

Chapter 5 - Inputs and fate of contaminants in the aquatic environment

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Recommendations

- *Funding bodies, particularly NERC, should:*
 - *prioritise research to identify emerging contaminants, such as pharmaceuticals, and establish the risks to aquatic systems.*
 - *provide funds to perform controlled studies aiming to understand the mechanisms underlying the fate of emerging substances in the environment and the effects of environmental variables on behaviour.*
 - *fund research to develop approaches to identify transformation products and to assess potential risks of these substances*
 - *provide funds and continuity to ensure that the results of the investigations into emerging contaminants are used to inform the development of new modelling approaches.*
 - *provide funds to identify the potential impact of climate change on contaminant fate and behaviour.*
- *Funding bodies, particularly NERC, and Government bodies notably the Environment Agency, should commission research into how, if possible, to assess the risk to environmental and human health of mixtures of chemicals, at low concentrations.*
- *Research councils fund projects to synthesise the current state of knowledge into the environmental fate of new chemistries; for example the behaviour of polar multifunctional substances.*
- *Policy makers need to understand and incorporate the complexity of the environment in the assessment of risk from contaminants.*

Executive Summary

An understanding of the inputs, fate, and subsequent exposure of aquatic systems to chemical contaminants is essential in determining and controlling the risks of the contaminants to environmental and human health. Our understanding of the major fate processes for many contaminant types is well developed, and experimental and modelling approaches are available to determine how a substance is going to behave in the environment and to establish the level of exposure. These draw on numerous disciplines from across the chemistry area. However, there are still many uncertainties and unknowns that need to be urgently addressed.

There are various sources of diffuse and point source contaminants that include inputs from farming, urban and domestic activities, industrial effluents, waste disposal and atmospheric deposition. In addition to these sources of conventional contaminants, is increasing concern over emerging pollutants. Pollutants impact on the provision and maintenance of sustainable water.

Broadly speaking, our understanding of the behaviour of conventional contaminants is well developed after years of study. Emerging contaminants of concern, including pharmaceuticals, veterinary medicines, personal care products and nano-materials, are far less well studied.

The processes most often involved in the breakdown of contaminants are photodegradation and aerobic and anaerobic action. All these processes can form a range of degradation products and consequently, the environment may be exposed to a mixture of the parent compound and any resulting transformation products. Additionally, there are biochemical transformations which are not necessarily classified as degradation; for example, the *in situ* methylation of heavy metals leading to the formation of toxic organometallic compounds. Whilst the fate and effects of many major groups of synthetic

chemicals are relatively well understood, the behaviour and effects of transformation products are less well studied¹. Information about the mechanisms and properties (e.g. persistence, mobility and toxicity) of transformation products is critical if we are to fully understand the behaviour of contaminants in the environment.

To predict environmental fate it is vital to understand how contaminants are transported around the environment, and the mechanisms for degradation and transformation. Physical and chemical properties of the compounds such as structure, functional groups, size, shape, volatility, charge, solubility, aggregation behaviour, and hydrophilicity, in addition to knowledge of the characteristics of the aqueous environment, are critical. These factors determine the extent to which the contaminant is partitioned between water, soil, air and biota. The physico-chemical properties are also valuable in predicting degradation mechanisms and potential degradation products.

Current approaches to environmental modelling are deterministic in nature and do not always consider temporal and spatial distributions of contaminants in the aquatic environment. Knowledge gaps include the environmental fate of nanoparticles and polar multi-functional substances, and the identification and risk analysis of transformation products. Current risk assessment in Europe focuses on single substances at fixed concentrations, whereas, in the environment, numerous substances of various concentrations will be present as a heterogeneous mixture. However, in the US the Environment Protection Agency also requires under the Food Quality Protection Act an assessment on "cumulative exposure" to pesticides that have common mechanisms of toxicity².

Temperature and precipitation changes due to global warming may affect the input of chemicals into the environment and their fate and transport in aquatic

¹ There are a few exceptions; for example pesticides where this information is required by legislation.

² <http://www.epa.gov/pesticides/cumulative/index.htm>

systems. There is a need to identify the potential impact of climate change on contaminant fate and behaviour.

Introduction

The input of contaminants to the environment could impact the sustainability of aquatic systems and water supplies. This chapter highlights the different sources of contaminants and identifies priority chemicals that are or may be posing impacts on the aquatic environment and potable water supplies. The chapter provides a brief description of the regulatory drivers and presents the main factors and processes affecting chemical exposure in aquatic systems. Modelling tools which can be used to predict the fate and pathways of pollutants are also described. Throughout the Chapter we have attempted to provide an overview of the current knowledge and then identify major research needs in order to protect the health of water bodies into the future.

Inputs of contaminants to the environment

There are various sources of contaminants which include diffuse and point-source pollution. They include discharges from farming activities (e.g. sewage sludge and manure application, sheep dipping chemicals etc.), urban and domestic inputs (e.g. highway runoff, home pesticide use, discharge from combined sewer overflows), industrial effluents, waste disposal (e.g. leachate from landfill sites) and atmospheric deposition. In addition to these sources of contaminants which are more conventional, there seems to be increasing concern on emerging pollutants. These sources of pollutants impact on the provision and maintenance of sustainable water. Table 1 summarises the various sources of contaminants in the environment which will be discussed in detail below.

Types of contaminants

Nutrients

Nitrogen and phosphorus are particularly important as both are implicated in aquatic eutrophication. Eutrophication and the associated ecological effects result in general decline in overall water quality, restricting its use for general and drinking purposes. Nutrients in agricultural runoff can arise from point or diffuse sources of pollution, with major point-sourced pollution incidents occurring due to poor containment of slurry or silage effluents. Such point sources of pollution are easy to identify and control. However the diffuse sources of pollution, such as losses of nutrients through leaching and in surface runoff (due to slurry, manure or fertiliser application on fields or unsafe disposals of sheep dips) are more difficult to assess and control (Hooda *et al.*, 2000).

Heavy metals

Soil acts as a long term sink of heavy metal accumulation as a net result of the different mobility and bioavailability of heavy metal in soils, leaching losses and plant uptake. The significance of the accumulation of heavy metal in soils can impact water supply via borehole abstraction and associated groundwater activities.

