- dichlorobenzamide, AMPA	Monitoring	Haarstad and Ludvigsen (2007)

France	Atrazine, metolachlor	desethyl-atrazine, ethane sulfonic acid, metolachlor oxanilic acid	Catchment monitoring	Baran et al. (2008; 2007; 2010)
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Table 3 Key metabolites assessed as having leaching potential from Figure 2

Parent compound	Key metabolite	DT ₅₀	K _{oc}
Chlorothalonil	2-amido-3,5,6-trichlo-4-cyanobenzenesulphonic acid	121	10
	3-carbamyl-2,4,5-trichlorobenzoic acid	103	77
Cymoxanil	2-cyano-2-methoxyiminoacetic acid	2.8	9
	3-ethyl-4-(methoxyamino)-2,5-dioximidazolidine-4-carboxamide	11.2	21.6
Cyproconazole	1H-1,2,4-triazol-1-ylacetic acid	15	8
Diflufenican	2-(3-trifluoromethylphenoxy)nicotinic acid	10.6	13
Florasulam	5-(aminosulfonyl)-1H-1,2,4-triazole-3-carboxylic acid	328	83
	N-(2,6-difluorophenyl)-8-fluoro-5-hydroxy[1,2,4]triazolo[1,5-c]pyrimidine-2-sulfonamide	23	21
Flufenacet	FOE oxalate	11	11
	FOE sulphonic acid	230	10
Fluoxastrobin	HEC-5725-des-chlorophenyl	67	60
Fluroxypyr	4-amino-3,5-dichloro-6-fluoro-2-pyridinol	37	4
Iodosulfuron-methyl- Na	2-amino-4-methoxy-6-methyl-1,3,5-triazine	181	97.7
Mesosulfuron-methyl	4,6-dimethoxypyrimidine-2-yl-urea	48	3
	Mesosulfuron	53	68
Metalddehyde	Acetaldehyde	18.5	1.5
Metsulfuron-methyl	Saccharin	150	5.2
Thiram	N,N dimethyl carbamosulfonic acid	38	33
Tribenuron-methyl	N-methyl triazine amine	165	89
	Saccharin	105	5.2

Table 4 Examples of models to calculate properties required to predict the fate and transport of contaminants

Model	Description	Parameters predicted	Reference
EPI-Suite	Fragment constant	KOW, solubility, hydrolysis rate	(Kavlock et al., 2008)
KNN	Atom-centred fragments	indirect photolysis, biodegradation, and hydrolysis	(Kühne et al., 2007)
SPARC	Fundamental chemical structure theory (LFER & PMO)	Thermodynamic properties Physicochemical properties	(Hilal et al., 2005; Whiteside et al., 2006)
CATABOL	Degradation simulator using hierarchy of abiotic and enzymatic reactions	Biotransformation pathways and metabolites	(Jaworska et al., 2002)
SAR/QSAR type	Molecular connectivity Structural activity relationship	Physical and chemical properties, environmental fate, ecological effects and health effects of organic	(Sabljić, 2001; Walker et al., 2002; Cronin et al., 2003)

Table 5 Organic micropollutants detected in UK surface water (LOD = limit of detection; TW = wastewater treatment works)

