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**Sources and Impacts of Past, Current and Future
Contamination of Soil**

Appendix 2 : Organic Contaminants

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Note on the report structure and content

This report forms an Appendix to the SID 5 Research Project Final Report for Defra Project code SP0547: Sources and Impacts of Past, Current and Future Contamination of Soil. The report here deals specifically with sources of organic inputs to soil and their potential impacts on soil quality, environment and human health. An extensive review of published literature, web information and unpublished reports was completed. The data were organised into three main sections in the report providing: (1) an overview of the identified key groups of organic compounds that may potentially enter soil; (2) a detailed, and as far as possible, quantitative assessment of the extent of the inputs of these contaminant groups from different source pathways; and (3) an assessment of the potential impacts of selected, important groups or specific contaminants on soil, environment and health. The appendices to this report present a list of categories of different compounds, the inventory of reviewed concentration data in environmental media; a list of legislation relating to organic contaminants that has direct or indirect implications for their transfer to soil; a list of chemicals of potential concern for the environment and procedures and legislation relating to pesticides and their approval.

EXECUTIVE SUMMARY

1. Introduction

Soil is potentially the recipient of inputs of a very large number of organic contaminants (OC). In the past effort has concentrated on examining the fate of OC in the aquatic environment and the potential for direct impact on human health *via* the food chain. Only more recently has attention focused on the impacts of OC on soil. For the purposes of this report, OC inputs to soils were divided into seven broad groups:

- Persistent organic pollutants (POPs);
- Bulk chemicals used in industry and domestically;
- Pesticides;
- Human pharmaceuticals;
- Veterinary medicines;
- Biocides and personal care products (PeCPs);
- Endocrine disrupting chemical (EDCs)

2. Sources of OC inputs to soil

Potential sources of OC inputs to soil include: atmospheric deposition, sewage sludge, livestock manure, compost, other 'wastes', pesticides and irrigation water. A brief summary is provided below.

Atmospheric deposition Information on atmospheric emissions and concentrations of POPs, provides an indirect indication of POP inputs to soils. National emissions data is collected annually in accordance with international treaties to monitor and limit POP emissions. Inevitably, the UK is both a recipient of POPs from overseas and an exporter of emissions. Modelling of long-range transport and deposition of POPs (MSC-E, 2004) has provided reasonable predictions of actual and relative POP concentrations in UK air, soil and vegetation. In general, concentrations have decreased over time and illustrate the effectiveness of action taken during the 1980s and 1990s to curb emissions and reduce the environmental burden of some principal POPs (PCDD/Fs, PCBs and PAHs).

There are a variety of routes through which pesticides may enter the atmosphere including spray drift and volatilisation. Since the loss of spray means that chemicals are not being effective it is in the farmers' interest to minimise losses through appropriate operating practices. The use of aerial application of pesticides has declined substantially in the last 20 years, with applications in 2002 estimated to be equivalent of 0.01% of the total area of pesticide application (CSL, 2003c). Wet deposition is generally the most significant route for pesticide redeposition to soils (Dubus *et al.*, 2000).

Sewage sludge. Quality standards for various OC in sewage sludge for agricultural use have been established in a number of European countries. The range of OC with potential health or environmental implications is much greater than the number of PTEs in sludge which are routinely monitored and controlled. Indeed, 42 organic compounds are regularly detected in sludge (IC Consultants, 2001).

Many OC will adsorb to the sludge matrix, although a proportion of the volatile OC may be lost by volatilisation during wastewater and sludge treatment. Biodegradation during anaerobic digestion may also eliminate certain OC from sewage sludge, but in general destruction is typically only 15 – 35 %. Aerobic composting and thermophilic

digestion processes are generally more effective at OC degradation than mesophilic anaerobic digestion, particularly for industrial bulk chemicals such as the surfactants LAS and NPE. Thermal hydrolysis prior to conventional anaerobic stabilisation may have a significant influence on the removal of OCs from sludge, but the effects have yet to be investigated for this comparatively new treatment process.

Controls on POPs introduced between 1980-90 have been relatively effective and there have been significant reductions in the primary sources of PAHs, PCBs and PCDD/Fs (Smith, 2000). This has also lowered inputs to the urban wastewater (UWW) system and reduced concentrations in sewage sludge. Inputs of POPs to sewage sludge now principally reflect:

- Background inputs to the sewer from normal dietary sources;
- Background inputs by atmospheric deposition due to remobilisation/volatilisation from soil and cycling in the environment (e.g. PCBs, PCDD/Fs and PAHs);
- Atmospheric deposition from waste incineration (eg PCDD/Fs);
- Atmospheric deposition from domestic combustion of coal;
- Biodegradation during sludge treatment;
- Volatile solids destruction during sludge treatment.

PAHs are Water Framework Directive (WFD) priority hazardous substances and the aim is to cease emissions, discharges and losses of these compounds by 2020 (CEC, 2001). However, curbing the emissions of PAHs and PCDD/Fs from domestic coal burning would be technically difficult and incinerators are already subject to stringent air quality emission standards (EPCEU, 2000a). Consequently, there is probably little opportunity to further reduce the inputs and concentrations of PAHs, PCDD/Fs as well as PCBs in UWW and sewage sludge.

POPs generally strongly bind to the sludge solids and the body of scientific evidence suggests that there are no significant environmental consequences from PAHs, PCBs or PCDD/Fs when sludge is applied to agricultural land. In the light of these developments, it may be argued that these substances are no longer as environmentally important as they were. However, soil is a major repository for POPs and further investigations are necessary to improve understanding of the remobilisation and cycling processes that control diffuse inputs of these organic compounds to UWW.

Data on the concentrations of pharmaceuticals in materials applied to land is very limited for the UK. In general, studies suggest that the pharmaceuticals vary greatly in biodegradability and are present in sewage influents and effluents to various extents. Typically, 60 % of the compounds in the influent may be removed during wastewater treatment although there is a wide range of removal efficiencies from 7-99% (Ternes, 1998).

Recent investigations show that approximately 90% of potential oestrogenic activity in UWW is reduced by sewage treatment and that <3 % is transferred to the sewage sludge. Oestrogenic substances excreted in farm livestock manures are likely to represent a much greater loading onto soil compared to recycling sewage sludge in agriculture (IC Consultants, 2001).

There is concern over persistent pesticide compounds (particularly organochlorines) in sewage sludge due to potential soil accumulation and long-term impacts on the environment (Bowen *et al.*, 2003). Modern pesticides have been developed with improved biodegradabilities in wastewater treatment and in the environment in general, so their presence is less of a concern than in the past. Varying persistences and ecotoxicities have been reported (Boxall *et al.*, 2004). However, the implications

for soil quality arise more from direct applications of pesticides to crops and soils, and from the application of livestock manures rather than from inputs *via* agricultural application of sewage sludge. Indeed, the withdrawal of persistent pesticides from agricultural means they are unlikely to be detected in influents to urban wastewater treatment plants (Bowen *et al.*, 2003) or sludge.

Livestock manures. POPs are not considered to be a concern in livestock manures applied to land (e.g. Stevens and Jones, 2003).

Veterinary medicines are used extensively in livestock production and consequently are present in livestock excreta. Direct deposition or application of manures to land provides a direct route of entry to the soil. In the UK, approximately 40-45% of the 459t of therapeutic-use antimicrobials are administered to pigs, implying that areas of pig production will be most susceptible to impacts from manure antimicrobial compounds (Burch, 2003).

Excreta deposited directly in the field may contain much higher concentrations of antibiotics than manure from housed stock because there is no dilution with material from medication-free time periods or degradation during storage (Boxall *et al.*, 2004). De Liguoro *et al.* (2003) and Boxall *et al.* (2004) have demonstrated that processes occurring between excretion and manure application to the soil were very effective in reducing the load of a number of antibiotics. In contrast, ivermectin (an endectocide), tetracyclines and quinolones (both antibiotics) are highly persistent with half-life values of 100 days in manure.

Manure and slurry management practices designed to reduce the risks from microbial pathogens by ensuring adequate storage and composting (FSA, 2002) are also likely to reduce the concentrations of veterinary medicines in livestock manures, however, further work is recommended to fully assess their effectiveness.

Compost. A recent review (Amlinger *et al.*, 2004) has concluded that concentrations of PCBs, PCDD/F and PAHs in source separated biowaste and green waste composts were similar to background concentrations in soils, and that regular measurements of these compounds and the establishment of limit values were not required. However, due to the higher concentrations in mixed waste compost the authors recommended that these compounds should be monitored and their use limited to non-food areas. This would appear to be an overly precautionary measure given the absence of environmental effects of POPs, their accumulation in compost amended soil is negligible and the concentrations present in mixed waste compost are below conservative and risk-derived limits for POPs in sewage sludge intended for agricultural use. Groeneveld and Hébert (2005) also concluded that the inclusion of dioxins/furans, PCBs, or PAHs in compost quality criteria was not justified.

A number of chlorinated pesticides have been found in compost, but generally only in very small amounts, with biowaste composts having higher concentrations than green compost (Amlinger *et al.*, 2004; Brändli *et al.*, 2005). Comparisons of pesticide concentrations in feedstock with the composted end products showed that composting substantially decreases the concentrations of most compounds. Consequently, there is no need for regular analyses of adsorbable organohalogenes (AOX) or specific pesticides in composts. However, given the high persistence/toxicity of wood preservatives, a precautionary measure would be to exclude pesticide treated wood from the production of marketable compost products or for recycling in agriculture.

LAS, NPE, DEHP, PBDE are rapidly degraded under aerobic composting conditions and extremely low concentrations have been reported in the literature (Amlinger *et al.*, 2004). Thus there is no evidence of a need for general threshold or limit values in composts.

Fungicides, disinfectants and insecticides are used in mushroom production. The use of spent mushroom compost (SMC) in agriculture, gardening and landscaping means that any pesticide residues will be added to soil. However, the range and quantities of chemicals applied have diminished in recent years and mushroom production has declined to an extent in the UK. Nevertheless, the estimated production of mushroom compost applied to land remains a significant volume, equivalent to approximately 400,000 t y (fresh weight) and, given the uncertainty about the extent of its contamination with pesticide residues, a chemical survey of the material is warranted.

Other waste materials. Davis and Rudd (1997) reported that a large number of compounds (and their degradation products) could be associated with waste materials applied to land and considered that such wastes should be subject to a detailed evaluation and risk assessment.

Information on OC concentrations in industrial wastes spread to land was compiled from data from EU Member States by Gendebien (2001). With the exception of waterways dredgings, POPs were within the ranges measured in sewage sludge and greenwaste composts and would not be considered limiting to land spreading. However, only a limited range of compounds was examined and a broader survey of wastes from sources where OC contamination may arise is required.

A recent survey of land spreading practices for paper waste (Gibbs *et al.*, 2005) concluded that there was no evidence of any significant risks to the environment from OC in paper waste materials applied to land. This was confirmed by field investigations which demonstrated significant agronomic benefit from the application of paper sludge and concluded that detrimental effects on soil microbial activity were not important in the medium-to-long-term after application (Aitken *et al.*, 2002).

Pesticides. The Pesticide Safety Directorate commissions regular surveys of pesticide use across the agricultural and horticultural industry. In this study, only arable crops, and grassland and fodder crops have been examined in detail because of the area of land they encompass and the amount of plant protection products which are used.

Agrochemicals are applied at different times of year depending on the crop to be protected. The extent to which a pesticide will be washed into soil will in part be dependant on weather conditions and hence will vary through the seasons. Likewise, the amount of leaf on a crop will vary through the year further influencing the extent to which a pesticide will fall directly onto the soil.

Drift can occur to a greater or lesser extent with both spray and granular products, depending on the equipment used. This will both reduce the concentration reaching the soil at the point of application and increase the area of soil which may be affected by plant protection products (CSL, 2004).

Pesticide and veterinary medicine residue disposal. Farm operations are a significant source of pesticides to surface and groundwaters, although soil may also be at risk of contamination from pesticide residues during, for example, spray equipment washing and cleaning. Managed soil-bioreactor systems or reedbeds may have potential for treating pesticide residues from tanks and equipment washing for

example and require further evaluation to develop an engineered design specification for effective remediation of pesticide wastes to protect soil and the water environment.

Land treatment is the principal approach for disposing of sheep dip chemicals, with 116,454 t disposed annually in the UK (EA, 2003). The primary focus of current environmental control measures is to protect water resources from contamination by sheep dip chemicals (Defra, 2001), with disposal to land requiring authorisation from the Environment Agency (EA). However, land treatment should also account for the potential impacts on soil fauna and flora. For instance, diazinon, one of the main organophosphate pesticides used in sheep dip, is acutely toxic to earthworms and other invertebrates (Boxall *et al.*, 2004), although other soil biological compartments may be less sensitive to sheep dip chemicals. Further research is needed to assess the consequences of sheep dip disposal on soil biological processes and fertility, and to develop recommendations to minimise soil damage and assess recovery.

Irrigation water. Irrigation is used to only a limited extent in UK agriculture, on lighter soils and for high value crops. It is more widely used in horticulture, and golf course and landscape maintenance, but this water will normally be from the mains supply. Because river water is often polluted with pharmaceutical compounds from WWt discharges, irrigation water abstracted from rivers is a potential source of pharmaceutical inputs to soil.

Limited data on OC concentrations in surface and groundwater were used to try to establish the potential scale of OC inputs to soil from crop irrigation. These are unlikely to have significant toxicological or ecotoxicological impacts in the main. However, the addition of trace quantities of antibiotic residues through irrigation of surface waters receiving effluents from urban wastewater treatment could have implications for the wider development and dissemination of antibiotic resistant bacteria in the environment. However, the implications of OC inputs for soil quality arise more from direct application of pesticides to crops and soils, and in managed applications of organic sludges and livestock manures rather than from inputs *via* irrigation waters.

3. Effects of OC inputs on soil quality and function

Soil is an effective scavenger and sorptive medium for OC and acts as a long-term and major repository, although biodegradation will also take place. The behaviour of OC in soil depends on their physical and chemical properties and on the nature of the soil. The persistence of OC in the environment is one of the key properties used to determine its potential significance and long-term impact. Those that are highly resistant to breakdown are described as refractory or recalcitrant (Walker, 2001). Many are not photochemically stable and may be transformed when exposed to sunlight. Some, such as carbamates and pyrethroids are susceptible to hydrolysis especially at high pH. Highly halogenated compounds (e.g. some PCBs and dioxins) are resistant to oxidation and chemical degradation.

Some OC bind to soil organic matter (OM) or minerals and tend to be immobile and persistent. Metabolism is limited and they are therefore not freely accessible to soil enzymes (Walker, 2001). Heavy soils, high in OM and/or clay adsorb hydrophobic compounds that would be more mobile or bioavailable in light sandy soils, low in OM. In contrast, hydrophilic or polar compounds are less adsorbed to soil colloids and are both more rapidly degraded by soil enzymes and more readily lost in soil drainage.

Persistent organic pollutants. PCDD/Fs, PCBs, higher chlorinated CBs and most PAHs are highly persistent in soil, whereas lower chlorinated CBs and some types of PAH are only moderately sorbed. Soil sorption of these compounds is enhanced by sewage sludge applications (e.g. Zhang *et al.*, 2005). In general, highly sorbed POPs are less susceptible to leaching and transport. The lower chlorinated chlorobenzenes and most PAH congeners are highly volatile in soil (Wild *et al.*, 1995). The lighter PCB congeners are moderately volatile, whilst PCDD/Fs do not tend to volatilise.

Due to the strong soil sorption of most POPs, the potential for root uptake is limited (e.g. Fries, 1996; Smith, 2000). Moreover, most POPs are not efficiently translocated into the above ground plant parts (McCrary *et al.*, 1990 cited in Wild *et al.*, 1992). Volatile compounds are thought to be lost from the soil before having the opportunity to enter plant tissue *via* the roots (Wild *et al.*, 1995; Duarte-Davidson and Jones, 1996). However they can potentially enter plant tissues *via* foliar absorption (Duarte-Davidson and Jones, 1996) and there is substantial evidence to indicate that this is the primary mechanism of plant contamination. POPs have no reported detrimental effects on plant growth and the scientific literature consistently shows that there is effectively no crop uptake.

POP ingestion by grazing animals could be expected and their lipophilic properties may result in their accumulation in animal tissues and food products (Fries, 1996; Smith, 2000). Indeed this pathway is considered to represent the greatest risk for POP entry into the food chain from agricultural sources (Fries, 1996; Smith, 2000). However, PAHs do not appear to accumulate in animal tissue. Lusky *et al.* (1992 cited in Fries, 1996) found that the concentrations of PAHs in animal tissues were the same regardless of whether the animals had received high or low feed PAH concentrations. Whilst PCBs, PCDD/Fs and CBs are not metabolised and can accumulate in the food chain, the risks still appear to be extremely low, especially from contaminants in sewage sludge applications since measures in the Safe Sludge Matrix designed to further limit potential infections from pathogenic organisms that may be present in sludge, at the same time, also reduce the potential for animal ingestion of OC (eg grazing restrictions on sludge-treated pasture). Thus, the main route for POP accumulation in the food chain is via atmospheric deposition onto the soil. Since the 1977 UK ban on PCBs, the amount of these contaminants in soil has been greatly reduced and is now similar to values prior to the production of PCBs. Thus, the risks of transfer into the human food chain are minimal.

Reinecke and Nash (1984) found that acute exposure to TCDD at concentrations currently found in the environment did not present a risk to earthworms. However, chronic exposure to sublethal TCDD concentrations could cause accumulation in earthworms, and as earthworms are a major source of food for higher organisms, this could present significant ecological risks. Other studies have reported the accumulation of chlorobenzenes, chlorophenols and other PCDDs in earthworms (Belfroid *et al.*, 1995).

In terms of soil microorganisms, Chaudri *et al.* (1996) found that Aroclor 1016 (a mixture of PCB congeners) and anthracene (a PAH) had little or no effect on the soil rhizobial population. Aldrich and Daniel (2003) concluded that, for PCDD, PAH and PCB there was sufficient data to exclude an unacceptable risk to soil organisms from agricultural recycling of compost.

Pesticides. Approximately 85% of an applied pesticide may reach the soil where it is subject to biological or chemical transformation (Margni *et al.*, 2002). Some pesticides are mobile and readily degradable, while others are persistent and may accumulate and impact non-target soil organisms (HRI, 2002). Microbial degradation

is the key process affecting pesticide persistence in soil, susceptibility to leaching and entry into surface and ground waters (Aislabie and Lloyd Jones, 1995). Plant roots release substances that stimulate soil microbial and biochemical activity, enhancing pesticide degradation. Sludge application has also been shown to increase the degradation of some pesticides (Sanchez *et al.*, 2004). Sinclair and Boxall (2004) found that 30% of pesticide breakdown products were more toxic than the parent compound. In addition, the properties and persistence of the breakdown products may be such that environmental compartments are exposed to them to a greater extent than the parent compound, further increasing the potential impact.

Multiple pesticide applications may have an enhancing or deleterious effect on soil biological processes. Williams *et al.* (1996) suggested that in soils repeatedly exposed to pesticides, the microbial population becomes acclimated to more rapidly degrade them. However, multiple pesticide applications may also impair the soils ability to metabolise subsequent applications (HRI, 2002).

At normal application rates, herbicides and insecticides generally have little effect on soil ammonification or nitrification processes (Yamaoto, 1998; Wainwright, 1978). Fungicides have been reported to increase ammonification in soils (Wainwright and Pugh, 1973) and some older fungicides were significant nitrification inhibitors. However, newer compounds appear to have only marginal effects on nitrification (Wainwright, 1978). Insecticides generally have a minor influence on soil respiration (e.g. Lewis *et al.*, 1977). In contrast, fungicides have been found to initially decrease soil respiration rates, followed by a marked stimulation attributed to the increased activity of a few resistant microorganisms (Domsch, 1970 cited in Wainwright, 1978). Others (e.g. Smith and Woods, 1996) have reported reductions in the microbial biomass and increased respiration in pesticide treated soils.

The effects of insecticides on the growth and activities of soil organisms are not consistent. No negative effects of insecticides on soil organisms, microbial processes or crop productivity were found by Bromilow *et al.* (1996) or Das and Mukherjee (2000). In contrast, Kale *et al.* (1989) found that, whilst neither insecticides nor their metabolites had negative effects on *Rhizobium* sp. growth, *Azotobacter chroococcum* growth was inhibited, indicating that the chemicals may interfere with nitrogen fixing mechanisms. Moreover, after PCP was applied in sewage sludge, Chaudri *et al.* (1996) found a 99% reduction in soil rhizobia, with no evidence of recovery. However, production and use of PCP has been restricted in Europe since the 1980s. The compound was not detected in a contemporary survey of sewage influents in the UK (Bowen *et al.*, 2003).

Phenoxyalkanoic acid herbicides have been applied repeatedly on the same soil in many areas of the world with no negative impacts on soil fertility or ecology. Similarly, 35 years of annual 2,4-D field applications had no apparent effects on biomass N or N mineralization (Biederbeck *et al.*, 1987). Triazines have been found not to alter soil bacterial and fungal populations (Voets *et al.*, 1974). However, reductions in sporeformers (Audus, 1970), and nitrifying bacteria (e.g. Farmer *et al.*, 1965 cited in Voets *et al.*, 1974) have been observed. Voets *et al.* (1974) also studied the long term effects of atrazine and found reductions in the numbers of various soil organisms, and a large and persistent depression of certain soil enzymes.

Veterinary medicines. A significant portion of most drugs are excreted after administration to livestock, either as the parent substance or metabolites. Antibiotics are biologically active substances designed to affect microorganisms. They are usually mobile as their water solubility is high relative to the molecular weight. Many

medicines are lipophilic and persistent, with a high potential to bioaccumulate in the soil environment.

Most research on the health effects arising from the presence of antibiotics in the environment has focussed on the development of antibiotic resistant bacteria. When medicated livestock excrete drug metabolites, bacteria in the manure reconvert the metabolites into active compounds. Thus, manure application to agricultural soils can provoke pathogens and bacteria into developing drug resistance (Thiel-Bruhn, 2003). Antibiotic treatment also causes the formation of resistant microorganisms within the animal which can be transferred to the soil in the excreta. Even trace concentrations of active substances are sufficient to provoke resistance (Halling-Sørensen *et al.*, 1998). Microbial antibiotic resistance readily crosses species boundaries (Witte, 1998), allowing multiple-resistant strains of microorganisms to find their way into the food chain (Berger *et al.*, 1996 cited in Halling-Sørensen *et al.*, 1998). Indeed, the spread of antibiotic resistant human pathogens has been directly linked to the use of antibiotics in animal husbandry which have entered the water environment following manure application (Haller *et al.*, 2002). However, the development of resistance in soil bacterial populations appears to be a transient phenomenon. Recent studies show that, once the selection pressure from inputs of antibiotic compounds in livestock manures is removed, the resistance profiles of the soil community return to pre-treatment values (e.g. Sengeløv *et al.*, 2003)

The mobility and availability of veterinary medicines for uptake by soil organisms depends on the chemistry of the compounds and soil properties. In general, an antibiotic sorbed to soil demonstrates reduced antimicrobial activity. Desorption on the other hand reactivates antimicrobial potency (Lunestad and Goksøyr, 1990).

Antibiotics and other veterinary medicines and their metabolites vary in persistence (Kümpel *et al.*, 2001). Some compounds, such as ivermectin (an endoparasiticide), chlorotetracycline and amprolium (both antibiotics) persist for months, while others like tylosin, penicillin (both antibiotics) and nicarbazin (an endoparasiticide), degrade after a few days. Manure type also affects degradation, although breakdown rates in manure are generally faster than in soil (Loke *et al.*, 2000; Boxall *et al.*, 2004). Soil type and manure application timing may also affect the degradation rate of a compound (Boxall *et al.*, 2003a). Metabolites in general are less potent than the parent compounds, but may still be toxic. Thus, risk assessments based on the parent compound alone may underestimate actual potential effects on the soil environment.

There are very few reports of the detection of drug residues in food for human consumption arising from environmental contamination. Thiele-Bruhn (2003) concluded that plant uptake even of mobile antibiotics was small, although some effects on plant growth were apparent. There is as yet no evidence that bioaccumulation of some therapeutic compounds poses any significant health hazard to consumers.

A long-term priority is to reduce reliance on routine veterinary administration of antibiotics in livestock production. A more immediate practical option would be to adapt manure storage and composting practices to maximise antibiotic degradation. Spreading frequency and rates of application could also be modified to allow time for microbial populations to recover and avoid supporting a permanent reservoir of resistant bacteria in soil. Manure applications to agricultural land are restricted to limit inputs of nitrogen within Nitrate Vulnerable Zones (CEC, 1991). These measures could also provide a degree of indirect control to minimise the extent of antibiotic resistance and allow natural attenuation of antibiotic resistant soil bacterial

populations to take place. Further work is necessary to determine the potential impacts of current manure application practices on the development of antibiotic resistance in manure treated soil. Also, fundamental work is necessary to establish the risks and implications of disseminating antibiotic resistance from agricultural soil to livestock and the human population.

As antibiotics are designed to affect bacteria, they are naturally a potential hazard to soil microorganisms. However, published information on their effects on soil organisms and processes is inconsistent (Thiele-Bruhn, 2003). Some studies have reported that antibiotics inhibit microorganisms (e.g. Colinas *et al.*, 1994; Elvers and Wright, 1995) whilst others have reported enhanced microbial growth and activity (Höper *et al.*, 2002). Significant effects of pharmaceutical compounds on soil have generally only been observed for anthelmintic (deworming) compounds (Thiele-Bruhn, 2003) and anti-parasitic agents e.g. ivermectin.

In general, acute ecotoxicological effects of medicines are unlikely when mixed in soil (Boxall *et al.*, 2004). Some drugs (e.g. ivermectin) have been found to adversely effect insect (e.g. springtail and enchytraeid) survival and reproduction (Blume *et al.*, 1976; Wall and Strong, 1987). This is important because of potential effects on food chains that depend on these organisms (Davis *et al.*, 1999). Laboratory experiments have shown that certain compounds are potentially phytotoxic, although the concentrations used were often much larger than those in field soils (Thiele-Bruhn, 2003).

Phthalates. A large number of chemicals are used in industrial manufacturing processes and domestic products and potentially transfer to soil. However, plasticizers deserve special mention because they are ubiquitous in the built environment. They leach from plastic materials and can transfer to soil by the water and sludge application route. Di(2-ethylhexyl)phthalate (DEHP) is a WFD priority substance under review and there is a degree of controversy regarding its potential carcinogenicity and oestrogenic properties. However, the available evidence indicates that the risk to human health from diffuse environmental sources of DEHP is negligible. Biodegradation is the dominant loss mechanism of phthalates in soils. Microorganisms, particularly, bacteria and actinomycetes degrade phthalate esters and their metabolites. Various studies have shown that phthalate esters are not persistent and undergo relatively rapid degradation in soils (e.g. UKWIR, 1995). In general, phthalate esters are considered to be nonvolatile (Smith, 2000).

Plant growth studies show there is little uptake of DEHP via the roots (e.g. Schmitzer *et al.*, 1989), with the increased organic matter associated with sludge applications thought to reduce DEHP bioavailability. The low volatility of phthalates also restricts their potential for redeposition onto above-ground plant parts.

Phthalates are usually rapidly metabolised by livestock and there is no significant transfer from soil or sludge to food products (UKWIR, 1995; Fries, 1996; Smith, 2000). The principal route of human exposure to phthalates is probably from other sources such as food packaging. DEHP is widely used as a plasticizer of PVC and the most critical human exposure route to DEHP is from medical equipment. Phthalates have not been found to cause any significant adverse effects on soil microbial processes or on soil fertility. However, some authors have found that DBP and DEHP may accumulate in some mesofauna and represent a potential risk to these organisms (e.g. Hu *et al.*, 2005). If DEHP use were to be restricted in future, the implications for soil quality of alternative plasticizers should be assessed as much less is known about these potential replacement compounds compared to DEHP.

1. OVERVIEW OF ORGANIC CONTAMINANT INPUTS TO SOIL

1.1 Introduction

There are a large and diverse variety of chemicals and compounds that could be included in an assessment of the inputs of organic contaminants (OC) to soil. Some 90,000 industrial and domestically employed organic compounds have the potential to be found in wastes applied to land, for instance (O'Connor, 2005). In the last 20 to 30 years a considerable amount of work has been conducted on certain aspects of OC fate in the environment. This has focused largely on the aquatic environment and the potential for direct impact on human health *via* the food chain. More recently increasing attention has focused on the impacts of OC on soil quality and hence indirectly on human health, but the database is considerably more limited compared to that for the water environment. Table 1 gives typical background OC concentrations in soil for identified priority and potentially important compounds.

Table 1 Typical concentrations of organic contaminants in soils in $\mu\text{g kg}^{-1}$ ds (dry soil) (others indicated)

Compound	Area	Land use	Median/ 50%ile	90%ile
EOX ¹	rural area		0.3 mg kg ⁻¹	0.6 mg kg ⁻¹
	urban area		0.4 mg kg ⁻¹	0.9 mg kg ⁻¹
Phthalates (EPA 606)		arable land	786	1,262
		grassland	893	1,825
PAH (EPA 16)	rural soils		0.82	3.99
	urban soils		2.67	10.92
PCB (IUPAC 6)	rural soils		14	98
	urban soils		34	243
		arable land	10	40
		grassland	16	101
		private gardens	30	284
PCDD/F			2.44 ng ITeq(NATO) kg ⁻¹ dm n = 132	13.3 ng ITeq(NATO) kg ⁻¹ n = 132
HCB			<1.0	5.0
HCHsum			<1.0	4.3
DDTsum			3.6	45.5

(Source: UMEG, 1999; Litz, 1998; cit. in Erhardt & Prüeß, 2001 cited in Amlinger *et al.* 2004)

¹EOX is the sum of extractable organic halogen compounds

The exception to this is the investigation of OC concentrations in biosolids and their fate in soil. The consensus from that research is that the risk presented by organic chemicals in biosolids are small (Lester, 1983; Overcash, 1983; Davis *et al.*, 1984; Dean and Suess, 1985; Jacobs *et al.*, 1987; Rogers 1987; Webber and Lesage, 1989; Chaney, 1990ab; O'Connor *et al.*, 1991; Sweetman, 1991; Wild and Jones, 1991; Sweetman *et al.*, 1994; Smith, 1996; Carrington *et al.*, 1998; Smith, 2000;

Erhardt and Prüß, 2001). For example, a recent three year programme of field and glasshouse investigations in Denmark (Petersen *et al.*, 2003) examined the effects of sludge, household compost and solid pig manure application on soil properties and soil biota, the fate of selected OC (which included four principal groups or types of OC present in sludge: polycyclic aromatic hydrocarbons (PAH), di(2-ethylhexyl)phthalate (DEHP), nonylphenol and ethoxylates (NP + NPE) and linear alkylbenzene sulphonates (LAS)), and their potential for plant uptake. No accumulation of the OC in soil or plant uptake were detected and no adverse effects of waste application on soil or crop were found (Petersen *et al.*, 2003).

Extensive risk assessments and evaluations have been completed for biosolids. For example, US EPA, in developing the *Standards for the Use or Disposal of Sewage Sludge: Final Rules Part 503* (US EPA, 1993), screened approximately 200 pollutants and selected 31 for further evaluation, which included 18 organic compounds (US EPA, 1992abc). This list was later expanded to include an evaluation of dioxin and dioxin like substances (US EPA, 2003). Water Environment Association of Ontario (WEAO, 2001) recently reviewed the fate and significance of selected contaminants in sewage biosolids applied to land including:

- Trace organics, including volatile organic contaminants (VOCs), polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs) and pesticides;
- Linear alkylbenzene sulphonate (LAS) surfactants;
- Endocrine disrupter compounds (EDCs) including alkylphenol surfactants (APs) and oestrogenic hormones;
- Dioxins and furans (PCDD/Fs)

The World Health Organisation (WHO) has developed human-health related guidelines for 24 groups of organic compound for sewage sludge applications to agricultural land (Chang *et al.*, 2002). UK Water Industry Research has funded extensive research programmes on OC in urban wastewater and sludge (eg UKWIR, 1995; Bowen *et al.*, 2003). The European Commission has also reviewed the significance of OC in sewage sludge and following application to agricultural land (Erhardt and Prüß, 2001; IC Consultants, 2001). A summary of current knowledge of the concentrations of potentially 'dangerous' substances in sewage sludge was recently compiled for the UK Environment Agency (Rogers *et al.*, 2001). Consequently, it has been relatively easy to obtain data from the literature concerning the concentrations of organic compounds in biosolids. This extensive database of information therefore provides a bench-mark for considering the wider assessment of the significance of OC entering soil. In stark contrast, however, the amount of data available concerning the OC content for other materials applied to land is relatively limited by comparison.

Organic contaminants entering soil fall into three principal categories:

1. Persistent organic pollutants (POPs), which have been recognised as important environmental contaminants for several decades, are well characterised and many protocols are in place to eliminate, or limit their use.
2. Compounds which are partially or wholly regulated, but whose environmental concentrations or impact may not be fully characterised. These include human pharmaceuticals, veterinary medicines, and also certain agrochemicals.
3. There is also a category of compounds the use of which is only lightly regulated or unregulated and the environmental impact of which is either unknown or just becoming understood. These include, many bulk chemicals used in industry or

domestically (eg flame retardants, solvents, surfactants and their residues, plasticizers), personal care products (PeCPs) and endocrine disruptors (EDC). However, the environmental impacts of certain compounds within these groups have been well characterised recently, eg the surfactant linear alkylbenzene sulphonate (LAS), the surfactant residue nonyl phenol (NP) and also the plasticizer di(2-ethylhexyl)phthalate (DEHP).

A literature review was conducted to source data concerning the concentrations of OC in materials routinely applied to soil, directly applied to soil *via* land management practices such as pesticide use and irrigation, and deposited on land via deliberate or accidental release to the environment. The detailed, quantitative assessment of these different pathways is given in Section 2 of the report. Five broad categories of OC have been identified:

- Persistent organic pollutants (POPs);
- Bulk chemicals used in industry and domestically;
- Pesticides;
- Human pharmaceuticals;
- Veterinary medicines;
- Biocides and personal care products;
- Endocrine disrupting chemical (EDCs).

The availability of data concerning these categories of compound varies greatly both in terms of the concentrations present in different media and their fate, behaviour and impact on different compartments of the environment. All the categories have been widely studied in the aquatic environment, but the availability of data in solid matrices is much poorer. Table 2 illustrates the availability of data for different media and compounds included in this study.

Table 2 Summary of data availability

	POPs	Industrial and bulk chemicals	Pesticides	Human Pharmaceuticals	Vet medicines	Biocides & PCPs
Atmospheric deposition	●	●	●	□	□	□
Sludge	●	●	●	●	○	●
Manure	●	●	●	□	●	□
Industrial waste	●	○	○	○	○	○
Compost	●	●	○	□	○	□
Dredgings	●	●	○	○	●	○
Irrigation	●	●	●	●	●	○
Usage data available	□	Yes	Yes	Some	Yes	No

● Good , ● moderate, ● poor, ○ none, □ not relevant

A list of organic compounds and abbreviations generally used in the literature to described them is give in Annex A. A summary of the concentration data available on

pharmaceutical compounds in different water samples is presented in Annex B. The complete inventory of concentration values for OC in different media is given in Annex C.

Few data were available for OC concentrations in many materials which are applied to land, most particularly industrial wastes. Some limited values are available for certain wastes spread on land in the survey completed by Gendebien *et al.* (2001) for DG Environment, and these are presented later in the report (Section 2.5). Aitken *et al.* (2002) also supply a qualitative assessment of the likely concentrations of organic contaminants in a range of these wastes (Table 3). More recently, Amlinger *et al.* (2004) reviewed the published data on organic compounds in biowastes and composts for DG Environment (Section 2.4) and also commented on the paucity of results. Whilst the absence of routine monitoring data on OC concentrations in these materials spread on land may raise concerns about the potential quality and impacts of the wastes, and restricts the development of an inventory of inputs to soil, it is not considered to affect this substantially since the quantities applied to land are relatively small (Table 4). As indicated in Table 3, OC are not likely to represent a significant issue for many industrial wastes and biowastes applied to land as they do not come into direct contact with organic chemicals, such as in a manufacturing process, or from urban or industrial discharges. Exceptions include residuals from processes where bleaching, colouring or preservation agents and pesticides may be used. It is also conceivable that composted green wastes from urban areas may contain elevated concentrations of combustion by-products from atmospheric deposition or absorption (eg PAHs) and compost produced using the organic fraction from mechanically segregated municipal waste to contain contaminants associated with household hazardous waste (HHW).