Heavy metal input to agricultural soils originates from various sources including atmospheric deposition, biosolids, livestock manures, inorganic fertilisers and lime, industrial by-products and composts. These sources of heavy metal input can contribute to significant levels of Zn, Cu, Ni, Pb, Cd, Cr, As and Hg (Nicholson *et al.*, 2006). Atmospheric deposition was the main source of most metals entering agricultural land representing 49% of total Zn inputs of 5040t/year, 39% of Cu inputs of 1620t/year and 54% of Cd inputs of 40t/year. Livestock manures and biosolids were also important sources representing 37 and 8% of total Zn inputs, 40 and 17% of Cu and 10 and 4% of Cd inputs respectively (Nicholson *et al.*, 2006).

Endocrine disruptors

Around 100 000 man-made chemicals are in everyday use, many of which are disposed via the sewer system (and hence enter the sewage treatment works) and it is readily apparent that it is likely, even probably definite that very many chemicals and their intermediary degradation products, are entering most rivers continuously. These chemicals can have different types of activity (e.g. estrogenic, anti-androgenic) and cause their effects through different mechanisms of action (i.e. be agonists, or antagonists, of endogenous hormones, or affect hormone synthesis and/or metabolism) (Sumpter, 2005).

Estrogenic chemicals have been widely investigated compared to any of the others. Their significance came to attention of scientists when "feminised" wildlife was discovered. The causative chemicals at least in domestic sewage treatment works effluents (in England) appear to be the natural steroid estrogens 17β -estradiol (E2) and estrone (E1), and the synthetic steroid estrogen ethinyl estradiol (EE2) as reported by Desbrow *et al.* (1998). The former two chemicals are natural hormones and the last one is the active ingredient of the contraceptive pill. All are presumably excreted by people (primarily females) and incompletely degraded in sewage treatment works and hence are present in effluents.

Although most focus has been on estrogens and estrogenic effects (e.g. feminisation), there is also strong evidence that chemicals with androgenic and anti-androgenic activities are present in the aquatic environment. The first realisation that this was so, arose from the discovery that some paper and pulp mill effluents were masculinising fish living downstream of where the effluent entered the river (Howell *et al.*, 1980). The causative chemical in these effluents is likely to be a phytosterol (Durhan *et al.*, 2002).

17β -trenbolone (a synthetic androgen) which is a metabolite of a steroidal growth promoter administered to cattle has shown to be potent in the aquatic environment. This potent androgenic chemical is present in relatively high concentrations in waters receiving cattle feedlot effluent and is probably responsible for the masculinisation of fish observed at these locations (Wilson *et*

al., 2002). Hanselman *et al.*, (2003) demonstrated field studies which show that manure-borne estrogens are sufficiently mobile and persistent to impact surface and groundwater quality. Radiotracer studies showed that cattle excrete estrogens mostly in faeces (58%), whereas swine and poultry excrete estrogens mostly in urine (96% and 69% respectively). However these ratios change during pregnancy. Since urine and faeces are not usually handled separately in commercial animal production systems, the route of excretion would not appear to be an important environmental consideration (Knight, 1980).

A wide variety of man made chemicals have been shown to possess androgenic and/or anti-androgenic activity. These chemicals include chlorinated pesticides such as DDE and lindane and fungicides such as vinclozolin and herbicides such as linuron and diuron, as well as some of the phthalate plasticisers. Tributyltin (TBT) also causes androgenic effects to molluscs. TBT is the active ingredient used in many anti-fouling paints used on ships' hulls (Sumpter, 2005).

Persistent Organic Pollutants (POPs)

Under the United Nations Economic Commission for Europe (UN/ECE), chemicals which are POPs should demonstrate potential for long range transboundary atmospheric transport, toxic to human and/or environment, persistent and bioaccumulative. The list of POPs include aldrin, chlordane, DDT, polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and a more comprehensive list can be obtained from Harrad (2001). The Stockholm Convention, a global agreement on POPs came into force in 2004 and acts as a driver for implementation of safe levels of POPs in the environment. It is important to consider the impacts of POPs because of its implication to terrestrial and aquatic environment.

Pesticides

Pesticides in soils are widely studied because they are used widely to control pests that affect agricultural crops and pests in the home, yards and gardens. The

fate of pesticides in soil is controlled by chemical, biological and physical dynamics of this matrix. These processes can be grouped into those that affect persistence, including chemical and microbial degradation and those that affect mobility, involving sorption, plant uptake, volatilization, wind erosion, runoff and leaching.

Pesticides are degraded by chemical and microbiological processes. Chemical degradation occurs through reactions such as photolysis, hydrolysis, oxidation and reduction. Biological degradation takes place when soil microorganisms consume or break down pesticides. These microorganisms are mainly distributed in the top centimetres of the surface layer of the soil, where the organic matter acts as food supply. The extent of degradation ranges from formation of transformation products (TPs) to decomposition in inorganic products (Andreu and Pico, 2004).

In addition, some pesticides are chiral molecules. In that way, environmental studies have historically neglected to determine the adverse effects associated with particular enantiomers, including persistence in various environmental media. The racemic signature remains unchanged by physico-chemical removal mechanisms. However, microbial degradation and biological metabolism may be enantio-selective, and result in different effects and fates in the environment (Monkiedje *et al.*, 2003)

The movement of pesticides is determined by solubility, soil-sorption constant (K_{oc}), the octanol/water partition coefficient (K_{ow}) and half life in soil (DT_{50} or $T_{1/2}$). Pesticides can enter aquatic systems via spray drift surface runoff or drainflow. The potential for transport to aquatic systems is highly dependent on the chemical properties and the nature of the soil environment. A pesticide is able to contaminate groundwater (leaching) if its sorption coefficient is low, its half-life long and its water solubility high. This is quite frequent because pesticides are increasingly polar, hydrosoluble and thermolabile to diminish their toxicity and

to facilitate their disappearance from the environment; at the same time, they must persist long enough to enable acceptable pest control.

Emerging environmental contaminants

Our understanding of the inputs and behaviour of nutrients, pesticides, heavy metals and selected POPs is well developed and these groups have been investigated for many years. However, there is now increasing interest in classes of substances that have not yet been extensively studied. This class of substances is often referred to as the 'emerging environmental contaminants' and includes pharmaceuticals, veterinary medicines, personal care products and the nanomaterials.