Site	Source	Compounds detected	Reference
England and Wales	Contaminated & control sites	polychlorinated dibenzo-p-dioxins and dibenzofurans detected in all sediments sampled	Rose et al. (1994)
Thames in south west London and rural river	WTW	ibuprofen, paracetamol and salbutamol quantified in all samples. mefenamic acid (NSAID) in 70% of samples. propranolol (β -blocker) <LOD	Bound and Voulvoulis (2006)
Tyne Estuary	WTW	clotrimazole, dextropropoxyphene, erythromycin, ibuprofen, propranolol, tamoxifen, trimethoprim quantified clofibric acid, diclofenac, mefenamic acid, paracetamol <LOD	Roberts and Thomas (2006)
Tees, Mersey, Aire river and estuary	Industry?	APEs detected above threshold	Blackburn et al. (1999)
Taff & Ely, South Wales	WTW	trimethoprim, erythromycin, amoxicillin, paracetamol, tramadol, codeine, naproxen, ibuprofen, diclofenac, carbamazepine, gabapentin most frequently detected 41 others detected including illicit drugs	Kasprzyk-Hordern et al. (2008)
Inland streams	WTW	ibuprofen, mefamic acid, diclofenac, propranolol, dextropropoxyphene, erythromycin, trimethoprim, acetyl-sulfamethazole detected paracetamol, lofepramine not detected	Ashton et al. (2004)
Ouse, west Sussex	WTW	bisphenol A, oestrone, 17 β -oestodiol consistently detected propranolol, sulfamethoxazole, carbamazepine, indomethacine, diclofenac variably detected mebeverine, thioridazine, tamoxifen, meclofenamic acid <LOD	Zhang et al. (2008)
UK		Diuron	Alvarez et al. (2004)
Stream, Tunbridge Wells	Storm event, Fruit growing	simazine, diuron, NP, endosulfan sulphate, pendimethalin	Thomas et al. (2001)
Thames, 1988-1997		atrazine, simazine, lindane	Power et al. (1999)

Table 6 Summary of emerging contaminant detections in European groundwater

Location	Source	Compounds detected (Range of concentrations (ng L ⁻¹))	Reference
Eastern England	STW	Pharmaceuticals (<20-max): Ibuprofen (5044), erythromycin (1022), dextropropoxyphene (682), diclofenac (568), mefenamic acid (366), propranolol (215), acetyl-sulfamethoxazole (239), trimethoprim (42)	Hilton et al. (2003)
Berlin, Germany	STW	Pharmaceuticals (0-mean): clofibric acid (7300), clofibric acid derivative (2900), propyphenazone (1465), phenazone (1250), salicylic acid (1225), primidone (690), genistic acid (540), N-methylphenacetin (470), diclofenac (380), gemfibrozil (340), ibuprofen (200), fenofibrate (45), ketoprofen (30).	Heberer (2002)
Leipzig, Germany	STW	Bisphenol A (~7000), NP (~1000), caffeine (~140), carbamazepine (~90), tonalide (~6), galoxalide (~2.8)	Musolff et al.(2009)
Halle, Germany	STW	Bisphenol A(<1-1136), carbamazepine (<2-83), galaxolide (3-19)	Osenbrück et al. (2007)
Baden-Württemberg, Germany	STW	Maximum concentrations: amidotrizoic acid (1100), carbamazepine (900), diclofenac (590), sotalol (560), sulfamethoxazole (410), iopamidol (300), anhydro-erythromycin (49), phenazone (25).	Sacher et al. (2001)
France	Regional survey	Hormones (0.4 to 4): levonorgestrel (4), progesterone (1.6), testosterone (1.4); Pharmaceuticals (0 to 14): oxazepam (14), carbamazepine (10.4), acetaminophen (10.3), metformin (9.9), diclofenac (9.7), salicylic acid (metabolite) (6.5), atenolol (5.5), sulfamethoxazole (3).	Vulliet and Cren-Olivé (2011)

Table 7 Data from UK Environment Agency Monitoring for compounds with >20 detections in groundwater over the period 1992 to 2009