Table 3 Assessment of likely concentrations of organic contaminants in a range of organic wastes (Aitken *et al.*, 2002)

Waste	<u>Risk</u>
Waste soil or compost	L
Waste wood, bark or other plant matter	L
Waste food, drink or materials used in their preparation	L
Blood and gut contents from abattoirs	L
Waste lime	L
Lime sludge from cement manufacture or gas processing	L
Waste gypsum	L
Paper waste sludge, waste paper and de-inked paper pulp	M
Dredgings from any inland waters	L
Textile waste	M
Septic tank sludge	M
Sludge from biological treatment plants	M
Waste hair and effluent treatment sludge from tanneries	M

Notes:

L = Low unlikely to be a problem

M = Moderate a possible problem unless strict precautions are followed

H = High likely to be a serious problem unless strict precautions are carried out

Where data were limited or absent, the potential for given substances to present a significant hazard has been assessed in part by considering the quantities

manufactured or used, where this data is available. The potential for a substance to impact the environment will be influenced in part by how widely it is used, the quantities manufactured, and its degradation or persistence in different environmental compartments. For instance, pharmaceuticals, both human and veterinary, are absorbed to varying degrees within the body and may be excreted either as the original chemical or in a partially metabolised form. The impact of both active ingredient and its metabolites therefore need to be considered when investigating the impact of compounds on soil function and health (Section 3.3).

Table 4 Quantities of wastes applied to land in the UK annually

Material	Type	Quantity (000 t fw)	Rate (t ha ⁻¹ fw)
Compost	Green waste	1200	36
	Mushroom	400	
Sewage sludge ¹		824	6
Industrial waste	Food	1409	nd
	Paper - primary	258	69
	Paper - secondary biological	205	33
	Paper - secondary chem/phys	236	69
	Textile	3.5	nd
	Leather	0.3	nd
	Cement lime sludge	12.2	nd
	Biological treatment sludge	4.3	nd
	Other organic	5050	nd
Manures	Dairy slurry	13979	63
	Beef slurry	2896	71
	Pig slurry	2011	36
	Dairy FYM	7957	42
	Beef/sheep FYM	20361	42
	Pig FYM	3463	36
	Layer	978	16
	Broiler	1771	8

Notes:

1 dry weight not fresh weight

The section of this report relating to OC inputs is structured in such a way as to maintain clarity across a broad ranging subject. Each category of organic contaminant is considered for each type of material applied to land (Section 2). The exception is agrochemicals, which are applied directly and not *via* another medium.

The behaviour of organic compounds in soil depends on their physical and chemical properties and on the physical, chemical and biological nature of the soil. Polarity is a key determinant of the environmental fate of organic chemicals. Broadly speaking, the more polar a compound the higher is its water solubility and *visa versa*. Compounds of low polarity tend to be lipophilic and of low water solubility i.e. hydrophobic. The balance between the lipophilicity and hydrophilicity of a compound is indicated by its octanol-water partition coefficient (K_{OW}), which is determined when equilibrium is reached between the two adjoining phases i.e. K_{OW} = concentration of compound in octanol/concentration in water. K_{OW} values for highly lipophilic compounds are very large and hence are commonly expressed as log values to the base 10.

Log K_{OW} has been used extensively to estimate the environmental fate of organic compounds. In general, compounds with high K_{OW} values have a greater tendency to adsorb onto soil particles and organic matter. Lipophilic, hydrophobic compounds tend to be less readily broken down by biological processes, hence K_{OW} values can be used as an indication of the environmental persistence of a compound. Where no data is available on the concentrations of compounds entering soils, K_{OW} values can potentially be used to identify compounds of concern which may merit more targeted investigation of their presence in materials applied to land. The sorption behaviour of OC according to K_{ow} values is described as follows (IC Consultants, 2001):

Log K_{ow} < 2.5	low sorption potential
Log K_{ow} > 2.5 and < 4.0	medium sorption potential
Log K_{ow} > 4.0	high sorption potential

Organic carbon-water partition coefficient (K_{oc}) is the ratio between the concentration of a compound on organic carbon (mg/g) and the concentration in water (mg/ml). In general, compounds with higher K_{oc} values tend to adsorb more strongly onto organic carbon, whilst those with lower K_{oc} values are more readily leached. Hence, the K_{oc} value provides an indication of the likelihood of leaching through soil. As with K_{ow} , K_{oc} values can vary over several orders of magnitude and therefore are expressed usually on a log scale.

Vapour pressure is defined as the pressure exerted by a chemical on the vapour state on its own liquid or solid surface at equilibrium and is another key determinant of chemical environmental fate. Vapour pressure is related to temperature and liquids boil at temperatures which raise their vapour pressure to the same as atmospheric pressure. Some solids pass directly from solid state to the vapour state and many pesticides that exist as solids at normal pressure and temperature conditions will sublime under field conditions. Volatilisation is a major source of pesticides loss from crop surfaces and soil. High vapour pressure values indicate that a compound will readily volatilise. As a general guide, compounds with a Henry's Law constant $>10^{-3}$ atm ($\text{mol}^{-1} \text{m}^{-3}$) can be removed by volatilisation (IC Consultants, 2001). The significance of volatilisation losses of specific organic compounds during sewage treatment can be predicted based on Henry's constant (H_c) and K_{ow} (IC Consultants, 2001):

$H_c > 1 \times 10^{-4}$ and $H_c/K_{ow} > 1 \times 10^{-9}$	high volatilisation potential
$H_c < 1 \times 10^{-4}$ and $H_c/K_{ow} < 1 \times 10^{-9}$	low volatilisation potential

The chemical stability of a compound will also influence its environmental fate. Those that are highly resistant to breakdown are described as refractory or recalcitrant. (Walker, 2001). Many are not photochemically stable and may be oxidised or undergo molecular rearrangement when exposed to sunlight. Some, such as carbamates and pyrethroids are susceptible to hydrolysis especially under conditions of high pH. Highly halogenated compounds such as higher chlorinated PCBs and dioxin tend to be resistant to oxidation and other mechanisms of chemicals degradation. The presence of charged groups will also influence the behaviour of a chemical in the environment. Some pollutants exist as anions or cations in solution which may become bound to organic macromolecules or minerals of the opposite charge in soil or sediments (Walker, 2001).

Hydrophobic compounds of high K_{OW} become very strongly adsorbed to soil colloids and consequently tend to be immobile and persistent. Strong adsorption and low solubility means they are not leached through the soil profile. Metabolism is limited as they are tightly bound and, therefore, are not freely available to enzymes of soil

organisms. Even where enzymes systems can access them, breakdown is extremely slow (Walker, 2001). Heavy soils, high in organic matter and/or clay, adsorb hydrophobic compounds that will be more mobile or bioavailable in light sandy soils, low in organic matter. In contrast, hydrophilic or polar compounds are less adsorbed to soil colloids and are consequently both more rapidly degraded by soil enzymes and more readily lost in soil drainage.

The persistence of an organic compound in the environment is one of the key properties used to determine the potential significance and long-term impact of its emission. This is usually based on a measured half-life value determined by controlled incubation in soil, for instance, under laboratory conditions. However, these are regarded as conservative as the persistence of OC in the field is often overestimated by models based on laboratory determined degradation half-lives (Beulke *et al.*, 2000).

1.2 Persistent organic pollutants

Persistent organic pollutants (POPs) are organic compounds of natural or anthropogenic origin that resist photolytic, chemical and/or biological degradation (UNEP, 1999). They are characterised by low water solubility and high lipid solubility, which gives them high potential for bioaccumulation. POPs are semi-volatile, allowing them to be transported long distances from the original source via the atmosphere and the aquatic environment. Consequently, POPs are widely distributed and may be found at locations where they have never been used. Estimated UK emission sources to the environment are listed in Table 5.

The persistent organic pollutants considered within this report fall into three main categories (Brändli *et al.*, 2003):

- Ubiquitous compounds with ongoing release from primary sources mainly due to anthropogenic production such as emissions from incineration of fuel e.g. polycyclic aromatic hydrocarbons, (PAHs) or from volatilisation or leaching of high volume chemicals, e.g. flame retardants;
- Ubiquitous compounds banned for production, but still present in anthropogenic repositories (e.g. building parts) and in natural sinks like sediments, soils or water bodies due to their high persistence, e.g. polychlorinated biphenyls, (PCBs);
- Pesticides or biocides, which in contrast to the former two categories, are released to the environment deliberately due to application.

Some POPs have been deliberately produced for use within industry, including organo-chlorine pesticides, polychlorinated biphenols (PCBs) and polychlorinated naphthalenes (PCNs), though their use is now limited by international treaty (Annex D). Others, such as brominated flame retardants (BFRs) are still produced in large quantities – 69,000 t worldwide in 1999 (Eljarrat and Barceló, 2004) (see Section 1.3). A third group are formed accidentally or as a by-product of industry or combustion processes. These include polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polycyclic aromatic hydrocarbons (PAHs). Dioxins and furans are frequently lumped together as PCDD/Fs and together with PCBs, PCNs and BFRs go under the collective name of halogenated aromatic hydrocarbons (HAHs) (BFRs will be dealt with here as ‘industrial bulk chemicals’ as they are still in active production).

Table 5 UK emissions of key POPs in 2002 listed by UN/ECE category (NAEI, 2003)

2002	PCDD/Fs		BaP ¹		PAH		PCBs	
BY UN/ECE CATEGORY	g TEQ y ⁻¹	%	t	%	t	%	kg	%
Combustion in Energy Prod								
Public Power	31	10			4		51	3
Petroleum Refining Plants	11	4			3			
Other Combustion & Trans.					1		3	0
Combustion in Comm/Res								
Residential Plant	64	20	2.9	31	408	20	10	1
Comm/Agricul Combustion	15	5			2		1	0
Combustion in Industry								
Iron & Steel Combustion	24	8			15	1	28	2
Non-Ferrous Metals	13	4			144	7		
Other Ind. Combustion	50	16					1049	72
Production Processes								
Iron & Steel	9	3					140	10
Non-Ferrous Metals	6	2	0.7	7	114	6		
Processes in Industry	3	1	0.2	2	65	3		
Solvent Use					69	3		
Road Transport								
Combustion	3	1	0.5	5	1051	52		
Vehicle Fires	9	3						
Other Trans/Machinery					4			
Waste			2.0	21	65	3		
Landfill	1							
Waste Incineration	70	22					149	10
Other Waste Treat. & Disp.							20	1
Agriculture								
Nature	6	2	2.9	31	95	5		
TOTAL	316		9		2039		1452	

Notes:

1 Emissions of BaP (benzo(a)pyrene) are included in the 16 PAH emissions, but it is an important pollutant, and is therefore also reported in its own right

Controls on the emissions of POPs (Annex D) have substantially reduced their release, however, there is an ongoing discrepancy in data pertaining to their release and their deposition. It is generally felt that this is most likely to be the result of the recycling and re-entrainment, such that measured deposition data is the sum of primary source releases and the flux attributable to recycling of previously deposited POPs. A study of PCBs by Eduljee (1988 cited Eduljee, 2002) determined that about 1% of the deposition flux in the UK was accounted for by emissions from primary sources with the remaining deposition, equal to about 12 t per annum, attributable to volatilisation from the land mass. Harrad *et al.* (1994) revised this to 40 t per annum volatilisation from land as compared with 3.9-4.8 t per annum from primary sources. From a source-sink mass balance, Harrad *et al.* (1994) estimated that the bulk of the contemporary UK environmental burden of Σ PCBs was associated with soil. The

contemporary flux of Σ PCBs to the UK surface was estimated to be 19 t y^{-1} , compared to an estimated annual flux to the atmosphere of 44-46 t. Volatilisation from soil (88.1 %) was identified as the main source of PCBs to the atmosphere (Harrad *et al.*, 1994).

Eljarrat and Barceló (2003) summarised the available data on contributions to total toxicity and concluded that the most important contributory pollutants in sediment and sludge samples are PAHs>PCNs>PCDD/Fs>PCBs>PBDEs.

PCDD/Fs are formed during thermal processes where chlorine is present. The quantity of chlorine required for PCDD/F formation can be small, hence, there is the potential for many processes to emit these compounds. They can also be released to the environment from some chemical processes. Waste incineration and coal combustion are the principal sources (Table 5; Figure 1). Incineration and other high temperature processes were identified as major sources of PCDD/Fs to the environment by Jones and Bennett (1989), but stricter controls are now in place to limit emissions from mass burn incineration, incineration of hazardous waste and cocombustion of solid waste (EPCEU, 2000a).

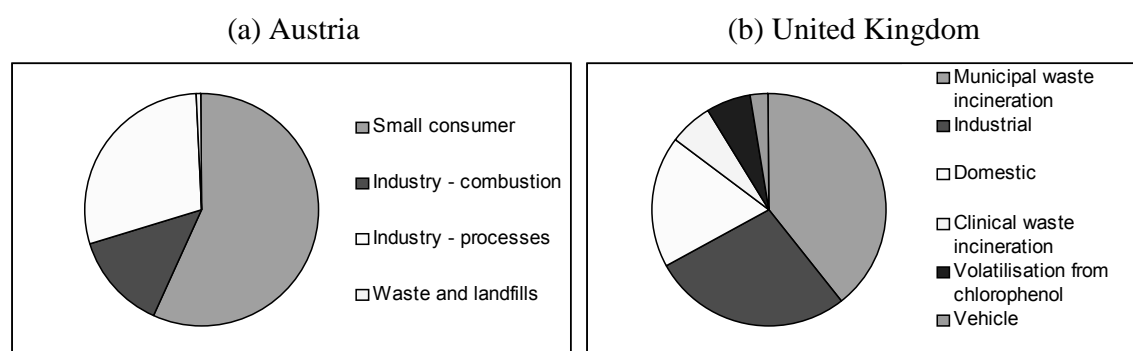


Figure 1 Sources of dioxin emissions (% of total emitted) in (a) Austria in 1998 and (b) UK in 1991 (IC Consultants, 2001)

Dioxins and furans constitute a group of lipophilic, persistent, ubiquitous and bioaccumulative compounds of high toxicity, high chemical stability and extremely low water solubility that are subject to long range transport. Only 17 of the 75 dioxin congeners and 135 furan congeners, those that are chlorine substituted at all four lateral positions, the 2,3,7,8- substituted congeners, are of particular interest due to their toxicity. For practical reasons, the analysis of PCDD/F is generally restricted to the eight tetra- to heptachlorinated homologue sums and the 17 2,3,7,8-substituted congeners. The 25 separate concentrations produced in such an analysis are often condensed to a single number, the toxicity equivalent (TE), which is calculated by totalling the products of the concentration of the analyte and the toxicity of the analyte relative to 2,3,7,8-TCDD, the most toxic PCDD/F congener. These relative toxicities are referred to as toxicity equivalency factors (TEFs) (McLachlan *et al.*, 1996).

Emissions of importance are those of the 7 PCDDs and 10 PCDFs as defined by the NATO/CCMS (1988) international toxic equivalent (I-TEQ) scheme. In 1998, a WHO scheme was also launched, but differs in the value given for three of the 17 compounds specified within the scheme. Many compounds have dioxin-like characteristics, though are not necessarily yet included in any conventions to limit their use (Table 6).

Table 6 Some compounds which have dioxin-like properties (Eljarrat and Barceló, 2004)

Dioxin like compounds	Abbreviation
Polychlorinated biphenyls	PCBs
PXDDs/PXDF	X = chlorine, bromine or fluorine
Alkyl-substituted dioxins & furans	R-PCDD/PCDF
Polychlorinated naphthalenes	PCNs
Polychlorinated dibenzothiophenes	PCBT
Polychlorinated thianthrens	PCTA
Terphenyl & polychlorinated terphenol	PCT
Hexachlorobenzene	HCB
Polybrominated diphenyl ether	PBDE
Polychlorinated azobenzoles	PCA
Polychlorinated dibenzothiophens	PCDT

Most industries are negligible sources of PCDD/Fs to municipal wastewater treatment works (WwTW), either because they have no PCDD/Fs in their processes, because the PCDD/Fs in their processes do not enter their wastewater effluent streams, or because the PCDD/Fs in their wastewater effluent are removed in on-site treatment facilities. Nevertheless, industrial sources of PCDD/F to wastewater can be important. A survey of sources of PCDD/F in German sewage sludges was carried out by Klöpffer *et al.* (1990 cited McLachlan *et al.*, 1996). Their estimates of the annual fluxes of PCDD/F from different industries to WwTW are summarised in Table 7. These individual fluxes were compared with the total annual flux of PCDD/F in West German sewage sludge that they estimated to be 50 kg. The textile industry was identified as the most important industrial source of PCDD/Fs to WwTWs. Based on elevated sewage sludge concentrations in s impacted by the textile industry, the annual discharges in former West Germany were estimated to be 3.4-6.5 kg PCDD/F per year, accounting for about 10% of the estimated annual PCDD/F load in West German sewage sludge. It was suggested that pentachlorophenol (PCP), which contains trace quantities of PCDD/Fs was a major source of contamination within the textile industry, and the possibility of imported cotton containing PCDD/F from chlorinated defoliants used in cotton production was mentioned. A number of chemical additives used in textile finishing were also considered, but no evidence was found indicating that they were making a significant contribution to the textile industry emissions. Surface run-off represented the largest input from diffuse sources, due to deposition onto paved surfaces from combustion processes.

Polychlorinated biphenyls (PCBs) were widely used industrial chemicals, the primary uses of which were dielectric fluids in electrical transformers and capacitors, hydraulic fluids, cutting and lubricating oils, and additives in a wide range of materials including paints, sealants and adhesives. Their use has been banned since the late 1970s. There are 209 congeners, all of which have low solubility and vapour pressure and are highly soluble in non-polar solvents, oils and fats (Eljarrat and Barceló, 2004). They have high thermodynamic stability and environmental degradation is extremely slow. The most significant are 12 congeners with similar toxicological properties to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2378-TCDD), the most toxic of the dioxins.

Table 7 Estimated annual fluxes of PCDD/F from selected different industries and surface runoff to MWTPs in Germany (Klöpffer *et al.* 1990 cited McLachlan *et al.*, 1996)

Source	Annual PCDD/F flux to WwTWs (g) (maximum estimates)
Textile industry	6500
PCP	1800
Formation within MWTP	800
Flocculating agents in MWTP	500
Pulp and paper industry	140
Metal working industry	4
Cleaning of tank cars	0.14
Surface runoff	16000

Polychlorinated naphthalenes (PCNs) have been used in a variety of industries. The most important uses are cable insulation, wood preservation, engine oil additives, electroplating masking compounds, feedstock for dye production, dye carriers, capacitors and refractive testing oils. Their chemical structure is similar to that of PCBs. PCNs are widely considered to be associated with cancer and chronic liver disease. The total UK production has been estimated at 6,650 t (NAEI, 2003), but they have not been produced in the UK for over 30 years. Consequently, current potential sources are expected to be dominated by the disposal routes of capacitors and engine oil, where it is thought the majority of the PCNs produced were used. Another potential source of PCNs may be the incineration industry, PCNs have been found in fly ash and flue gas in waste incinerators. Landfills are also expected to be a source of PCN emissions (NAEI, 2003).

PCNs have been found in emissions from incinerators and are thought to be produced from the combustion of PAHs. Therefore, PCNs could potentially be produced from other high temperature combustion processes. As the information regarding the emission of PCNs in the UK is relatively sparse, no emission estimate is currently available.

Polycyclic aromatic hydrocarbons (PAHs) are a large group of chemical compounds with a similar structure comprising two or more joined aromatic carbon (benzene) rings. Different PAHs vary both in their chemical characteristics and in their environmental sources. They are derived from both endogenous and anthropogenic sources and are found in the environment, both as gases and associated with particulate material. Many PAHs have strong carcinogenic properties, the most potent being benzo[a]anthracene, benzo[a]pyrene and dibenz[ah]anthracene (NAEI, 2003). The semi-volatile property of PAHs makes them highly mobile throughout the environment *via* deposition and re-volatilisation between air, soil and water bodies. Road transport combustion is currently the largest source of PAH emissions contributing 52% of the emissions in 2002. Domestic combustion and other forms of industrial combustion were the next largest sources of emissions in 2002 (NAEI 2003) (Table 5).

1.3 Bulk industrial and domestic chemicals

A large array of organic chemical compounds are manufactured for industrial and domestic purposes. It would not be possible here to consider all the manufactured bulk chemicals and compounds have been selected on the basis of their recognised significance in urban wastewater and water systems and atmospheric emissions as potential routes of entry of contaminants into soil. For example, a recent comprehensive investigation of diffuse and industrial inputs of priority substances to wastewater treatment works (WwTW) in the UK (Bowen *et al.*, 2003) provides an illustration of potentially important OC that may enter soil eg through the irrigation route via surface water influenced by treated effluent discharges from WwTW and from land spreading sewage sludge. This also follows recommendations that Pollutant Release and Transfer Registers (PRTRs) (which are a catalogue or register of potentially harmful pollutant releases or transfers to the environment from a variety of sources) for land should be equivalent to that for water, or a derivative of the water list (EA, 2005). Currently there 104 substances included in the proposed changes to the UK PRTR water for 2005 to 2007 (EA, 2005), which, with the exception of 10 inorganic elements, are OCs. The list includes industrial bulk chemicals as well as POPs and pesticide compounds. The UK Chemicals Stakeholder Forum (CSF) (Defra, 2005a) has developed a set of criteria, based on persistence, bioaccumulation and toxicity properties (see Box 1), and applied this to high volume production chemicals ($>1000 \text{ t y}^{-1}$) used in the UK. Approximately 70 compounds or compound groups meet the criteria (Defra, 2005a). The full list of compounds of concern identified by the CSF are presented in Annex E.

Box 1

UK Chemicals Stakeholder Forum criteria for concern:

Persistence (P), bioaccumulation (B) and toxicity (T) criteria for identifying substances of concern:

- $P = t_{1/2} \text{ water} > 2 \text{ months}$ or $t_{1/2} \text{ soil/sediment} > 6 \text{ months}$;
- $B = \log K_{ow} > 4$ or Bioconcentration Factor (BCF) > 500 where data are available. If experimental BCF is < 500 , Log K_{ow} does not apply;
- $T = \text{Acute L(E)C}_{50} < 1 \text{ mg/l}$ or long term NOEC $< 0.1 \text{ mg/l}$ OR category 1 or 2 carcinogen, mutagen or reprotoxin and category 3 mutagens;

OR evidence of endocrine disrupting effects.

Criteria for substances of highest concern:

- $P = t_{1/2} \text{ marine water} > 60 \text{ days}$, fresh water $> 40 \text{ days}$ or $t_{1/2} \text{ marine /sediment} > 180 \text{ days}$, freshwater sediment $> 120 \text{ days}$;
- $B = \log K_{ow} > 4.5$ or Bioconcentration Factor (BCF) > 2000 where data are available. If experimental BCF < 2000 , Log K_{ow} does not apply;
- $T = \text{Acute lethal (effect) concentration L(E)C}_{50} < 0.1 \text{ mg/l}$ or long term no observable effect concentration, NOEC $< 0.01 \text{ mg/l}$ OR category 1 or 2 carcinogen, mutagen or reprotoxin, and category 3 mutagens and reprotoxins;

OR evidence of endocrine disrupting effects.

Some of the largest volumes of bulk chemicals produced include surfactant compounds used in the production of detergents, plasticizing agents and solvents.

The estimated consumption of surfactant compounds in Europe is presented in Table 8. The total consumption of surfactant chemicals for industrial and domestic purposes was 1.7 M t in 2000, 85 % of which was used in domestic products. Much attention has focussed on the potentially environmental impacts of linear alkyl benzene sulphonate (LAS) as this agent was included as a regulated substance in Danish controls for agricultural recycling of sludge and was proposed for inclusion in a revision of Directive 86/278/EEC for agricultural use of sludge (CEC, 1986; EC, 2000). However, LAS is not generally regarded as toxic; it is not identified as a Priority Hazardous Substance within the Water Framework Directive (WFD) and it is not included in the UK PRTR or recognised as a chemical of concern by the UK CSF. Whilst, LAS is a major surfactant, the compound only represents one of a range of chemicals used in large volumes in the manufacture of detergents. An extensive literature is available on the ecotoxicological behaviour of LAS and a risk assessment on the compound, revising an earlier risk assessment based on incomplete data (Jensen *et al.*, 2001a), will be published shortly by the Expert Group on Risk Assessment of Sewage Sludge within the Environment and Health Task Force of the International Life Sciences Institute (ILSI) - Europe. This follows up the publication of a conceptual framework for risk assessment for organic chemicals in sewage sludge for agricultural use (Schowanek *et al.*, 2004) and shows that the compound is not hazardous to soil or plant processes when applied to soil at contemporary concentrations present sludge. The species-sensitivity distribution, which gave a $PNEC_{\text{Soil}}$ (Predicted No Effect Concentration is the chronic HC_5 hazardous concentration protecting 95% of soil species) of 5.2 mg LAS kg^{-1} dry soil (ds), and provided the basis to the Danish sludge limit for LAS (2600 mg LAS kg^{-1} dry solids (DS) from 1997, which was reduced to 1300 mg LAS kg^{-1} DS in 2000), is being revised. The new $PNEC_{\text{Soil}}$ is approximately 30 mg LAS kg^{-1} ds (pers. com. PH Krogh, NERI, Denmark), which equates to a sludge limit concentration of approximately 11,000 mg LAS kg^{-1} DS; the maximum value reported recently in UK sludge is 10,500 mg kg^{-1} (Bowen *et al.*, 2003). Consequently, the presence of apparently relatively large concentrations of LAS in sludge does not represent a significant risk to the fertility or ecological performance of agricultural soil when sludge is recycled as a fertiliser and soil conditioner to farmland.

Other comprehensive risk assessments have also been completed or updated (HERA, 2004; OECD, 2005) which conclude that the ecotoxicological parameters of LAS have been adequately and sufficiently characterised and that the ecological risk of LAS is judged to be low. The HERA Project (<http://www.heraproject.com/>) is a voluntary industry programme to carry out Human and Environmental Risk Assessments on ingredients of household cleaning products and was a partnership established in 1999 between the makers of household cleaning products (A.I.S.E) and the chemical industry (Cefic), who supply the raw materials for these products. However, in contrast to LAS, there is little published information available evaluating the behaviour of other surfactants in soil and policies or controls limiting the use of LAS will lead to its substitution with compounds that are potentially less well characterised or understood in terms of their potential impacts on soil. Currently HERA has completed a programme of risk assessments for compounds in household cleaning products, concluding they do not generally represent a risk to human health or the environment. The following organic chemicals have been evaluated:

- Alcohol ethoxysulphates
- Alkali silicates
- Alkyl sulphate

- Amine oxides
- Amylase/lipase/cellulase
- Boric acid
- Citric acids / salts
- Cocamidopropyl betaine
- Diethyleneglycol n-butylether
- Ester quats
- Fatty Acid Salts
- Fluorescent brightener FWA-1
- Fluorescent brightener FWA-5
- Hydroxycitronellal
- Isoeugenol
- Isopropyl alcohol
- Linear alkylbenzene sulphonate
- Perboric acid, sodium salt, mono and tetrahydrate
- Phosphonates
- Polycyclic musk AHTN
- Polycyclic musk HHCB
- Propylene glycol n-butylether
- Protease
- Secondary alkane sulfonate (SAS)
- Sodium tripolyphosphate (STPP)
- TAED
- Xylene / cumene / toluene sulphonate

Table 8 Estimated consumption of surfactants in detergents (CETOX 2000)

Surfactant	Europe annual consumption in 2000 (t)	
	Household products	Industrial products
Anionic Surfactants, subtotal	780,000	128,000
Linear alkyl benzene sulphonate (LAS)	330,000	80,000
Alkyl ethoxylate sulphates (AES)	123,000	-
Alkyl sulphonate (AS)	117,000	-
Secondary alkane sulphonate (SAS)	55,000	-
Soap	134,000	22,000
Other	21,000	26,000
Non-ionic Surfactants, subtotal	530,000	96,000
Alcohol ethoxylates + Acrylic acid (AE + AA)	455,000	-
Alkyl-C12/14(glucopiranoside)1.2 (APG)	28,000	-
Fatty acid glucamide (FAGA)	28,000	-
Other	19,000	-
Cationic surfactants, subtotal	98,000	17,000
Amphoteric surfactants, subtotal	40,000	7000
Total	1,448,000	248,000

Nonyl phenol ethoxylates (NPEs) were used extensively as surfactants, but are Water Framework Directive (WFD) Priority Hazardous Substances (EPCEU, 2000b –

see Annex F for the full list of priority substances) and a draft limit was proposed in the EC Working Document on Sludge 3rd Draft (WDS) (EC, 2000) due to concerns regarding the endocrine disrupting properties exhibited by nonylphenols (NPs) (the breakdown products of NPEs). It is included in the proposed UK PRTR list for water and NP is on the UK CSF list of chemicals of concern. The use of NPEs in surfactants is therefore decreasing, with voluntary removal from the market already occurring in many cases, including the UK where a Voluntary Agreement on risk reduction for NP and NPEs has been established (Defra, 2004a). Nonetheless, in a screening study of chemicals in influents, effluents and sewage sludge at UK wastewater treatment works (WwTW), Bowen *et al.* (2003) detected NPEs at all works at concentrations ranging from 1.0 to 350 $\mu\text{g l}^{-1}$ with an average value of 79.5 $\mu\text{g l}^{-1}$. There was no correlation between levels and runoff or industrial inputs. In a literature study, Bowen *et al.* (2003) observed that average values were reported in influent over a very wide range from 0.01 $\mu\text{g l}^{-1}$ to levels in excess of 1 g l^{-1} . In sludge, reported NPE concentrations (including NPE and nonylphenol) ranged from 10 to over 1000 mg kg^{-1} , indicating that many UK and European sludges would exceed a limit of 10 mg kg^{-1} discussed by the EC in proposals for the future revision of the Sludge Directive (EC, 2000), which mirrored the limit adopted in Danish controls on agricultural use of sludge. Octyl phenols, which are a related group of chemicals used as surfactants, are a group of WFD Priority Substances under review, but were not detected in the screening study of UK WwTW (Bowen *et al.*, 2003). Octyl phenols are included on both proposed UK PRTR for water (including octyl phenol ethoxylates) and the UK CSF lists. The UK Voluntary Agreement on risk reduction for NP and NPEs also includes this group of compounds (Defra, 2004a). Bowen *et al.* (2003) concluded that, given the wide range of reported concentrations in urban wastewaters, and likely future restrictions on NPE discharges, further assessment of the sources of NPEs in wastewaters was required.

Plasticisers and additives are added to plastic polymers to give plastics useful properties such as colour, resistance to fire, strength and flexibility. Over 90% of plasticizers used are phthalate based compounds and in Western Europe about one million t of phthalates are produced each year, of which approximately 90% are used to plasticize PVC (polyvinyl chloride) (CSTEE, 1999). The annual global production of DEHP has been estimated to be approximately 2 million t (Koch *et al.*, 2003ab). Concentrations of phthalates in PVC range from 15-50%. There are five phthalate plasticizers: di(2-ethylhexyl) phthalate (DEHP, sometimes also referred to as DOP), diisodecyl phthalate (DIDP) and diisononyl phthalate (DINP), butyl benzyl phthalate (BBP) and di-n-butyl phthalate (DBP). Of these five phthalates, DEHP is the most commonly used and accounts for 51% of the market (HSDB, 2000). Phthalates are not chemically combined with PVC and are slowly released to the environment during use or after disposal, to landfill for example. DEHP is a WFD Proposed Priority Substance and a draft limit was proposed for sludge (EC, 2000); DEHP is regulated under Danish legislation for agricultural use of sludge. DEHP is on the proposed UK PRTR for water, but does not appear on the UK CSF list. It is one of the most frequently detected and highly concentrated priority pollutants in industrial and municipal sludges. Concentrations in US sludge are reported to range from 0.3 to 1020 mg kg^{-1} DS with a weighted average value of 110 mg kg^{-1} DS (US EPA, 1992c). Given the ubiquitous use of phthalates and their potential to transfer to the environment, and they have been regulated in sludge and are under review with regard to the WFD, it is surprising that their significance in the environment has not been more fully considered, compared to surfactant compounds for example. An assessment of the impacts of DEHP and other phthalates used as plasticizers on soil quality and human health is therefore presented in Section 3.4.

Solvents are extensively used chemicals within industry and can be discharged in effluents from industrial processes. Concentrations of solvents in crude sewage collected during the screening study reported by Bowen *et al.* (2003) varied widely between sites and substances. Benzene and dichloroethane were almost entirely below the limit of detection (LOD) at most works, and carbon tetrachloride was not detected at any works. Trichloroethene and tetrachloroethene were detected at 14 and 21 works (out of a total of 30 works sampled), respectively, and dichloromethane and trichloromethane (chloroform) were detectable in most influent samples up to approximately $5 \mu\text{g l}^{-1}$. All these compounds, except for dichloroethane are listed on the proposed UK PRTR for water (EA, 2005); benzene, dichloromethane and trichloromethane are WFD Priority Substances (Annex F). There was little or no evidence of a correlation between runoff in the sewage and solvent concentrations, nor any trend between concentration and percentage industrial effluent for the solvents. This was consistent with earlier work by Wilson *et al.* (1994), which also found no apparent relationship between concentrations of 15 important volatile organic compounds (VOC) (e.g. chloroform, benzene, toluene) in 12 liquid digested sewage sludges and the volume of industrial input to the WwTW, influent treatment, population served and sludge dry solids content. The WwTW in that study served representative rural, urban and industrial catchments in north-west England. Bowen *et al.* (2003) considered the widespread use of these compounds as degreasing agents and solvents (e.g. engine cleaning, glass degreasing, paints, varnishes) as the likely cause for their presence in crude sewage. The screening study indicated that some Priority Substances are present at measurable concentrations. Given the volatile nature of these compounds a significant reduction in concentrations would be anticipated as a result of standard WwTW processes. Because significant losses of these compounds occur by volatilisation (and biodegradation), Wilson *et al.* (1994) concluded that normal rates of sludge application to agricultural land would not increase the VOC content of the soil to levels which may cause concern for human health and the environment. Webber and Goodin (1992) confirmed from a laboratory incubation study of the persistence of VOCs in sludge-treated soils that sludge VOCs do not present a hazard to agriculture. Indeed, any elevation in soil concentrations in solvents or other VOCs, arising, for example, from spreading sewage sludge on agricultural land, is likely only to be transient due to rapid volatilization losses and degradation (Jin and O'Connor, 1990).

Other substances used as intermediates, for instance as part of a production/synthesis process, include hexachlorobutadiene (HCBd) (proposed UK PRTR list for water) and C10-13 chloroalkanes (on both the UK PRTR and UK CSF lists (see Annex E). Bowen *et al.* (2003) did not detect either group of compound in influents to WwTW and concluded that, because they were largely used as intermediates in industrial processes, they were unlikely to be present in significant quantities in diffuse inputs to sewerage systems. According to Lecloux (2004) the commercial production of HCBd has been virtually eliminated in Europe. Consequently, these compounds would be unlikely to represent a risk to soils.

Flame retardants are employed within textiles, plastics, packaging material, polymer foam for use in furniture and upholstery, electronic equipment, aircraft and motor vehicles. There are about 30 different aromatic, aliphatic and inorganic flame retardants, most of which contain halogens (Litz, 2002). Greatest concern relates to polybrominated diphenyls, which have similar properties to PCBs, and whose use is fairly restricted, polybrominated diphenyl ethers (PBDEs) and tetrabromobiphenol A (TBBP-A) which are similar to dioxins in their characteristics. Thus, they are persistent in the environment and have the potential to bioaccumulate. Brominated flame retardants may make up as much as 10-30% of the plastics used, for example, in printed circuit boards, computer housings and other electronic equipment (Eljarrat

and Barceló, 2004). At the moment, PentaBDE is not listed in the UNECE POP protocol or in the UNEP POP convention. Brominated flame retardants have been included in the list of priority pollutants of the Commission for the Protection of the Marine Environment of the North-East Atlantic (OSPAR).

The commercial PBDEs most widely used are nominally deca-, octa- and penta-brominated forms. The penta-BDE formulation consists of about 41% tetra-BDE, mainly BDE-47 and 45% penta-BDE, predominately BDE-99 and BDE-100. The deca-BDE formulation is 98% BDE-209 (Eljarrat and Barceló, 2004). The yearly market demand for pentaBDE in the year 2000 was estimated to be around 200 t in Europe and 8,300 t in the US. It is now produced in USA, Japan and Israel, but consumption has apparently decreased since 1998. Annual release to the environment during production processes are estimated to be around 180 kg y⁻¹ to waste water and 150 kg y⁻¹ to air. Most of the inputs to the environment come from volatilisation during the service life of the foam, from weathering and wearing of the products in which the foam is present and during disposal and recycling operations.

PDBEs are regarded as persistent due to their low volatility and water solubility and high octanol/water partition coefficient. Log *K*_{OW} for penta- and decabrominated congeners are 7.42 and 11.15, respectively (Litz, 2002). PBDE enters the environment via water, sewage sludge, accidents and in gaseous form.