Pharmaceutical compounds

Pharmaceutical products are widely used in the human health sector and in the animal husbandry. These substances have been designed to be biologically active and to cause very specific effects. The pharmaceuticals and their metabolites are excreted via faeces and urine and end up in the aquatic environment, either by discharge after passage of a sewage water treatment plant (STP), or by run-off from the surface, leaching via the soil or drainage to the surface water after spreading of manure on the land (Derksen *et al.*, 2004).

Human pharmaceuticals comprise a very diverse group of substances. The most important groups described in literature are fibrates and β -blockers (to treat cardiovascular diseases and high blood pressure), antiepileptics, analgesics (painkillers), cytostatics (to treat cancer), antibiotics (e.g. amoxicillin), hormonal substances (e.g. steroids), antidepressants, iodinated X-ray contrasting agents and bronchospasmolytics (asthma). Other regularly used human pharmaceuticals are pharmaceuticals to treat the gastrointestinal system as well as sleeping pills. Of the latter substances however, no or only very limited inventories of their presence and their effects in the aquatic environment have been described in the literature (Derksen *et al.*, 2004). The concentrations are usually low, ranging from

the detection limit and several hundred ng/l, with several substances peaking above the µg/l in surface water.

Details on different pharmaceutical substances in the environment in terms of their occurrence, fate and toxic effects is summarised by Halling-Sorensen *et al.* (1998). Metabolite compounds are formed due to degradation of the more complex parent compound by microbial activity. The toxicity of parent and metabolite compounds differs. Halling-Sorensen *et al.* (1998) stress the importance of considering the toxicity of both parent and metabolite compound in terms of environmental risk assessment.

Hirsch *et al.*, (1999) have demonstrated the presence of veterinary medicines in water bodies and the accumulation of medicine from surface waters by fish, shellfish and crustaceans (Samuelsen *et al.*, 1999).

Personal care products

Parabens (alkyl- *p*-hydroxybenzoates) are one of the most widely and heavily used suites of antimicrobial preservatives in cosmetics (skin creams, tanning lotions etc.), toiletries, pharmaceuticals and even foodstuffs (up to 0.1% wt/wt). Although the acute toxicity of these compounds is very low, it displays weak estrogenic activity in several assays (Daughton and Ternes, 1999).

Triclosan is an antiseptic agent that has been widely used for almost 30 years in a vast array of consumer products. The use of triclosan in commercial products includes footwear (in hosiery and insoles of shoes), hospital handsoaps, acne creams and rather recently as a slow-release product called Microban, which is incorporated into a wide variety of plastic products from children's toys to kitchen utensils such as cutting boards (Daughton and Ternes, 1999). Many of these uses can result in direct discharge of triclosan to sewage systems and as such this compound can find its way into receiving waters depending on its resistance to microbial degradation.

Another group of personal care products that can be introduced directly to the environment via volatilisation into air is musk. Musks (fragrances) are ubiquitous, persistent, bioaccumulative pollutants that are sometimes highly toxic; amino musk transformation products are toxicologically significant.

Veterinary compounds

Veterinary medicines are widely used to treat disease and protect the health of animals. Dietary enhancing feed additives (growth promoters) are also incorporated into the feed of animals reared for food in order to improve their growth rates. Release of veterinary medicines to the environment occurs both directly, for example the use of medicines in fish farms, and indirectly, via the application of animal manure (containing excreted products) to land or via direct excretion of residues onto pasture (Boxall et al., 2003; Boxall et al., 2004b; Jørgensen and Halling-Sørensen, 2000).

Nanomaterials

Nanomaterials apply to particles ranging in size from 1 to 100 nanometers. One key concern about nanoparticles is their potential to invade the body, either through skin contact or by inhaling airborne particles. There is also concern about moderate toxicity to some aquatic species that fish feed on, raising the concern that nanomaterials may accumulate in the food chain (Toensmeier, 2004). Examples of nanomaterial use include nanoscale titanium-dioxide particles, for example, are used in cosmetics and sun blocks and nanosized silica acts as filler in several consumer products including dental filling (Mraz, 2005).

Increasingly more companies are now producing nanoparticles in powders, sprays and coatings that are being used in a variety of products, including automobile parts, tennis rackets, scratch-proof eye glasses, stain-repellent fabrics, self-cleaning windows and sunscreens (Brüske-Hohlfeld *et al.*, 2005).

The fate and transport of these nanomaterials in the environment is of growing concern and there isn't any legislation at the moment to control its production.

However in the US, the EPA and OSHA are funding studies on the health and environmental risks posed by nanomaterials. The UK's Royal Society of Engineering and the European Union are calling for rules to protect humans and the environment from nanomaterials (Mraz, 2005).

Transformation products

For most contaminants, aerobic and anaerobic degradation will occur via a series of reactions resulting in the formation of a range of degradation products (e.g Roberts, 1998; Roberts and Hutson, 1999). Consequently, the environment may be exposed to a mixture of the parent compound and any resulting transformation products. Whilst the fate and effects of many major groups of synthetic chemical are relatively well understood, with a few exceptions, the behaviour and effects of degradates have been more or less ignored. Transformation products can be present at higher levels in environment than the parent and in some instances can be more persistent, more mobile and more toxic (Boxall et al., 2003; Andreu and Pico, 2004; Table 2).

Which contaminants should we be focusing on?

It can be seen from the previous sections that a vast number of chemicals have the potential to be released to the environment and it has been long recognised that it will be impossible to experimentally assess every one of these. There is therefore increasing interest from policy makers and other stakeholders in the development of methods for prioritising those substances that pose the greatest potential risk to environmental systems. A number of previous studies have been performed to identify priority emerging environmental pollutants (e.g. Boxall et al., 2003; Thomas et al., 2004; Capelton et al., 2006; Sinclair et al., 2006; Sanderson et al., 2003). These have considered a range of classes (veterinary and human medicines and degradates), different exposure pathways and have been aimed at different protection goals (Table 3). The outputs from these projects may provide a useful starting point for future research.