Type	Name	Detects	Sites	Max conc (µg/L)	Use
Pharmaceuticals and personal care products	DEET	280	280	6.5	Insect repellent
	Propylparaben	68	68	5.5	Personal care
	Methylparaben	44	44	5	Personal care
	Trimipramine	34	34	0.26	Antidepressant
	Carbamazepine	32	32	3.6	Antiepileptic
	Oxybenzone	32	32	70.4	Personal care
	1,3-Dicyclohexylurea	27	27	0.41	Blood pressure/hypertension
	Isopropyl myristate	22	22	0.39	Personal care
	Triclosan	22	22	2.11	Antibacterial
	Coumarin	20	20	0.42	Anticoagulant
Lifestyle and food additives	Caffeine	722	720	4.5	Coffee and tea
	Nicotine	107	107	8.07	Tobacco ingredient
	2,6-di-t-butyl-4-methylphenol (BHT)	106	106	7.0	Food additive
	2,6-di(t-butyl)-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one (BHT analogue)	79	79	4.2	Food additive
	1(3H)-Isobenzofuranone (phthalide)	59	56	9.3	Food additive
	Cotinine	40	40	0.4	Nicotine metabolite
	Vanillin	31	31	1.08	Food additive
	p-acetylacetophenone	30	30	9.42	Food additive
	Dimethyldisulfide	22	22	9.48	Food additive
Alkyl phosphates and resins	Tributylphosphate	450	450	2.5	Solvent, plasticiser & anti-foaming
	Bisphenol A	209	206	9.3	Resin precursor
	2-ethylhexyl diphenyl phosphate	68	68	2.7	Flame retardant plasticiser
	Tris(2-dichloroethyl)phosphate	54	54	4.9	Flame retardant plasticiser