Five of the most important brominated compounds have been prioritised for detailed environment and human health risk assessment at European level (under the Existing Substances Regulation). Two of these compounds PentaBDE and OctaBDE were banned (at any concentration >0.1 % by mass) from the European market from August 2004 (EPCEU, 2003) (http://europa.eu.int/eur-lex/pri/en/oj/dat/2003/l_042/l_04220030215en00450046.pdf). Risk assessments for the others are still underway and so decisions on whether risk reduction measures are needed have not yet been made. Information on the risk reduction strategies for PentaBDE and OctaBDE is available from Defra at <http://www.defra.gov.uk/environment/chemicals/>. PentaBDE is a Water Framework Directive (WFD) priority hazardous substance (Annex F) and is listed by the UK Chemical Stakeholder Forum (CSF) as a chemical of concern (Annex E) (Defra, 2005a). Brominated diphenyl ethers are on the proposed UK PRTR for water (EA, 2005).

The consequences of brominated flame retardants for health and the environment has received increasing attention in the scientific literature. A series of reviews were recently published in a special volume of Environment International (Volume 29, Issue 6, Pages 663-885) on The State-of-Science and Trends of BFRs in the Environment (Letcher, 2003). The published literature on BFRs in the environment is also reviewed by de Wit (2002).

Chlorobenzenes (CBs) were used mainly as intermediates in the synthesis of pesticides and other chemicals; 1,4-DCB is used in deodorants and as a moth repellent. The higher chlorinated benzenes (TCBs and 1,2,3,4-TeCB) have been used as components of dielectric fluids. Chlorobenzenes have been identified as one of the potentially important groups of POPs in sewage sludge and sludge-treated soil (Wang and Jones, 1994a; Beck *et al.*, 1995). Atmospheric deposition is also recognised as a mechanism of entry to soil and this was a potentially important route at the time of peak CB production (Beck *et al.*, 1995). However, CBs were virtually absent from WwTW influents in the screening study by Bowen *et al.* (2003) due to their withdrawal from use. Any occurrence was likely to be associated with industrial rather than diffuse sources. All TCB isomers, PCB and HCB are included on the UK

proposed PTRT list for water (EA, 2005) and therefore would also potentially be included on a future list for soil.

Pentachlorophenol (PCP) was principally used for timber preservation and as a textile preservative, but production in the EC was banned in 1992 and its use as a chemical intermediate in the chemical industry was banned in 2000. This compound entered urban wastewater collection systems from industrial releases, and also from diffuse inputs in surface-water run-off. Its high persistence and toxicity was a concern for land spreading sewage sludge (as with most OCs, partitioning to the sludge organic matter is a main removal mechanism) (Bellin *et al.*, 1990). However, Bowen *et al.* (2003) reported that PCP was not detected in any of the influent samples in the screening study of UK WwTW and concluded that, whilst small scale import apparently continues (mainly for the preservation of industrial textiles), the widespread occurrence of PCP in WwTW effluent (and sludge) is considered extremely unlikely. Thus, the potential risk to soil quality from inputs of this compound have been significantly curbed and no longer represent a concern. PCP is a proposed UK PRTR list compound (EA, 2005).

A final compound to be considered here is methyl tertiary butyl ether (MTBE), which is used widely as an oxygenate of unleaded petrol to prevent engine 'knock'. It can be blended with petrol in any proportion up to 15 % to achieve the required octane level of the fuel. Commercial production of MTBE started in Europe in 1973 and in the US in 1979. Total worldwide production capacity in 1998 was 23.5 million t and the actual production was 18 million t (EFOA, 2005). The estimated annual production of MTBE in the EU today is 3 million t and current demand in Europe is estimated at 2.6 million t. Although EU legislation permits the use of MTBE at up to 5 % by volume in petrol, on average levels of MTBE used in EU (~1.6 %) and UK petrol (<1 %) are substantially less. The compound is not included in current lists of potential pollutants, but was raised as a compound of interest during management meetings of this project and therefore transport emissions of MTBE to soil from combustion of unleaded petrol were considered. MTBE is highly soluble in water and mobile in soil; it is generally reported as recalcitrant and there are no widely accepted estimates of the half-life (Squillace, 1998). It is regarded as a widespread point and non-point source contaminant in groundwater in the US and contamination incidents have led to California phasing out MTBE in petrol by 2003 and the US Congress is considering introducing legislation to substantially reduce or eliminate the use of MTBE in petrol because of the risk to groundwater (UKPIA, 2005). In Europe, MTBE was included in a priority list identifying substances requiring attention and a risk evaluation was completed (CEC, 2001a). This concluded that MTBE was not carcinogenic, mutagenic or a reproductive toxin and therefore did not represent a risk to human health or require further risk reduction measures to protect the terrestrial environment. Measures were considered necessary to prevent spillages and leakage of underground storage tanks to protect groundwater with respect of taste and odour in accordance with a key objective of Community legislation to prevent all anthropogenic inputs, including MTBE, to groundwater (CEC, 2001a).

1.4 Pesticides

Routes of entry of agricultural pesticides into soil are:

- direct application;
- *via* throughfall while being applied to crops;
- *via* the irrigation or flooding of agricultural land with surface or groundwater containing pesticides, and

- via rainfall containing pesticides.

Drift from the site of application can occur to a greater or lesser extent with both spray and granular products, depending on the equipment used. This will both reduce the concentration reaching the soil at the point of application and increase the area of soil which may be potentially impacted by plant protection products (CSL, 2004a). The physico-chemical and uses of some of the main pesticides in the UK are listed in Table 9.

Table 9 Physicochemical characteristics of some pesticides widely used in the UK (Brown *et al.*, 2002)

Common name	Soil sorption (K_{oc} ml g ⁻¹)	Soil half-life (days)	Vapour pressure (Pa)	Main uses in UK
Aldicarb	30	30	1.3×10^{-2}	root vegetables
Atrazine	100	41	3.9×10^{-5}	maize, nursery, non-agricultural
Bentazone	42	12	1.7×10^{-4}	legumes
Bromoxynil	190	10	6.3×10^{-6}	cereals, maize
Chlorothalonil	1380	30	7.6×10^{-5}	cereals, vegetables, fruit
Dimethoate	20	7	2.5×10^{-4}	cereals, potatoes, sugar beet, vegetables, fruit, nursery, grassland
Ethofumesate	203	30	3.9×10^{-4}	sugar & fodder beet
Flutriafol	231	500	7.1×10^{-9}	cereals
Isoproturon	120	30	3.2×10^{-6}	cereals
Lindane	1100	400	5.6×10^{-3}	cereals, grassland, vegetables, fruit, storage & non-agricultural
Linuron	400	60	5.1×10^{-5}	cereals
MCPA	20	25	2.3×10^{-5}	cereals, grassland
Mecoprop	20	21	3.1×10^{-4}	cereals, grassland
Simazine	130	49	1.6×10^{-6}	maize, nursery, non-agricultural
Triallate	2400	82	1.6×10^{-2}	cereals, vegetables
Trifluralin	8000	60	6.1×10^{-3}	cereals, oilseed rape, sugar beet, vegetables

The general pattern of pesticide use in the last ten years has been for the area treated to be increased, but the quantity of active ingredient used at each application to decrease. This is mainly due to the introduction of products which are active at much lower rates of application and to growers using fungicides and herbicides at reduced rates per hectare (CSL, 2003ab). For example, between 1992 and 2002, the average quantity of fungicide active ingredient applied to wheat has fallen from 0.35 kg ai ha⁻¹ to 0.13 kg ai ha⁻¹ and the overall use of fungicides has decreased by 34%, even though the area sprayed has increased by 20% (CSL 2003ab).

The use of organochlorine and organophosphate insecticides across all arable crops has decreased by 83% and 75%, respectively, since 1992. Over the same period the use of pyrethroid insecticides, which are applied at lower rates, has increased by

44% (CSL 2003ab). The quantity of herbicides used has remained fairly static over the same ten year period, but the area to which they are applied has increased by 38%, due to increased use of sulfonylurea products which are applied at lower rates. The amount of growth regulators used has increased by 21%, nematicides by 27% and molluscicide use has increased by almost four times.

The area of arable crops, excluding set-aside, has decreased by 9% since 1992. Thus, the area of land potentially impacted by pesticide inputs should have decreased by a similar amount. This is certainly the case where the subsequent land use does not involve pesticide applications. However, in practice, repeated applications of pesticide to the same land are summed together in pesticide use statistics to give a total area of treated land, so these data require careful interpretation as they suggest the actual area receiving pesticide treatment has increased when this may not actually be the case.

In broad summary, more frequent lower level pesticide application has become the norm for fungicides, insecticides and herbicides, while there has been an increase in the amount of growth regulators, molluscicides, nematicides and seed treatments used. More frequent application of active ingredients at lower rates may actually reduce any impact on soil fauna through enabling resistant populations to develop under lower dose regimes, such that subsequent applications can be more easily metabolised. Seed treatments have the potential to have the greatest effect on soil processes since they are applied to the surface of seeds which are then drilled into the soil. Hence, no breakdown in the chemistry of the seed treatment will have taken place before it comes into contact with soil and the chemical is purposefully in a concentrated form in the immediate vicinity of the seed.

1.5 Human pharmaceuticals

Antibiotics are widely used in human and animal medicine yet, despite their relatively high usage, very little information on the environmental release of these substances is available (Halling-Sørensen *et al.*, 1998). They are used in both human and veterinary medicine to treat or prevent microbial infections.

The impact of medicines on the environment will depend on:

- The quantity used;
- The degree of metabolism in the human/animal;
- Any degradation during storage of manure prior to land spreading;
- Toxicity of the substance to terrestrial organisms.

Figure 2 shows the main routes by which drugs can enter soil.

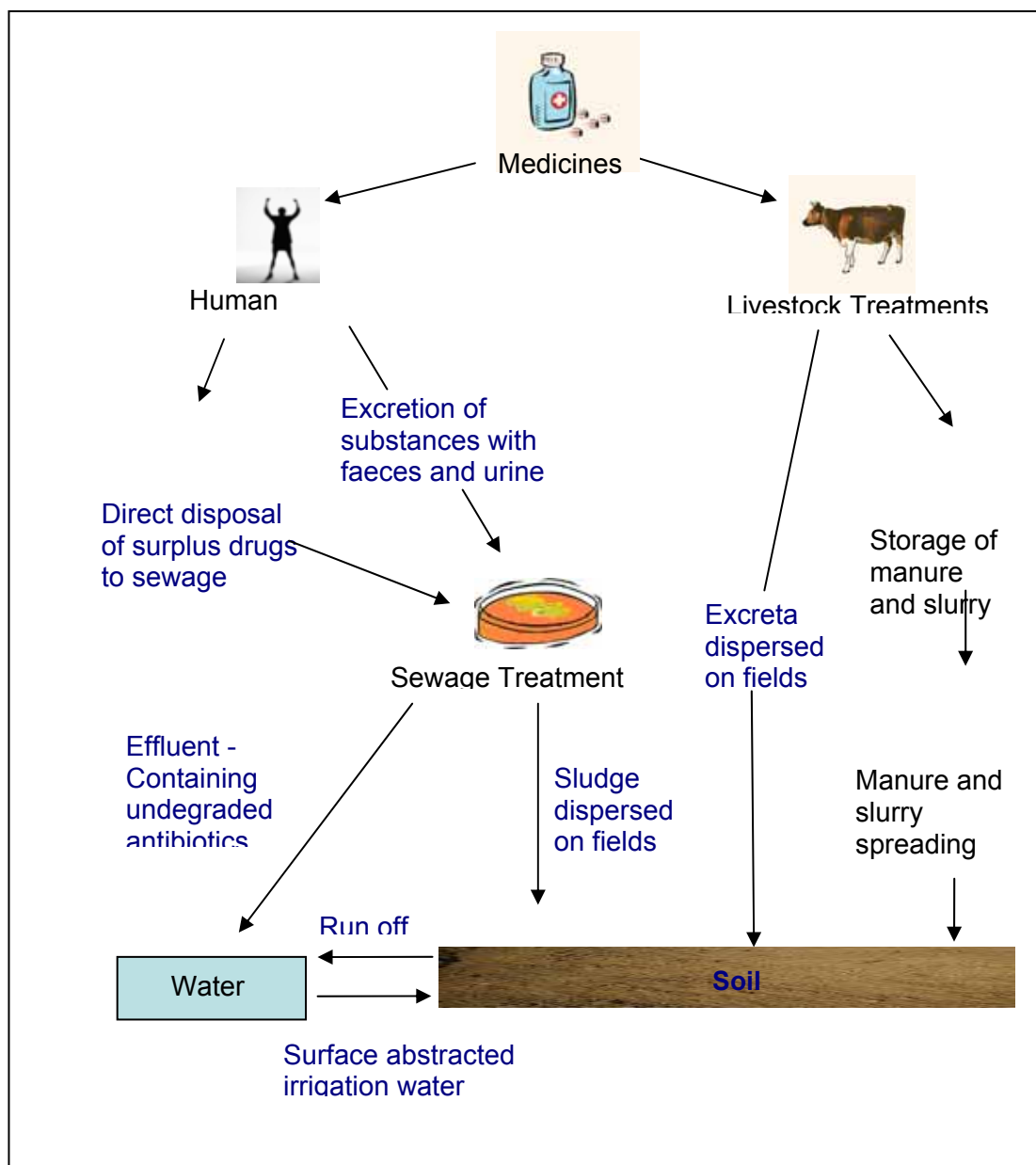


Figure 2 Main exposure routes of veterinary and human medicinal substances in the environment (adapted from Halling-Sørensen *et al.*, 1998)

The extent to which a pharmaceutical compound, whether human or veterinary, may be detected in the environment will depend on several factors, including:

- The extent to which it is absorbed and transformed within the body;
- Its degradability;
- The prevalence of its use; and
- The total mass used.

These characteristics can be employed to gauge the potential for a particular compound to be present in the environment, where specific concentration data are not available.

After entering the human body, medical substances are excreted through the urine and faeces. Prior to excretion, however, some of the compound may be metabolised

in the body. The excreta may therefore contain a mixture of unchanged compound and metabolites. These metabolites may also be harmful to the environment. For most antibiotics, for instance, 30 to 90% of an administered dose is excreted with the urine as an active substance (Halling-Sørensen *et al.*, 1998).

Once chemicals enter the sewer system and into the WwTW they can undergo a number of possible fates:

1. Microorganisms in the WwTW degrade the drug and its metabolites converting it into carbon dioxide and water. This is what happens in the case of aspirin.
2. The drug or metabolites do not degrade in the WwTW. They persist, and will be present in the sludge. The sludge may then be applied to agricultural land. Depending on the ability of the drug to bind to sludge, the drug may adsorb onto soil or leach into groundwater or a surface water source.
3. The drug or metabolites in the WwTW do not degrade. They are also polar and do not adsorb to the sludge matrix. As a result, the chemicals enter the aquatic water course with the treated wastewater effluent. If this water is then used for irrigation, pharmaceutical compounds will once again enter the soil.

Many pharmaceuticals are employed for both human and animal health and hence it is not necessarily possible to differentiate between the sources of some pharmaceuticals entering the soil environment. In Europe, two thirds of all antibiotics are used in human medicine and one third for veterinary purposes. Antibiotics are the third biggest group of pharmaceuticals used in human medicine at 6% of all prescriptions (Diaz-Cruz and Barceló, 2004). In veterinary medicine, antibiotics comprise 70% of all drugs used.

Over 3000 active substances are licensed in the UK for use as human pharmaceuticals (Ayscough *et al.*, 2000). In 2004, a total of 1548 different pharmaceutical chemicals were prescribed in the UK, excluding those for which less than 50 prescriptions were issued (PCA, 2005). Of that number, 143 were prescribed one million times or more. Data on the quantity of drugs used in the UK is relatively difficult to obtain. Drugs may be dispensed *via* high street pharmacies, *via* pharmacies associated with hospitals or doctors' practices, or bought over the counter, and the methods for accounting for these various route differ between these sources. No data is collected concerning over the counter sales of pharmaceuticals.

Data on hospital prescribing is collected on a commercial basis by IMS Health *via* the Hospital Pharmacy Audit Index (HPAI). The HPAI is based on issues of medicines recorded on hospital pharmacy systems and refers to all medicines supplied to wards, departments, clinics, theatres, satellite sites, and to patients in out-patient clinics and on discharge.

Tables 10 and 11 list the quantities of most commonly used human drugs in the UK in 1995 and 2000. Very few of those most commonly used drugs in 1995 are on the list for those most frequently used in 2000. This demonstrates the need to obtain up-to-date data for 2005 to accurately review which drugs may be found most widely in the environment.

Table 10 Human pharmaceuticals used in quantities of one tonne or more per annum in the UK (data from 1995) (Webb, 2000)

Pharmaceutical	Purpose	Quantity (t yr ⁻¹)
Paracetamol	analgesic	2000
Aspirin		770
Metformin		106.1
Cimetidine		72
Ranitidine		69
Erythromycin		67.7
Naproxen		60.6
Dextroproxyphene		42.5
Oxytetracycline		33.7
Quinine		29.7
Theophylline		21
Lithium salts		20.53
Metronidazole	antibiotic	15.5
Iopromide		11.9
Propanolol	β blocker	11.8
Verapamil		9.9
Amitiptyline		5.5
Tetracycline		4.7
Omeprazole		3.9
Thioridazine		3.8
Chloroquine		2.9
Gabapentin		2.6
Etidronic acid		2.1
Fluoxetine		2
Phenobartitol		1.7
Tramadol		1.7
Clofibrate	lipid regulator	1.5
Paroxetine		1.3
Orphenadrine		1.1

Table 11 Top 25 most widely used pharmaceuticals by weight in England in 2000 (Jones *et al.*, 2002)

Compound name	Therapeutic_use	Amount used per year (kg)
Paracetamol	Analgesic	390,954
Metformin hydrochloride	Antihyperglycaemic	205,795
Ibuprofen	Analgesic	162,209
Amoxycillin	Antibiotic	71,466
Sodium valproate	Anti-epileptic	47,479
Sulphasalazine	Antirheumatic	46,430
Mesalazine (systemic)	Treatment of ulcerative colitis	40,421
Carbamazepine	Anti-epileptic	40,348
Ferrous sulphate	Iron supplement	37,538
Ranitidine hydrochloride	Anti-ulcer drug	36,319
Cimetidine	H ₂ receptor antagonist	35,654
Naproxen	Anti-inflammatory	35,065
Atenolol	β -blocker	28,976
Oxytetracycline	Antibiotic	27,195
Erythromycin	Antibiotic	26,483
Diclofenac sodium	Anti-inflammatory and Analgesic	26,120
Flucloxacillin sodium	Antibiotic	23,381
Phenoxymethylpenicillin	Antibiotic	22,227
Allopurinol	Anti-gout drug	22,095
Diltiazem hydrochloride	Calcium antagonist	21,791
Gliclazide	Antihyperglycaemic	18,783
Aspirin	Analgesic	18,105
Quinine sulphate	Muscle relaxant	16,731
Mebeverine hydrochloride	Antispasmodic	15,497
Mefenamic acid	Anti-inflammatory	14,522

The data concerning the presence of human pharmaceuticals in the UK environment is limited. Ayscough *et al.* (2000) conducted a review on behalf of the Environment Agency (EA), of the occurrence, fate and behaviour of pharmaceuticals in the environment. This highlighted the lack of up-to-date data for the UK, some being ten years old, but the majority being over twenty years old, prompting the EA to initiate a programme of screening of selected pharmaceuticals in the aquatic environment. This was followed by a targeted programme of monitoring of twelve compounds and their metabolites at five WwTW (Hilton *et al.*, 2003).

Nine of the twelve compounds were detected in final effluent and in receiving waters. Tamoxifen was found only on two occasions and lofepramine and paracetamol were not detected at all. The probable reason for the former drug not being detected was probably due to the analytical techniques were not sufficiently sensitive. Paracetamol has the highest usage of any drug in the UK at 2,000 t y⁻¹ (Webb, 2000) and has been reported to be readily degradable after acclimatisation during sewage treatment. It is excreted mainly as glucuronides and sulphate conjugates with only 5 % excreted as the parent compound (Hilton *et al.*, 2003). Its low excretion rate and

high degradability are the most likely reasons for paracetamol not being detected, despite the high rate of use. Thus, there is the potential for many types of human pharmaceutical compound to enter the soil (Figure 2) in trace concentrations in irrigation and sludge applications, for instance.

1.6 Veterinary medicines

Human antibiotics are used only therapeutically, but veterinary antibiotics are widely used in feed additives on a precautionary basis, to maintain animal health and prevent infection, particularly in intensive production systems that are vulnerable to health problems due to the high population density of animals. As Intensive and housed production systems use more medicines routinely, wastes from these sources tend to contain significant residues of drugs and medicines. They are also used as growth promoters in farm animals. For example, animals receiving antibiotics in their feed gained 4-5% more body weight than untreated animals (Witte, 1998).

The term “antimicrobial agent” describes any substance of natural, synthetic or semisynthetic origin that is used to kill, or inhibit the growth of, microorganisms (bacteria, fungi, protozoa and viruses). They are compounds which, at low concentrations, exert an action against microorganisms and exhibit selective toxicity towards them. Antimicrobials include: antibiotics, disinfectants, preservatives and other substances. Antibiotics are substances with antibacterial effects. Coccidiostats are not related to any product currently used in human therapy and are used exclusively in animals to prevent coccidiosis, particularly in poultry. Major veterinary medicine groups and applications, and a list of major veterinary compounds used in the UK are presented in Tables 12 and 13, respectively.

Obtaining information on the usage of individual medicines is difficult, which makes the design of monitoring and experimental studies problematic (Boxall *et al.*, 2003a). However, limited information on the sale and usage of the different chemical classes is available. For instance, sales of certain medicines are reported to the Veterinary Medicines Directorate (VMD), an Executive Agency of the DEFRA, protecting public health, animal health, the environment and promoting animal welfare by assuring the safety, quality and efficacy of veterinary medicines in the UK (<http://www.vmd.gov.uk/>).

Table 14 shows the sale volumes of some of the main veterinary antibiotic compounds. Data on the number and quantity of products sold by group in the UK are shown in Table 15 and Table 16.

Most antibiotics are water soluble and readily excreted either as the parent compound eg tetracyclines, sulfonamides and β -lactam antibiotics, or as metabolites eg sulfonamides and macrolides. Those which are less water soluble such as tylosin and tiamulin ($\log K_{OW}$ 1.83 and 5.93, respectively) are excreted in the faeces (Table 17) (Halling-Sørensen *et al.*, 2001).

Table 12 Major veterinary groups and applications, with example medicines used in the UK and Netherlands (from Boxall *et al.*, 2003a).

Groups	Purpose	Examples
Antimicrobials	Substances that kill microorganisms or suppress their multiplication or growth.	Amoxicillin, dihydrostreptomycin, enrofloxacin, lincomycin, oxytetracycline, sulfadiazine, tylosin.
Endectocides	Antiparasitic agents used to control internal and external parasites.	Ivermectin, pyrantel, triclabendazole.
Coccidiostats and antiprotozoals	Chemical agents effective against the control of infections of the intestinal tract caused by single-cell parasites; used in all areas of farming, especially poultry.	Amprolium, clopidal, dimetridazole, narasin, nicarbazin
Antifungals	Agents that kill or control fungi.	Chlorhexidine, griseofulvin, miconazole
Aquaculture treatments		Amoxicillin, azamethipos, cypermethrin, emamcetin, florfenicol, hydrogen peroxide, oxolinic acid, oxytetracycline
Hormones	Active regulatory chemicals that signal the coordination of cellular functions	Altrenogest, estradiol benzoate, ethinyl estradiol, methyltestosterone, melatonin, progesterone
Growth promoters	Used to promote the growth of food producing animals	Flavophospholipol, monensin, salinomycin
Anaesthetics	Used to anaesthetize animals	Halothane, isoflurane, lidocaine/lignocaine, procaine
Euthanasia products	Used to kill sick animals	Pentobarbitone sodium
Tranquilizers	Used to sedate animals	phenobarbitone
NSAIDS	Nonsteroidal anti-inflammatory agents that work by inhibiting the production of prostaglandins	Phenyl butazone
Enteric bloat preparations	Used to treat bloat, mainly in cattle	Dimethicones, poloxalene

Table 13 Major veterinary medicines in use in the UK (Boxall *et al.*, 2004)

Group	Chemical class	Major active ingredients
Ectoparasiticides	Organophosphates	Diazinon
	Synthetic pyrethroids	Flumethrin Cypermethrin
	Amidines	Amitraz
Antibiotics	Tetracyclines	Oxytetracycline Chlortetracycline Tetracycline
	Sulphonamides	Sulphadiazine Sulphadimidine Formosulphathiazole
	β -Lactams	Amoxicillin Procaine penicillin Procaine benzylpenicillin
	Aminoglycosides	Dihydrostreptomycin Neomycin Apramycin
	Macrolides	Tylosin
	Fluoroquinolones	Enrofloxacin
	2,4-Diaminopyrimidines	Trimethoprim
	Pleuromutilins	Tiamulin
	Lincosamides	Lincomycin Clyndamycin
Endectocides	Macrolide endectins	Ivermectin Doramectin Eprinomectin
	Pyrimidines	Pyrantel Morantel
	Benzamidazoles	Triclabendazole Fenbendazole
	Others	Levamisole Nitroxylin
Hormones		Altrenogest Progesterone Medroxyprogesterone Delmadinone Methyltestosterone Estradiol benzoate Ethenyl estradiol
Antifungals	Biguanide/ gluconate Azole Others	Chlorhexidine Miconazole Griseofulvin
Anesthetics		Isoflurane Halothane Procaine Lido/lignocaine
Euthanasia products		Pentobarbitone
Analgesics		Metamyzole
Tranquilizers		Phenobarbitone
NSAIDs		Phenylbutazone Caprofen
Enteric bloat preparations		Dimethicone Poloxalene

Table 14 Annual consumption of antibiotics for veterinary medicine, especially livestock, in the EU and UK

	EU 1999 (t)	UK 2000 (t)
Therapeutics	3902	437
Tetracyclines	2575	228
Sulphonamides	78	94
Aminoglycosides	1564	12
β-lactams	351	49
Macrolides	468	41
Others	234	12

Table 15 Number and quantity of veterinary products sold by group in the UK in 2003 (VMD, 2004)

Group of Veterinary Product Sold	Number of Products Sold by Group	Quantities sold in the UK (t ai)*
Therapeutic Antimicrobials comprising:	358	456
Tetracyclines	49	212
<i>Trimethoprim/Sulphonamides</i>	50	89
<i>β-lactams</i>	124	62
<i>Aminoglycosides</i>	45	21
<i>Macrolides</i>	20	60
<i>Fluoroquinolones (kg ai)</i>	34	1388
<i>Others</i>	36	12
Therapeutic Antiprotozoals	14	2
Therapeutic Antifungals	16	2
Antimicrobial Growth Promoters	3	36
Coccidiostats	11	241
Total		737

Notes:

* t ai - tonnes active ingredient

Of the total quantity of therapeutic antimicrobials sold 30 t were for non-food animal use and 28 t could be used by either food or non-food animals.

Table 16 Annual sales in the UK of antimicrobial therapeutic products by sub-chemical grouping (VMD, 2004)

Sub-chemical grouping	t ai y⁻¹
Trimethoprim/Sulphonamides	89
<i>Trimethoprim</i>	15
<i>Sulphonamides</i>	74
β-Lactams	62
<i>Cephalosporins</i> all generations of cephalosporins are included in this group	3
<i>Penicillins</i> includes potassium penicillin, benzyl penicillin, procaine penicillin, benzathine penicillin	16
<i>Others</i> includes cloxacillin, amoxycillin, ampicillin, nafcillin, penicillamine hydrochloride	43
Aminoglycosides	21
<i>Streptomycins</i>	7
<i>Neomycin and Framycetin</i>	5
<i>Others</i> includes gentamicin, apramycin and spectinomycin	9

Notes:

t ai, tonnes active ingredient

For animals at pasture, veterinary compounds are excreted directly to soil. As in humans, the excreta may be made up of a mixture of the parent compound and its metabolite. In cases where animals are housed, the manure and slurry produced is collected and applied to land as fertilizer after a period of storage. There is some evidence that antibiotics may also enter the environment as aerosols and dusts, but entry from this route is considered to be insignificant (Boxall *et al.*, 2003a) compared to the main entry routes shown in Figure 2.

The resources to monitor all of the antibiotic compounds used as veterinary medicines are not available. Therefore, compounds with the greatest potential for impacting the environment need to be identified and prioritised. Boxall *et al.* (2003b) proposed a 2 stage scheme for identifying such priority veterinary compounds.

The first stage involved assessing the potential for compounds to enter the environment in significant amounts. This was a two step process. Firstly, groups of substances were ranked according to their usage. Those used in quantities greater than 10 t per y were classed as high. Those used in quantities between 1 and 10 t per y were classed as medium, while those with less than 1 tpa were classed as low. Compounds for which usage could not be determined were classed as unknown.

The second part of Stage 1 involved assessing the potential for substances to enter the environment. This assessment was based on information on the target treatment group, the route of administration, metabolism in the animal and the potential for the substance to be degraded during slurry or manure storage. Taking these factors into consideration, substances were classified as having high, medium, low or unknown potential to enter the environment.

Table 17 K_{ow} and excretion rate in pigs and cattle of parent compound and metabolites for some commonly used veterinary antibiotics and half lives measured in manures under laboratory conditions. (Halling-Sørensen *et al.*, 2001)

Antibiotic	log K_{ow}	Excretion rate in urine except where stated (% of dose)
Sulfonamides	Half lives = 30 days	
Sulfadiazine	0.12 +/- 0.26	90
Sulfatroxazole		90
Sulfadoxine	0.34 +/- 0.43	90
Sulfapyrazole	1.98 +/- 0.50	90
Tetracyclines	Half lives = 100 days	
Tetracycline	-1.19 +/- 0.71	
Chlortetracycline	-0.04 +/- 0.72	65
Oxytetracycline	-1.22 +/- 0.75	65
β-lactam antibiotics	Half lives = 5 days	
Benxylpenicillin (penicillin-G)	1.67 +/- 0.20	90
Amoxicillin	0.61 +/- 0.38	90
Ampicillin	1.35 +/- 0.38	90
Penethamate	2.41 +/- 0.86	
Quinolones	Half lives = 100 days	
Enrofloxacin	2.53 +/- 0.75	35
Macrolides	Half lives = 21 days	
Tylosin ¹	2.5 +/- 0.84	100
Aminoglycosides	Half lives = 30 days	
Dihydrostreptomycin	-3.57 +/- 1.01	95, 5 in faeces
Miscellaneous		
Spectinomycin	0.83 +/- 0.72	100
Tiamulin ¹	5.93 +/- 0.62	No value given
Trimethoprim	0.79 +/- 0.38	65
Lincomycin	0.52 +/- 0.68	20, 75 in faeces

Note:

¹The data abstracted from Table 13.1 in Halling-Sørensen *et al.* (2001) on excretion of these antibiotic compounds may be in error and actually refer to excretion in the faeces

Stage 2 was a hazard assessment for compounds with high, medium or unknown potential to enter the environment and of high, medium, low or unknown usage. The exception was compounds with medium potential and low usage. All compounds with a low potential to enter the environment were not required to undergo hazard assessment. This scheme is shown in Figure 3.

In the hazard assessment, each compound was given a hazard classification of very high, high, medium, low or unknown, according to the criteria outlined in Table 18.

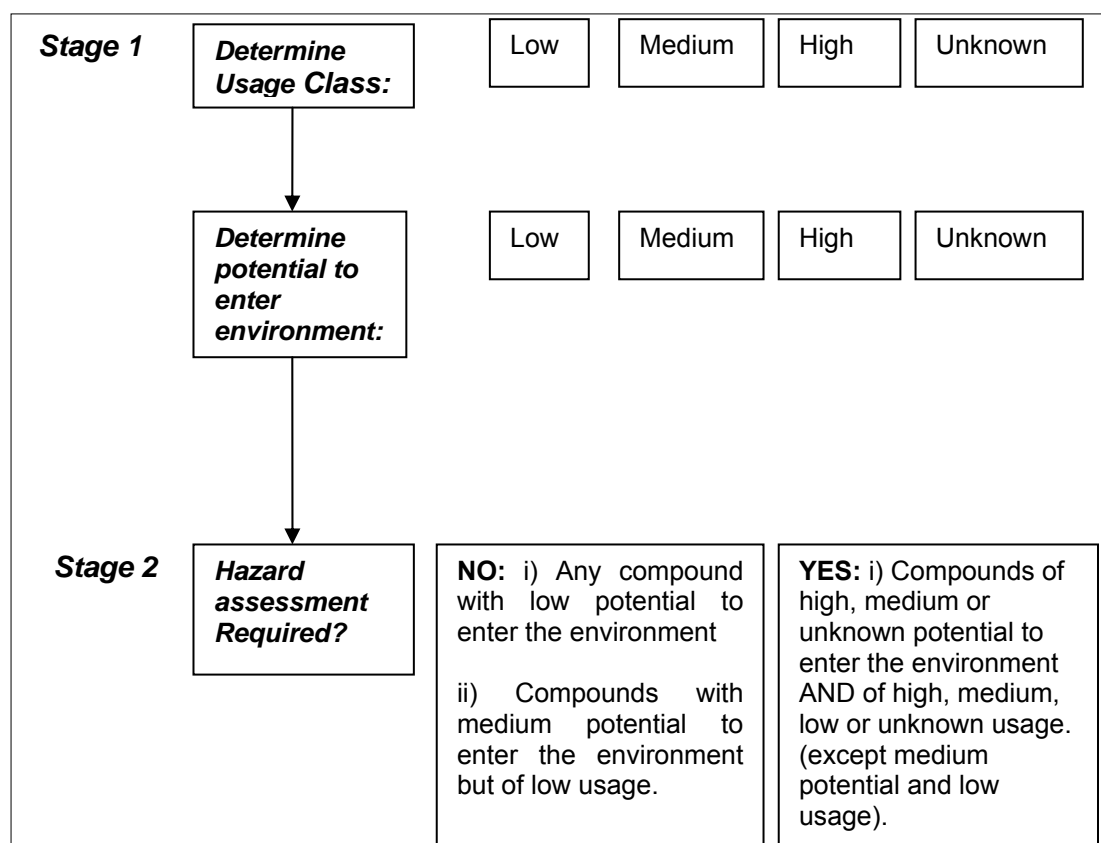


Figure 3 Identification procedure for priority veterinary compounds (Boxall *et al.*, 2003b)

Table 18 Classification criteria for ecotoxicity of veterinary compounds (Boxall *et al.*, 2003b)

Hazard Classification	Aquatic Toxicity ^a	Terrestrial Toxicity ^b
Very High	≤ 0.1	≤ 10
High	$> 0.1 \leq 1$	$> 10 \leq 100$
Medium	$> 1 \leq 100$	$> 100 \leq 1000$
Low	> 100	> 1000
Unknown	No data available	

Notes

- a Based on a OECD system harmonising system for the classification of chemicals which are hazardous for the aquatic environment;
- b Based on a proposed EU hazard assessment scheme for the terrestrial environment.

The compounds identified as having the greatest potential to cause environmental impacts from this prioritisation exercise are listed in Table 19. Those compounds whose usage and potential to enter the environment were unknown, are also included in this list. They may not actually cause adverse impacts on the environment, but are included as a precautionary measure.