Regulation of environmental contaminants

For new substances, a company is usually required to assess the impact of the product on the environment before it can be registered. This assessment involves a consideration of the potential exposure to the ingredients in the product as well as the potential effects of the ingredients on organisms. During the registration process for new pesticides, veterinary medicines, biocides and pharmaceuticals, it is necessary to generate information on the fate of the substances in the environment in order to determine the magnitude and potential for exposure. For example, under EU Directive 2001/82/EC as amended by Directive 2004/28/EU it is necessary, when applying for marketing authorisation for a veterinary product, to provide “tests assessing the potential risks posed by the medicinal product for the environment. This impact should be studied and consideration shall be given on a case-by-case basis to specific provisions seeking to limit it.” The Annex to the Directive states that the assessment of environmental risk should be carried out in two phases. There are provisions in the veterinary directive to refuse an application for a marketing authorisation on the ground of a serious risk to the environment. The data required usually include information on volatility, the persistence of a substance in soil, sludge or sediment-water systems and on the sorption behaviour of the substance to soils and/or sediments.

The new **Registration, Evaluation, Authorisation and Restriction of Chemicals** (REACH) regulation will be EU’s most comprehensive and complex piece of legislation. The main purpose of REACH is to improve standards in the area of environmental and health protection. About 30,000 substances (with a volume > 1 metric ton per year) are expected to fall under registration requirements. In their registration of dossiers, manufacturers and importers must provide information about the chemical identity of the substance in question; its physical-chemical, toxic and ecotoxic properties, its classification and labelling and the ways in which it is used. REACH also focuses on emerging contaminants. Annex XIV of the REACH regulation contains a list of substances that to be studied in the framework of the authorisation period. This current list which is

empty is anticipated to have approximately 1000 names as potential/emerging contaminants (Lahl and Hawxwell, 2006).

An understanding of the fate and transport of a contaminant is also important to support a number of other regulatory drivers including the Water Framework Directive; the Nitrates Directive; the Drinking Water Directive; the Bathing Waters Directive; the Habitats Directive and international conventions such as the Stockholm Convention (for Persistent Organic Pollutants) and the Convention for the Protection of the Marine Environment of the North-East Atlantic (also known as the "OSPAR Convention"). For example, the Water Framework Directive requires water bodies to be in good ecological status by 2015. In order to achieve this, it will be necessary to identify the major chemical, physical and biological stressors within catchments.

These policies and directives (as mentioned above) act as important drivers to ensure that sufficient measures are taken to ensure that the environment is managed in a sustainable way.

Fate and transport processes

Once released to the aquatic environment, a chemical will be distributed around the different environmental compartments (including air, water, soil, sediment and biota) and may be degraded. In this section, we provide an overview of the properties and processes affecting exposure of aquatic systems. It is essential to have an understanding of the fate of a contaminant in order to determine what are the risks to environmental and human health.

(a) Distribution in the aquatic environment

The main processes affecting distribution in aquatic systems are sorption, volatilisation, bioaccumulation and biomagnification.

A contaminant may adsorb or absorb from the water phase to solid material (e.g. suspended solids, biota, sediment) in aquatic systems. The sorption behaviour of

a contaminant is typically described by the sorption coefficient (K_d) or the organic-carbon sorption coefficient (K_{oc}) that can be determined experimentally using batch studies (e.g. OECD 106) or column studies. For neutral organic substances, sorption will typically occur via hydrophobic interactions and a strong relationship exists between a substances hydrophobicity and sorption behaviour – hydrophilic substances tending to sorb to a lesser extent than hydrophobic substances. However for ionic and charged species (e.g. many pesticide classes, pharmaceuticals, veterinary medicines and surfactants), interactions with particulate material can occur through other mechanisms including electrostatic attraction, surface bridging or hydrogen bonding (e.g. Tolls, 2001). For these substances, the characteristics of the aquatic environment (including pH, ionic strength, metal oxide content, cation exchange capacity) will be very important as they can significantly affect the sorption behaviour (Ter Laak et al., 2006).

Many substances will transfer from aquatic systems to the air by volatilisation. The volatility of a contaminant is related to a substances aqueous solubility and vapour pressure and is described by the Henry's Law Constant (HLC). The HLC can tell us about the behaviour of a substance in different water types. For example, substances with an HLC of greater than $1 \text{ Pa m}^3 \text{ mol}^{-1}$ will volatilise from shallow water whereas a HLC of $10 \text{ Pa m}^3 \text{ mol}^{-1}$ would need to be reached for volatilisation to occur from deeper water bodies.

The potential for a substance to be taken up into biota will be determined by the properties (size, shape, hydrophobicity, solubility and speciation) of the chemical, the characteristics of the exposure environment (pH, suspended solids concentration, ionic strength) and the physiological and behavioural characteristics of the organism of interest (including lipid content, feeding behaviour and habitat). Uptake is usually described by the bioconcentration factor (BCF). For neutral organic substances, there is a strong positive relationship between the octanol-water partition coefficient and BCF although

this relationship falls down for highly hydrophobic substances ($\text{Log Kow} > 6$) possibly due to steric or solubility issues.

For nanomaterials, aggregation behaviour will also be important in determining environmental behaviour. Available data indicate that, following release to water, nanoparticles (including carbon nanotubes, nanoscale zerovalent iron, titanium dioxide and fullerenes) will aggregate to some degree (e.g. Fortner *et al.*, 2005; Phenrat *et al.*, 2007; Dunphy *et al.*, 2006). Aggregates may then settle out (Brant *et al.*, 2005). The degree of aggregation and the size range of the aggregates is dependent on the characteristics of the particle (i.e. type, size, surface properties and, for metal particles, the intrinsic magnetic moment) and the characteristics of the environmental system (including pH, ionic strength and dissolved organic carbon content)(Hyung *et al.*, 2007; Phenrat *et al.*, 2007; Dunphy *et al.*, 2006). Environmental transport studies indicate that nanoparticles will exhibit differing mobilities in the soils and waterbodies and in water treatment processes compared to their corresponding parent form. The behaviour of nanoparticles in environmental systems is therefore highly complex and appears to be dependent on not only the particle type but also the particle size.

These properties can be determined experimentally or, alternatively, by predictive models. For example, a number of quantitative structure-property relationships (QSPRs) are available for estimating volatilisation, water solubility, sorption and bioconcentration from chemical structure (e.g. Karickhoff, 1995; Meylan *et al.*, 1992). These models often work very well for several classes of contaminants (e.g. the neutral organic compounds) in simple environmental systems but often fall down when used to predict the behaviour of other classes of contaminants in complex environmental systems. In the future, by performing controlled experiments to fully understand the underlying mechanisms that determine fate in the environment, it may be possible to develop improved predictive approaches that are applicable to a wider range of substances and systems.