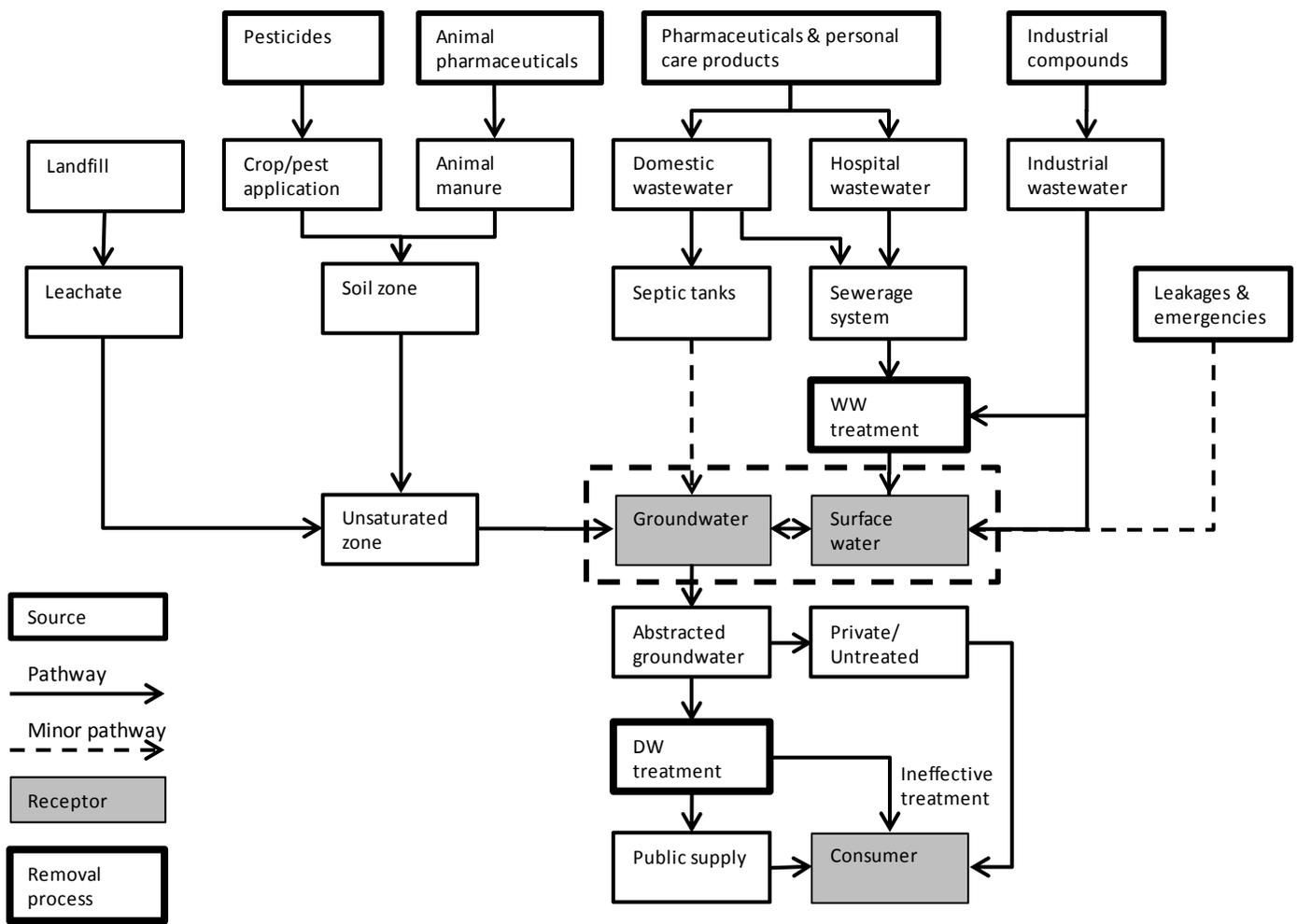


Figure 1 Sources (bold) and pathways for emerging contaminants to reach various receptors (grey)

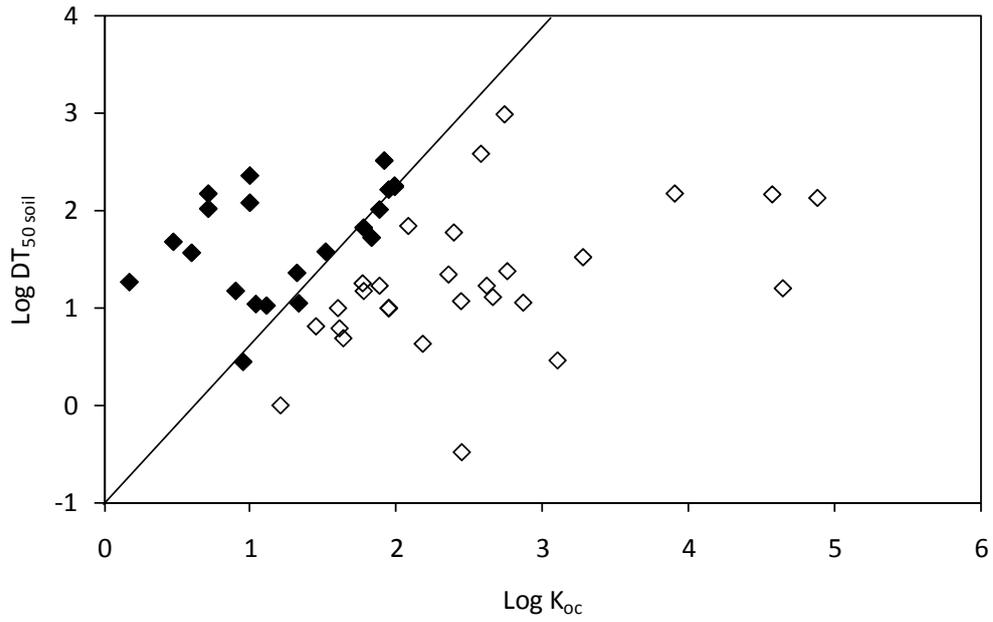


Figure 2 Classification of leaching probability of all compounds using K_{oc} and DT_{50} (after Worrall et al, 2000). Compounds with solid symbols assessed as leachers