Table 19 Prioritisation assessment for veterinary medicinal products that have the potential to enter the environment (Boxall *et al.*, 2003b)

Therapeutic group	Chemical group	Major usage products	Potential to reach environment	Usage class	Hazard to terrestrial organisms
Antimicrobials	Tetracyclines	Oxytetracycline Chlortetracycline Tetracycline	High High High	High	Low Very high Unknown
	Potentiated sulphonamides	Sulphadiazine Trimethoprim Baquiloprim	High High Unknown	High	High Unknown Unknown
	β -lactams	Amoxicillin Procaine penicillin Procaine benzylpenicillin Clavulanic acid	High Unknown Unknown Unknown	High	Unknown Very high Unknown Unknown
	Aminoglycosides	Dihydrostreptomycin Neomycin Apramycin Flavomycin	High High High Unknown	High	Unknown Unknown Very high Unknown
	Marcolides	Tylosin Monensin Salinomycin sodium Flavophospholipol	High Unknown Unknown Unknown	High	Low Very high Very high Unknown
	Pleuromutlins	Tiamulin	Unknown	Medium	Medium
	Lincosamides	Lincomycin Clyndamycin	Unknown Unknown	Medium	Very high Unknown
Endoparasiticides	Pyrimidines (wormers)	Morantel	Medium	Medium	Unknown
	Pyrethroids (sheep dips)	Cypermethrin Flumethrin	High High	Medium	Unknown Unknown
	Azoles (wormers)	Triclabendazole Fenbendazole Levamisole	Medium Unknown Unknown	Medium	Unknown Unknown Unknown
	Macrolide endectins	Ivermectin	Medium	Medium	Very high

Table 19 (Continued)

Therapeutic group	Chemical group	Major usage products	Potential to reach environment	Usage class	Hazard to terrestrial organisms
Endoparasiticides -coccidiostats		Amprolium Clodol Lasalocid sodium Maduramicin Nicarbazin Robenidine hydrochloride	Medium Unknown Unknown Medium Unknown Unknown	High	Very high Unknown Unknown Very high Unknown Unknown
Other Antibiotics		Cephalexin Florfenicol Tilmicosin Oxolinic acid Lido/lignocaine hydrochloride	Unknown High Unknown High Unknown	Medium	Unknown Very high Unknown Unknown Unknown
Endoparasiticides	Others	Nitroxynil	Unknown	Medium	Unknown
Antimicrobials	Flouroquinolones	Enrofloxacin Sarafloxacin	High High	Medium	Unknown Very high
Enteric preparations		Dimethicone Poloxalene Toltrazuril Decoquate Diclazuril	Unknown Unknown Unknown Unknown Unknown	Low	Unknown Unknown Unknown Unknown Unknown
Ectoparasiticides		Phosmet Piperonyl butoxide	High Medium	Unknown/Low	Unknown Unknown
	Amidines (sheep dip)	Amitraz	High	Unknown	Unknown
Ectoparasiticides		Delamethrin Cypermazine	High High	Unknown	High Unknown
Ectoparasiticides	Organophosphate	Diazinon	High	High	Very high

1.7 Biocides and personal care products

Biocides and personal care products (PeCPs) are widely used in domestic products, including furnishings, clothing as well as hygiene products. They are discharged with urban wastewater (UWW) and, therefore, potentially enter soil when sewage sludge is recycled to agricultural land or from inputs in surface water receiving treated effluents from WwTW, used as irrigation.

Triclosan is an antimicrobial agent used in a wide range of medicinal and consumer care products. Triclosan is added as a preservative or as an antiseptic agent in medical products such as hand disinfecting soaps, medical skin creams, and dental products. It is also found as an antimicrobial active component in many everyday household and consumer care products such as toothpaste, mouthwash and soaps, as well as in household cleaners. Even textiles, such as sportswear, bed cloths, shoes, and carpets can contain triclosan. European consumption of triclosan is about 350 t per annum (Singer *et al.*, 2002). The widespread use of triclosan means that it is inevitably discharged to WwTW and into surface waters where there are concerns about its impact on certain algae species (Singer *et al.*, 2002).

Triclosan is a chlorinated phenoxyphenol with a pKa of 8.1. The pH of surface water exerts a significant influence on its speciation and its fate and behavior (Singer *et al.*, 2002). The relatively high octanol-water partition coefficient ($\log K_{ow} = 5.4$) of its protonated form can lead to sorption to particles. Moreover, as the dissociated form of triclosan absorbs sunlight, photodegradation maybe a possible elimination process for the compound in surface water. On the other hand, triclosan is relatively stable against hydrolysis. Singer *et al.* (2002) examined the transformation of triclosan through wastewater treatment (WwT) processes and found 79% was biologically degraded within the plant, 15% associated with the sludge and 6% was released in final effluent. Although degradation rates were high, the high usage of triclosan means that loads in treated effluents ranged from 30 to 210 mg of triclosan per 1000 persons per day. Degradation in soil is also rapid with reported half-lives in the range 17.4 – 35.2 days (Danish EPA, 2003). The concentrations of triclosan in different media are listed in Table 20. A terrestrial risk assessment of triclosan recently completed by the Danish EPA (Danish EPA, 2003) indicated that the concentrations measured in sewage sludge in the US and Sweden could have negative effects on soil organisms immediately after application. The collection of more data on triclosan concentrations in UK sludge is required. Also, the risk assessment protocol of Schowanek *et al.* (2004), for deriving quality standards for organic contaminants in sludge for use in agriculture, should be applied to this compound to determine its potential significance and impact on soil quality.

Descriptions of common additives in some personal care products are given in Table 21.

1.8 Endocrine disrupting chemicals (EDCs)

4-*tert*-Nonylphenol is a significant industrial xenobiotic oestrogen mimic which has been implicated as the dominant endocrine disruptor in certain industrialised river reaches. Apart from hot spots associated with particular industries, the oestrogenic alkylphenols, bisphenol A and phthalates, that were suspected DEC (although this is no longer the case – see Section 3.4) are present in effluent and receiving water at concentrations below that which would give cause for concern (Johnston and Jürgens, 2003).

Other more bioaccumulative compounds such as polybrominated flame retardants, dioxins, and furans may possess some endocrine active properties. The possibility of additive effects may mean that low concentrations of xenobiotic endocrine active substances will have a cumulative negative effect (Johnson and Jürgens, 2003).

Concentrations of potentially endocrine active substances in different environmental media are presented in Table 22.

Table 20 Concentrations of Triclosan in different media (Singer *et al.*, 2002; Danish EPA, 2003)

Matrix	Minimum	Maximum	Mean	No of data points
Sewage influent	0.07 µg l ⁻¹	14000 µg l ⁻¹		
Sewage effluent	42 ng l ⁻¹	213 ng l ⁻¹	116 ng l ⁻¹	7
River water	50 ng l ⁻¹	2300 ng l ⁻¹		
Sediment	1 µg l ⁻¹	35 µg l ⁻¹		
Activated sludge	0.028 mg kg ⁻¹ DS	4.2 mg kg ⁻¹ DS		
Trickling or other bio-filter sludge	0.38 mg kg ⁻¹ DS	15.6 mg kg ⁻¹ DS		
Soil from industrially contaminated area	<3 µg kg ⁻¹ ds	15 µg kg ⁻¹ ds		
Uncontaminated forest soil	<3 µg kg ⁻¹ ds			

**Table 21 Description of common additives in some personal care products
(from Xia *et al.*, 2005)**

Fragrances	
Distribution of the use of synthetic musks in personal care products: candles, air fresheners, and aroma therapy = 41%, perfumes, cosmetics, and toiletries = 25%, soaps, shampoos, and detergents = 34% (Fragranced Products Information Network, 2004).	
Active compound	log K_{OW}
Musk ketone	3.48
Musk xylene	3.46
Galaxolide (HHCB)	4.60
Tonalide (AHTN)	4.84
Phantolide (AHMI)	4.53
Traseolide (ATII)	4.72
Celestolide (ADBI)	4.37
Cashmeran (DPMI)	4.84
Flame retardants	
Used as additive in flexible polyurethane foam, in textile coatings and coatings for furniture, and in plastics for electrical and electronic equipment, wire, and cable insulation and electrical connectors, automobiles, and construction and building materials (Bromine Science and Environmental Forum, 2004). The current estimated worldwide growth for flame retardants is 4% per year. Distribution of the 1.14 million Mg global consumption of flame retardants in 1998: Al-, Mg-, and N-based = 56%, Br-based = 23%, P-based = 15%, Cl-based = 6% (Clariant, 2004). Worldwide market demand for PBDEs in 2001 was 67 440 Mg, 83% of which was in the Americas (Hites, 2004).	
Active compound	log K_{OW}
Tetrabromobisphenol A	0.39–5.34
Polybrominated diphenylether (commercially available PBDEs primarily consist of penta-, octa-, deca- PBDE)	log K _{OW} μ 5.74, log K _{OW} = 0.621(Br) + 4.12 Braekevelt <i>et al.</i> , 2003)
Polybrominated biphenyl	>4.0
Pentabromochlorocyclohexane	4.01
Hexabromocyclododecane	4.98
Pentabromotoluene	4.57
Tetrabromophthalic anhydride	3.17
Tris(2,3-dibromopropyl)phosphate	>4.0

Table 21 (Continued)

Disinfectants, antiseptics and pesticides		
Active compound	Log K_{ow}	Characteristics
Triclosan (2,4,4_-trichloro-2_-hydroxy diphenyl ether)	2.39–4.54	Bactericide added in detergents, dishwashing detergents, laundry soaps, deodorants, cosmetics, lotions, creams, toothpastes and mouthwashes, footwear, and plastic wear. It interferes with an enzyme crucial to the growth of bacteria.
Biphenylol	2.67–2.98	Bactericide and virucide added in dishwashing detergents, soaps, general surface disinfectants in hospitals, nursing homes, veterinary hospitals, commercial laundries, barbershops, and food processing plants. It is used to sterilize hospital and veterinary equipment
Chlorophene	3.37–3.78	Bactericide and fungicide added in disinfectant solutions and soaps
DEET (<i>N,N</i> -diethyltoluamide)	2.44	Pesticide added in insect repellent
Butylparaben (alkyl- <i>p</i> -hydroxybenzoates)	1.49–3.26	Fungicide added in cosmetics, toiletries, and food
Surfactants		
Active compound	Log K_{ow}	Characteristics
Alkylphenol polyethoxylates (usually branched nonyl or octyl; ethoxylate units = 1–20)	>4.5	Nonionic surfactants added in detergents
Sodium dodecylbenzenesulfonate	water soluble	Ionic surfactants added in detergents
Benzalkonium chloride	water soluble	Ionic surfactants added in detergents, preservative and disinfectant in contact lens solutions

Table 22 Concentrations of endocrine active substances in different environmental media (various sources cited Johnson and Jürgens, 2003)

Compound	Domestic effluent	Industrially impacted effluent	Sewage sludge	Surface water	Sediment
	$\mu\text{g l}^{-1}$ ^a	$\mu\text{g l}^{-1}$ ^a	$\mu\text{g g}^{-1}$ dry wt	$\mu\text{g l}^{-1}$ ^a	$\mu\text{g g}^{-1}$ dry wt
Nonylphenol	<0.02–69	142–330	8–4000	<0.01–644	<0.0015–72
Octylphenol	0.005–1.7	0.26–9	<0.01–20	<0.005–13	<0.002–1.8
Bisphenol A	<0.0001–4.5	<0.01–8	0.004–1.36	<0.0001–1.4	<0.001–0.19
Phthalates DEHP^b DBP^c, BBP^d	<0.1–30.5	<0.1–80.5	0.19–154	<0.1–98	<0.01–8.4
Brominated flame retardants BDE-47 BDE-99, BDE-100			0.015–0.12		<0.0002–0.9

Notes:

- a May include chemical sorbed to suspended particles.
- b di(2-Ethylhexyl)phthalate (see Section 3.4.2 for further discussion)
- c di-*n*-Butylphthalate.
- d Benzylbutylphthalate.

2 SOURCES OF ORGANIC CONTAMINANTS TO SOIL

2.1 Atmospheric

There is a considerable amount of information concerning the atmospheric concentrations of organic chemicals of interest. However, this data is not readily transferable into mass of deposited compound on soil. Deposition can be derived from air concentrations, but the main problem is that deposition of organics is very difficult to reliably measure (Sweetman 2005, University of Lancaster, pers com). Thus, published data concerning emissions to or depositions on land from the atmosphere may be regarded as providing an indication of chemicals that are potentially active in the biosphere or impacting on soil processes.

2.1.1 Persistent organic pollutants - POPs

National emissions data is collected annually in accordance with international treaties signed by the UK to monitor and limit emissions of POPs (Table 23). There is considerable uncertainty associated with the accuracy of this data (Table 24). It is also not possible to say what proportion of the emissions will be deposited on soil. Inevitably, the UK is both a recipient of POPs from overseas and a portion of that emitted is exported beyond the UK, as illustrated for benzo[a]pyrene (B[a]P) in Table 25. The European average B[a]P deposition is 0.5 g km^{-2} per month.

Table 23 Total UK emissions of POPs in 2002 (NAEI, 2003)

Pollutant	Total 2002 UK emission	
Polycyclic aromatic hydrocarbons (PAHs) (USEPA 16) ¹	2039	tonnes
Dioxins and Furans (PCDD/F)	316	I-TEQ grams
Polychlorinated biphenyls (PCBs)	1.45	tonnes
Pesticides		tonnes
- lindane (γ -HCH)	16	
- pentachlorophenol (PCP)	437	
- hexachlorobenzene (HCB)	0.31	
Short Chain Chlorinated Paraffins (SCCPs)	1	tonnes
Polychlorinated Naphthalenes (PCNs)	NE ²	
Polybrominated Diphenyl Ethers (PBDEs)	13.8	tonnes

Notes:

1 US EPA priority pollutants listing of 16 PAHs.

2 Not estimated

A unique feature of POPs is their ability for re-emission (Section 1.2). To evaluate long-range transport and deposition of POPs multi-compartment approach has been developed by the Meteorological Synthesizing Centre-East (MSC-E) (Moscow, Russia) (MSC-E, 2004). MSC-E is an international centre within the Co-operative Programme for Monitoring and Evaluation of Long-Range Transmission of Air Pollutants in Europe (EMEP) and was established in 1979. The Centre has developed a model of atmospheric transport and deposition of POPs (MSCE-POP) based on advective transport and turbulent diffusion of pollutants within the atmosphere. The MSCE-POP model is a three-dimensional multi-compartment model operating within the geographical scope of the EMEP region with a spatial resolution $50 \times 50 \text{ km}^2$. The model considers main environmental compartments (atmosphere, soil, seawater, vegetation) and includes basic processes describing

POP emission, long-range transport, deposition, degradation, and gaseous exchange between the atmosphere and the underlying surface (Figure 4). MSCE-POP model domain covers the troposphere, upper layer of soil of 20 cm, and the seawater compartment within the model grid.

Table 24 Uncertainty of the emission inventories for persistent organic pollutants (NAEI 2003)

Pollutant	Estimated uncertainty %
Benzo[a]pyrene	-70 to +200
Dioxins and furans	-50 to +100
Polychlorinated biphenyls	-40 to + 70
Pentachlorophenol	-80 to +200
Hexachlorohexane	-80 to +300
Hexachlorobenzene	-70 to +200
Short-chain chlorinated paraffins	-90 to +1000
Pentabromodiphenyl ether	-90 to +1000
Polychlorinated naphthalenes	not estimated

Table 25 Net deposition of benzo(a)pyrene in the UK from the air (kg)

	Deposition from UK sources	Imports from overseas
United Kingdom	1239	
Germany	54	39
France	62	113
Atlantic	222	
North Sea	256	
Other	311	94
Ireland		38
Belgium		39
Net total deposition from air in UK		1562

Source: http://www.emep.int/index_pollutants.html

The following processes affecting the long-range transport of POPs are included in the model:

Atmosphere:

- advective transport and turbulent diffusion;
- partitioning between the gaseous and particulate phase;
- wet and dry deposition of POP in particulate and gaseous phase to the underlying surface;
- degradation.

Vegetation:

- gaseous exchange with the atmosphere;
- degradation;
- defoliation and transfer to upper soil layer.

Soil:

- gaseous exchange with the atmosphere;
- partitioning in soil between the gaseous, solid and liquid phases;
- vertical transport due to convective water fluxes, diffusion, and bioturbation;
- degradation.

A description of the model can be found at:

http://www.msceast.org/events/review/pop_description.html

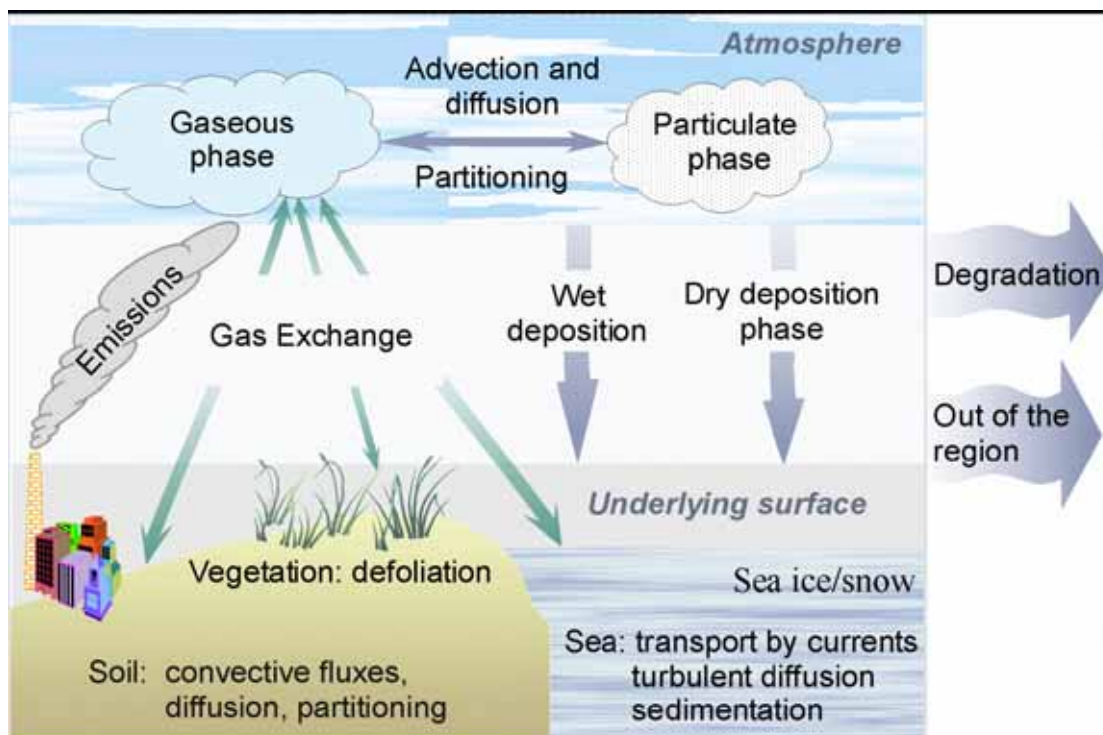


Figure 4 The scheme of processes included in the MSCE-POP model of POP transport, deposition and soil accumulation

Based on these assumptions and emissions data (eg Pacyna *et al.*, 1999), POP (HCB and PCBs: 1998 emissions data; PCDD/Fs, B[b]F, B[k]F and B[a]P: 2001 emissions data) concentrations have been predicted for air, soil and vegetation compartments in the UK environment (Table 26 and 27) (see: http://www.msceast.org/countries/United_Kingdom/index.html).

Table 26 Modelled UK atmospheric concentrations of key POPs in 2004 (ng m⁻³) except where stated

Substance	Minimum	Maximum	Mean
PCDD/Fs (fg TEQ/m ³)	0.21	7.56	3.23
HCB	0.04	0.749	0.0495
PCBs	0.0152	0.21	0.11
PAH - B[b]F	0.0211	0.51	0.12
PAH - B[k]F	0.0148	0.37	0.16
PAH - B[a]P	1.62	19.83	14.66

Source: http://www.msceast.org/countries/United_Kingdom/index.html#popaver

Table 27 Modelled total emissions and soil concentrations of key POPs for UK in 2004 (mg kg⁻¹; for PCDD/Fs: pg TEQ g⁻¹)

Compound	Label	Mean ¹	Minimum ²	Maximum ²	Total emissions (t y ⁻¹)
Dioxins and furans	PCDD/F	0.80	3.56x10 ⁻²	1.68	341.3 ⁽³⁾
Hexachlorobenzene	HCB	0.38	8.70x10 ⁻³	1.31	0.5
Polychlorinated biphenyls	PCBs	33.22	0.33	61.72	3.7
Benzo[b]fluoranthene	B[b]F	3.92	0.32	7.64	5.9
Benzo[k]fluoranthene	B[k]F	2.43	0.15	4.75	12.0
Benzo[a]pyrene	B[a]P				7.2

Notes:

Source: http://www.msceast.org/countries/United_Kingdom/index.html#popaver

1 mean over whole country

2 min and max values within the country

3 g TEQ y⁻¹

Whilst precise matching with contemporary spot measurements of these compounds in the different media would not be expected, the predicted values fall within the range of measured results from the UK (http://www.msceast.org/countries/United_Kingdom/index.html). Further time trend analyses are also available (except for B[a]P) showing changes in environmental emissions and concentrations for the selected POPs since 1970 (Figures 5-7). Whilst there are limitations to modelling POP concentrations in the environment, the results provide a reasonable reflection of actual and relative concentrations of the various contaminants in the different environmental media and how these have changed with time. In particular, this provides a graphic illustration of the impact and effectiveness of action taken during the 1980s and 1990s to curb emissions and reduce the environmental burden of these principal POPs. Thus, the modelling results show that emissions and predicted concentrations in air and soil of all POPs examined have declined significantly since the 1970s. The reduction in soil concentrations (Figure 7) is consistent with the net loss and export of POPs from UK soils reported for compounds where detailed quantitative sink-source relations have been investigated, such as for PCBs (Harrad *et al.*, 1994). Alcock *et al.* (1993) suggest that the dramatic reduction in Σ PCB concentrations, that have declined to values similar to the early 1940s (approx. 20-30 $\mu\text{g kg}^{-1}$) from a peak of 140-560 $\mu\text{g kg}^{-1}$ in the late 1960s/early 1970s, is explained by volatilisation and subsequent long-range transport. The reduction in concentrations of individual PAH congeners in soil (Figure 7) is also consistent with the declining burden of these compounds in the UK environment and losses from soil by biodegradation and volatilisation (Wild and Jones, 1995).

PCB concentrations in air vary seasonally with concentrations being greater in the summer months due to higher temperatures increasing volatilisation losses from soil. However, Robson and Harrad (2004) found that soil concentrations also followed a similar seasonal pattern, though the reasons were not clear since greater volatility due to higher temperatures would suggest a lowering of soil concentrations.

The EU POLMIT (POLMIT, 2002) project obtained information on road and vehicle emissions of pollutants to identify their relative importance as a source of terrestrial pollution. Annual loadings of pollutants into the local roadside environment were monitored at a range of sites across Europe, including heavy metals and PAHs.

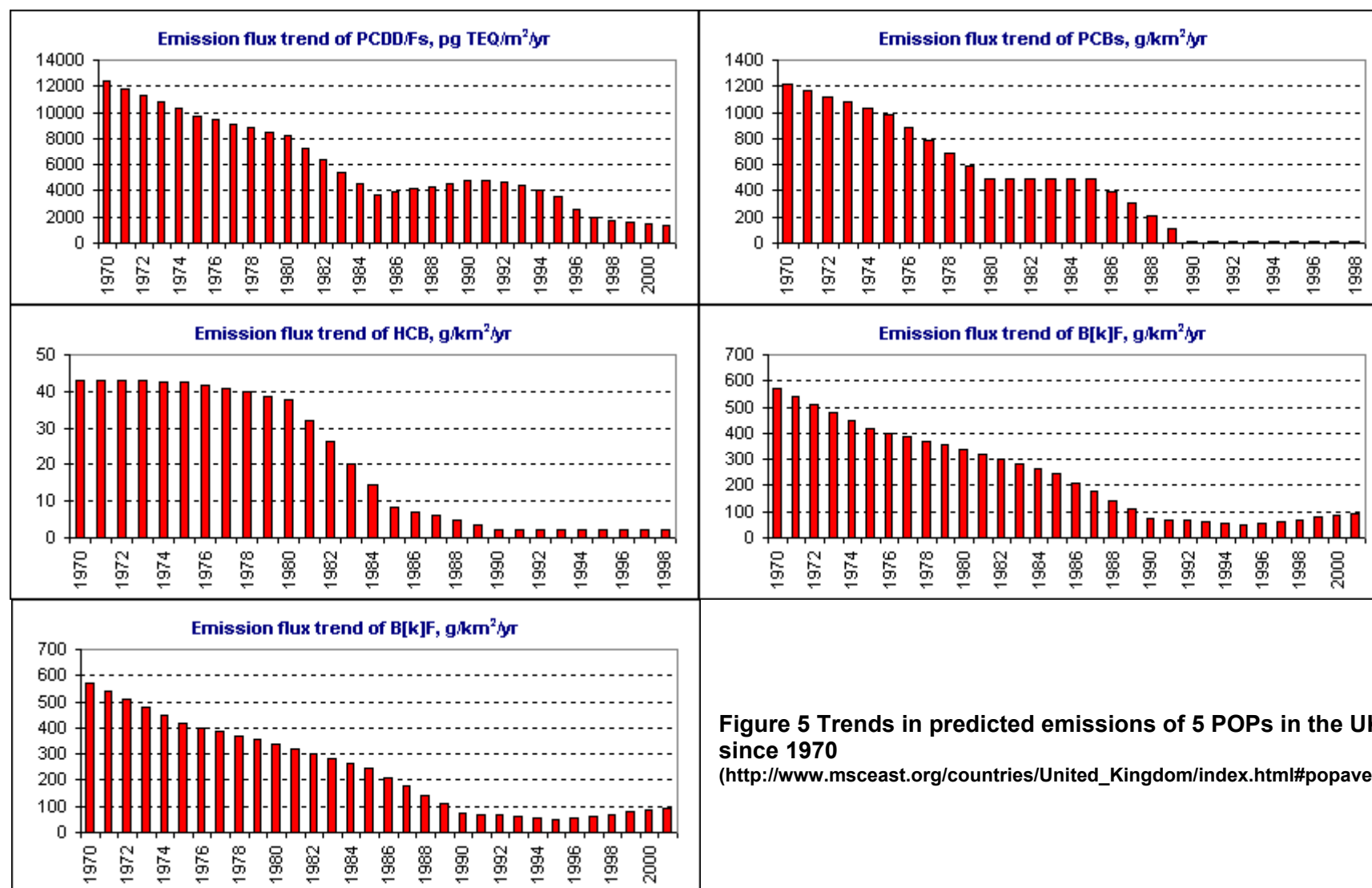


Figure 5 Trends in predicted emissions of 5 POPs in the UK since 1970
http://www.msceast.org/countries/United_Kingdom/index.html#popaver

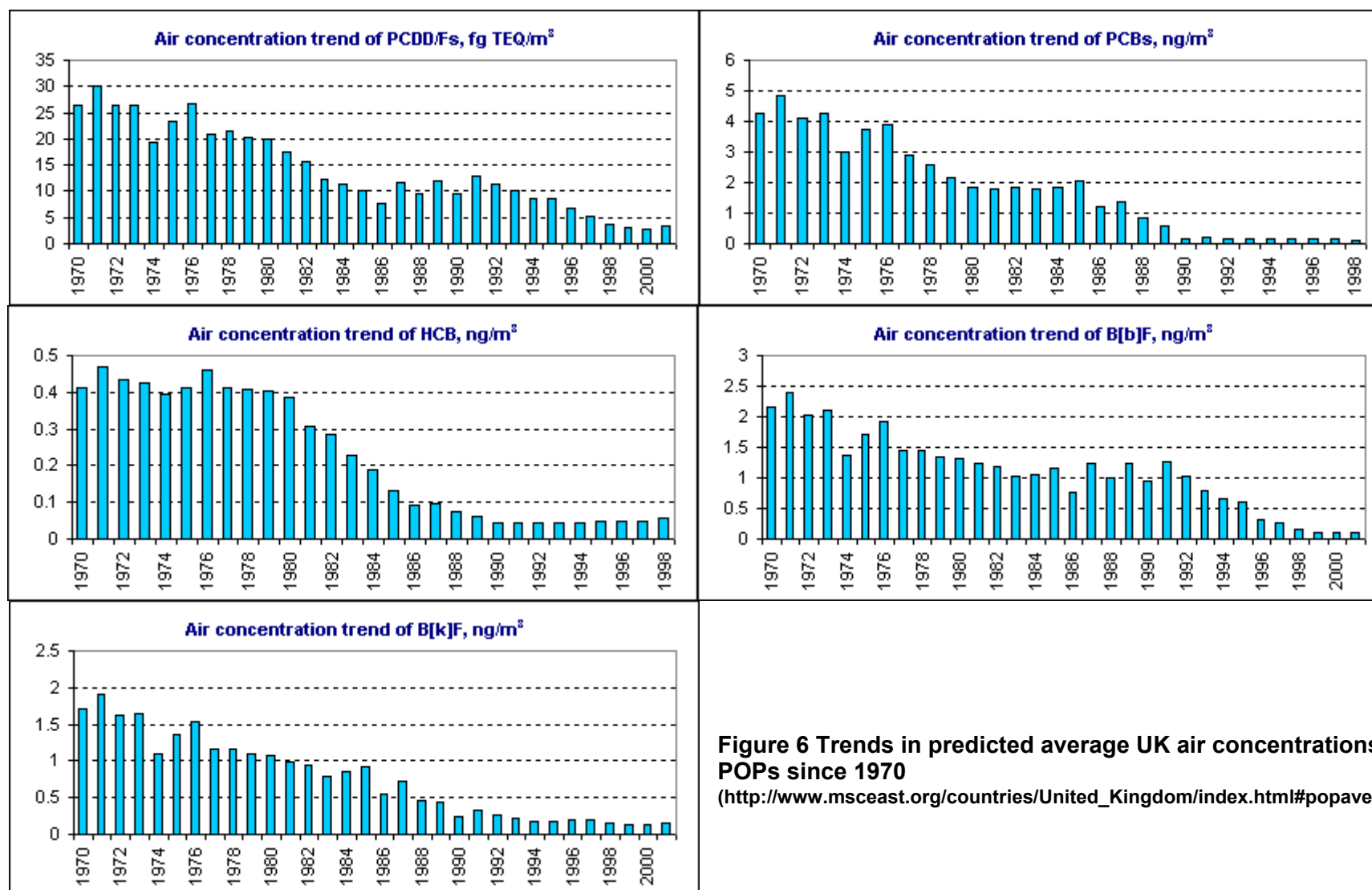


Figure 6 Trends in predicted average UK air concentrations of 5 POPs since 1970
 (http://www.msceast.org/countries/United_Kingdom/index.html#popaver)

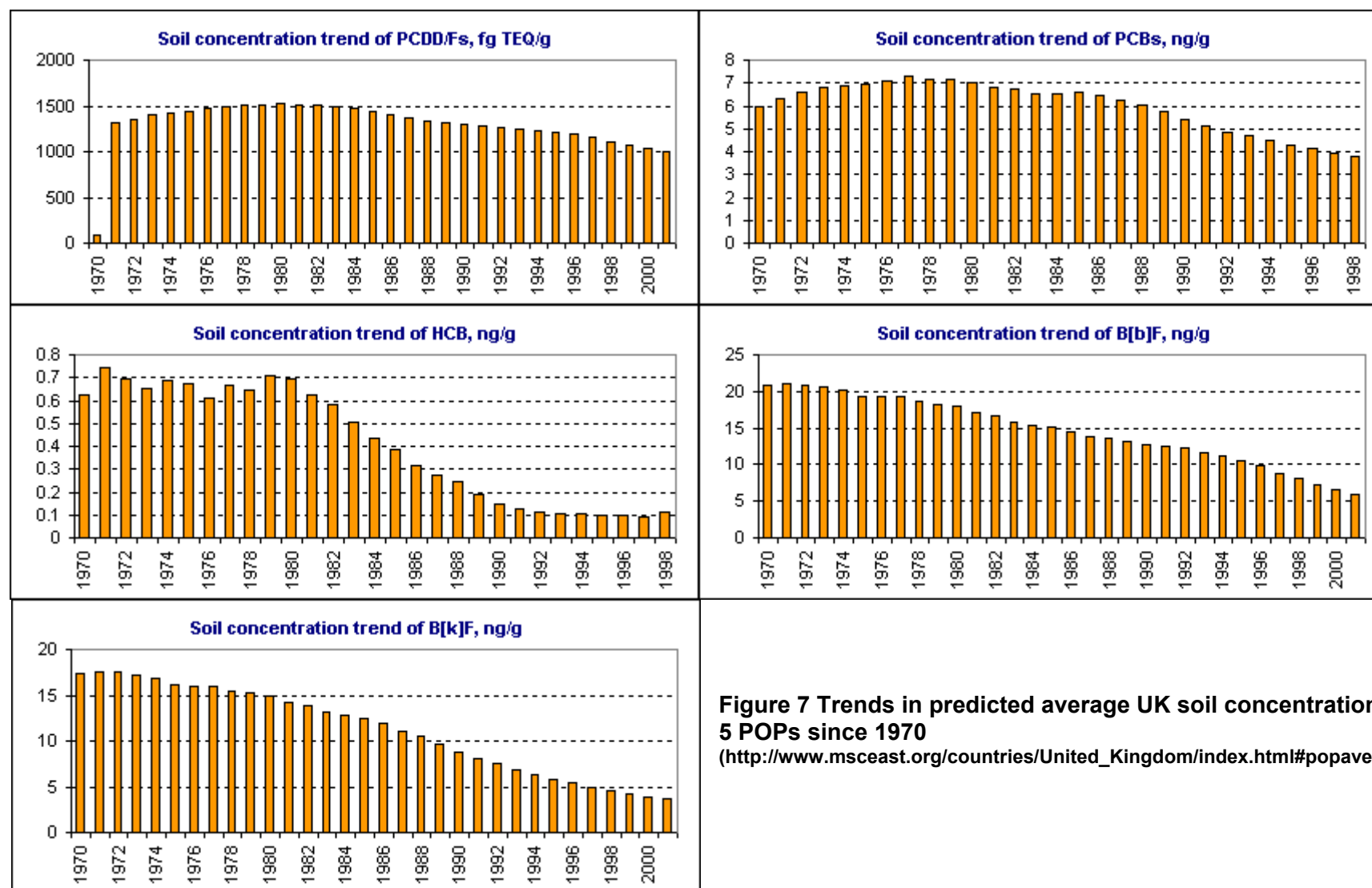


Figure 7 Trends in predicted average UK soil concentrations of 5 POPs since 1970
http://www.msceast.org/countries/United_Kingdom/index.html#popaver

Emission rates (mass per km of road per year) of Σ PAHs calculated from literature data were 65 - 721 g km⁻¹ y⁻¹ from one carriageway (downwind side) only. Data collected from the UK sites are presented in Table 28. These data are regarded only as estimates due to sampling difficulties. Only 10% of the emitted PAHs were recovered in the vicinity of the road suggesting either that it was dispersed beyond the measurement zone, that it was rapidly degraded *in situ* or was degraded during sample storage. In terms of total PAH emissions to the atmosphere, Wild and Jones (1995) estimated that vehicles represented approximately 10 % of the total release of PAHs to the UK atmosphere.

Table 28 Estimated PAH emissions rates from roads (g km⁻¹ road y⁻¹) (POLMIT, 2002)

PAH	Reading	Oxford
Fluoranthene	318	252
Benzo[a]pyrene	34	27
Indeno[1,2,3]pyrene	20	16
Benzo[g,h,i]perylene	116	96
Benzo[k]fluoranthene	32	26
Naphthalene	183	146
Total PAH	703	562

Emissions from vehicles deposited on motorway surfaces (primarily petroleum derived products like diesel fuel and motor oil) are collected in run-off lagoons where the contaminated sludge is deposited and is removed intermittently for disposal (Durand *et al.*, 2004). This restricts the inputs of contaminants from major highway surfaces into neighbouring soils.

2.1.2 Pesticides

Emission of pesticides into the atmosphere can result from spray drift and volatilisation, from post-application volatilisation from treated crops and soil, from wind erosion of soil particles carrying sorbed pesticides and from re-suspension of pesticides previously deposited from the atmosphere. Wet deposition in precipitation is generally the most significant and differs little from total deposition since dry deposition has been found to be very small (Dubus *et al.*, 2000).

Pesticides enter rainfall largely through spray becoming airborne causing the loss of chemicals off site and subsequent deposition in rainfall elsewhere. Since the loss of spray means that chemicals are not being effective it is in the farmers' interest to minimise such losses through appropriate operating practices.

The use of historical data to determine potential pesticide inputs to soil from rainfall is potentially unsound since the technology used to apply products is likely to have improved and the concentration of products used in tanks has decreased substantially in the last ten years (CSL, 2003ab). Consequently, the data provided in Table 29 provide only a limited view of current concentrations of pesticides found in rainfall.

Dubus *et al.* (2000) conducted a review of pesticides in rainfall across Europe on behalf of MAFF examining 28 studies in 10 countries. Maximum reported concentrations in rainwater were 10 to 1110 ng l⁻¹ for atrazine, 94 to >1000 ng l⁻¹ for simazine, 26 to 800 ng l⁻¹ for terbutylazine, 140 to 6200 ng l⁻¹ for dichlorprop, 20 to 833 ng l⁻¹ for lindane, 110 to 3190 ng l⁻¹ for MCPA, 32 to >1000 ng l⁻¹ for mecoprop and 125 to >1000 ng l⁻¹ for isoproturon. Only three UK based studies were available to be reported (Table 29).