(b) Persistence in the aquatic environment

A number of abiotic and biotic degradation processes may occur in aquatic systems. The major biotic processes include hydrolysis and direct and indirect photodegradation. Direct photodegradation is primarily due to blue or UV light and only occurs in chemicals that can absorb light energy. It is often seen in double bond systems e.g. alkenes, polycyclic aromatic hydrocarbons, aldehydes and ketones, selected pesticides. Indirect photodegradation occurs when light-absorbing molecules (plant pigments, humics) absorb photons and transfer energy to the chemical of interest. It may also occur when highly reactive species (usually oxygen containing e.g hydroxy radical) are formed. The potential for a substance to photodegrade will be determined by the characteristics of the environment including light intensity, water depth and turbidity. The net result of hydrolysis is that a water molecule and a contaminant molecule is split. The process generally occurs in alkyl halides and esters and ester analogues and is often catalysed by H^+ or OH^- so the pH of the system is very important in affecting degradation rate.

Biotic processes include aerobic and anaerobic degradation. Generally, biodegradation is mediated by bacteria and fungi although other organisms (e.g. plants, invertebrates and fish) may accumulate and subsequently metabolise a substance. Fungi are aerobic whereas bacteria are active in both aerobic and anaerobic environments. Biodegradation often mediates reactions that are energetically favourable and is accomplished by enzymes. Aerobic biodegradation involves aerobic bacteria that require free oxygen to decompose organic material. This is an autocatalytic reaction in that it produces new microbes. Anaerobic degradation is performed by a completely different group of microbes – oxygen is toxic to them. The bacteria utilize oxygen bound in other substances and oxidise organic matter in the complete absence of oxygen. Examples of substances that are anaerobically degradable include chlorinated solvents and highly chlorinated PCBs.

A range of standardised experimental approaches is available for assessing the abiotic and biotic persistence of a substance in the aquatic environment. For example, studies in water/sediment systems using radiolabelled compounds can provide information on not only the distribution of a chemical in an aquatic system but also on the nature of the degradation products. One of the major challenges in assessing the impact of degradation products is identifying the structure of the degradates. Degradation route studies are complex and costly and it is often very difficult to identify the minor degradates in a particular system (Boxall et al., 2004a). An alternative to experimental testing may be to use structure-biodegradability relationships (SBRs) to predict degradation rates and pathways from the chemical structure of the parent compound. A number of systems have been developed for doing this including BESS (Punch et al., 1996) and CATABOL (Jaworska et al., 2002). CATABOL is a probabilistic approach to modelling biodegradation based on aerobic microbial transformation pathways generated from MITI-I tests and expert judgement (Jaworska et al., 2002). As well as providing information of degradation pathway the system also provides information on degradation route. An evaluation against experimental degradation data (Jaworska, 2002) indicated that the system can correctly identify 98% of ready biodegradable substances and 96% of non-ready degradable substances. CATABOL has been evaluated for determining transformation pathways for pesticides in soil (Sinclair and Boxall, 2003). Comparison of predictions with experimental observations indicated that only 24% of experimentally derived transformation products are predicted correctly. Further development of this and other expert systems is therefore required before they can usefully be used to assess degradates.

(c) Assessing exposure in real environmental systems

It can be seen from the above that a range of processes will affect the exposure of aquatic systems to chemical contaminants. By using complex experimental studies, including microcosm/mesocosms, controlled field studies and monitoring studies, it is possible to investigate the interactions of these processes within a system. These types of study are costly, time-consuming and

often difficult to interpret. However, by applying environmental models it is possible to use basic fate data in order to predict exposure in the real environment. A wide range of models are available that have been developed for different chemical types, which vary in terms of complexity and which operate at a range of temporal and spatial scales. Table 4 provides a summary of some major models that are used to determine fate and transport of pollutants at various scales. This list is not meant to be exhaustive but provides an indication of the different models used to provide predictions of contaminant exposure.

Conclusions and Research priorities

An understanding of the inputs, fate and subsequent exposure of aquatic systems to chemical contaminants is essential in determining and controlling the risks of the contaminants to environmental and human health. Our understanding of many of the major fate processes for many contaminant types is well developed and experimental and modelling approaches are available to determine how a substance is going to behave in the environment and to establish the level of exposure. These draw on many disciplines in the chemistry area. However, there are still many uncertainties and unknowns that need to be urgently addressed. We would advocate that work focuses on the following broad areas:

- Previously ignored and emerging contaminants – Over the past five years a significant amount of work has been done on some of the emerging contaminants (including degradates, pharmaceuticals, personal care products, emerging POPs (flame retardants, PFOS)). However, there are still many substances that we know very little about (e.g. the nanoparticles). Research should be performed to identify and prioritise these in order to establish the risks to aquatic systems
- Environmental fate of new chemistries - Whilst we have a good understanding of the behaviour of small neutral compounds, our understanding of the behaviour of polar multifunctional substances is much less well developed. Our understanding of nanoparticle behaviour

is non-existent. Research in this area is disparate so there is a need to synthesise work to date as well as to perform controlled studies to understand the mechanisms underlying the fate of these substances in the environment and the effects of environmental variables on behaviour. Results of these types of investigations should be used to inform the development of new modelling approaches.

- Transformation products – The impact of transformation products has been more or less ignored. Work is required to develop approaches to identify transformation products and to assess potential risks of these substances.
- Environmental complexity – When assessing the risks of a contaminant, we tend to ignore the complexity of the environment. For example: risk assessments will generally consider single substances yet in the real environment a large number of substances will be present; effects testing is done over short durations at constant concentrations yet exposure concentrations will be variable and could be prolonged; and current approaches to environmental modelling are deterministic in nature and do not always consider temporal and spatial distributions of contaminants in the aquatic environment. We need to begin to try to better understand this environmental complexity in order to protect the health of the aquatic environment into the future.
- Climate change – It is anticipated that the winters will become wetter and summers will become drier and warmer. These changes are likely to affect the inputs of chemicals into the environment and to affect the fate and transport in aquatic systems. There is therefore an urgent need to identify the potential impacts of climate change on contaminant fate and behaviour.

References

Adriaanse, P.I., 1996. Fate of pesticides in field ditches: the TOXSWA simulation model. SC-DLO Report 90, DLO Winand Staring Centre for Integrated Land, Soil and Water Research, Wageningen, the Netherlands, 241 pp.