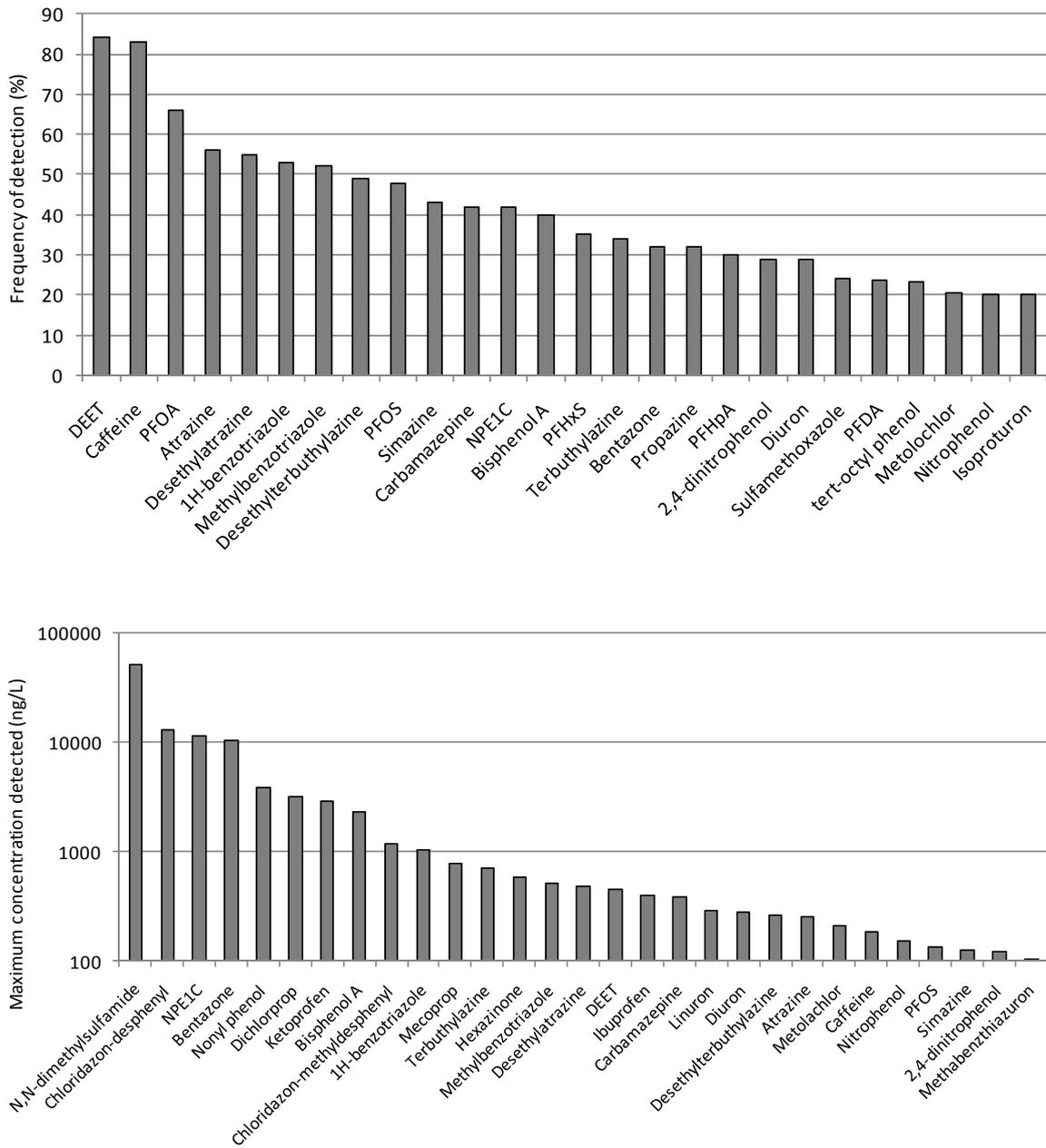


Figure 3 Frequency of detection and maximum detected concentrations in European groundwater (from Loos et al., 2010)