Table 29 Pesticides reported in studies of rainfall concentrations of pesticides in the UK (Dubus *et al.*, 2000)

Pesticide	Type	Reference
Aldrin ^a (organochlorine)	insecticide	Harris <i>et al</i> 1992
Atrazine ^b	herbicide	Clark and Gomme 1991 ^c , Fisher <i>et al</i> 1991 ^c , Gomme <i>et al</i> 1991 ^c , Harris <i>et al</i> 1992
Chlorothalonil	fungicide	Clark and Gomme 1991, Fisher <i>et al</i> 1991, Gomme <i>et al</i> 1991,
Dimethoate	insecticide	Clark and Gomme 1991, Fisher <i>et al</i> 1991, Gomme <i>et al</i> 1991
HCH (Lindane) ^d	insecticide	Clark and Gomme 1991, Fisher <i>et al</i> 1991, Gomme <i>et al</i> 1991, Harris <i>et al</i> 1992, Johnson <i>et al</i> 1996
Isoproturon	herbicide	Clark and Gomme 1991, Fisher <i>et al</i> 1991, Gomme <i>et al</i> 1991, Harris <i>et al</i> 1992
Mecoprop	herbicide	Clark and Gomme 1991, Fisher <i>et al</i> 1991, Gomme <i>et al</i> 1991
Simazine ^b	herbicide	Harris <i>et al</i> 1992
Triallate	herbicide	Clark and Gomme 1991, Fisher <i>et al</i> 1991, Gomme <i>et al</i> 1991

Notes:

- a banned since 1991
- b no longer in general use
- c all three papers report the same data for all pesticides
- d banned since 1981

Of the 46 pesticides for which data were reported as having been recently detected in rainwater at sites in Europe, 19 of them can be found in the top 50 most widely used pesticides in Great Britain in the most recent Pesticide Survey (CSL, 2003)

The use of aerial application of pesticides has declined substantially in the last 20 years. In 1985, a total of 470,551 ha were applied aerially with insecticides, acaricides and fungicides predominating. By 1992, this fell to 25,418 ha with fungicides and herbicides predominating, while by 2002, only 4,406 ha were aerially applied, with the herbicide asulam used to control bracken. Over the same period the area treated with herbicide reached a maximum of 8,048 ha. Aerial applications in 2002 have been estimated to be equivalent of 0.01% of the total area of pesticide application, excluding seed treatments, to agricultural and horticultural land in Great Britain in that year (CSL, 2003c). The only other crops to receive significant application by air in recent years are potatoes, with a limited amount of application to upland grazing.

2.2 Sewage sludge

2.2.1 General

A difficulty in comparing concentrations of OC from different sources is the different ways in which data are reported, namely the labels applied to the compounds; some are reported as different groups of congeners and some as individual chemicals. It therefore makes it very difficult to combine data from different sources. Nevertheless, sewage sludge represents the most comprehensive data set on OC concentrations (Table 30, Annex C) and quality standards for various OC have been established in a number of European countries for agricultural use (Table 31). Following detailed risk assessment US EPA decided that the regulation of OC was unnecessary to protect human health and the environment when sewage sludge was used as a soil amendment (US EPA, 1992). Therefore, OC were deleted from the Final Part 503 Standards for the Use or Disposal of Sewage Sludge (US EPA, 1993).

Table 30 Summary of organic compounds found in sewage sludge in the UK (mg kg⁻¹ DS except where indicated) (from UKWIR, 1995; Jones and Northcott, 2000; IC Consultants, 2001; Rogers *et al.*, 2001; Bowen *et al.*, 2003; Stevens *et al.*, 2003; Gawlik and Bidoglio, 2004) (The inventory of concentration data is listed in Annex C)

Substance	Minimum	Maximum	Mean
Non-halogenated monocyclic aromatics	0.025	22.1	2.29
Monocyclic aromatic (chloro- and nitro-anilines)	0.0001	192000	125.83
Monocyclic aromatics	0.004	2.6	0.1427
Alkyl and aromatic amines/imines	0.01	3.8	1.34
Organotin	0.01	1.3	0.36
Halogenated aliphatics	0.00002	16.6	1.0178
Carbonyl	1.4	23	10.1
∑ Polycyclic aromatic hydrocarbons	6.4	72	130
∑ Polychlorinated biphenyls	0.054	0.93	0.22
PCDD/Fs	2.4 pg kg ⁻¹	80000 ng kg ⁻¹	2178 ng kg ⁻¹
TEQ contribution attributable to the PCDD/Fs & PCBs	0.7	680	36.5
Aroclor mixtures	0.00002	23.1	0.023
Organochlorine pesticide	0.00001	2.2	0.035
Linear alkybenzene sulphonate	2100	10500	
Di(2-ethylhexyl)phthalate	0.3	1020	110 (median)
Nonylphenols and nonylphenol ethoxylates	256	824	351
Chlorinated paraffins	0.9	6000	171
Nitro musks	2.1	99	32
Chlorinated phenols	0.09	52.6	
Polychlorinated naphthalenes	0.05	0.19	0.083
Polychlorinated <i>n</i> -alkanes C10-13	6.9	200	42
Polychlorinated <i>n</i> -alkanes C14-17	30	9700	1800

Table 31 Standards for maximum concentrations of organic contaminants in sewage sludge (mg kg⁻¹ DS except PCDD/F: ng TEQ kg⁻¹ DS) (EC, 2000; Smith, 2000; Düring and Gath 2002; US EPA 2003)

	AOX	DEHP	LAS	NP/NPE	PAH	PCB	PCDD/F
EU ^a	500	100	2600	50	6 ^b	0.8 ^c	100
Denmark		50	1300	10	3 ^b		
Sweden				50	3 ^d	0.4 ^c	
Lower Austria	500					0.2 ^e	100
Germany	500					0.2 ^e	100
France					9.5 ^f	0.8 ^{cg}	
USA							300 ^h

Notes:

a proposed but not confirmed (EC, 2000)

b sum of 9 congeners: acenaphthene, fluorene, phenanthrene, fluoranthene, pyrene, benzo(b+j+k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, indeno(1,2,3-c,d)pyrene.

c sum of 7 congeners: PCB 28, 52, 101, 118, 138, 153, 180

d sum of 6 congeners

e each of the 6 congeners: PCB 28, 52, 101, 138, 153, 180

f sum of 3 congeners: fluoranthene, benzo(a)fluoranthene, benzo(a)pyrene

g for pasture the limit is 0.5 mg kg⁻¹ DS

h following detailed risk assessment US EPA final decision was not to regulate PCDD/Fs (US EPA, 2003, for further discussion see Section 3.1.3)

A list of the general properties and potential environmental consequences of the main identified OC in sewage sludge are presented in Table 32.

A set of preliminary, health related numerical limits for OC (as well as potentially toxic elements (PTEs)) in soil have been developed by WHO (Chang *et al.*, 2002) for land application of wastewater and sewage sludge, with particular relevance to sludge and wastewater reuse in developing countries (Table 33). The limits were developed considering only the food chain transfer of pollutants *via* the waste → soil → plant → human route based on potential pollutant intakes from consumption of grain, vegetable, root/tuber, and fruit. This was on the basis that food chain transfer is the primary route of human exposure to environmental pollutants. Based on a global diet, daily intake of grain/cereal, vegetable, root/tuber, and fruit account for about 75% of daily adult food consumption. The exposure scenario assumed that most exposed individuals were the adult residents (60 kg in body weight) of a land application area whose entire consumption of grain, vegetable, root/tuber, and fruit were produced from the soils affected by the waste streams. Their daily intake of pollutants from consumption of grain, vegetable, root/tuber, and fruit foods was assumed to account for 50% of the acceptable daily human intake (ADI). The remaining 50% of the ADI was credited to the background exposure.

Compared with the small number of PTEs of concern in wastewater and sludge which are routinely monitored and controlled, the range of organic contaminants present in these media, with the potential to exert a health or environmental hazard, are significantly more diverse. For example, approximately 140 organic compounds have been identified in urban wastewater samples in Sweden and more than 330 organic substances have been determined in German sewage sludge. Forty two organic compounds are regularly detected in sludge (IC Consultants, 2001).

Table 32 Properties, occurrence, degradation and transfer of organic contaminant groups found in sewage sludge (Smith, 1996, quoted from Arthur Andersen on behalf of DG Environment, 2001; cited by Amlinger *et al.*, 2004) compared to data of biowaste and greenwaste compost

Compound Group	Physico-chemical properties	Conc. in compost	Conc. in sludge	Degradation	Leaching Potent.	Plant uptake	Transfer to animals
Polynuclear aromatic hydrocarbons (PAHs)	Water soluble/volatile to lipophilic	BWC: 0.8-4.5 mg kg ⁻¹ GC: 1.7-3.8 mg kg ⁻¹	1-10 mg kg ⁻¹	Weeks → 16 years Strongly adsorbed by soil O.M.	None	Very poor	Possible but rapidly metabolised
Polychlorinated Biphenyls (PCBs)	Complex, > 200 congeners low water solubility, highly lipophilic and semi-volatile	BWC: 0.03-0.86 mg kg ⁻¹ GC: 0.015-0.48 mg kg ⁻¹ mixed BWC/MC: 0.02-1.68 mg kg ⁻¹	1-20 mg kg ⁻¹	Very persistent Half-life ca. 12 years Strongly adsorbed by soil O.M.	None	Root retention Foliar absorption Minimal root uptake and translocation	Possible into milk/tissues via soil ingestion Long half-life
Polychlorinated dibenzo-P-dioxins and Furans (PCDD/Fs)	Complex, 75 PCDD congeners, 135 PCDF congeners, Low water solubility, highly lipophilic and semi-volatile	BWC: 4.3-17.5 ng I-Teq kg ⁻¹ GC: 3.6-13 ng I-Teq kg ⁻¹	Very low <few µg kg ⁻¹	Very persistent Half-life several years Strongly adsorbed by soil O.M.	None	Root retention Foliar absorption Minimal root uptake and translocation	Possible into milk/tissues Via soil ingestion Long half-life
Phthalate acid esters	Generally lipophilic, hydrophobic and non-volatile	DEHP: 0-69.6 mg kg ⁻¹ Means: BWC: 1.4-9.6 mg kg ⁻¹ GC: 0.4-2.9 mg kg ⁻¹	High 1-100 mg kg ⁻¹	Rapid Half-life <50 days	None	Root retention Not translocated	Very limited
Linear alkylbenzene-sulphonates (LAS)	Lipophilic	Only one investigation > 0: 9-396 mg kg ⁻¹ Mean: 41 mg kg ⁻¹	Very high 50-15000 mg kg ⁻¹	Very rapid in aerobic environment	None	None	None
Alkylphenols	Lipophilic	~ 200 µg kg ⁻¹	100-3,000 mg kg ⁻¹	Rapid < 10 days	None	Minimal	Minimal
Organochlorine pesticides	Varied, lipophilic to hydrophilic, some volatile	0.6 – 100 µg kg ⁻¹	<Few mg kg ⁻¹	Slow > 1 year Loss by volatilisation	None	Root retention Translocation not important Foliar absorption	Via soil ingestion persistent in tissues
Monocyclic aromatics	Water soluble and volatile	n.i.	<1-10 mg kg ⁻¹	Rapid	Moderate	Limited due to low persistence Rapidly metabolised	Rapidly metabolised
Chlorobenzenes	Water soluble/volatile to lipophilic	HCB 0-156 µg kg ⁻¹	<0.1-50 mg kg ⁻¹	Lower mol wt types lost by volatilisation Higher mol wt types persistent	High to low	Possible via roots and foliage Maybe metabolised	Important for persistent compounds
Short-chained halogenated aliphatics	Water soluble and volatile	n.i.	0-5 mg kg ⁻¹	Lower mol wt types lost by volatilisation Higher mol wt types persistent	Moderate	Foliar absorption Possible translocation	Low
Aromatic and alkyl amines	Water soluble and low volatility	n.i.	0-1 mg kg ⁻¹	Slow	High	Possible	Low
Phenol	Varied, lipophilic high water solubility and volatile	n.i.	0-5 mg kg ⁻¹	Rapid	Moderate to low	Possible via roots and foliage	None

BWC...Biowaste Compost (including source separated organic household/kitchen waste); GC...Green Compost (from garden and park waste only); n.i. ... not identified in literature

Table 33 WHO health-related guideline maximum permissible pollutant concentrations of soils receiving sewage sludge and/or untreated municipal wastewater (Chang *et al.*, 2002)

Organic compound	Soil concentration (mg kg ⁻¹)
Aldrin	0.48
Benzene	0.14
PAH (as benzo(a)pyrene)	16
Chlorodane	3
Chlorobenzene	211
Chloroform	0.47
Dichlorobenzene	15
2,4 – D	0.25
DDT	1.54
Dieldrin	0.17
Heptachlor	0.18
Hexachlorobenzene	1.40
Pyrene	41
Lindane	12
Methoylechlor	4.27
Pentachlorophenol	14
PCBs	0.89
Tetrachloroethane	1.25
Tetrachloroethylene	0.54
Toluene	12
Toxaphene	0.0013
2,4,5 – T	3.82
Trichloroethane	0.68
Phthalate	13,733
Styrene	0.68
Dioxins	0.00012

IC Consultants (2001) give an overview of the fate of OCs during wastewater and sludge treatment processes. Sewage sludge is treated to reduce its fermentability, nuisance and vector attraction and to aid its management and acceptability for use on agricultural land. These processes include physical, chemical and microbiological treatment of the sludge that may influence the loss, or potential formation, of organic contaminants. Loss mechanisms include:

- Volatilisation;
- Biological degradation;
- Abiotic/chemical degradation (e.g. hydrolysis);
- Extraction with excess liquors;
- Sorption onto solid surfaces and association with fats and oils.

The sorption of organic contaminants onto the sludge solids is determined by physico-chemical processes and can be predicted for individual compounds by the octanol-water partition coefficient (K_{ow}). During primary sedimentation, hydrophobic contaminants may partition onto settled primary sludge solids and compounds can be grouped according to their sorption behaviour based on the K_{ow} value (Section 1.1)

Many sludge organics are lipophilic compounds that adsorb to the sludge matrix and this mechanism limits the potential losses in the aqueous phase in the final effluent. A proportion of the volatile organics in raw sludge, including benzene, toluene and the dichlorobenzenes, may be lost by volatilisation during wastewater and sludge treatment at thickening, particularly if the sludge is aerated or agitated, and by dewatering. The significance of volatilisation losses of specific organic compounds during sewage treatment can be predicted based on Henry's constant (H_c) and K_{ow} (Section 1.1). However, biodegradation is also important in removing volatile organic contaminants during secondary biological wastewater treatment (WwT).

Mesophilic anaerobic digestion is the principal sludge stabilisation process adopted in most European countries and many organic contaminants are biodegraded under anaerobic conditions and this is enhanced by increasing retention time and digestion temperature. Biodegradation during anaerobic digestion may eliminate certain organic contaminants from sewage sludge, but in general the destruction achieved is typically in the range of 15 – 35 %. Aromatic surfactants, including LAS and 4-nonylphenol polyethoxylate (NP_nEO) are not fully degraded during sewage treatment and there is significant accumulation in digested sludge. For example, mass balance calculations suggest that approximately 80 % of LAS is biodegraded during the activated sludge process and 15-20 % is transferred to the raw sludge, although near complete biodegradation (97-99 %) is also reported in some cases. Approximately 20 % of LAS in raw sludge may be destroyed by mesophilic anaerobic digestion. The compounds, nonylphenol monoethoxylate (NP_1EO) and nonylphenol diethoxylate (NP_2EO) are formed during sewage treatment from the microbial degradation of NP_nEO . These metabolites are relatively lipophilic and accumulate in sludge and are also discharged in the treated effluent from WwT. Approximately 50 % of the NP_nEO in raw sewage is transformed to NP by sludge digestion.

Lower molecular weight phthalate esters and butyl benzyl phthalate are completely degraded in 7 days by anaerobic digestion at 35°C and should be removed by most municipal anaerobic digesters. The extent and rate of biodegradation of organic compounds during anaerobic digestion is apparently related to the size of alkyl side chains and compounds with larger C-8 groups are much more resistant to microbial attack. Therefore, di-n-octyl and DEHP are more persistent and are not removed by conventional anaerobic treatment of sludge. Phthalate esters are rapidly destroyed under aerobic conditions, however, and biological WwT (eg activated sludge process) can usually achieve >90% removal in 24 h. In soil, the reported half-life of DEHP is <50 d (for further discussion see Section 3.4.1).

Composting is a thermophilic aerobic stabilisation process and has the potential to biodegrade relatively persistent organic compounds in sludge. Thermophilic aerobic digestion processes and sludge storage for three months can achieve similar overall removal rates for OC as those obtained with mesophilic anaerobic digestion. Thermal hydrolysis conditioning of sludge prior to conventional anaerobic stabilisation may have a significant influence on the removal of OC from sludge, but this is a comparatively new enhanced treatment process and effects on the destruction of OC have yet to be investigated.

A detailed overview of the significance of OC in urban wastewater and sludge was undertaken by IC Consultants (2001), on behalf of DG Environment and a principal output from that work was an assessment of the significance of OCs and of potential opportunities to reduce contamination and this is shown in Tables 34 and 35.

Table 34 Assessment of the significance of organic contaminants entering urban wastewater and sewage sludge (IC Consultants, 2001)

Contaminant	⁽¹⁾ Content in WW/sludge	⁽²⁾ Priority hazardous substance	⁽³⁾ Destruction in treatment		Accumulation (Yes, Y; No, N)		Background inputs (Yes, Y; No, N)	⁽⁴⁾ Overall significance	
			Wastewater	Sludge	Biological	Soil		Wastewater	Sludge
LAS	H	N	H	L Anaerobic H Aerobic	N	N	N	H	L
NPE	M - H	Y	M	L Anaerobic H Aerobic	N	N	N	H	L
DEHP	M	(Y)	M	L Anaerobic M Aerobic	N	N	N	H	L
PAHs	L - M	Y	L	L	Y	Y	Y	L	L
PCBs	L	N	L	L	Y	Y	Y	L	L
PCDD/Fs	L	N	L	L	Y	Y	Y	L	L
Pharmaceuticals	L	N	M	M	N	N	N	M	L
Oestrogenic:									
Endogenous	L	N	M - H	M - H	Y	N	Y	H	L
Synthetic	L	N	L - M	L - M	Y	N	N	H	L

Notes:

(1)Concentration ranges for sludge: L<1 mg kg⁻¹ DS; M<100 mg kg⁻¹ DS; H>100 mg kg⁻¹ DS. Concentrations in wastewater are small (mg l⁻¹) and highly variable, but will follow a similar general pattern to sewage sludge;

(2)European Commission Amended Proposal for a European Parliament and Council Decision establishing the list of priority substances in the field of water policy (COM(2001)17 final of 16 January 2001) (CEC, 2001b);

(3)Approximate indicative ranges: L < 20 %; M = 20 – 60 %; H > 60 %

(4)Significance rating: Low, L; Moderate, M; High, H

LAS Linear alkylbenzene sulphonates

NPE Nonylphenoethoxylates

DEHP Di-(2-ethylhexyl)phthalate

PAHs Polycyclic aromatic hydrocarbons

PCBs Polychlorinated biphenyls

PCDDs Polychlorinated dibenzo-p-dioxins

PCDFs Polychlorinated dibenzo-p-furans

Table 35 Sources and control of organic contaminants entering urban waste water and sewage sludge (IC Consultants, 2001)

Contaminant	Commercial		Run-off		Domestic	
	Relative importance	Opportunity to reduce	Relative importance	Opportunity to reduce	Relative importance	Opportunity to reduce
LAS	H	M	L	L	H	M
NPE	H	M	L	L	H	L
DEHP	H	M	L	L	M	M
PAHs	L	L	H	L	L	L
PCBs	L	L	H	L	L	L
PCDD/Fs	L	L	H	L	L	L
Pharmaceutical	H	M	L	L	H	M

LAS Linear alkylbenzene sulphonates
 NPE Nonylphenolethoxylates
 DEHP Di-(2-ethylhexyl)phthalate
 PAHs Polycyclic aromatic hydrocarbons
 PCBs Polychlorinated biphenyls
 PCDDs Polychlorinated dibenzo-p-dioxins
 PCDFs Polychlorinated dibenzo-p-furans

There has been much debate about the relevance of quality standards for sludge (see Smith 2000 for an overview). The general consensus that has emerged is that they are not a priority for regulation and proposals (EC, 2000) to revise the current Directive on agricultural use of sludge (86/278/EEC; CEC, 1986), which, amongst other issues included standards for OC (Table 31), have not been taken further, but could be revisited in a future revision of this legislation. Furthermore, the EC JRC recommended that routine monitoring of dioxins (PCDD/F), PCBs and PAHs in sludge used for agricultural purposes was unnecessary. However, the JRC did raise questions about the safety of detergent residues applied to soil in sludge, due to concerns about their solubility and potential to impact aquatic systems (Erhardt and Prüß, 2001). However, the consensus of scientific opinion is that detergent residues in sludge do not pose a significant environmental or health risk (see Section 1.3). It is also emphasised that, following a detailed risk assessment, the US EPA deleted OC from the controls regulating the use of sludge in the US (US EPA, 1993), and, after a second round risk assessment, a proposed limit for dioxin and dioxin-like substances in sludge were also recently withdrawn (US EPA, 2003).

2.2.2 Persistent organic pollutants (POPs)

Source and emission controls on POPs were introduced between 1980-90 to curb environmental releases due to concerns about the extent of their occurrence and potential toxicity. This legislation has been relatively effective and there are several reliable examples in the literature (eg see Smith, 2000) illustrating significant reductions in the primary sources of PAHs, PCBs and PCDD/Fs and this has lowered inputs to the urban wastewater (UWW) system and reduced concentrations in sewage sludge (Table 36). For example, discharges of PCBs to UWW declined by >99 % in the Rhine region of France between 1985 to 1996 due to stricter industrial source control and PAHs were also reduced by >90 % over the same time period (IC Consultants, 2001). The principal inputs of these contaminants to UWW are from atmospheric deposition onto paved surfaces and run-off.

Table 36 Mean concentrations of organic contaminants in German sewage sludges in 1988/89 and compared with data from sources published till 1996 (Leschber, 1997 cited Smith, 2000)

Contaminant	1988/89	1991/96
Adsorbable organo-halogens	250-350	140-280
Polychlorinated biphenyls ⁽¹⁾	<0.1	0.01-0.04
Polycyclic aromatic hydrocarbons ⁽¹⁾	0.25-0.75	0.1-0.6
Di(2-ethylhexyl)phthalate	50-130	20-60
Nonylphenol	60-120	-
Dioxins and furans	<50	15-45

Units: mg kg⁻¹ ds except dioxins and furans, ng TEQ kg⁻¹ ds

⁽¹⁾Single congeners

Controls on combustion and incineration emissions and the production of certain potentially contaminated chlorinated pesticides have markedly reduced the release of PCDD/Fs to the environment. The emission controls have had a positive effect on the quality of sewage and PCDD/F concentrations have declined significantly. For example, the average PCDD/F concentration in sludge sampled from Spanish WwTW declined from an average value of 620 ng kg⁻¹ TEQ reported for the period 1979 – 1987 to 55 ng kg⁻¹ TEQ in 1999 (IC Consultants, 2001). In the case of sludge from a major London WwTW (Figure 8), PCDD/F concentrations decreased by >97 % in the past 40 years from 166 ng kg⁻¹ TEQ in 1960 to 4.2 ng kg⁻¹ TEQ in 1998. Typical PCDD/F concentrations reported in sewage sludge are significantly below the highly precautionary standard for agricultural utilisation (100 ng kg⁻¹ TEQ) proposed by the EC (Table 31). Indeed, the proposed numerical limit was unlikely to restrict land application yet the cost of PCDD/F analysis is high and routine monitoring of sludge for its PCDD/F content is impractical with limited statistical validity so there would appear to be no justification to require routine monitoring of these POPs in sewage sludge recycled to agricultural land.

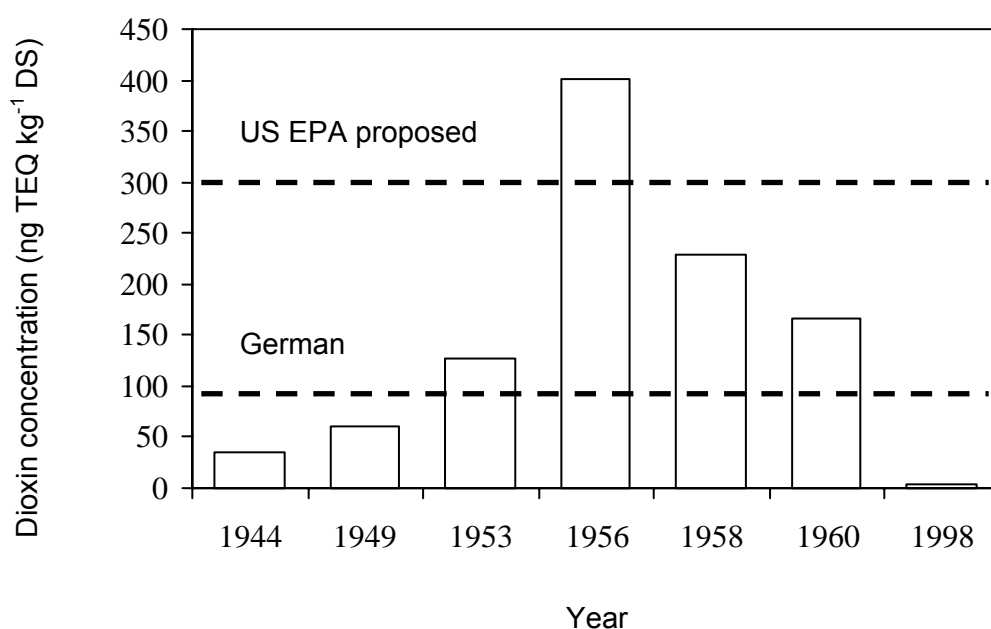


Figure 8 Dioxin content of archived samples of sewage sludge from a WWTW in West London, UK (Note: US EPA retracted the proposed limit – see Section 3.1.3) (Smith, 2000)

Historic pollution levels are important for OC as well as potentially toxic elements. For example PCBs, which are no longer used, largely result from volatilisation from soil and are found in similar concentrations generally at all WwTW (IC Consultants, 2001). This suggests either that sources are diffuse and spread evenly or that this is due to general background concentrations. Soil is an effective scavenger and sorptive medium for OC and acts as a long-term and major repository, although biodegradation also takes place. Contemporary remobilisation by volatilisation from soil and redeposition onto surfaces and consequential collection by UWW systems is a major source of these compounds entering sewage sludge.

Controls on the use and emissions of POPs have significantly reduced industrial inputs of these substances to sewer. Therefore, the concentrations present in sludge principally reflect:

- Background inputs to the sewer from normal dietary sources ;
- Background inputs by atmospheric deposition due to contemporary remobilisation/volatilisation from soil and cycling in the environment (eg PCBs, PCDD/Fs and PAHs);
- Atmospheric deposition from waste incineration (eg PCDD/Fs);
- Atmospheric deposition from domestic combustion of coal;
- The extent of biodegradation of OC during sludge treatment, which is limited for most persistent compounds;
- The extent of volatile solids destruction during sludge treatment, which increases the concentration of conservative persistent organic compounds in sludge.

Polycyclic aromatic hydrocarbons are WFD priority hazardous substances and the aim will be to achieve cessation of emissions, discharges and losses of these compounds by 2020 (COM(2001) 17 final; CEC, 2001b). However, curbing the emissions of PAHs and PCDD/Fs from domestic coal burning would be technically difficult and incinerators are already subject to stringent air quality emission standards (EPCEU, 2000a). Consequently, there is probably little opportunity to further reduce the inputs and concentrations of PAHs, PCDD/Fs as well as PCBs in UWW and sewage sludge. Furthermore, the compounds are effectively removed by WwT processes because they strongly bind to the sludge solids minimising the discharge in treated effluent. The increasing amount of scientific investigation also shows there are no significant environmental consequences from PAHs, PCBs or PCDD/Fs when sludge is used on farmland as a fertiliser (see Section 3.1). In the light of such developments, and their physico-chemical behaviour, it may be argued that these substances are no longer as environmentally important as they were in the past. Consequently, routine monitoring of these compounds in sludge for agricultural application is unnecessary (Erhardt and Pr   , 2001). Nevertheless, soil is a major repository for POPs and further investigations are necessary to improve understanding of the remobilisation and cycling processes in the environment that control diffuse inputs of these organic compounds to UWW.

Recent data on POPs are available from a major monitoring programme of WwTW influents and effluents in the UK (Bowen *et al.*, 2003). Those results for POPs are presented in Table 37, which also includes a summary of concentration values in influents, effluents and sludge, obtained from published literature. PAHs are WFD Priority Substances and had draft limits proposed in the EC working document on sludge (WDS) (EC, 2000). In the screening study PAHs were detected in the majority of samples. Total PAH values of up to 0.8 $\mu\text{g l}^{-1}$ were measured in influents, with highest individual PAH concentrations occurring for acenaphthalene (up to 0.35 $\mu\text{g l}^{-1}$). The greatest frequency of occurrence was observed for the lower molecular weight 2- and 3-benzene ringed PAHs, suggesting that inputs were dominated by petroleum sources rather than combustion-derived processes.

Comparison of PAH values with runoff percentage failed to show any correlation. This may have been a result of taking composite samples leading to dilution of runoff with crude sewage during dry periods. PAHs occur both naturally through volcanic activity and forest fires, and anthropogenically through the burning of fossil fuels and are widespread throughout the environment at low but detectable concentrations. Their presence in fuel and generation during the combustion of fossil fuels means that they would be expected to be present in runoff from roads. Focused sampling of runoff within a catchment, and collation of literature data on runoff, in future work should provide a better estimate of the contribution of runoff to PAH loads at WwTW.

Table 37 Summary of PAH, PCB and dioxin concentrations in influents and effluents to UK WwTW and in sewage sludge (Bowen *et al.*, 2003)

Information source	Screening Study on WwTW influent			Literature Review (Values are averages unless otherwise stated)		
Determinand	Max ($\mu\text{g l}^{-1}$)	Mean ($\mu\text{g l}^{-1}$)	No. of works	Influent ($\mu\text{g l}^{-1}$)	Effluent ($\mu\text{g l}^{-1}$)	Sludge (mg kg^{-1} DS)
Total PAH	0.771	0.28	25	0.79 - 51.8 (3)	0.418 - 30.8 (2)	6.4 - 72.3 (2)
Acenaphthalene	0.345	0.108	17	NR	NR	1.45 – 4.02
Fluorene	0.271	0.088	17	NR	NR	1.95 – 7.48
Phenanthrene	0.279	0.082	16	NR	NR	3.9 – 10.6
Fluoranthene	0.173	0.036	4	NR	NR	2.18 – 10.5
Pyrene	0.192	0.035	5	NR	NR	0.001 – 7.8
Benz(a)anthracene	0.084	0.029	3	NR	NR	NR
Naphthalene	0.066	0.027	2	NR	NR	NR
Anthracene	0.05	0.026	1	NR	NR	NR
Acenaphthylene	<0.05	<0.05	0	NR	NR	NR
Chrysene	<0.05	<0.05	0	NR	NR	NR
Benz(b)fluoranthene, Benz(k)fluoranthene	<0.05	<0.05	0	NR	NR	0.3 – 5.9
Benz(a)pyrene	<0.05	<0.05	0	0.022 (1)	0.005 (1)	0.78 – 10.79
Indeno(1,2,3-cd)pyrene	<0.05	<0.05	0	0.015 (1)	0.005 (1)	0.67 – 2.0
Dibenz(a,h)anthracene	<0.05	<0.05	0	NR	NR	NR
Benz(g,h,i)perylene	<0.05	<0.05	0	NR	NR	0.76 – 5.7
Polychlorinated biphenyls	0.006 ¹	0.0027 ¹	2 ¹	0.04 (1)	0.01 (1)	0.05 – 0.5 (4)
Dioxins (PCDD/F)	NM	NM	NM	0.024-16.9 (1) (Range)	NR	23 – 357 (>10 EU refs)

Notes: Literature review values are averages reported in separate papers unless otherwise stated. Values for influent and effluent are not necessarily from the same reference. NR – No references. NM – No Measurement. ¹ 7 PCBs analysed. Of these only PCB153 was detected (at 2 works).

For total PAHs, average influent values reported in the literature were lower than the average from the screening study. Perhaps this may be related to the higher predominance of coal burning in the UK compared to other European countries where data are available. For individual PAHs, the only substances for which comparisons could be made were benz(a)pyrene and indeno(1,2,3-cd)pyrene which are reported in the literature in low concentrations (0.022 and 0.015 $\mu\text{g l}^{-1}$, respectively), but were not detected in the screening study where the limit of detection (LOD) was 0.05 $\mu\text{g l}^{-1}$.

Regarding the predominance of lower molecular weight PAHs observed in the screening study, a similar distribution was noted in a survey of sewage effluents carried out by Eaganhouse and Kaplan (1982, cited Bowen *et al.*, 2003), where levels in the $\mu\text{g l}^{-1}$ range were observed. However, the fact that the higher molecular weight PAHs would partition more strongly to the sludge, owing to their higher organic carbon:water partition coefficients, may have been a contributing factor to the distribution in effluent.

PCBs comprise a group of 209 compounds which, as a group, had draft limits proposed in the EC WDS, but are not WFD Priority Substances. Seven compounds were analysed in the screening study described by Bowen *et al.* (2003). Of these only PCB153 was detected and only at 2 works, with the maximum concentration being $0.006 \mu\text{g l}^{-1}$. Only one literature study was found that included data for PCBs in WwTW influent with the average value reported of $0.01 \mu\text{g l}^{-1}$ being slightly higher than that found in the screening study. The use of PCBs is now banned but they are persistent in the environment and prone to recycling. Recent data (Jones and Northcott, 2000) indicate that PCB concentrations in UK sewage sludge are unlikely to exceed the proposed EC limit of 0.8 mg kg^{-1} DS (EC, 2000).

Dioxins, or more formally polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs) are a further group of substances that had draft limits proposed in the EC WDS but are not WFD Priority Substances. They are formed as a by-product of the combustion and manufacture of some aromatic chlorinated organic chemicals. Dioxins were not analysed in the screening study reported by Bowen *et al.* (2003) due to the very high cost of analysis and availability of literature information for the main fate compartment, namely sludge. In the literature review, one study reported values in influent in the range $0.024\text{--}16.9 \mu\text{g l}^{-1}$. With regards to sludge, recent data from the UK indicate that a minority of sludges (around 15%) would exceed the proposed EC limit of $100 \text{ ng TEQ kg}^{-1}$ DS. However, due to restrictions on many of the source chemicals for PCDD/Fs and PCBs, it is likely that concentrations in the environment, and in sludge, will continue to decline with time (Figures 5 – 7).

2.2.3 Pharmaceuticals

Data concerning the concentrations of pharmaceuticals in materials applied to land is very limited for the UK. There is limited toxicity data available for pharmaceuticals in the terrestrial environment (Jones *et al.*, 2002) though there are a reasonable amount of data for the aquatic environment.

Jones *et al.* (2002) modelled the fate of the 25 most commonly used pharmaceuticals through wastewater treatment works (WwTW). They found that the majority of substances would not be degraded within WwTW, nor would they be sorbed onto sludge and hence would be discharged in effluent. The fate model for paracetamol indicated that 98.1% of the drug entering a WwTW would exit in the final effluent. This contradicts the measurements by Hilton *et al.* (2003), however, that show paracetamol is readily degradable and hence rarely found in sewage effluents. Hilton *et al.* (2003) also suggest that tertiary treatment of wastewater increases the removal of pharmaceuticals from the final effluent, but do not indicate whether degradation is increased or if the pharmaceuticals are found in the sludge instead. Stumpf *et al.* (1998) found isoprofen removal to be 75% in an activated sludge process, but only 22% degraded by biological filtration. Maximum values in average loads of up to 3 kg day^{-1} for salicylic acid in the influent and up to 114 g day^{-1} for carbamazepine in the effluent from WwTW have been recorded (Ternes, 1998).

In the absence of measured data concerning the concentration of pharmaceuticals in sewage sludge, it is possible to calculate a theoretical maximum value based on the mass of active ingredient used and its rate of excretion. This provides an indication of the potential maximum concentration of active ingredient per tonne of sludge

produced annually. Using standard application rates a maximum application rate of pharmaceutical active ingredient may be calculated. This figure would take no account of the degradation of the active ingredient in the sewage treatment works and assumes that it is sorbed entirely onto the sludge biomass. As indicated above, studies suggest that the pharmaceuticals vary greatly in biodegradability and are present in sewage influents and effluents.

Tables 10 and 11 provide consumption data on commonly used human pharmaceuticals and Tables 38 - 40 their excretion rates. A study examining the amounts of antibiotics in human faeces found trimethoprim and doxycycline at concentrations between 3-40 mg kg⁻¹ and erythromycin at concentrations around 200-300 mg kg⁻¹ (Hirsch *et al.*, 1999). Elimination at treatment plants is usually incomplete, ranging between 60-90% (Ternes, 1998). Table 41 provides an indication of the potential input of selected pharmaceuticals to soil in sewage sludge if all of the excreted active ingredient is sorbed unaltered onto sludge solids within the treatment works. This is a worst case scenario since the evidence is that pharmaceuticals are only sorbed to sludge to a small extent and biodegradation takes place to a varying extent. A more realistic, but still precautionary calculation is to assume that 20% of the active ingredient entering the treatment works is sorbed onto sludge and hence may be applied to soil. These figures are also offered in Table 41.