Adriaanse, P.I., 1997. Exposure assessment of pesticides in field ditches: the TOXSWA model. Extended summary SCI Pesticide Group Meeting Ecotoxicology of Organic Compounds in the Aquatic Environment. *Pestic. Sci.* 49, 210-212.

Andreu V. and Pico Y. (2004). Determination of pesticides and their degradation products in soil : critical review and comparison of methods. *Trends in Analytical Chemistry*, 23(10-11), 772-789.

Boesten J. and Gottesburen B. (2000). Testing PESTLA using two modellers for bentazone and ethoprophos in a sandy soil. *Agricultural Water Management* 44(1-3): 283-305.

Boxall, A.B.A., Fenner, K., Kolpin, D.W., Maund, S. (2004a) Environmental Degradates of Synthetic Chemicals: Fate, Effects and Potential Risks. *Environmental Science and Technology* 38(19): 369A-375A.

Boxall, A.B.A., Fogg, L.A., Kay, P., Blackwell, P.A., Pemberton, E.J., Croxford, A. (2004b) Veterinary medicines in the environment. *Reviews in Environmental Contamination and Toxicology*. 180: 1-91.

Boxall, A.B.A., Kolpin, D., Halling Sørensen, B., Tolls, J. (2003) Are veterinary medicines causing environmental risks? *Environmental Science and Technology*. 37(15): 286A-294A.

Brant J., Lecoanet H., Wiesner M.R. (2005). Aggregation and deposition characteristics of fullerene nanoparticles in aqueous systems. *Journal of Nanoparticle Research*. 7 (4-5), 545-553

Brüske-Hohlfeld I., Peters A. and Wichmann H.E. (2005). Do nanoparticles interfere with human health ? *GAIA* 14(1) : 21-23.

Capelton, A., Courage, C., Rumsby, P., Stutt, E., Boxall, A., Levy, L. (2006) Prioritising veterinary medicines according to their potential indirect human exposure and toxicity profile. *Toxicology Letters* 163(3): 213-223.

Carsel R.F., Imhoff J.C., Hummel P.R., Cheplick J.M. and Donigan A.S.J. (1998). PRZM-3, A model for predicting pesticide and nitrogen fate in the crop root and unsaturated soil zones : User manual for release 3.0, National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, Georgia, USA (available at <http://www.epa.gov/ceampubl/gwater/przm3/index.htm>)

Cunningham, V.L. (2003) The PhATE Model: Estimating the Distribution of Pharmaceuticals in the Environment, *Southwest Hydrology*, 2, 20-21

Daughton C.G. and Ternes T.A. (1999). Pharmaceutical and Personal Care Products in the Environment : Agents of Subtle Change ? *Environmental Health Perspective Supplements*, 107 (S6), 1-35.

Derksen J.G.M., Rijs G.B.J. and Jongbloed R.H. (2004). Diffuse pollution of surface water by pharmaceutical products. *Water Science and Technology* 49 (3), 213-221.

Desbrow C., Routledge E.J., Brighty G.C., Sumpter J.P., Waldock M. (1998). Identification of estrogenic chemicals in STW effluents In : Chemical fractionation and in vitro biological screening. *Environ. Sci. Technol.* 32 : 1549-1558.

Dunphy Guzman KA, Finnegan MP, Banfield JF (2006) Influence of surface potential on aggregation and transport of titania nanoparticles. *Environmental Science and Technology* 40: 7688-7693.

Durhan E., Lambright C., Wilson V., Butterworth B.C., Kuehl D.W., Orlando E.F., Guillette L.J. Jr., Gray L.E. Jr. Ankley G.T. (2002). Evaluation of androstenedione as an androgenic component of river water downstream of a pulp and paper mill effluent. *Environ. Toxicol. Chem.* 21 : 1973-1976.

Eljarrat, E., Barcelo, D. (2003) Priority lists for persistent organic pollutants and emerging contaminants based on their relative toxic potency in environmental samples. *Trends in Analytical Chemistry* 22(10): 655-665.

Fortner JD, Lyon DY, Sayes CM, Boyd AM, Falkner JC, Hotze EM, Alemay LB, Tao YJ Guo W, Ausman KD, Colvin VL, Hughes JB (2005) C-60 in water: nanocrystal formation and microbial response. *Environmental Science and Technology* 39(11) 4307-4316.

Harrad S. (2001). The Environmental Behaviour of Persistent Organic Pollutants: In *Pollution: Causes, Effects and Control*. Harrison R.M. (ed). 445-447. The Royal Society of Chemistry.

Halling-Sorensen B., Nors Nielsen S., Lanzky P.F., Ingerslev F., Holten Lutzhoft H.C. and Jorgensen S.E. (1998). Occurrences, fate and effects of Pharmaceutical Substances in the Environment – A Review. *Chemosphere* 36(2), 357-393.

Hanselman T.A., Graetz D.A. and Wilkie A.C. (2003). Manure-borne estrogens as potential environmental contaminants : A Review. *Environmental Science & Technology*, 37(24) : 5471-5478.

Hirsch R., Ternes T., Heberer K., Kratz K. (1999). Occurrence of antibiotics in the aquatic environment. *Sci. Total Environ.* 225, 109-118.

Hooda P.S., Edwards A.C., Anderson H.A. and Miller A. (2000). A review of water quality concerns in livestock farming areas. *The Science of the Total Environment*, 250 : 143-167.

Horst M.M.S., Adriaanse P.I., Beltman W.H.J. and Van den Berg F. (2003). User Manual of TOXSWA, FOCUS version 1.1.1. Alterra Report 586, Alterra, Wageningen, the Netherlands.

Howell W.M., Black D.A., Bortone S.A. (1980). Abnormal expression of secondary sex characters in a population of mosquitofish, *Gambusia affinis holbrooki* : evidence for environmentally induced masculinization. *Copeia*. 676-681.

Hyung H, Fortner JD, Hughes JB, Kim JH (2007) Natural organic matter stabilizes carbon nanotubes in the aqueous phase. *Environmental Science and Technology* 41(1): 179-184.

Jarvis N and Larsson M (1998). The MACRO model (version 4.1). Technical description. Swedish University of Agricultural Sciences (SLU), Department of Soil Sciences, Uppsala, Sweden (available at <http://130.238.110.134:80/bgf/Macrothm/document.htm>.)