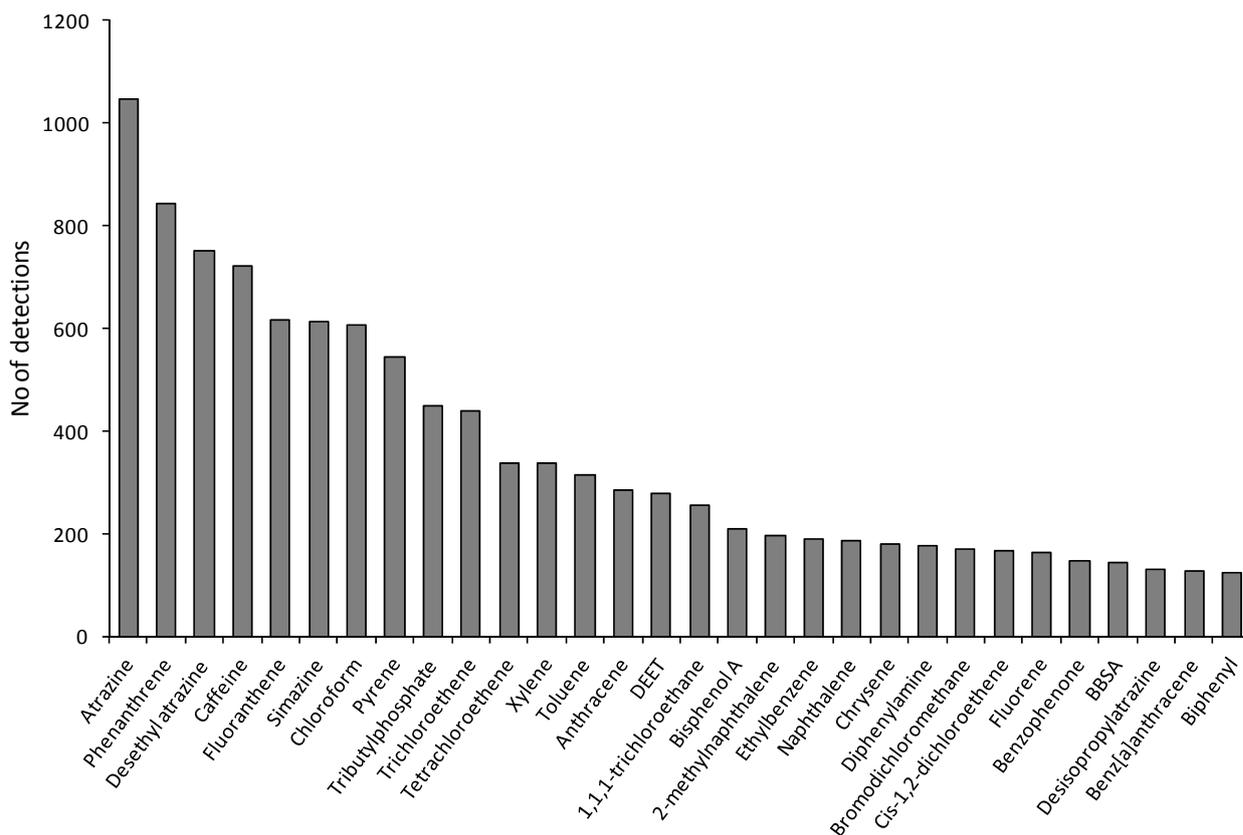


Figure 4 The top 30 most frequently detected compounds in the Environment Agency groundwater organic micropollutant database (DEET = N,N-dimethyl-toluamide, BBSA = N-butyl benzene sulphonamide)