Table 38 Typical excretion rates of human antibiotics (%) (Hirsch *et al.*, 1999)

Substance	%age excreted unchanged	Glucuronide	Other metabolites
Amoxicillin	80-90		10-20
Ampicillin	30-60		20-30
Chloramphenicol	5-10	70-90	
Chlortetracycline	>70		
Clarithromycin	>60		
Dicloxacillin	~65		~20
Doxycycline	>70		
Erythromycin	>60		
Minocycline	~60		~40
Oxacillin	~40		~60
Oxytetracycline	>80		
Penicillin G	50-70		30-50
Penicillin V	~40		~60
Roxithromycin	>60		
Sulfamethoxazole	~15		
Tetracycline	80-90		
Trimethoprim	~60		

Table 39 Excretion rates for some drugs for human use (Zuccato *et al.*, 2001)

Active ingredient	Percentage excretion as parent compound
Amiloride	Almost complete in urine, overall estimate 90%
Amoxycillin	60% after oral administration, in urine
Atenolol	90%, in urine
Captopril	40-50%, in urine
Ceftazidime	80-90%, in urine
Ceftriaxone	40-65%, in urine, part in faeces, overall estimate 70%
Digoxin	50-70%
Furosemide	Almost complete in urine, overall estimate 90%
Hydrochlorthiazide	Almost complete in urine, overall estimate 90%
Lincomycin	50% in urine
Lisinopril	Almost complete in urine, overall estimate 90%
Ranitidine	In urine, 30% after oral administration, 70% after parenteral administration (any route except oral), overall estimate 40%
Sobrerol	In urine, 13% after intravenous and 24% after oral administration, overall estimate 15%

In reality, of course, drugs are removed by WwT processes to a varying extent. The fate of pharmaceutical substances may be divided into three groups:

- Mineralisation to CO₂ and water, for example aspirin;
- Retained in sludge, if the compound is lipophilic and not readily biodegradable;
- Emitted to receiving water due to transformation into a more hydrophilic form but still persistent, for example clofibrate.

Typically, 60 % of the compounds in the influent may be removed although there is a wide range of removal efficiencies from 7-99% (Figure 9; Ternes, 1998). Compounds such as the analgesics, ibuprofen and naxoprofen, have removal efficiencies between 22-90 % and 15-78 %, respectively (IC Consultants, 2001). Richardson and Bowron (1985) investigated degradation of pharmaceuticals during WwT and found that many common compounds are biodegradable, although corticosteroid compounds and ethinyloestradiol, among others, are nonbiodegradable (Alcock *et al.*, 1999). Carbamazepine, clofibric acid, and phenazone also have very poor elimination efficiencies (Figure 9). Kümmerer (2000) investigated the biodegradability of two clinically important groups of antibiotics. Chinolones and nitromidazoles possess different chemical structures, activity spectra and modes of action and the study found low rates of biodegradation for ciprofloxacin, ofloxacin, and metronidazole. Also, the genotoxicity of these compounds remained unaffected during treatment and the different groups of antibiotics were active against bacteria present in wastewater. Polar antibiotics are not removed efficiently during WwT because elimination is mainly due to adsorption on activated sludge, which is mediated through hydrophobic interactions (Hirsch, 1999).

Table 40 Common pharmaceuticals found in sewage effluent and excretion rates in urine and faeces (Huschek *et al.*, 2004)

Active Substances	Sewage effluent ($\mu\text{g l}^{-1}$)	Median ($\mu\text{g l}^{-1}$)	Maximum ($\mu\text{g l}^{-1}$)	Excretion rate in urine, bile & faeces of parent drug & active metabolites (%)	Reference
Atenolol	0.19–0.27			90	
Bezafibrate	0.10–1.75	2.20	4.60	40	Ternes 1998
Bisoprolol	0.13	0.06	0.37	50	Ternes 1998
Carbamazepine	0.9–1.2	2.10	6.30	33	Ternes 1998
Clarithromycin	0.071	-	0.24	100	Hirsch <i>et al</i> 1999
Diclofenac	1.47–2.1	0.81	2.10	33	Ternes 1998
Erythromycin	0.15–0.43			25	
Ethinylestradiol		0.001	0.015	85	Ternes <i>et al</i> 1999
Gemfibrozil	0.28	0.40	1.50	76	Ternes 1998
Ibuprofen	0.054–0.35	0.37	3.40	1	Ternes 1998
Ibuprofen		0.34	1.90		Stumpf <i>et al</i> 1998
Ibuprofen-OH		0.92	5.96	>60	Stumpf <i>et al</i> 1998
Indomethacine	0.14	0.27	0.60	25	Ternes 1998
Metoprolol	0.99–1.18	0.73	2.20	33	Ternes 1998
Naproxen	0.1	0.30	0.52	10	Ternes 1998
Phenazone	0.09			3	Ternes 1998
Propranolol	0.056–0.09	0.17	0.29	NA	Ternes 1998
Propyphenazone	0.11			1	
Roxithromycin	0.11–0.52	0.68	1.00	100	Hirsch <i>et al</i> 1999
Sotalol	0.57–0.68	0.16	0.41	90	
Trimethoprim	0.16–0.42	0.32	0.66	64	Hirsch <i>et al</i> 1999

A screening programme of 49 different German WwTW effluents and river water sampling showed that lipid regulating agents were found in the majority of the effluents, and in many river samples, but in a much lower concentration (Ternes, 1998). Polar metabolites of the compounds were usually detected. For example, clofibrac acid was detected at concentrations up to $1.6 \mu\text{g l}^{-1}$ in WwTW effluent and in the ng l^{-1} range in rivers, which illustrates the importance of metabolites (Ternes, 1998). Anti-inflammatories, such as, ibuprofen and naproxen, were also detected. Diclofenac was present in the highest concentration at median values of $0.81 \mu\text{g l}^{-1}$ in treated effluent and $0.15 \mu\text{g l}^{-1}$ in rivers. In the case of betablockers, the highest median concentration was found for metoprolol at $0.73 \mu\text{g l}^{-1}$ in WwTW effluent and $0.45 \mu\text{g l}^{-1}$ in rivers. β 2-sympathomimetics were also present, but in very low concentrations. Anti-cancer agents such as cyclophosphamide and ifosamide were detected at values of $0.02 \mu\text{g l}^{-1}$ and $0.08 \mu\text{g l}^{-1}$, respectively in WwTW effluent; however, they were associated with presence of hospital effluents, and are, therefore, not widespread (Ternes, 1998). Carbamazepine, an anti-epileptic drug was widespread in the aquatic environment, with a high median value of $2.1 \mu\text{g l}^{-1}$ in effluent and $0.25 \mu\text{g l}^{-1}$ in rivers. Annual prescriptions of carbamazepine amount to

approximately 80 t y⁻¹ in Germany, however, it is metabolised and glucuronides are excreted. Treatment of wastewater cleaves these metabolites back to the parent compound, increasing environmental concentrations (Ternes, 1998).

Table 41 Potential maximum concentration of selected human pharmaceuticals in sludge if total mass excreted remains in sludge following wastewater treatment

	Quantity used in 2000 (kg) ¹	%age excreted	Mass to go into sludge (t) ²	Mass per t of sludge (g)	Mass per t sludge if 20% sorbed (g)
Amoxycillin	71,466	90-100	64.32	45	9.0
Atenolol	28,976	90	26.08	18	3.6
Carbamazepine	40,348	33	13.31	9.4	1.9
Diclofenac	26,120	33	8.62	6.1	1.2
Erythromycin	26,483	60	15.89	11	2.2
Ibuprofen	162,209	100	162.21	114	22.8
Naproxen	35,065	10	3.51	2.5	0.5
Oxytetracycline	27,195	80	21.76	15	3.0

Notes:

- 1 Jones *et al* 2002
- 2 Assuming a total UK sludge production of 1,422,000 t DS (Defra, 2006)

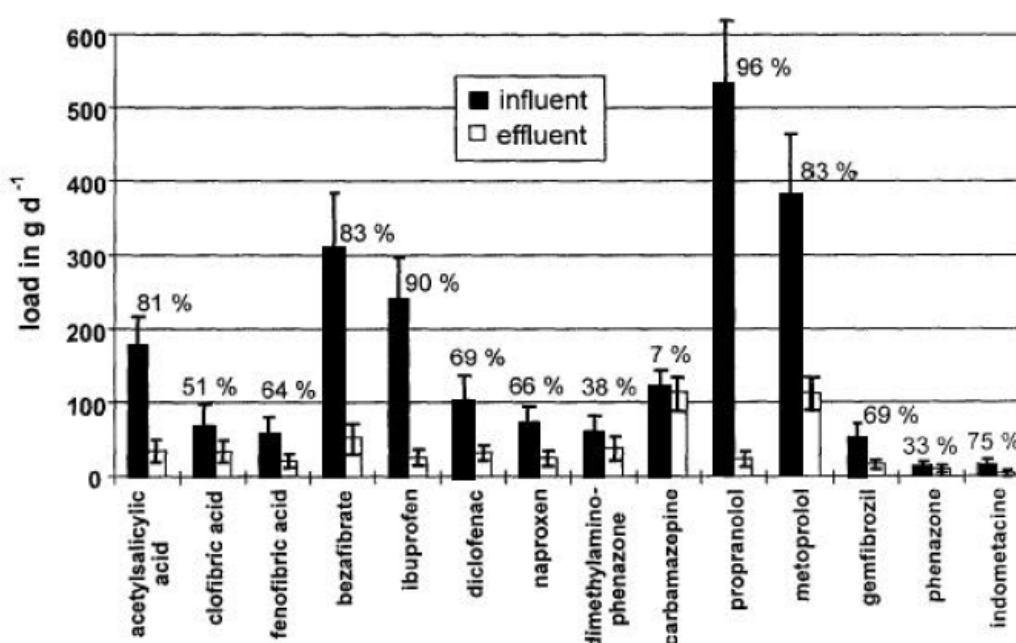


Figure 9 Elimination of different drugs during passage through a municipal wastewater treatment plant near Frankfurt/Main over 6 days (Ternes, 1998)

Consequently, river water is often polluted with traces pharmaceutical compounds. Most groups of compounds, i.e. antibiotics, antineoplastic agents, and ethinyloestradiol, have been detected between 5-10 ng l⁻¹. A study conducted by Richardson and Bowron (1985) investigated the exposure of human pharmaceuticals

in the river Lea in England and found that over 170 substances are used in excess of 1 t y^{-1} in the river's catchment. From this it was predicted that a concentration of at least $0.1 \text{ } \mu\text{g l}^{-1}$ was likely to occur in the river (Halling-Sørensen *et al.*, 1998). Thus, irrigation water abstracted from rivers represents a potential source of pharmaceutical inputs to soil.

The potential ecotoxicological significance of pharmaceuticals in sewage sludge used as an agricultural fertiliser, as well as any other type of OC applied to soil in sludge, needs to consider the persistence of the compound in soil. Table 42 gives the environmental persistence of a selection of major pharmaceutical compounds. This shows that, whilst some of the bulk use types (eg aspirin, ibuprofen, paracetamol) may be regarded as impersistent, persistences vary from <1 day to >1 year, which may be regarded as very persistent. Indeed, many pharmaceutical compounds have similar physico-chemical characteristics as other organic compounds, such as persistence and lipophilicity, but much less is known about their entry into the environment and subsequent fate (Alcock *et al.*, 1999). For instance, over 30% of all drugs produced between 1992 and 1995 were lipophilic with solubilities less than 100 mg l^{-1} (Halling-Sørensen *et al.*, 1998). For example, erythromycin and other drugs such as naproxen and sulphasalazine, have survived in the environment for over a year (Zuccato *et al.*, 2001). Clofibric acid was also found to survive for 21 years and, although its use has been stopped, it is still detected in rivers and lakes in Italy (Zuccato *et al.*, 2001).

Table 43 gives an overview of the present knowledge of the environmental fate of specific pharmaceuticals. Most hormones, such as oestrogen, are persistent in all areas and that most of the antibiotics used for human treatment are not biodegradable. The majority of other compounds used for human treatment are also non-biodegradable, with the exception of the following: paracetamol, nicotinamide, ibuprofen, caffeine, and aspirin. Lipid regulators, X-ray contrast media, antibiotics etc., are ubiquitous and extremely persistent in the environment, some are even present in drinking water: clofibric acid for example has been found at concentrations up to $0.27 \text{ } \mu\text{g.l}^{-1}$ in some German waters (IC Consultants, 2001). Only a fraction of the drugs on the market have been investigated regarding their occurrence in the environment.

Pharmaceutical substances have been found to be ubiquitous in soil samples due to excretion by livestock. They are excreted as inactive compounds but are reactivated by bacteria in the soil. However, the compounds used in veterinary treatment tend to be more biodegradable than human pharmaceuticals, although the rate of degradation depends on environmental conditions, such as pH, and temperature (Boxall *et al.*, 2004). This has caused an increase in drug resistance in the microflora of livestock and in soil, so increasing human exposure particularly to antibiotic resistant bacteria through the food chain (Halling-Sørensen *et al.*, 1998) (see Section 3.3.3).

Table 42 Environmental persistence given as $t_{1/2}$ of pharmacologically active substances, measures in the field or in laboratory conditions (multiple authors from Zuccato *et al.*, 2001)

Persistence	Active ingredient	Persistence	Active ingredient
<1 day	Aspirin	20-100 days	Cytarabine
	Diclofenac		Gemcitarabine
	Ephedrine		Mitoxantrone
	Furazolidone		Monensin
	Ibuprofen		Streptomycin
	Paracetamol		Sulfadiazine
	Penicillin		Treosulfan
	Theobromine		Trimethoprim
	Theophylline		Tylosin
	Florfenicole		Ceftiofur
1-19 days	Ivermectin	101-364 days	Flumequine
	Northisterone		Oxolinic acid
	5-Fluorouracil		Oxytetracycline
	Bacitracin		Sarafloxacin
	Bambermycin		
1 year +	Amitriptyline	Erythromycin	Pentoparbitol
	Clofibrate	Ifosfamide	Sulfadimidine
	Codeine	Meprobamate	Sulfamethoxazole
	Cyclophosphamide	Methyldopa	Sulfasalazine
	Diethylstilbestrol	Metronidazole	Tetracycline
	Dextropropoxyphene	Naproxen	Tolbutamide

Table 43 Pharmaceutical compounds identified in environmental samples (Daughton and Ternes, 1999)

Compound	Use/Origin	Environmental occurrence
Acetaminophen	Analgesic/anti-inflammatory	Removed efficiently by WwT, max. effluent $6 \mu\text{g l}^{-1}$, not detected in surface waters
Acetylsalicylic acid	Analgesic/anti-inflammatory	Ubiquitous, removal efficiency 81 %, max. effluent $1.5 \mu\text{g l}^{-1}$, in surface water $0.34 \mu\text{g l}^{-1}$
Betaxolol	betablocker	Max. effluent $0.19 \mu\text{g l}^{-1}$, in surface water $0.028 \mu\text{g l}^{-1}$
Benzafibrate	Lipid regulator	Removal efficiency 83 %, max. effluent $4.6 \mu\text{g l}^{-1}$, in surface water $3.1 \mu\text{g l}^{-1}$
Biphenylol	Antiseptic, fungicide	Extensive removal in
Bisoprolol	betablocker	Max. effluent $0.37 \mu\text{g l}^{-1}$, in surface water $2.9 \mu\text{g l}^{-1}$
Carazolol	Betablocker	Max. effluent $0.12 \mu\text{g l}^{-1}$, in surface water $0.11 \mu\text{g l}^{-1}$
Carbamazepine	Analgesic, anti-epileptic	Removal efficiency 7%, max. effluent $6.3 \mu\text{g l}^{-1}$, in surface waters $1.1 \mu\text{g l}^{-1}$
Chloroxylenol	Antiseptic	In influents and effluents $<0.1 \mu\text{g l}^{-1}$
Chlorophene	Antiseptic	Influent $0.71 \mu\text{g l}^{-1}$, removal not very efficient
Clenbuterol	β_2 -sympathomimetic	Max. effluent $0.08 \mu\text{g l}^{-1}$, in surface waters $0.05 \mu\text{g l}^{-1}$
Clofibrate	Lipid regulator	River water 40 ng l^{-1} , not detected in effluent or surface waters.
Clofibric acid	Metabolite of clofibrate	Removal efficiency 51 %, max. effluent $1.6 \mu\text{g l}^{-1}$, surface waters $0.55 \mu\text{g l}^{-1}$, up to 270 ng l^{-1} in German tap waters
Cyclophosphamide	antineoplastic	Max. effluent $0.02 \mu\text{g l}^{-1}$, not detected in surface waters, high in hospital sewage: up to 146 ng l^{-1}
Diatrizoate	X-ray contrast media	Resistant to biodegradation, median in German surface waters $0.23 \mu\text{g l}^{-1}$, locally very high concentrations can occur
Diazepam	Psychiatric drug	Max. effluent $0.04 \mu\text{g l}^{-1}$, not detected in surface waters.
Diclofenac-Na	Analgesic/anti-inflammatory	Removal efficiency 69 %, max. effluent $2.1 \mu\text{g l}^{-1}$, in surface waters $1.2 \mu\text{g l}^{-1}$
Dimethylaminophenazone	Analgesic/anti-inflammatory	Removal efficiency 38%, max. effluent $1 \mu\text{g l}^{-1}$, in surface waters $0.34 \mu\text{g l}^{-1}$
17α -ethinylestradiol	Oral contraceptive	Up to 7 ng l^{-1} in effluent, not detected in German surface waters above 0.5 ng l^{-1}
Etofibrate	Lipid regulator	Not detected in effluent and surface waters
Fenfluramine	Sympathomimetic amine	No studies but is known to be an endocrine-disrupting substance
Fenofibrate	Lipid regulator	Efficiently removed, max. effluent $0.03 \mu\text{g l}^{-1}$, not detected in surface waters
Fenofibric acid	Metabolite of fenofibrate	Removal efficiency 64%, max. effluent $1.2 \mu\text{g l}^{-1}$, in surface waters $0.28 \mu\text{g l}^{-1}$
Fenoprofen	Analgesic/anti-inflammatory	Not detected in U effluent or surface waters
Fenoterol	β_2 -sympathomimetic	Max. effluent $0.06 \mu\text{g l}^{-1}$, in surface waters $0.061 \mu\text{g l}^{-1}$
Fluorquinolone carboxylic acids	Antibiotics	Ubiquitous, led to resistance in pathogenic bacteria, strongly sorbs to soil
Fluoxetine	Antidepressant	No studies
Fluvoxamine	Antidepressant	No studies
Gemfibrozil	Lipid regulator	Removal efficiency 69 %, max. effluent $1.5 \mu\text{g l}^{-1}$, in surface waters $0.51 \mu\text{g l}^{-1}$
Gentisic acid	Metabolite of acetylsalicylic acid	Efficiently removed by WwT, max. effluent $0.59 \mu\text{g l}^{-1}$, in surface waters $1.2 \mu\text{g l}^{-1}$

Table 43 (Continued)

o-hydroxyhippuric acid	Metabolite of acetylsalicylic acid	Efficiently removed by WwT, not detected in effluent or surface waters
Ibuprofen	Analgesic/anti-inflammatory	Removal efficiency 90 %, max. effluent $3.4 \mu\text{g l}^{-1}$, in surface waters $0.53 \mu\text{g l}^{-1}$
Ifosamide	Antineoplastic	Max. effluent $2.9 \mu\text{g l}^{-1}$, not detected in surface waters, hospital sewage 24ng l^{-1} , totally refractory to removal by
Indomethacine	Analgesic/anti-inflammatory	Removal efficiency 75 %, max. effluent $0.60 \mu\text{g l}^{-1}$, in surface waters $0.2 \mu\text{g l}^{-1}$
Iohexol	X-ray contrast media	Very low aquatic toxicity.
Iopamidol	X-ray contrast media	Max. effluent $15 \mu\text{g l}^{-1}$, median $0.49 \mu\text{g l}^{-1}$
Iopromide	X-ray contrast media	Resistant to biodegradation, yields refractory, unidentified metabolites, max. effluent $11 \mu\text{g l}^{-1}$
Iotrolan	X-ray contrast media	Very low aquatic toxicity
Ketoprofen	Analgesic/anti-inflammatory	Max. effluent $0.38 \mu\text{g l}^{-1}$, in surface waters $0.12 \mu\text{g l}^{-1}$
Meclofenamic acid	Analgesic/anti-inflammatory	Not detected in effluent or surface waters
Metoprolol	betablocker	Removal efficiency 83 %, max. effluent $2.2 \mu\text{g l}^{-1}$, in surface waters $2.2 \mu\text{g l}^{-1}$
Nadolol	Betablocker	Max. effluent $0.06 \mu\text{g l}^{-1}$, not detected in surface waters
Naproxen	Analgesic/anti-inflammatory	Removal efficiency 66 %, max. effluent $0.52 \mu\text{g l}^{-1}$, in surface waters $0.39\mu\text{gl}^{-1}$
Paroxetine	antidepressant	No studies
Phenazone	Analgesic	Removal efficiency 33 %, max. effluent $0.41 \mu\text{g l}^{-1}$, in surface waters $0.95 \mu\text{g l}^{-1}$
Propranolol	Betablocker	Removal efficiency 96 %, max. effluent $0.29 \mu\text{g l}^{-1}$, in surface waters $0.59\mu\text{gl}^{-1}$
Propyphenazone	Analgesic/anti-inflammatory	Prevalent in Berlin waters
Salbutamol albuterol	β_2 -sympathomometic	Max. influent $0.17 \mu\text{g l}^{-1}$, in surface waters $0.035 \mu\text{g l}^{-1}$
Salicylic acid	Metabolite of acetylsalicylic acid	Up to $54 \mu\text{g l}^{-1}$ in effluent but efficiently removed in effluent, average in effluent $0.5\mu\text{gl}^{-1}$, in surface waters $4.1 \mu\text{g l}^{-1}$
Sulfonamides	Antibiotics	Present in landfill leachates
Terbutaline	β_2 -sympathomometic	Max. effluent $0.12 \mu\text{g l}^{-1}$, not detected in surface waters
3,4,5,6-tetrabromo-o-cresol	Antiseptic, fungicide	Found in influents and effluents in Germany $<0.1\mu\text{gl}^{-1}$
Timolol	Betablocker	Max. effluent $0.07\mu\text{gl}^{-1}$, in surface waters $0.01\mu\text{gl}^{-1}$
Tolfenamic acid	Analgesic/anti-inflammatory	Not detected in effluent or surface waters.
Triclosan	Antiseptic	$0.05\text{-}0.15 \mu\text{g l}^{-1}$ in water, very widely used.
Verapamil	Cardiac drug	No occurrence data

2.2.4 Endocrine disrupting chemicals (EDCs)

There is increasing concern about the widespread presence of oestrogenic, endocrine disrupting substances (Table 44) in wastewater and other water bodies. Natural, endogenous oestrogens (17 β -oestradiol and oestrone) and synthetic steroids such as ethinyloestradiol, which is the active oestrogenic component in oral contraceptives, are discharged in trace amounts in the effluent from WwTW and are primarily a concern due to possible endocrine disrupting effects on the aquatic ecosystem.

The daily production rate of natural oestrogens by humans is in the microgram range, up to 400 μg of 17 β -oestradiol for women (Ternes *et al.*, 1999). The maximum daily excretion rate is 64 μg for oestriol (Ternes *et al.*, 1999). Oestrogens are mainly excreted as inactive polar conjugates (Ternes *et al.*, 1999). Vitellogenin (precursor for production of yolk in all oviparous vertebrates) induction in male or juvenile fish has become a “biomarker” for the presence of oestrogenic substances in the aquatic environment (Larsson *et al.*, 1999). In the UK, caged fish downstream of a WwTW were found to produce vitellogenin. Two possibilities were investigated: the presence of ethinylestradiol and NPE. This prompted investigation of a Swedish WwTW, which on analysis of the effluent showed high concentrations of oestrogenic compounds (Larsson *et al.*, 1999). It was found that exposure to large amounts of ethinyloestradiol caused accumulation in fish, as fish concentrations were found to be 10^4 - 10^6 times higher than those detected in the water (Larsson *et al.*, 1999). The estimated use of ethinyloestradiol was equivalent to a theoretical mass of 3.5 mg day⁻¹, which is close to the mass found in the WwTW effluent (2.9 mg day⁻¹), indicating very limited degradation of this compound during treatment (Larsson, 1999).

Table 44 Categories of substances with endocrine-disrupting activities (Environment Agency, 1998 cited IC Consultants, 2001)

Category	Examples	Uses	Modes of action
Natural			
phytoestrogens	Isoflavones, lignans	Present in plants	Oestrogenic and anti-oestrogenic
Female sex hormones	17 β -oestradiol, oestrone	Produced in animals	Oestrogenic
Man-made			
Polychlorinated organic compounds	PCBs, dioxins	By-products from incineration and chemical processes	Anti-oestrogenic
Organochlorine pesticides	DDT, dieldrin, lindane	Insecticides	Oestrogenic and anti-oestrogenic
Alkylphenols	Nonylphenol	Production of NPE and polymers	Oestrogenic
Alkylphenol ethoxylates	NonylPhenol Ethoxylate (NPE)	Surfactant	Oestrogenic
Phthalates	Dibutyl phthalate	Plasticiser	Oestrogenic
Bi-phenolic compounds	Bisphenol A	In polycarbonate plastics and epoxy resins	Oestrogenic
Synthetic steroids	Ethinyl oestradiol	Contraceptives	Oestrogenic

Of these compounds, oestrogens are of a major concern, as they are excreted in an inactive form, but are found to be reactivated in sewage effluent. In the UK, analysis of sampled effluents found that natural hormones (17 β -oestradiol and oestrone) were present in the range 1.4 to 76 ng l⁻¹, whereas the synthetic hormone

(ethinyloestradiol) was only found in 3 out of the 7 effluents analysed and at comparatively low values: 0.2 to 7 ng l⁻¹ (Alcock *et al.*, 1999). The source of these is thought to be mainly from human excretion products. It was also found that the hormones were present in the biologically active form, suggesting that they had been transformed and reactivated after excretion (Alcock *et al.*, 1999).

In Germany, raw sewage was found to contain 0.015 µg l⁻¹ of 17β-oestradiol and 0.027 µg l⁻¹ of oestrone and it was also found that oestrone and 17α-ethinyloestradiol were not efficiently removed during WwT (Ternes *et al.*, 1999). In contrast, 17β-oestradiol and 16α-hydroxy-oestrone were eliminated with a higher efficiency of 64-68% (Ternes *et al.*, 1999) (Figure 10).

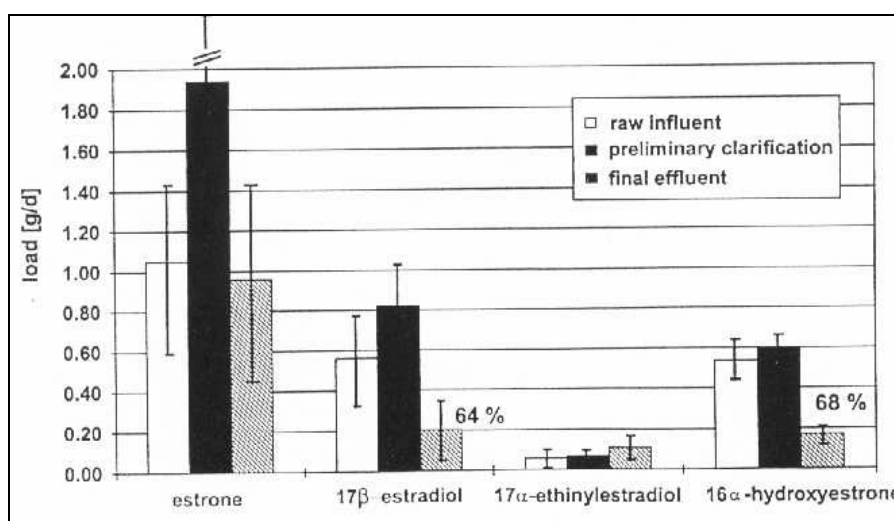


Figure 10 Elimination percentages and loads of estrogens during passage through a municipal wastewater treatment plant located near Frankfurt/Main over 6 days (Ternes *et al.*, 1999)

In discharges from the treatment plants, all compounds could be detected in the ng l⁻¹ range (Ternes *et al.*, 1999), however oestrone was predominant with concentrations up to 0.07 µg l⁻¹ and a median value of 0.009 µg l⁻¹. The compounds 17α-ethinyloestradiol and 16α-hydroxy-estrone were found at the detection limit of 0.001 µg l⁻¹ (Ternes *et al.*, 1999). Oestrone was the only compound detected in 3 of the 15 rivers sampled at concentrations between 0.7 and 1.6 ng l⁻¹ (Ternes *et al.*, 1999). This was consistent with the poorer degradation particularly of the natural oestrogenic compound, oestrone, observed in the treatment system. Nevertheless, the loads entering receiving waters were small. Therefore, it is the natural, endogenous hormones, oestrone and 17β-oestradiol, and to a much lesser extent the synthetic hormone ethinyloestradiol, that are considered primarily responsible for oestrogenic activity observed within treated sewage effluents. Approximately, 90 % of potential oestrogenic activity (based on 17β-oestradiol equivalency) in UWW is reduced by WwT and <3 % may be transferred to the sewage sludge (Young *et al.*, 1997). Oestrogenic compounds partition onto particulates and may be associated with sewage sludge, but there is no information on the amounts of endogenous oestrogens or ethinyloestradiol in sludge and only limited information on their biodegradation (Young *et al.*, 1997). However, this is unlikely to have significant environmental implications for use of sludge in agriculture (IC Consultants, 2001). Oestrogenic substances excreted in the wastes of farm livestock are likely to represent a much greater loading onto soil compared to recycling sewage sludge.

2.2.5 Pesticides

Interest in the presence of persistent pesticide compounds, particularly the organochlorine insecticide group of compounds, in sewage sludge has been shown alongside the other types of POP potentially present in sludge, due to concerns relating to soil accumulation and long-term impacts on the environment (Bowen *et al.*, 2003). Modern pesticide compounds have been developed with improved biodegradabilities during WwT and in the environment in general, so their presence is less of a concern in general than in the past. However, varying persistences and ecotoxicities are reported (Boxall *et al.*, 2004) and these give rise to important potential consequences for the environment. However, the potential implications for soil quality arise more from direct application to crops and soils and from application (managed and direct) of wastes to soil from livestock administered with these compounds rather from inputs *via* agricultural application of sewage sludge or irrigation waters.

During WwT processes, organic compounds are subjected to a variety of biological and physico-chemical attenuation processes. A major removal mechanism is sorption onto the sludge solids and, as a general rule, substantial association with sewage sludge is unlikely for substances whose octanol-water partition coefficients are <1000 ($\log K_{OW} < 3$). Partitioning of modern pesticide compounds currently licensed for use varies from negligible to approximately 30 % (Table 45).

Table 45 Percentage of pesticide substances expected to partition to sewage sludge based on octanol-water partitioning co-efficient (Rogers *et al.*, 2001)

Pesticide	Log K_{OW}	% predicted to partition to sludge solids
Atrazine	2.61	3
Azinphos methyl	2.7	4
Diazinon	3.8	34
Dichlorvos	1.43	0
Dimethoate	0.5	0
Linuron	3.2	12
Mecoprop	2.3	2
Mevinphos	3.13	10

Notes:

Above percentages were calculated assuming that the sludge solids content was 1000 mg l^{-1} , that $K_{OC} = K_{OW} \times 0.41$ and that the fraction of the organic carbon in sewage solids is 0.2.

Bowen *et al.* (2003) was only able to detect tributyl tin (TBT), which is a WFD Priority Hazardous Substance, of the principal pesticide and biocide compounds they screened for in UK WwTW influents and effluents (Table 46). The predominant route by which pesticides and biocides are likely to enter wastewater systems is *via* urban runoff from treated verges, paths and forecourts. The occasional detection of TBT at WwTWs is somewhat surprising given that the main use of this substance is in antifouling agents for boats and this has been restricted to professional application since 2000. A complete ban on the use of TBT for antifouling occurred from 2003, but the use of some products in timber treatment is still permitted.

With regard to the other pesticides, these are a combination of WFD Priority Substances and Dangerous Substance Directive List 1 substances. List 1

Substances such as DDT and organochlorines (aldrin, dieldrin, endrin and isodrin) are banned for use in the UK and would not be expected to be present with the exception, potentially, of inputs from historically contaminated land. Other pesticides, such as the triazines (atrazine and simazine) and the 'urons (diuron and isoproturon) are predominantly used in agricultural applications. The predominant route to the water environment is therefore likely to be *via* direct runoff from agricultural land. This is reflected in the literature where there are virtually no data reported on pesticide concentrations entering WwTW or in effluent or sludge.

Atrazine and simazine are now banned from amenity use (for example on hardstanding), but are present in some amateur pesticide products and these substances have occasionally been detected at WwTW in the past. The 'urons, in particular diuron, can be used in the urban environment for weed control. Although none of these substances were detected in the screening study, their possible presence in WwTW cannot be ruled out as they are likely to be applied seasonally.

Overall, however, the available data indicate that sewage sludge and receiving waters used for irrigation are unlikely to be significant sources of pesticide contaminants entering soil compared to the specific managed use of these compounds in agricultural and other land management situations.

Table 46 Summary of pesticide concentrations concentrations in influents and effluents to UK WwTW and in sewage sludge (Bowen *et al.*, 2003)

Information source	Screening study on WwTW influent			Literature review (Values are averages unless otherwise stated)		
Determinand	Max ($\mu\text{g l}^{-1}$)	Mean ($\mu\text{g l}^{-1}$)	No. of works	Influent ($\mu\text{g l}^{-1}$)	Effluent ($\mu\text{g l}^{-1}$)	Sludge (mg kg^{-1} DS)
Alachlor	<0.005	<0.005	0	NR	NR	NR
Trifluralin	<0.005	<0.005	0	NR	NR	NR
Simazine	<0.005	<0.005	0	NR	0.03	NR
Atrazine	<0.005	<0.005	0	NR	0.02	NR
HCH	<0.005	<0.005	0	NR	<LOD	NR
Aldrin	<0.005	<0.005	0	NR	NR	NR
Isodrin	<0.005	<0.005	0	NR	NR	NR
Dieldrin	<0.005	<0.005	0	NR	NR	NR
Endrin	<0.005	<0.005	0	NR	NR	NR
Endosulphan	<0.005	<0.005	0	NR	<LOD	NR
DDT	<0.005	<0.005	0	NR	<LOD	NR
Isoproturon	<2.0	<2.0	0	NR	NR	NR
Diuron	<1.0	<1.0	0	NR	NR	NR
TBT	0.063	0.013	3	0.06 – 0.2 (Range)	NR	0.3 – 0.1 (Range)

Notes:

Literature review values are averages reported in separate papers unless otherwise stated. Values for influent and effluent are not necessarily from the same reference. NR – No references.

2.2.6 Bulk chemicals

Other potentially important groups of OC entering urban wastewater were identified by IC Consultants (2001). Direct or indirect discharges of OC may arise from their use in commercial and domestic activities. For example, the principal emissions of DEHP occur from the use of finished products and major domestic inputs to UWW are floor and wall coverings and textiles with PVC prints. In Sweden, for example the domestic contribution was equivalent to approximately 70 % of the total load of phthalates to Gothenburg WwTW. Numerically, detergent surfactants and residues (LAS and NPE) are the most significant contaminants in sewage sludge (Table 30). Linear alkylbenzene sulphonate and NPE can be substituted in detergent formulations and alternative plasticizers would also need to be sought if DEHP is classified as a WFD Priority Hazardous Substance (it is currently under review; Annex F) in plastics manufacture to reduce emissions of this substance to water. The use of NPEs in detergents is likely to end with the implementation of European legislation to phase out discharges, losses and emissions of alkylphenolic compounds to the aquatic environment. A comprehensive independent review, also involving the detergent and plastics manufacturers, regarding the fate, behaviour, degradability, toxicity and environmental consequences of these and the alternatives compounds would provide information on the advantages and disadvantages of product substitution in detergent formulations and plastics manufacture as well as determine the implications for soil quality.