Jaworska, J., Dimitrov, S., Nikolova, N., Mekenyan, O. (2002) Probabilistic assessment of biodegradability based on metabolic pathways; CATABOL system. *SAR and QSAR in Environmental Research* 13(2): 307-323.

Jorgensen, S.E. and Halling-Sorensen, B., 2000. Drugs in the environment. *Chemosphere* 40 (7), 691–699.

Karickhoff, S.W. (1995) Pollutant sorption in environmental systems, in: Neely, W.B. and Blau, G.E. (Eds.), Environmental exposure from chemicals Volume 1. CRC Press, Boca Raton, pp 49-64.

Knight W.M. (1980). In. Estrogens in the Environment Dev. Toxicol. Environ. Sci. 5, McLachlan J.A. (Ed). Elsevier, New York. 391-401.

Lahl U. and Hawxwell K.A. (2006). REACH – The New European Chemicals Law. Environment, Science and Technology, December, 7115-7121.

Leistra, M., van der Linden A.M.A., Boesten J., Tiktak A. and van den Berg F. (2000). PEARL model for pesticide behaviour and emissions in soil-plant systems. Description of processes. Alterra report 13, RIVM report 711401009, Alterra, Wageningen, 107 pp.

Mraz S.J. (2005). Nanowaste : Thenext big threat ? Machine Design, November 17, 46-53.

Meylan, W.M., Howard, P.H. and Boethling, R.S. (1992) Molecular topology/fragment contribution method for predicting soil sorption coefficients. *Environmental Science and Technology* **26**: 1560-1567.

Monkiedje A., Spiteller M. and Bester K. (2003). Degradation of racemic and enantiopure metalaxyl in tropical and temperate soils. *Environmental Science & Technology*, 37(4):707-712.

Nicholson F.A., Smith S.R., Alloway B.J., Carlton-Smith C. and Chambers B.J. (2006). Quantifying heavy metal inputs to agricultural soils in England and Wales. *Water and Environment Journal*, 20 : 87-95

Phenrat T, Saleh N, Sirk K, Tilton RD, Lowry GV (2007) Aggregation and sedimentation of aqueous nanoscale zerovalent iron dispersions. *Environmental Science and Technology* 41: 284-290.

Plant J.A., Korre A., Reeder S., Smith B., Voulvoulis N. (2005). Chemicals in the environment : implications for global sustainability. *Applied Earth Sciences (Trans. Inst. Min. Metall. B)*. 114, B65-B97.

Punch, B., Patton, A., Wight, K., Larson, B., Masscheleyn, P., Forney, L. (1996) A biodegradation evaluation and simulation system (BESS) based on knowledge of biodegradation pathways. In Peijnenberg, W.J.G.M., Damborsky, J. (Eds) *Biodegradability prediction*. Kluwer Academic Publishers, Dordrecht, p 65-74.

Roberts, T.R. (1998) *Metabolic pathways of agrochemicals, Part 1: Herbicides and plant growth regulators*. The Royal Society of Chemistry, Cambridge, UK.

Roberts, T.R., Hutson, D.H. (1999) *Metabolic pathways of agrochemicals, Part 2: Insecticides and fungicides*. The Royal Society of Chemistry, Cambridge, UK.

Samuelsen O., Lunestad B., Husevag B., Holleland T., Ervik A. (1999). Residues of oxolinic acid in wild fauna following medication in fish farms. *Dis. Aquat. Organisms* 12: 111-119.

Sanderson H., Johnson, D.I., Reitsma, T., Brain, R.A., Wilson, C.J., Solomon, K.R. (2003) Ranking and prioritisation of environmental risks of pharmaceuticals in surface waters. *Regulatory Toxicology and Pharmacology* 39: 158-183.

Sumpter J.P. (2005). Endocrine disrupters in the aquatic environment: An overview. *Acta Hydrochim. Hydrobiol.* 33(1) : 9-16.

Sinclair C.J., Boxall A.B.A. (2003). Assessing the Ecotoxicity of Pesticide Transformation Products. *Environ. Sci. Technol.*; 2003; 37(20), 4617 - 4625;

Sinclair, C.J., Boxall, A.B.A., Parsons, S.A., Thomas, M. (2006) Prioritization of pesticide environmental transformation products in drinking water supplies. *Environmental Science and Technology*. Published online December 2006.

Ter Laak T.L., Gebbink W.A., Tolls J. (2006). Estimation Of Soil Sorption Coefficients Of Veterinary Pharmaceuticals From Soil Properties. *Environmental Toxicology and Chemistry*. 25(4), 933–941

Tiktak A., F. van den Berg, J.J.T.I. Boesten, Leistra M., A.M.A. van der Linden and D. van Kraalingen (2000). Pesticide Emission Assessment at Regional and Local Scales: User Manual of Pearl version 1.1. RIVM Report 711401008, Alterra Report 28, RIVM, Bilthoven, 142 pp.

Toensmeier P.A. (2004). Nanotechnology faces scrutiny over environment and toxicity. *Plastics Engineering*, Nov 60, 11; ABI/INFORM Trade & Industry.

Tolls J. (2001). Sorption of Veterinary Pharmaceuticals in Soils: A Review. *Environ. Sci. Technol.*, 35(17), 3397 – 3406.

Van den Berg F. and Boesten J.(1998). Pesticide leaching and accumulation model (PESTLA) version 3.4.b Description and user's guide. Winand Staring Centre for Integrated Land, Soil and Water Research, Agricultural Research Department, Wageningen, The Netherlands, 150 pp.

Wagner J. O. and Koormann F. (1999). GREAT-ER 1.0 Technical Manual. Institute of Environmental Systems Research. University of Osnabruck

Wilson V.S., Lambright C., Ostby J., Gray L.E. Jr. (2002). In vitro and in vivo effects of 17 β -trenbolone : a feedlot effluent contaminant. *Toxicol. Sci.* 70: 202-211.