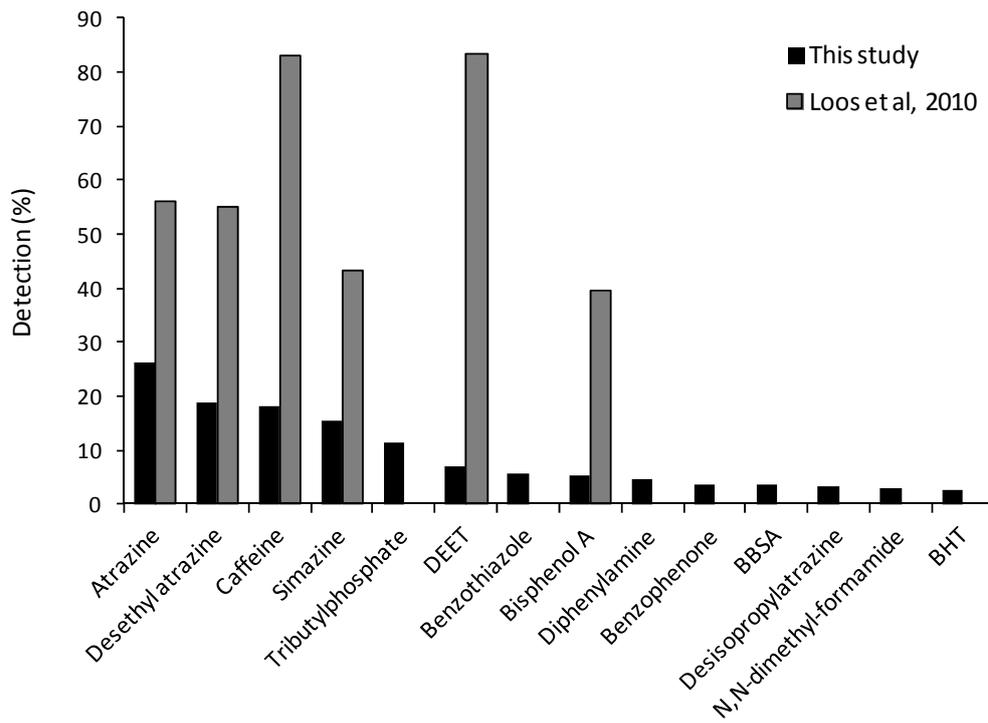


Figure 5 Top 15 polar compounds detected in England and Wales groundwater from this study compared with Loos et al 2010

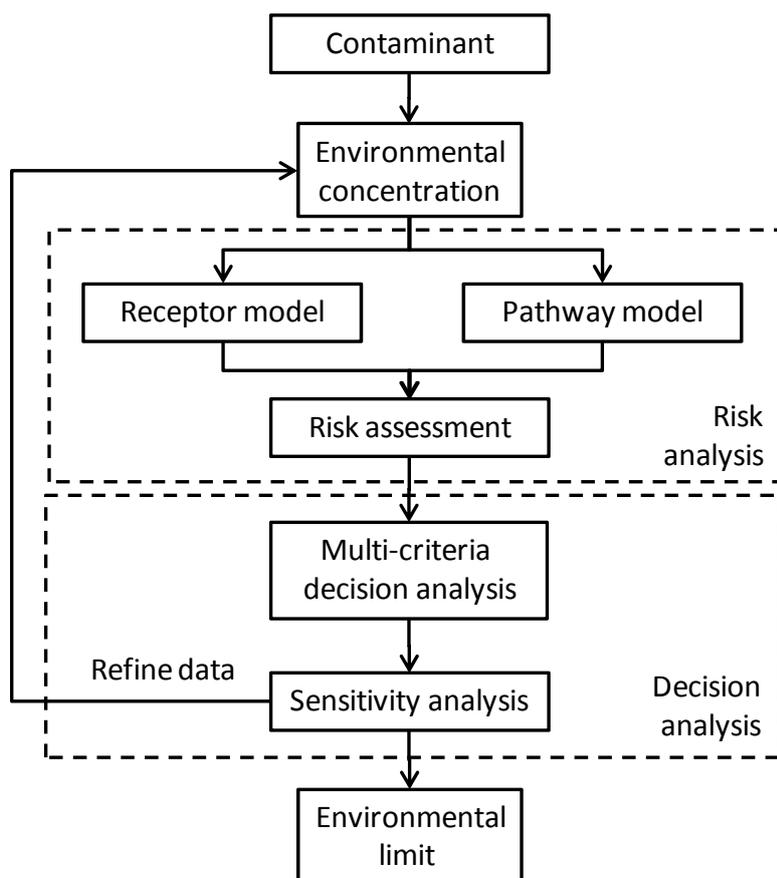


Figure 6 Flow chart showing risk-based decision analysis (adapted from Khadam and Kaluarachchi, 2003)