2.2.7 Other compounds

A group of emerging compounds of potential significance in urban wastewater (UWW) were identified by IC Consultants (2001) and Stevens *et al.* (2003) due to their persistence during wastewater or sludge treatment, persistence in soil or toxicity in the environment:

1. Little is known about the fate and behaviour in UWW of the large number (>200) of commercial chlorinated paraffin formulations in use as plasticisers in PVC and other plastics, extreme pressure additives, flame retardants, sealants and paints.
2. The polybrominated diphenyl ethers (PBDEs) are a group of compounds used for flame retardation in furnishings, textiles and electrical insulation and their use has expanded due to fire regulation requirements and the increased use of plastic material and synthetic fibres. A survey in Sweden indicated concentrations of PBDE congeners in sludge were between 15 and 19 $\mu\text{g kg}^{-1}$, respectively. PBDEs are on the WFD list of proposed priority hazardous substances, the CSF list of chemicals of concern (Defra, 2005a) and the UK proposed PRTR for water (EA, 2005). Action was taken in Europe to prohibit the use of pentaBDE and OctaBDE and the placing on the market of articles containing one or both of these substances taking effect from 15 August 2004 (EPCEU, 2003). Therefore, emissions to UWW and presence in sludge is expected to decrease.
3. Polychlorinated naphthalenes (PCNs) are released into the environment by waste incineration and landfill disposal of items containing PCNs. Concentrations in sewage sludge may be in a similar range to individual PCB congeners. A survey of Swedish sludges indicated that PCN concentrations were in the range 1.6 mg kg^{-1} DS. Stevens *et al.* (2003) reported the mean ΣPCN concentration measured in digested sludge samples from 14 UK WwTW was 83 $\mu\text{g kg}^{-1}$ DS (Table 30) Some PCN congeners have dioxin like activity and have been assigned TCDD toxic equivalent values similar to those for coplanar PCBs and so have toxicological interest.

4. A small amount of Quintozene (pentachloronitrobenzene) is produced in the EU (21.5 t y^{-1}) and it is registered for use in the UK, Spain, Greece and Cyprus. It has low water solubility and half-lives in soil are reported to be in the range 5 – 10 months.

5. Polydimethylsiloxanes (PDMS) are nonvolatile silicone polymers used in industrial and consumer products including lubricants, electrical insulators and antifoams. They are hydrophobic and partition onto the sludge solids and concentrations in N American sludge are reported to be in the range $290 - 5155 \text{ mg kg}^{-1}$. However, PDMS do not bioconcentrate or exhibit significant environmental toxicity, but they are relatively persistent in soil and can take months to years to degrade.

6. Nitro musks (chloronitrobenzenes) are a group of synthetic dinitro- trinitro-substituted benzene derivatives used as substitutes for natural musk in perfumed products. In Europe, current consumption is estimated to be 124 t y^{-1} for musk ketone and 75 t y^{-1} for musk xylene and the release of these compounds to the environment is dominated by domestic discharges in wastewater. The average sum of detectable synthetic musk concentrations measured in UK sewage sludges by Stevens *et al.* (2003) was 32 mg kg^{-1} (Table 30). Nitro musks were not detected as these have now largely been replaced by polymusk compounds in Europe because of concerns regarding the safety and bioaccumulation of nitro musks (Stevens *et al.*, 2003),

7. Polychlorinated *n*-alkanes (PCAs) are used as extreme pressure additives in metal working fluids, flame retardants in rubbers and textiles, plasticizers/flame retardants in paints, coatings and sealant/adhesives, and as fat liquoring agents in leather processing. Stevens *et al.* (2003) detected very high concentrations of PCAs in UK sludge and considered this as indicative of chemicals with numerous and ongoing diffuse sources. Total concentrations of the short- (C10-13) and medium (C14-17) chained PCAs ranged between $7 - 200 \text{ mg kg}^{-1} \text{ DS}$ and between $37 - 9700 \text{ mg kg}^{-1} \text{ DS}$, respectively. The presence of significant concentrations in sludge derived from treating entirely domestic sources indicated PCAs may be present in some household products entering the wastewater stream. Their occurrence in sludge in larger amounts than other groups of compounds, such as PCBs and organochlorine pesticides that have largely been phased out, is expected as PCAs have been widely used. Nichols *et al.* (2001) detected short- and medium chained PCAs in sediment ($<0.2-65.1 \text{ mg kg}^{-1} \text{ dw}$), water ($<0.1-1.7 \mu\text{g l}^{-1}$), fish ($<0.1-5.2 \text{ mg kg}^{-1} \text{ fw}$), benthos ($<0.05-0.8 \text{ mg kg}^{-1} \text{ fw}$), digested sludge ($1.8-93.1 \text{ mg kg}^{-1} \text{ DS}$) and earthworms ($<0.1-1.7 \text{ mg kg}^{-1} \text{ fw}$), and concluded that they were widely distributed in the UK environment, although it was not possible to assess the risks posed to wildlife or humans from their continued use. Interestingly, PCAs were not detected in the same soil ($<0.1 \text{ mg kg}^{-1} \text{ ds}$) that the earthworms were exposed to, suggesting bioaccumulation of PCAs from soil receiving sludge. However, short-chained PCAs (C10-13) are classified as WFD priority hazardous substances and are identified as compounds posing extremely high hazard levels, equivalent to the properties of POP-like compounds. Therefore, chloroalkanes (C10-13) will become subject to severe restrictions within the Community (CEC, 2001) so their concentrations in the environment should be expected to decline in future.

2.3 Livestock manures

2.3.1 Persistent organic pollutants

Stevens and Jones (2003) quantified PCDD/Fs in samples of cattle, pig, sheep and chicken manure. TEQs ranged from 0.19 ng TEQ kg⁻¹ DS for pig manure to 20 ng TEQ kg⁻¹ DS for one cattle manure sample. Exposure assessments showed that spreading cattle manure (or sewage sludge) did not increase the PCDD/F TEQ background exposure. It was concluded that application of cattle manure to agricultural land does not make a significant contribution to human exposure to PCDD/Fs. Consequently, POPs are not a concern for livestock manures.

2.3.2 Veterinary medicines

Veterinary medicines are used extensively in livestock production to treat disease and protect the health of domestic animals. Consequently, medicinal compounds are present in the excreta of farm animals and direct deposition or managed application of manures to land provides a direct route of entry to the soil (Figure 2). In the UK, approximately 40-45% of the therapeutic use of the 459 t of antimicrobials used are administered to pigs. This suggests that areas of pig production or where pig slurry is regularly applied will be most liable to impact from the presence of antimicrobial compounds in manures (Burch, 2003). Boxall *et al.* (2003a; 2004) reviewed the use and environmental significance of veterinary medicines in the UK. This included a literature survey of compound concentrations in different media. The majority of data reported from UK sources were for surface and groundwaters and sediments (Table 47). Data for soil concentrations and those materials added to soil such as manures were largely absent for the UK. The available data presented by Boxall *et al.* (2003a; 2004) for soil and animal manures are listed in Table 48.

Haller *et al.* (2002) considered six different sources of slurry from cattle and pig farms that had been using medicinal feed during a study to develop analytical techniques appropriate for assessing antibiotic concentrations in manures (Table 49). Sulfamethazine was detected in all six samples while five samples contained its metabolite N-acetyl-sulfamethazine in concentrations 2 to 50 times below the concentrations of the parent compound. Although this metabolite itself is not antimicrobial, Berger *et al.* (1986) (cited Haller *et al.*, 2002) showed that it is transformed into its parent compound in manure and hence has the potential to exert an antimicrobial action. Total active sulfonamide concentrations (sulfamethazine + sulfathiazole) were greater than 20 mg kg⁻¹ (fresh weight). Minimum inhibition concentrations for sulfonamides eg for *E. coli*, are <1 mg kg⁻¹ and with manure applications of 50 m³ ha⁻¹, sulfonamide residue inputs to soil of 1 kg ha⁻¹ may not be unusual (Haller *et al.*, 2002) and may therefore exert a toxic effect on the soil microbial community.

The slurry in each sampling pit had been collected over a period of time, including when no medicines were being administered. Consequently, the manure was diluted with material from medication free time periods. The extent to which antibiotic contaminated slurry is diluted in this way depends on the size of the slurry storage tank, relative to the period over which the drug is being administered, and the rate of slurry production. Further, degradation will take place during the storage period, regardless of any dilution. This suggests that manure excreted directly in the field has the potential to contain much higher concentrations of antibiotic than material from housed stock, which may be diluted with uncontaminated slurry (Boxall *et al.*, 2004).

Table 47 Summary of measured environmental concentrations of veterinary medicines detected in surface and groundwater and sediment (ng l⁻¹ unless otherwise stated) (Boxall *et al.*, 2004)

Veterinary medicine	Surface water	Ground water	Sediment
Chlorfenvinphos	up to 30800	up to 70	
Chloramphenicol	0.06 µg l ⁻¹	-	-
Chlortetracycline	0.5 µg l ⁻¹	0.17-0.22 µg l ⁻¹	-
Coumaphos	30	-	-
Cypermethrin	1-85100	-	-
Desmethyldamino metabolite	-		>0.5
Diazinon	3-0.58 x 106	up to 216	-
Emamectin benzoate	nd	-	0.25-2.73
Fenchlorphos	<10-777	-	-
Flumethrin	1-2190	-	-
Ivermectin	-	-	trace-6.8 ng g ⁻¹
Monensin	-	-	
Oxolinic acid	-	-	<0.05-0.2 µg g ⁻¹
Oxytetracycline		0.15-0.19 µg l ⁻¹	0.1-285 µg g ⁻¹
Propetamphos	- up to 19.2 x 106	up to 489	
Sulphamethazine	-	00.08-0.16 µg l ⁻¹	-
Tetracycline	-	0.11-0.27 µg l ⁻¹	-
Tylosin		0.13-0.42±0.47 µg l ⁻¹	

Table 48 Concentrations of veterinary medicines found in soil and manures (from Boxall *et al.*, 2004)

Compound	Therapeutic use	Concentration detected (ng l ⁻¹ unless otherwise stated)	LOD (ng l ⁻¹ unless otherwise stated)	Country
Soil				
Chlortetracycline	Antibiotic	0.7±0.2-9.5±2.8 µg kg ⁻¹	0.7 µg kg ⁻¹	Germany
		<1-26.4 µg kg ⁻¹	1 µg kg ⁻¹	Germany
		1.2-41.8 µg kg ⁻¹	1 µg kg ⁻¹	Germany
Ivermectin	Endectocide	0.1-2 µg kg ⁻¹	1 µg kg ⁻¹	USA
Monensin	Coccidiostat	0.8-1.08 mg kg ⁻¹	-	Canada
Oxytetracycline	Antibiotic	0.9±0.1-8.6±4.5 µg kg ⁻¹	0.7 µg kg ⁻¹	Germany
Tetracycline	Antibiotic	1.2±0.1-12.3±5.6 µg kg ⁻¹	0.7 µg kg ⁻¹	Germany
		<1-32.2 µg kg ⁻¹	1 µg kg ⁻¹	Germany
		1.1-39.6±33.6 µg kg ⁻¹	1 µg kg ⁻¹	Germany
Tylosin	Antimicrobial	nd/trace	0.2 µg kg ⁻¹	Germany
Cattle faeces/manure				
[¹⁴ C]ceftiofur	Antibiotic	11.3-216.1 mg kg ⁻¹ (equivalent)	-	USA
Chlortetracycline	Antibiotic	7.6±2.7 µg kg ⁻¹	-	Germany
Ivermectin	Endectocide	12-75 µg kg ⁻¹	10 µg kg ⁻¹	USA
		0.3± 0.0-9.0±0.7 mg kg ⁻¹	0.03 mg kg ⁻¹	Denmark
		0.2-3.8 mg kg ⁻¹ (dry wt)	-	Tanzania
		0.07-0.36 mg kg ⁻¹ (wet wt.)	-	Australia
		0.353 mg kg ⁻¹	-	USA

Table 48 (Continued)

Compound	Therapeutic use	Concentration detected (ng l-1 unless otherwise stated)	LOD (ng l-1 unless otherwise stated)	Country
Cattle faeces/manure				
Ivermectin	Endectocide	13-80 µg kg ⁻¹	-	USA
		0.24-0.27	-	USA
Monensin	Coccidiostat	0.7-4.7		Canada
Sulphadimethoxine	Antimicrobial	300-900 mg kg ⁻¹		Italy
Tetracycline	Antibiotic	2.5±1.2 µg kg ⁻¹		Germany
Pig faeces/manure				
Chlortetracycline	Antibiotic	3.4-1001.6 µg kg ⁻¹	-	Germany
Ivermectin	Endectocide	0.22-0.24 mg kg ⁻¹	-	USA
Tetracycline	Antibiotic	44.4-132.4 µg kg ⁻¹	-	Germany
Sheep faeces/manure				
Ivermectin	Endectocide	0.63-0.714 mg kg ⁻¹	-	USA
Poultry faeces/manure				
Chlortetracycline	Antibiotic	22.5 µg g ⁻¹	-	Canada
[14C]narasin	Antibiotic	1±0.3-725±60.3 µg kg ⁻¹ (equivalent)	-	USA
Horse faeces/manure				
Ivermectin	Endectocide	0.05-8.47 µg g ⁻¹	0.05 µg g ⁻¹	USA

Table 49 Sulfonamide and trimethoprim residues in manure samples (mg kg⁻¹ fresh weight, n=51) (Haller *et al.*, 2002)

Compound	Mother pigs with farrows			Fattening pigs			Fattening calves
	A	B	C	D	E	F	
Sulfamethazine	8.7	(8.9)	5.5	3.3	0.23	0.13 (0.11)	3.2
4 N -Acetyl-sulfamethazine ¹	2.6	(2.7)	0.59	0.15	nd	det	det
Sulfathiazole	12.4	(12.4)	det	nd	0.10	0.17 (0.17)	nd
Trimethoprim		det	nd	nd	nd	nd	nd
Dried mass content (%)	3.3		3.4	1.8	3.7	3.2	1.1

Notes:

Results determined by external calibration (and determined by standard addition in parenthesis for samples A and E).

det = Detected, but below 0.1 mg kg⁻¹ and therefore not quantified.

nd = Not detected; Sulfaguanidine, sulfadiazine, sulfamethoxazole and sulfadimethoxine were not detected in any of the samples.

¹ metabolite of sulfamethazine.

De Liguoro *et al.* (2003) conducted a study of the fate of oxytetracycline and tylosin in intensive calf farming. Fifty simmental calves were treated for 5 days with 60 mg kg⁻¹ day⁻¹ of oxytetracycline (OTC). After 15 days the animals were treated for 5 days with 20 mg kg⁻¹ day⁻¹ of tylosin (TYL). Tylosin degraded rapidly, and was not detected in manure 45 days after cessation of treatment and no trace of the compound was detected in soil or surrounding water. The half-life of OTC in manure was 30 days and the compound was still detectable in this matrix after 5 months maturation. However, in the manured soil OTC was detected at concentrations at least 10 times lower than the European Agency for the Evaluation of Medicinal Products threshold (100 µg kg⁻¹) requiring phase II environmental risk assessment. Oxytetracycline was not detected in the water courses (detection limit 1 µg l⁻¹). These results demonstrated that the processes occurring between faeces production and application of manure to the soil are very effective in reducing the load of TYL and OTC in the environment. The persistences of a range of commonly used classes of antibiotic veterinary medicines in manure were reported by Boxall *et al.* (2004) and are listed in Table 50. These show that sulfonamides, aminoglycosides, β-lactams, and macrolides have half-lives of 30 d or less and are therefore likely to be significantly degraded during manure or slurry storage, which is typically for an average period of 6 and 9 months, respectively. In contrast, ivermectin, tetracyclines and quinolones are highly persistent with half-life values of 100 days in manure. Thus, draft manure and slurry management practices recommended by the Food Standards Agency to mitigate risks from microbial pathogens (FSA, 2002), by ensuring adequate storage and composting (eg >3 months storage; composting solid manures by turning to achieve >55 °C for 3 days), are also likely to reduce the concentrations of veterinary medicines in livestock manures. Further work is therefore recommended to assess the effectiveness of livestock manure management methods at enhancing the degradation of veterinary medicines.

Table 50 Persistence of major classes of veterinary medicines in manure (Boxall *et al.*, 2004)

Chemical group	Compound	t _{1/2} (d)	Persistence class
Aminoglycosides	Unspecified	30	Moderately persistent
Beta-lactams	Unspecified	5	Slightly persistent
Macrolides	Tylosin	<2	Not persistent
	Unspecified	21	Slightly persistent
Macrolide endectins	Ivermectin	>45	Moderately persistent
Quinolones	Unspecified	100	Very persistent
Sulphonamides	Sulfachloropyridazine	<8	Slightly persistent
	Unspecified	30	Moderately persistent
Tetracyclines	Unspecified	100	Very persistent
Others	Amprolium	>8	Slightly persistent
	Meticlorpindol	>8	Slightly persistent
	Nicarbazin	>8	Slightly persistent

Note: Classification of persistence (DT₅₀ is the time (days) taken for 50 % of a compound to decay – half-life):
 impersistent, DT₅₀<5 d;
 slightly persistent, DT₅₀ 5-21 d;
 moderately persistent, DT₅₀ 22-60 d;
 very persistent, DT₅₀>60 d.

2.4 Compost

2.4.1 Compost production in UK

Current statistics on compost production in the UK are reported by Slater *et al.* (2005). The survey of UK composting shows the amount of material composted increased by 20 % between 2001/2 and 2003/4 to 1.97 million t. Of the 1.97 Mt of wastes composted, 73% was household waste, 4% municipal non-household waste and 23% commercial wastes. During 2003/04 there was an expansion in composting garden waste, which accounted for 95% of municipal wastes composted, and virtually all household wastes composted. Approximately 1.2 Mt of compost was produced, of which, the largest fraction was used as soil conditioners (61 %), followed by mulches (16 %). Other fractions including growing media constituent and ingredients in manufactured topsoil, whilst turf dressings accounted for the remainder. Compost products are distributed to several markets and outlets. Agriculture is both the largest and the fastest growing outlet. Approximately 40 % of composted product went to agriculture in 2003/04 reflecting an increase in on-farm composting. A further 36 % was utilised in markets with a sales value including horticulture, landscaping and domestic gardening. Quality assurance of composted products is also expanding with over 850,000 t of material complying with at least one independently certified standard. The utilisation of composted products in landfill engineering fell by 18% from 2001/2 and, when combined with product used in land restoration, accounted for the remaining 24 %.

2.4.2 Standards for organic contaminants in compost

An extensive review of compost standards within the EU, North America and Australasia has been prepared by Hogg *et al.* (2002) on behalf of the Waste

Resources Action Programme (WRAP; www.wrap.org.uk). Some countries have established limit values for OC in compost and the European Commission proposed limits for PAHs and PCBs in stabilised biowastes (EC, 2001), including composts and digestates, in its preliminary proposals for a Biowaste Directive (Table 51). The Commission is not currently proceeding with its earlier plan for a Biowaste Directive or for EU-wide compost quality standards. In Germany and the Netherlands no limit values for OC were considered necessary because of the low level that has been detected in composts derived from the source-separated materials. The Federal German Council, however, requested the German Federal Government to investigate the need for limit values for harmful organic compounds before 31 December 2002. Analyses of the pesticide content in bio- and green waste in Germany and Luxembourg have also shown that very low concentrations are present. The UK BSi *Specification for Composted Materials*, Publicly Available Specification 100 (PAS100) which was revised in 2005 (BSi, 2005) does not include limits for OC in compost. In Australian state guidelines for biosolids, limit values appear for PCBs and for a number of pesticide (usually herbicide) products. Typically, these limits cover lindane, heptachlor, DDT and derivatives, and the drins (aldrin, dieldrin, etc.). Indeed, a number of local regulations exist concerning the use of pesticides in gardens, partly related to concerns for the fate of these once composted. It is notable also that Denmark, with its high rate of composting of garden waste, has tight legislation concerning pesticides and recently implemented a ban on the use of garden pesticides.

Pesticides of concern which have been frequently detected in composts include: carbaryl, atrazine, chlordane, 2,4-D, dieldrin, chlorpyrifos, diazinon, malathion, and others (Swedish EPA, 1997). Degradation-resistant herbicides have been identified as a source of plant phytotoxicity of composts, even at very low concentrations and this raises the possibility that all composts may be required to pass a bio-assay to assure absence of potential to harm plants (Hogg *et al.*, 2002).

Table 51 Limit values for organic contaminants in compost (Hogg *et al.*, 2002)

OC type	Austria	Denmark	Luxembourg	EU ⁸
	<i>Mixed MSW compost only</i>	<i>Biowaste compost (1 analysis per year)</i>	<i>Guide values for fresh and matured compost</i>	<i>Stabilised biowaste⁹</i>
PCB ¹	1 mg kg ⁻¹ DS		0.1 mg kg ⁻¹ DS (4 analysis per year)	0.4 mg kg ⁻¹ DS
PCCD/F ²			20 ng kg ⁻¹ DS (4 analysis per year)	
Dioxins	50 ng ITEQ kg ⁻¹ DS			
PAH ³	6 mg kg ⁻¹ DS	3 mg kg ⁻¹ DS	10 mg kg ⁻¹ DS (2 analysis per year)	3 mg kg ⁻¹ DS
AOX ⁴	500 mg kg ⁻¹ DS			
Hydrocarbons	3000 mg kg ⁻¹ DS			
LAS ⁵		1300 mg kg ⁻¹ DS		
NPE ⁶		30 mg kg ⁻¹ DS		
DEHP ⁷		50 mg kg ⁻¹ DS		

Note:

¹ PCB: Polychlorinated biphenyls; ² PCCD/F: Polychlorinated dibenzofuran; ³ PAH: polycyclic aromatic hydrocarbons; ⁴ AOX: Absorbable organic halogens; ⁵ LAS: linear alkylbenzene sulphonates; ⁶ NPE: nonylphenol; ⁷ DEHP: Di (2-ethylhexyl) phthalate.

⁸Working Document Biological Treatment of Waste 2nd Draft (EC, 2001) (The European Commission is not currently proceeding with its earlier plan for a Biowaste Directive or for EU-wide compost quality standards)

⁹Normalised to an organic matter content of 30 % DS.

In the US, the banning of chemicals that enter compost has been discussed, in Washington State and New York, for certain herbicides that are very persistent to degradation (e.g., chlorpyralid and picloram). Research into the fate of these chemicals in compost suggests they may decompose slower in compost than in natural soils (Hogg *et al.*, 2002). The debate on how to rationalise banning a particular use, but to permit another similar use has influenced pesticide policy development in Denmark and is now being considered in the US. This may require an assessment of the final fate of the treated plant residues and if composting is to be the destination, then the use of these types of pesticide compound may be unsuitable. Pesticide products for garden use provide advice on the time intervals required before composting plant residues, eg lawn clippings, following treatment with residual herbicides, for instance.

2.4.3 Biowaste, green and mixed municipal waste-derived compost

A recent extensive review of heavy metals and organic compounds from composted wastes used as fertilisers was reported by Amlinger *et al.* (2004). This primarily reports on the quality of compost from source separated collection schemes and considered:

- Biowaste compost (BWC) from organic household waste including kitchen waste;
- Green compost (GC) from garden and park waste materials (grass clippings, bush and tree cuttings, leaves, flowers etc.);
- Mixed municipal solid waste-derived compost (MSWC);
- The stabilised organic waste fraction from mechanical biological treatment plants (MBTC).

Selection criteria for the evaluation of OC were set based on their potential occurrence in compost, the availability of published data, knowledge of physico-chemical properties and feasibility of chemical analysis. The compounds considered were:

- Polychlorinated biphenyls (PCB),
- Polychlorinated dibenzodioxins and dibenzofurans (PCDD/F),
- Polycyclic aromatic hydrocarbons (PAHs),
- Chlorinated pesticides and adsorbable organic halogen (AOX) (*aldrin, biphenyl, o-phenylphenol chlordane, dieldrin, endrin, heptachlor, DDT [1,1,1-trichlor-2,2-bis(p-chlorophenyl)ethan], lindane, HCH-isomers [hexachlorcyclohexan], hexachlorobenzene, hexachlorobenzol, heptachlor, pentachlorophenol, pyrethroides, thiabendazole*),
- Linear alkylbenzene sulphonates (LAS),
- Nonylphenol (NPE),
- Di (2-ethylhexyl) phthalate (DEHP),
- Butylbenzyl phthalate (BBP),
- Dibutyl phthalate (DBP).

Soil accumulation scenarios were performed for: PCBs, PCDD/F and PAHs, since these compounds are the best documented and show comparatively high persistency.

Conclusions for the key substances covered by reliable literature data in the area of organic waste and its recycling via composting were:

PCB: Since PCBs have been excluded from industrial processes since the 1980s a continuous reduction in their occurrence in the environment can be expected. In general, they were detected in higher concentrations in composts stemming from urban areas. Some, but not all, investigations reviewed showed higher concentrations in biowaste than in green compost. PCB content in composts from mixed municipal solid waste was approximately 50 to 100-fold higher than that found in compost from source separated bio and green waste. The observed reduction of PCBs during composting was up to a maximum of 45 % through either biodegradation or volatilisation. However, there are considerable uncertainties since, given the concurrent mineralisation/volatilisation of part of the organic substrate, generally higher concentrations tended to be found in compost than in feedstock. Degradation occurs mainly for congeners with lower chlorination. Input of PCBs to soil from compost was considerably less than atmospheric deposition rates. Assuming a half-life ($t_{1/2}$) of 12 years reported in literature, and average concentrations in composts, no accumulation in soils can be expected. Even in a worst-case scenario ($t_{1/2}$ =50 years) the soil precautionary reference value of the German Soil Protection Ordinance (0.05 mg kg^{-1}) would not be reached within 100 years also assuming a comparatively high PCB concentration of 0.1 mg kg^{-1} DS in compost.

PCDD/F: The concentration of PCDD/F in composts mainly depended on the background concentrations in the soil and the source material following diffuse emissions in the catchment area of the composting plant. A differentiation between urban and rural areas could not be clearly identified. Mean values of several investigations demonstrated a trend towards lower values in green compost than in biowaste compost. A trend of continuous decrease of PCDD/F values over time in composts was observed. PCDD/F content in composts from mixed municipal solid waste was typically 50 to 100 times higher than in compost from source separated bio- and green waste. In general PCDD/F tended to concentrate during the degradation process, mostly due to the mass loss during mineralisation of organic matter. Biowaste and green waste feedstocks showed generally lower concentrations than the finished composts. The reported initial generation during the rotting process only contributed to a negligible degree to dioxin content in composts and only occurred with temperatures were $>70^\circ\text{C}$ in the presence of primary substances such as *trichlorophenol* and *pentachlorophenol*. Higher temperatures are sought only for a short period to ensure sanitisation, although many regulations require 55 to 60°C to be reached for hygienisation. Most tests conducted during the composting process of biowaste showed an increase of hepta- and octa- PCDD. On the other hand, the content of low chlorinated PCDD/PCDF decreased during the composting process (thereby leading to a decrease in overall toxicity). PCDD/F input to soil by regular compost application was estimated to be in the same range as, or slightly higher than, mean atmospheric deposition rates. However, none of the scenarios modelled showed long term accumulation of PCDD/F in soil, even when no decay in soil was assumed. In most cases a decrease in soil concentration was found as, despite the long half-life of these compounds, this more than compensates for the inputs through atmospheric deposition and compost application.

PAHs: The relevant spatial and temporal variability of PAH may be explained by seasonal differences in the composition of the raw material, by different collection capture areas or individual contamination with extraneous materials (e.g. ashes). From the literature considered, higher concentrations for urban areas than for rural areas can be assumed. There was only a slight trend indicating higher values in

biowaste compost than in green compost. PAH concentrations in organic wastes were higher than in compost. PAH content in composts from mixed municipal solid waste was typically 1 to 10 times higher than in compost from source separated bio- and green waste. Though PAHs show a high persistency in soils they undergo an effective reduction under aerobic degradation conditions by up to 70 %. This includes volatilisation as well as biodegradation, which is a particularly effective loss mechanism during the maturation stage of composting. Though a certain accumulation of PAHs may occur in soils with low background concentrations (ca. < 0.5 mg kg⁻¹ DS) precautionary soil threshold values would not be attained even in the long term.

Overall, the review concluded that concentrations of PCBs, PCDD/F and PAHs in BWC and GC were similar to background concentrations in soils. This lead to the conclusion that regular measurements of PCBs, PCDD/F and PAHs and the establishment of limit values for these compounds are not required for the safe use of compost derived from source separated organic waste materials. Due to the comparatively higher concentrations found in mixed waste compost, however, Amlinger *et al.* (2004) recommended that these compounds should be monitored when mixed waste compost is used as a soil amendment. They recommended the use of mixed waste compost should be limited to non-food areas such as land reclamation of brown fields and surface layers on landfill sites or on noise protecting walls beside roads or railways. However, this would appear to be an overly precautionary restriction on the use of composted municipal waste products. There is no evidence that POPs are detrimental to soil or human health (Section 3.1) and concentrations in the environment and municipal solid waste are declining due to source and emission controls. This is further emphasised as the theoretical accumulation models for POPs in compost amended soil reported by Amlinger *et al.* (2004) showed no long-term build up or impact on soil quality under highly conservative, worse-case conditions (Figure 11). Furthermore, the maximum concentrations of PCDD/Fs measured in compost derived from mixed waste collection systems, that were available in the literature reviewed by Amlinger *et al.* (2004), were below the most conservative limits for these POPs in sewage sludge (Table 31). Maximum PCB and PAH concentrations also fall within risk derived limits for these contaminant groups for the most sensitive environmental exposure pathways (US EPA, 1992b; Chaney *et al.*, 1997), which are also applicable to MSWC (Chaney and Ryan, 1993).

The conclusions from the soil accumulation modelling for these contaminants were that:

- (1) For PCB no accumulation would occur under realistic half-time assumptions ($t_{1/2}$ = 12 years). Half-life degradation would fully compensate inputs by deposition and compost. Only a moderate increase in soil concentration could be expected when very compost concentrations were assumed. When a worst case scenario of a half-life of $t_{1/2}$ = 50 years was assumed, accumulation occurred when starting at low background soil concentration. Nevertheless a low soil guide value of 0.05 mg PCB kg⁻¹ was not exceeded.
- (2) PCDD/F: No accumulation occurred in any of the scenarios. In most of the cases a considerable decrease in soil concentration was observed, even assuming an unrealistic, conservative degradation rate of $t_{1/2}$ = 100 years.
- (3) Though a certain accumulation of PAHs was predicted to occur in soils with low background concentrations (ca < 0.5 mg kg⁻¹ ds.) precautionary soil threshold values would not be reached in the long term.

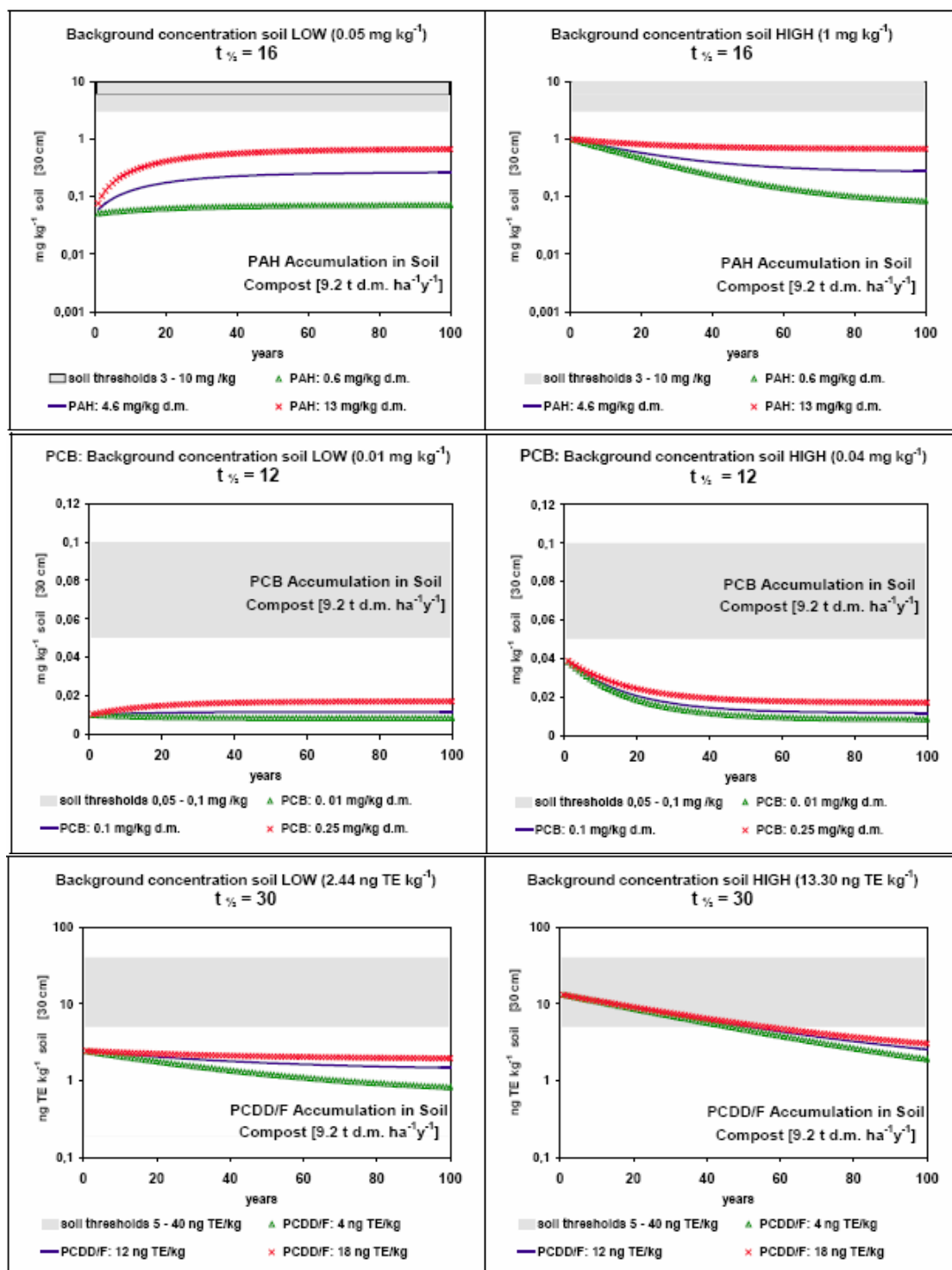


Figure 11 Theoretical changes in PAH, PCB and PCDD/F concentrations in soil following repeated annual applications of compost (Amlinger *et al.*, 2004)

Thus, under the worse-case conditions assumed in the soil accumulation scenarios, the changes in soil concentrations of PCDD/Fs, PCBs and PAHs from compost application were of no concern compared to precautionary soil threshold values and, compared to atmospheric deposition, the input by compost was considered as very low (PCB) at a similar level (PAH) or slightly higher (PCDD/F).

Groeneveld and Hébert (2005) measured the concentrations of dioxins/furans, dioxin-like PCBs and PAHs in 14 composts produced in the provinces of Québec and Nova-Scotia, Canada. Dioxins and furans were low, with an average of 9.7 ng I-TEQ kg⁻¹ DS, and a range of 1.0 to 31 ng I-TEQ kg⁻¹. All composts met the Québec C2 criteria for dioxins and furans of 50 ng I-TEQ kg⁻¹ or less, and 86 % met the C1 criteria of 17 ng I-TEQ kg⁻¹ or less. Dioxin/furans in all the compost samples tested were between 10 and 300 times lower than the risk based limit of 300 ng TEQDFP (TEQDFP-WHO98, sum of dioxins (D), furans (F) and dioxinlike compounds (P)) originally proposed by the U.S. Environmental Protection Agency (USEPA). On average, dioxin-like PCBs represented less than 20 % of the TEQDFP total. The PAH content was generally low, over 96 % of all analyses were below either the detection or quantification limit. Groeneveld and Hébert (2005) therefore concluded that the inclusion of dioxins/furans, PCBs, or PAHs as parameters in compost quality criteria was not justified.

Brändli *et al.* (2005) compiled literature data on some priority POPs in compost and its main feedstock materials from more than 60 reports. Median concentrations of $\Sigma 16$ PAHs, $\Sigma 6$ PCBs and $\Sigma 17$ PCDD/Fs were higher in green waste (1803, 15.6 $\mu\text{g kg}^{-1}$ dry wt., and 2.5 ng I-TEQ kg⁻¹ dry wt.) than in organic household waste (635, 14.6 $\mu\text{g kg}^{-1}$ dry wt., and 2.2 ng I-TEQ kg⁻¹ dry wt.) and kitchen waste (not available [NA], 14.9 $\mu\text{g kg}^{-1}$ dry wt., 0.4 ng I-TEQ kg⁻¹ dry wt.) (Figures 12 - 14). The POP concentrations in foliage were up to 12 times higher than in other feedstock materials. In contrast, compost from organic household waste and green waste contained similar amounts of $\Sigma 16$ PAHs, $\Sigma 6$ PCBs, and $\Sigma 17$ PCDD/Fs (1915, 39.8 $\mu\text{g kg}^{-1}$ dry wt., and 9.5 ng I-TEQ kg⁻¹ dry wt. and 1715, 30.6 $\mu\text{g kg}^{-1}$ dry wt., and 8.5 ng I-TEQ kg⁻¹ dry wt., respectively). Concentrations of three-ring PAHs were reduced during the composting process, whereas five- to six-ring PAHs and $\Sigma 6$ PCBs increased by roughly a factor of two, due to mass reduction during composting. $\Sigma 17$ PCDD/Fs accumulated by up to a factor of 14. Urban feedstock and compost had higher POP concentrations than rural material, corresponding to the pattern observed in other environmental compartments. The highest concentrations of POPs were usually observed in summer samples, in accordance with observed seasonal fluctuations in the environment for PCBs, but not for PAHs and PCDD/Fs. Median compost concentrations of POPs were greater by up to one order of magnitude than in arable soils, as the primary recipients of compost, but were well within the range of many urban soils.