Table 1: Sources of contaminants into the aquatic environment (adapted from Hooda et al (2000) and Plant et al (2005))

Emission type	Contaminant class	Major examples
Diffuse – agriculture and urban	Pesticides	Herbicides (e.g. glyphosate, atrazine, simazine, isoproturon), Fungicides (e.g. Cu)
	Nutrients	N, P
	Heavy metals	Cd, Cu, Zn , Pb, As
	Human pharmaceuticals	Carbamazepine, chlorhexidine, fluoxetine, cotinine, fluoxetine
	Veterinary medicines	Antibiotics, coccidiostats, ecto- and endo- parasiticides
	Personal care products	Methyl paraben, Sodium Lauryl Sulphate, triclosan
	POPs	Dioxins, furans, PCBs, aldrin, chlordane, DDT
Point-source – agriculture	Pesticides	Herbicides (e.g. glyphosate, atrazine, simazine, isoproturon), Fungicides (e.g. Cu)
	Veterinary medicines	Growth hormones (manure borne estrogens), roxarsone (As containing feed additive in poultry), coccidiostats (to overcome poultry intestinal parasites), antibiotics
Sewer discharge	Pesticides (home use)	Weed killers, herbicides, fungicides
	Heavy metals	Cd, Cu, Zn, Hg, Pb

	Human pharmaceuticals	Fibrates and β -blockers (CV and HP), antiepileptics, analgesics (painkillers), antibiotics (e.g. amoxicillin), hormonal substances (e.g. steroids), antidepressants, iodinated X-ray contrasting agents and bronchospasmolytics (asthma) Methyl paraben, Sodium Lauryl Sulphate, triclosan Dioxins, furans, PCBs, aldrin, chlordane, DDT <i>E.coli, Salmonella, Cryptosporidium</i>
	Personal care products	musks, triclosan, surfactants
	POPs	flame retardants (e.g. PFOS, PFOA, PBDE)
	Nanoparticles	TiO ₂ , fullerenes, Ag
Industrial discharges	Industrial chemicals	
Waste disposal	Pesticides	Similar to above
	Heavy metals	
	Human medicines	
	Personal care products	

POPs

Nanoparticles

Incinerators and power POPs
stations

Dioxins, furans

Table 2. TPs of different pesticides in soils in the last five years (adapted from Andreu and Pico, 2004)

Pesticide	K_{oc} (ml/g OC)	T_{1/2} (days)	TPs	Characteristics
<i>Organochlorines</i>				
DDT	635,000	3000	DDE, DDD	Toxic, persistent, bioaccumulable
Endosulfan	12,400	50	Endosulfan sulphate	Persistent
<i>Organophosphorus</i>				
Diazinon	1000	40	2-Isopropyl-6-methyl-4-pyrimidinol	Hydrolysis product
Glyphosate	24,000	47	Aminomethylphosphonic acid	More toxic
<i>Carbamates</i>				
Carbofuran	14-160	30-117	3-Hydroxycarbofuran 3-Ketocarbofuran	Hydrolysis products, toxic Little persistent
<i>Triazine herbicides</i>				
Simazine	130	60	Monodeethylsimazine	More toxic
Atrazine	100	60	Deethylatrazine Deisopropylatrazine	More toxic
<i>Urea pesticides</i>				
Isoproturon	66	15-40	4,4-diisoprylazobenzene	Less toxic

Chloroacetanilide herbicides

Metolachlor	90	26	2-Ethyl-6-methylalinine Metholachlor ethane sulfonic acid	Detected more often in groundwater
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Table 3. Previous horizon scanning studies for emerging environmental contaminants

Study	Emerging contaminant class	Protection goal	Exposure pathways	Parameters
Boxall et al., 2003	Veterinary medicines	Environmental	Soil, Surface water	Usage, Ecotoxicity
Thomas et al., 2004	Human medicines	Environmental	Surface water	Usage, Ecotoxicity, Therapeutic dose
Capelton et al., 2006	Veterinary medicines	Human	Drinking water, Vegetables, Meat, Fish	Usage, Toxicity
Sinclair et al., 2006	Degradates	Human	Drinking water	Usage, Sorption, Persistence, Toxicity
Sanderson et al., 2003	Human medicines	Environmental		Usage, Exposure, Ecotoxicity
Eljarrat and Barcelo, 2003	Dioxin-like compounds	Human	sediments, sludge	Chemical analysis, toxicity

Table 4: Summary of different models used at various scales

Scale	Process	Model example	Description	Reference
Field	Leaching	PESTLA – PEST icide L eaching and A ccumulation	Models movement of contaminant from soil surface to depth.	Van den Berg & Boesten (1998); Boesten & Gottesburen (2000)
		PEARL – P esticide E mission A ssessment at R egional and L ocal Scales	Routinely used in risk assessment of pesticides.	Leistra <i>et al.</i> (2000); Tiktak <i>et al.</i> (2000)
	Runoff	PRZM – P esticide R oot Z one M odel	Models movement of contaminant over the soil surface to adjacent waterbodies. Routinely used in risk assessment of pesticides.	Carsel <i>et al.</i> (1998)
	Drainflow	MACRO – Pesticide fate in macroporous soil	Models movement of contaminant from soil surface to field drainage systems. Routinely used in risk assessment of pesticides.	Jarvis & Larsson (1998)

Catchment	Fate in ditch	<p>TOXSWA - TOXic substances in Surface WAters</p> <p>GREATER – Geography Referenced Regional Exposure Assessment Tool for European Rivers</p>	<p>Models distribution and fate of a compound in a small water body comprising water, sediment and suspended sediment. Routinely used in risk assessment of pesticides.</p> <p>Models of the distribution and fate of a chemical in water at the catchment level. Most often applied in the assessment of chemicals emitted via wastewater discharges (e.g. surfactants, pharmaceuticals)</p>	<p>Adriaanse (1996); Adriaanse (1997); Horst <i>et al</i> (2003)</p> <p>Wagner & Koorman (1999)</p> <p>http://www.greater.org/files/techmanual.pdf</p>
		<p>PhATE – Pharmaceutical Assessment and Transport Evaluation</p>		Cunningham (2003)
Local	Fugacity		<p>Models fate of a substance in a ‘unit world’ comprising soil, sediment, water, air and biota. Used in the assessment of industrial chemicals</p>	<p>Prof Miriam Diamond (University of Toronto, Canada)</p>

Regional	Fugacity	Models fate of a substance in a 'unit world' comprising soil, sediment, water, air and biota. Used in the assessment of industrial chemicals
Global	Fugacity	Models fate of a substance in a 'unit world' comprising soil, sediment, water, air and biota. Used in the assessment of industrial chemicals