Therefore, of the seven types of feedstock examined by Brändli *et al.* (2005), foliage contained the highest concentrations of PAHs, PCBs and PCDD/Fs. Bark, shrub clippings and grass exhibited the lowest concentrations of POPs, followed by kitchen waste, organic household waste and green waste. The elevated concentrations of these semi-volatile compounds in green waste and foliage may be explained by the efficient filter characteristics of these materials. Organic household waste and green waste composts contained similar amounts of POPs, because the former is often blended with significant amounts of green waste to achieve an aerobic composting process. Whereas the PAH concentration in compost fell between the amounts measured in the different feedstocks, PCBs in compost were at the higher end of feedstock concentrations. This suggests degradation/volatilisation of the lower PAH congeners, but this was not apparent for heavier PAHs and PCBs or for PCDD/Fs.

The increase in PCDD/F concentrations in compost, compared to feedstock materials was larger than could be accounted for by the mass balance and loss of volatile solids during composting. Comparison of the main POP compound classes investigated suggested that atmospheric deposition may be a relevant input source for most of these semi-volatile pollutants. PAH or PCB concentrations may also be elevated possibly due to inputs from traffic emission, ashes or impurities, or also due to pesticide applications.

Data for PCBs and PCDD/Fs in compost derived from greenwaste are reported by Defra (2004b) and are listed in Table 52. These values are consistent with the concentration ranges reported by Amlinger *et al.* (2004) in Table 32.

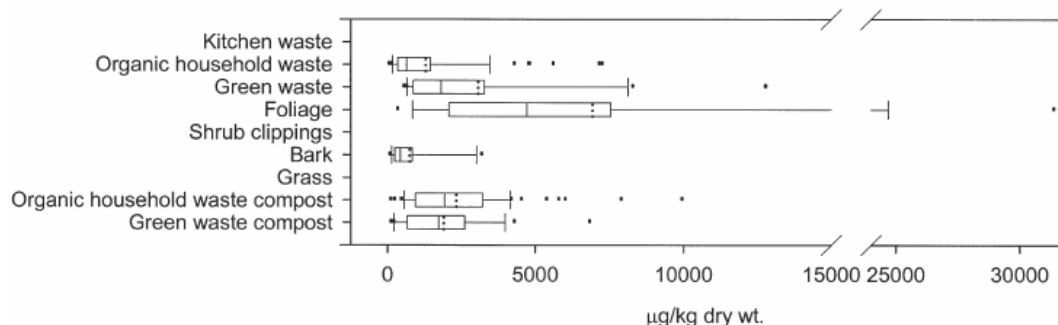


Figure 12 Sum of 16 USEPA polycyclic aromatic hydrocarbons ($\Sigma 16$ PAHs; $\mu\text{g kg}^{-1}$ dry wt) in kitchen waste (not available [NA]), organic household waste ($n = 69$, one study only), green waste ($n = 31$), foliage ($n = 13$, one study only), shrub clippings (NA), bark ($n = 18$, one study only), grass (NA), compost containing organic household waste ($n = 78$), and compost originating from green waste ($n = 23$). Line: median; dotted line: mean; box: 25th and 75th percentile; lines with whiskers: 10th and 90th percentile; dots: outside values (Brändli *et al.*, 2005)

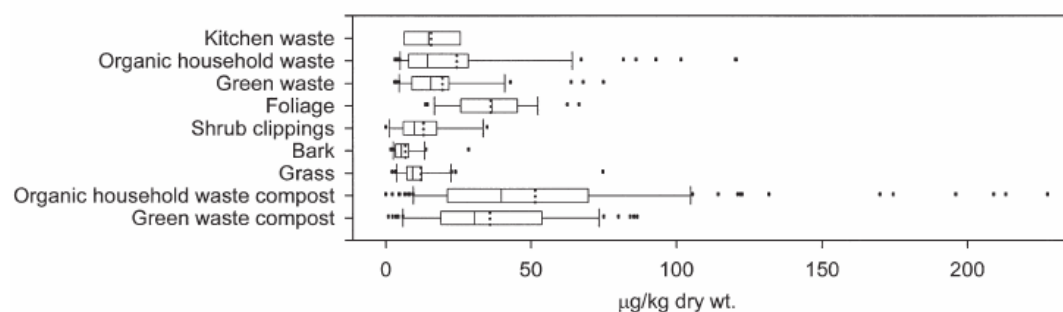


Figure 13 Sum of six polychlorinated biphenyls ($\Sigma 6$ PCBs; $\mu\text{g kg}^{-1}$ dry wt) in kitchen waste ($n = 8$, one study only), organic household waste ($n = 82$), green waste ($n = 41$), foliage ($n = 29$), shrub clippings ($n = 12$, one study only), bark ($n = 20$), grass ($n = 39$), compost containing organic household waste ($n = 124$), and compost originating from green waste ($n = 55$). Line: median; dotted line: mean; box: 25th and 75th percentile; lines with whiskers: 10th and 90th percentile; dots: outside values (Brändli *et al.*, 2005)

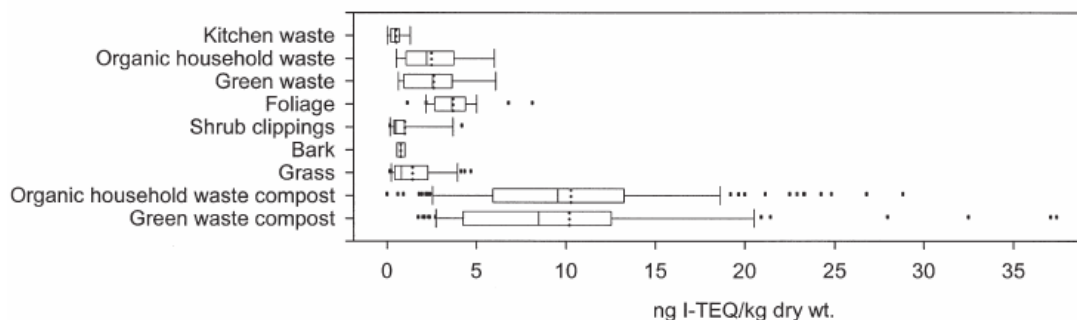


Figure 14 Sum of 17 polychlorinated dibenzo-*p*-dioxins and -furans ($\Sigma 17$ PCDD/Fs; ng international toxicity equivalent [I-TEQ] kg^{-1} dry wt.) in kitchen waste ($n = 9$, one study only), organic household waste ($n = 9$), green waste ($n = 9$), foliage ($n = 28$), shrub clippings ($n = 12$, one study only), bark ($n = 4$), grass ($n = 36$), compost containing biowaste ($n = 124$), and compost originating from green waste ($n = 61$). Line: median; dotted line: mean; box: 25th and 75th percentile; lines with whiskers: 10th and 90th percentile; dots: outside values (Brändli *et al.*, 2005)

Table 52 PCB and PCDD/F concentrations in compost derived from green waste (Defra, 2004b)

Contaminant	Emissions per t of waste processed (g t^{-1})			UK impacts
	Minimum	'Best estimate'	Maximum	
PCBs	0.018	0.06	0.102	36 kg y^{-1}
PCDD/Fs (ng TEQ)	1.2	17	34	18 mg TEQ y^{-1}

AOX and Pesticides: The majority of chlorinated pesticides are banned in the EU. A considerable number have been analysed in compost (Table 53), but they are rarely detected and only in very small amounts (Amlinger *et al.*, 2004; Brändli *et al.*, 2005). Generally biowaste composts have larger concentrations than green compost. Organochlorine pesticides, pyrethroides and thiabendazole were below related limit values for fertiliser regulations or were close to the lowest detection limit (Amlinger *et al.*, 2004). The variety of compounds within the group of chlorinated pesticides and absorbable organic halogens (AOX) gives a wide range of properties and related behaviour during composting. Comparisons of the pesticide concentrations in feedstock versus the end composted products showed that composting tends to substantially decrease the concentrations of most compounds. Frequently, thermophilic process conditions were favourable to breakdown the investigated substances. Specific case studies on chlorophenols consistently indicated their high degradability during composting. Therefore, they are not considered as substances with priority for analysis in compost or digestate from anaerobic treatment. In general, the patterns of pesticide degradation in composting parallel the patterns found in soil, but in several studies, pesticide compounds disappeared faster during composting than they typically do in soils, as indicated by their soil half-life values. From the literature reviewed it was concluded that there is no indication for the need for regular analyses of AOX or specific pesticides. This is mainly based on general low background concentrations (Table 32) as well as degradation behaviour during composting. However, given the high persistence/toxicity of compounds used for wood preservation, a precautionary measure would be to exclude pesticide treated wood from the production of marketable compost products or any recycling in

agriculture. Biphenyl, a fungicide used widely in citrus production, was detected in all composts (Table 52) and it is suggested that the main route of entry is via organic household wastes (Brändli *et al.*, 2005). Other citrus fungicides (eg *o*-phenylphenol and thiabendazole) were also detected in compost whereas pesticides such as cyfluthrin, deltamethrin and fenpropathrin, were rarely measured and reported (Table 53).

Table 53 Organochlorine pesticides and other compounds in compost (Brändli *et al.*, 2005)

	Median concentration [†] µg/kg dry wt.	Number of samples analyzed	Number of detections	Number of reports [‡]
Organochlorines				
Aldrin	0	88	6	5
Chlordane	0	97	22	7
Dieldrin	0	91	37	6
Endosulfan	0	45	5	3
Endrin	0	87	36	5
Heptachlor	0	53	9	6
Heptachlorepoxyd	0	49	11	5
Σ DDT§	8.1	66	55	4
Σ hexachlorohexane (HCH)	0	45	13	3
Hexachlorobenzene (HCB)	1.2	142	98	10
Pentachlorobenzene	0.7	47	36	4
Pentachlorophenol	14	100	98	7
Tetrachlorobenzene	0.4	33	26	2
Other compounds				
Biphenyl	48.5	28	28	2
Cyfluthrin	0	15	3	1
Deltamethrin	0	15	4	1
Fenpropathrin	0	15	5	1
<i>O</i> -phenylphenol	20	28	21	2
Thiabendazole	7.1	23	13	3
Di(2-ethylhexyl)phthalate (DEHP)	300	79	64	7
Polybrominated diphenylethers (PBDE)#	12.2	12	12	1

[†] Median is zero if more than 50% could not be quantified.

[‡] For detailed references see Table 1.

[§] Sum of *o,p'*-DDD, *o,p'*-DDE, *o,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, and *p,p'*-DDT.

^{||} Sum of α-, β-, γ-, and δ-HCH.

[#] Sum of IUPAC congeners #17, #28, #47, #66, #71, #85, #99, #100, #138, #153, #154, #183, and #190.

LAS, NPE, DEHP, PBDE: The Danish Decree for the agricultural use of sewage sludge and waste derived composts is the only regulation that specifies limit values for LAS, NPE, DEHP. Those compounds are rapidly degraded under aerobic composting conditions. Extremely low concentrations were found in the literature reviewed by Amlinger *et al.* (2004). Thus, there is no evidence of a need for general threshold or limit values. The median concentration of DEHP in compost reported by Brändli *et al.* (2005) was 300 µg kg⁻¹ DS. The DEHP content was larger in compost containing organic household waste (1300 µg kg⁻¹ DS) than in green waste compost (84 µg kg⁻¹ DS). This indicated a potentially larger plastic content of organic household waste compared to green waste. Polybrominated diphenylethers (PBDEs) are used as flame retardants and are detected at increasing concentrations in the environment and were present at 12.2 µg kg⁻¹ DS in compost (Brändli *et al.*, 2005).

2.4.4 Mushroom compost

Fungicides, disinfectants and insecticides are used in mushroom production. The spent mushroom compost (SMC) may then be applied to land and is frequently marketed for horticultural use. The use of SMC in agriculture, gardening and landscaping means that any pesticide residues contained therein will be added to soil with the SMC.

The mushroom industry in Great Britain is dominated by about 15 very large scale producers. MAFF statistics indicated that annual fresh mushroom production in Great Britain was just under 80,000 t in 1999. Production in Northern Ireland is much more diffuse with a large number of relatively small scale growers whose combined production is approximately 40% of that in Great Britain.

Mushroom production is approximately 25-30 kg m⁻² of compost (Mushroom Bureau <http://www.mushroom-uk.com/education/growing.htm>). Matured product yields around 1.4 m³ t⁻¹ and has a density of 0.7. Fresh SMC has a density of 0.55 to 1.8 m³ t⁻¹.

The amount of SMC produced by the industry can be approximated from mushroom production data. Thus, fresh mushroom production of 1,000 lbs per week (equivalent to 453 kg per week), the unit traditionally used in the industry, generates between 160 and 170 m³ fresh spent mushroom compost (SMC) per year (DETR, 2000a). This is equivalent to one tonne of mushrooms generating 7-7.5 m³ of SMC, equivalent to about 394,000 m³ of SMC in 2003 (Table 54). Mushroom production in the UK fell by about 32% between 1999 and 2003 (Table 54) and it follows that compost production would fall similarly. No figures are available for 2003 SMC production hence the same proportionate distribution between outlets has been assumed for 2003 (Table 54). Equally, no specific data were available for the amount of SMC used in agriculture so it has been assumed that spreading to agricultural land accounts for the SMC not used in the other three outlets. By this calculation, agriculture utilised about 50% of SMC produced annually. The estimated annual total production of SMC is in the range 400,000-600,000 t and therefore represents a relatively significant quantity compared to other industrial and biowastes applied to land (Table 4).

Table 54 Production of mushrooms and spent mushroom compost in 1999 and 2003 (from DETR, 2000a; Defra 2005b)

	1999	2003
Mushroom production (t y⁻¹)	79,439	53,345
Compost make (m³ y⁻¹)	556,073-595,792	387,415-400,087
Adjusted compost make (m³ y⁻¹)^a	575000	394000
Outlets		
Gardeners	77500	53104 ^b
Local authorities	14000	9593 ^b
Landscape industry	190500	130534 ^b
Agricultural land ^c	293000	200769

Notes:

- a amount of compost generated annually rounded to average of range
- b figures calculated from 1999 ratios
- c assumed from difference between total amount of compost generated and that used in other outlets.

Pesticides are applied predominantly as sprays or drenches (43%) or in irrigation systems (47%) with aerosol and wash-down methods accounting for 5% each. Insecticides and disinfectants are used between crops and hence are applied directly to the compost and surrounding trays, boxes and ancillary equipment. Pesticides are used at all stages of crop production. Fruiting bodies, ie mushrooms, are present on the compost surface for only about two weeks of the crop production cycle. On average, crops receive two treatments of disinfectant, one of insecticide and one of

fungicide, during each crop cycle (CSL, 2004b). The use of pesticides by the mushroom industry in Great Britain is shown in Table 55.

Table 55 Use of pesticides on mushrooms grown in Great Britain 2003 (CSL 2004)

	Treated square metres	kg active substance used
Disinfectant		
Formaldehyde	459,883	4,040
Sodium hypochlorite	3,080,175	893
All disinfectants	3,540,058	4,933
Fungicides		
Carbendazim	353,647	426
Prochloraz	3,832,452	1,775
Pyrifenox	142,084	142
All fungicides	4,328,183	2,343
Insecticides		
Bendiocarb	357,958	28
Diflubenzuron	338,653	298
Other insecticides	23,485	1
All insecticides	720,096	326
All registered pesticides ¹	8,667,543	7,603
Biological control agents		
Steinernema feltiae	675,569	
Heterorhabditis megidas	5,695	
All biological control agents	681,264	
All non-registered substances ²	5,668,350	152,039

Notes:

- 1 Registered pesticide refers to those active substances and formulations approved under the Control of pesticides Regulations (COPR) 1986 as amended and the Plant Protection Products Regulations (PPPR) 2003.
- 2 Non-registered substances does not infer non-approved use of pesticides but refers to the use of chemicals and biological control agents which do not come under COPR (1986) or PPPR (2003).

Whilst mushroom production has fallen by about 30 % since the 1999 survey, over the same period the mass of pesticide active ingredient use has decreased by 68%. This is accounted for by a fall in insecticides use of 82%, disinfectants by 74% and fungicides by 26%, largely due to the withdrawal of the Approval of several active ingredients, with no replacement alternative compound approved for these particular uses. In both the 1999 and the 2003 surveys, there was no record of the use of compost sterilants, though their use was recorded in previous surveys (CSL, 2004b). The use of organophosphates and organochlorines is also absent from the 2003 survey data.

In conclusion, SMC is likely to potentially contain pesticides and residues of other chemicals, but the range and quantities of chemicals applied appear to have diminished in recent years due to the withdrawal of pesticides previously approved for use in mushroom production. Nevertheless, given the uncertainty about the extent

of the contamination of mushroom compost with pesticide residues a chemical survey of the material is warranted.

2.5 Other waste materials

2.5.1 General assessment of OCs in industrial wastes applied on land

A wide range of organic wastes are applied to land as organic amendments (Table 4). Data were sought concerning the concentration of the organic contaminants of interest to this study present in these materials. Davis and Rudd (1997) reported that a large number of compounds could be associated with specific waste materials:

- Waste soil or compost may contain persistent organics including residues of non-approved or prescribed compounds (Red List), such as DDT, lindane and other substances;
- Antibiotics and other medicinal compounds may be present in products derived from animal, fish and pharmaceutical waste;
- Waste wood and paper may contain traces of persistent preservatives such as pentachlorophenol (PCP);
- Biosludges and septic tank sludges contain dichlorobenzene used in toilet disinfectants and alkyl benzenes used in detergents;
- Wastes derived from any process involving combustion could contain PCDD/Fs and PAHs.

Also, the presence of degradation products derived from the above must be considered. Davis and Rudd (1997) considered that, where a waste arises from a process such as those listed above, it should be subjected to a detailed evaluation and risk assessment.

Naturally occurring organic compounds such as oils and fats may be present in large concentrations in dairy, wool scouring, abattoir, meat processing, oil crushing and rendering wastes (Davis and Rudd, 1997). Above about 4 % fat or oil content detrimental effects on plant growth have been observed. The oil or fat appears to coat the soil particles, effectively producing a waterproof barrier. Plant roots are not able to extract water and stunting or die-back can occur. Further additions of water do not improve water absorption by the soil. Microbial breakdown of the fat or oil may cause temporary anaerobic conditions to develop which may also cause crop damage. Pretreatment of these wastes is recommended to reduce the fat or oil content to <4 % by separation and alternative disposal of this component of the waste (Davis and Rudd, 1997).

There is very little quantitative data in the published scientific literature on OC concentrations in industrial wastes that may be potentially landspread, but some information has been compiled from reported national surveys from individual EU Member States by Gendebien (2001). The full range of waste types and data, where reported, is given in Table 56.

Table 56 Organic contaminant concentrations in industrial wastes spread on land (mg kg⁻¹ DS, unless otherwise stated) (Gendebien, 2001)

Waste type and contaminant	Min	Max	Mean
Abattoir waste – blood			
PAHs			
Σ7PCBs			
Abattoir waste – stomach contents			
Fluoranthene	<0.1	<0.5	
Benzo(b)fluoranthene	<0.1	0.4	
Benzo(a)pyrene	<0.1	0.6	
Σ7PCBs	<0.0007	0.2	
Abattoir waste - sludge			
Fluoranthene	<0.1	<0.5	
Benzo(b)fluoranthene	<0.1	0.4	
Benzo(a)pyrene	<0.1	0.6	
Σ7PCBs	<0.0007	0.2	
Food and drink industry sludge			
Fluoranthene	0.01	0.3	0.2
Benzo(b)fluoranthene	0.01	0.05	0.04
Benzo(a)pyrene	0.01	0.06	0.04
Σ7PCBs	0.02	0.21	0.07
Pulp and paper industry sludge			
Fluoranthene	0.01	<0.1	<0.05
Benzo(b)fluoranthene	<0.005	0.04	<0.02
Benzo(a)pyrene	<0.005	0.03	<0.02
Σ7PCBs	0.002	<1	<0.5
Tannery sludge			
PAHs			
Σ7PCBs			
Textile waste			
Fluoranthene			0.06
Benzo(b)fluoranthene			0.05
Benzo(a)pyrene			0.02
Σ7PCBs			0.01
Wool scourers waste			
Fluoranthene	<0.01	0.04	
Benzo(b)fluoranthene	<0.01	<0.01	
Benzo(a)pyrene	<0.01	0.01	

Table 56 (Continued)

Σ7PCBs	<0.05	<0.05	
Decarbonation sludge			
PAHs			
Σ7PCBs			
Dredgings from waterways			
ΣPAH	0	203	16
Σ7PCBs			
Phenols	2.1	292	23.4
Waste lime (cement manufacture and gas processing)			
PAH			
Σ7PCBs			
Waste gypsum			
PAH			
Σ7PCBs			
Slag from steel industry			
PAH			
Σ7PCBs			
Waste bark and other plant materials¹			
Σ6PAHs			0.6
ΣPCBs			0.008
PCDD/F greenwaste (ng TEQ kg ⁻¹ ; +/- sd)			4.96 +/- 3.56
PCDD/F bark (ng TEQ kg ⁻¹ ; +/- sd)			1 +/- 0.57

¹ Amlinger *et al.* (2004)

With the exception of dredgings from waterways, the above data for POPs are within the ranges measured in sewage sludge and good quality greenwaste composts (Table 32 and Section 2.4.2) and would not be considered problematic or limiting to land spreading. However, the range of compounds examined is limited and a broader spectrum analytical survey is required of wastes originating from sources where potentially significant contamination with OC may arise, as indicated above. A more detailed review of the origin and chemical treatments involved in producing different residuals from industrial processes is required to determine the specific OC that should be determined for particular types of waste; the following example for textile wastes provides an illustration.

2.5.2 Textile wastes

Surfactants are used widely in the textile finishing industry. All types of surfactants (anionic, nonionic, cationic, and amphoteric) are used, though anionic and non-ionic substances dominate. Surfactants in the textile industry serve mainly as detergents, wetting agents, de-aeration agents, leveling, dispersing and softening agents, emulsifying and spotting agents, anti-electrostatics, foaming and defoaming agents,

after-treatment agents for improving dye fastness improvement and accelerating dye fixing (OECD, 2004).

Biocides are used on textiles to control bacteria, fungi, mold, mildew, and algae to control the problems of deterioration, staining, and odours that they cause. About 5 % of textiles are finished with biocides for the consumer end-use (OECD, 2004). In the carpet industry biocides play an important role to impart wool fibre lifetime. Mothproofing agents formulated from synthetic pyrethroids (permethrine and cyfluthrin) are used against a range of textile pests. Permethrine-based formulations account for approximately 90 % of the market (OECD, 2004).

In addition to the intentional application of biocides to textiles, biocides may be present on textiles for the following reasons:

- Biocides in textile auxiliaries to improve their storage stability (preservation agents);
- Biocides in raw cotton fibres (insecticides (organochlorines, organophosphates, pyrethroids, and carbamates), herbicides, harvest aid chemicals)
- Greasy wool contains residues of biocidal chemicals used to prevent or treat infestations of sheep by external pests (ectoparasites), such as ticks, mites, and blowfly. Like the natural by-products they are removed in wool scouring and load the wastewater. Biocide content of the wools processed varies widely, according to the countries of origin of the wools:
 - Organochlorines: 0.2–5 g t⁻¹ greasy wool
 - Organophosphates: 1-19 g t⁻¹ greasy wool
 - Pyrethroids: 0.05-6.3 g t⁻¹ greasy wool.

Biocides typically used in the textile industry include (OECD, 2004):

- 2,2'-Dihydroxy-5,5'-dichlorodiphenylmethane
- 2-Phenylphenol
- Sodium-2-phenyl-phenolate.
- Quaternary ammonium salts
- Copper-8-quinolinolate
- Dichlorophen
- Zinc naphthenate
- Thiobendazole
- Organotin compounds
- 2,4-Dichlorobenzyl alcohol
- 2-Bromo-2-nitropropane-1,3-diol.

2.5.3 Paper wastes

Gibbs *et al.* (2005) recently performed a survey of land spreading practices for paper waste, which included the collation of chemical analysis data on paper wastes provided by paper mills. Returns from the paper mills contacted during the study indicated that OC did not appear to be a problem in paper waste materials spread on agricultural land in England and Wales. Of the 28 mills using spreading to agricultural land as a recovery route for their paper wastes, 15 had undertaken analyses for the presence of OC. On all occasions, the concentrations of organic contaminants in the paper wastes were below laboratory detection limits, although it was not specified which OC were measured. Gibbs *et al.* (2005) concluded that there was no evidence to indicate any significant risks to the environment from potential OC that may be present in paper waste materials applied to land in the UK.

This was confirmed by on-farm field investigations reported by Aitken *et al.* (2002), which demonstrated significant agronomic benefit from the application of paper sludge. No negative effects were observed based on three assays for soil microbial activity (soil microbial biomass, mineralisable N and soil respiration rate). It was concluded that detrimental effects on soil microbial activity were not important in the medium-to-long-term after application.

2.5.4 Controlling the application of industrial wastes on land

Gendebien (2001) proposed a scheme for managing and controlling the spreading of wastes to land. The proposal would band waste into broad groups and all materials would be subject to overall generic controls. Further specific controls would apply to each group according to their properties. The proposals included the following main groups:

Class 1 Farm residues recycled on the farm of production e.g. manure from animals grazing *in situ*.

Class 2 Benign wastes containing negligible amounts of contaminants e.g. green waste, biological sludge from food waste treatment.

Class 3 Wastes which may contain contaminants (pathogens, heavy metals and other potentially toxic elements, OC) e.g. dredgings from waterways, tannery waste, paper waste.

Progressively more detailed information would be required according to the class of waste for instance:

Class 1 Source of waste (address of place of production or treatment centre, and quantity of waste arising tonne/annum). Extent of treatment e.g. storage for 3 months at ambient temperature.

Class 2 As for Class 1 plus basis for benefit to agriculture e.g. content of plant nutrients and lime (nitrogen, phosphorus, potassium, calcium, magnesium, sulphur, trace elements), organic matter, dry solids, pH value. Evidence that the waste contains only negligible concentrations of contaminants.

Class 3. As for Class 1 plus basis for benefit to agriculture: content of plant nutrients etc. as for Class 2 plus content of contaminants (pathogens – most probable numbers; concentrations of heavy metals, other potentially toxic elements and OC). Evidence that the waste is free of contaminants other than those specified.

As regards the *Class 3* wastes, Gendebien (2001) considered that the quality rules in Directive 86/278/EEC (landspreading of sewage sludge) could provide the basis for deciding on acceptability for landspreading, but this would not include OC. Further advice on identifying those compounds which could be significant as contaminants of a particular waste stream is given by Davis and Rudd (1997), and this is principally determined from knowledge of the process producing the waste.

These measures go further than the Environment Agency may currently require in issuing exemptions for land spreading industrial wastes according to paragraph 7 of Schedule 3 of the Waste Management Licensing Regulations (WMLR) 1994, but provide a more comprehensive and robust assessment of the quality and suitability

for land spreading of specific industrial wastes that originate from processes that may lead to contamination with OCs.

2.6 Pesticides

2.6.1 Use for pest control

The Pesticide Safety Directorate commissions regular surveys of pesticide use across the agricultural and horticultural industry. These cover the sectors listed in Table 57. It is beyond the capacity of this study to review pesticide use across the entire agricultural and horticultural industry. Consequently, only the most significant sectors have been looked at in detail, namely arable crops, and grassland and fodder crops. These are the most significant sectors because of the area of land they encompass and the amount of plant protection products which are used. The most recent surveys conducted for arable crops and for grassland and fodder crops, were undertaken in 2004, but the results will not be published until late 2005.

Upto date pesticide usage data for other sectors has been difficult to obtain. The DETR (2000b) study undertaken as a preliminary to the development of a pesticide tax provides some data, largely from the British Agrochemicals Association, (BAA) now the Crop Protection Association. The BAA data was judged to be consistent, but not complete since the BAA does not represent the entirety of the pesticide industry in the UK. That said, the BAA estimates that its figures refer to approximately 95% of the market (DETR, 2000b).

Data reviewed by the study from the Office of National Statistics (ONS) differed substantially from figures from both the BAA and the UK Agricultural Supply Trade Association trade associations, and also appeared to be at odds with the Pesticide Use Survey (DETR, 2000b). The data from DETR (2000b), presented in Table 57, provide an indication of the relative scale of use of plant protection products in the different sectors and supports the decision of this study team to concentrate efforts to review pesticide inputs to soil within the agricultural sector.

The Pesticide Usage Surveys of arable crops are conducted every other year and those for grassland and fodder crops every four years. Amongst other things, they report on the mass of active compound used for specific active ingredients on particular crop types. Table 58 is a short extraction from these reports. The full tables run to several pages (CSL 2003ab). It is also possible to conduct an online search of the pesticide usage statistics (<http://pusstats.csl.gov.uk/index.cfm>).

It is not appropriate to assume that there is a direct relationship between the mass of product used and the area of land receiving product. The loading of grassland and fodder crops with pesticide products is substantially lower than arable crops. The total mass of pesticide product applied to grassland and fodder crops is approximately 904 t compared with 27,764 t applied to arable crops (Table 58), yet the total area of land under grassland and fodder crops is over twice that under arable crops (Table 59).

Many agrochemicals for which there is data in the scientific literature have been withdrawn from the market, or banned by EU legislation in recent years. Annex G lists those substances which have been banned from use. Table 60 indicates the key products used on grassland and fodder crops in terms of amount of active ingredient applied and similar information is presented for arable crops in Table 61.

Table 57 Pesticide use (t active ingredient per y) (DETR, 2000b)

Product type	Non-agricultural	Agricultural	Garden & household	Industrial, amenity & forestry	Agricultural & horticultural
Herbicides	623	9,621	2,019	625	11,160
Fungicides	31	6,303	39	94	6,032
Insecticides	12	1,167	154	17	1,055
Growth regulators	9	2,582			2,744
Soil sterilants		434			
Molluscicides		264			140
Desiccants		32			
Repellents		4			
Biological control agents		2			
Others			73	8	1,074
Total	675	20,409	2,285	744	22,205
Year & source:	1995 Produce Studies		1997 BAA ¹		

Notes:

<http://www.defra.gov.uk/environment/chemicals/pesticides/pesticidestax/19.htm>

¹ Now the Crop Protection Association

Key spraying months for wheat are October and November when the majority of herbicides and insecticides are applied, and March through to June when fungicide and growth regulators predominate, though herbicides continue to be applied and June sees a greater period of insecticide use (CSL, 2003b). The pattern of application is similar for all cereals except for spring sown barley. The major spray application period for linseed, potatoes, peas, beans, and sugar beet is spring and early summer. Applications to oilseed rape are spread more evenly throughout the year with the lowest months being December, January, February and June (CSL, 2003b).

The extent to which a pesticide will be washed into soil will in part be dependant on weather and hence will vary through the seasons. Likewise, the amount of leaf on a crop will vary through the year further influencing the extent to which a pesticide will fall directly onto the soil.

Drift from the site of application can occur to a greater or lesser extent with both spray and granular products, depending on the equipment used. This will both reduce the concentration reaching the soil at the point of application and increase the area of soil which may be potentially impacted by plant protection products (CSL, 2004a).

Table 58 Summary of pesticide treatment regime applied to agricultural land in 2002 by product category (CSL, 2003ab)

Product type	Active ingredient applied (t)	Spray hectares ¹	Area of crop treated (%) ²	Average no. of spray rounds ³
Arable crops				
Fungicides	3,454.58	14,608,423	82.3	2.4
Growth regulators	3,187.39	4,131,261	51.4	0.8
Herbicides	8,815.04	14,676,412	93	2.7
Insecticides & nematicides	473.26	4,155,770	62.5	1.1
Molluscicides and repellents	362.91	1,100,071	16.5	0.3
All seed treatments	355.72	4,428,705	88.5	na
Sulphur	304.07	85,490	-	-
Desiccants	10,771.60	72,648	0.4	<0.1
All pesticides	27,724.57	43,258,781	-	5.3
Grassland and fodder crops (kg) ⁴				
Fungicides	13,015	71,884	0.3	0.2
Growth regulators	5,278	8,348	0.1	<0.1
Herbicides	834,665	847,588	4.9	1.4
Insecticides & nematicides	11,832	32,492	0.2	0.1
Sulphur	1,294	462	<0.1	<0.1
Molluscicides and repellents	11,226	23,074	0.2	<0.1
All seed treatments	26,531	301,757	45.4	na
All pesticides	903,841	1,285,605	-	1.6

Notes:

1 Spray hectares is a function of the both the area of land in receipt of a pesticide and the number of times that pesticide is applied in a single year.

2 The percentage areas of each crop treated with the different product categories.

3 The mean number of spray applications in the cropping year.

4 Indicates number of passes of application machinery as some herbicides may be applied using weed wipers and some insecticides/molluscicides as granules or pellets

Table 59 Area of grassland, fodder and arable crops grown in Great Britain in 2002 (CSL, 2003ab)

Grassland and Fodder crops	hectares	Arable	hectares
Maize	120,996	Wheat	1,989,471
Turnip & swede	15,003	Winter barley	541,769
Fodder beet & mangolds	5,928	Spring barley	530,777
Kale, cabbage and rape	9,721	Oats	123,205
Other crops for stock feeding	22,336	Rye	4,966
Stubble turnip and catch crops	30,610	Triticale	13,850
Grassland less than 5 years old	1,093,699	Oil seed rape	356,780
Permanent pasture	4,714,794	Linseed	14,826
Rough grazing	4,286,389	Potatoes ware	138,004
		Potatoes seed	16,290
		Peas	84,765
		Beans	164,184
		Sugar beet	169,148
		Set-aside	608,100
All grassland and fodder crops	10,299,456	All arable crops	4,756,081

2.6.2 Disposal of pesticide and veterinary medicine residues

Farm yard operations are a significant source of entry of pesticides into surface and groundwaters. Whilst this is principally a concern for water resource protection, soil may also be at risk of contamination from dilute or concentrated pesticide residues during, for example, spray equipment washing and cleaning activities. However, on-farm bioremediation systems may have significant potential to mitigate these problems, using an engineered bio-bed constructed from composted materials, straw and topsoil (Defra, 2003). Further development work is required to produce an effective on-farm bioreactor system for treating pesticide residues.

Land treatment is also the principal approach for disposing of sheep dip chemicals. Currently, 116,454 t of sheep dip waste is disposed annually in the UK (EA, 2003). The primary focus of environmental control measures here is to protect water resources from contamination by sheep dip chemicals (Defra, 2001). The *Groundwater Protection Code: Use and Disposal of Sheep Dip Compounds* (Defra, 2001) requires that, prior to landspreading, conditions should be checked to ensure the land is in an appropriate state to receive used dip. Spreading should not be carried out if, for example, the land is waterlogged or frozen, cracked following dry weather or has been recently drained. Mixing used dip with controlled volumes of slurry or water in a vacuum tanker for achieving the correct spreading rate is permissible and a typical dilution regime is one part used dip to three parts water or slurry. Disposal by mixing used dip with the contents of a slurry store is not acceptable. Disposal of used dip onto land requires a prior written authorisation from the Environment Agency.

In addition to protecting the water environment, land treatment should also have regard for the potential impacts of sheep dip chemicals on soil fauna and flora. For instance, diazinon, one of the main organophosphate pesticides used in sheep dip, is

acutely toxic to earthworms and other terrestrial invertebrates (Boxall *et al.*, 2004). However, other soil biological compartments may be less sensitive to sheep dip chemicals. For example, Aitken *et al.* (2002) did not detect any significant effects of diazinon or cypermethrin (the active ingredient of synthetic pyrethroid) disposal to soil in sheep dip on the microbial biomass, respiration activity or N mineralization and both compounds degraded rapidly in the treated soils. Approximately 0.5 % of the diazinon and 1.4 % of the cypermethrin originally applied was found in the top soil between 30 and 62 days after sheep dip application. There was some evidence of an adverse effect of diazinon on the functional microbial diversity of soil, measured by the Biolog assay, but there was no correlation with the concentration of the active ingredients and it was concluded this behaviour could have been related to some other aspect of the waste.

Table 60 Key products used on grassland and fodder crops in terms of amount of active ingredient applied (>10,000 kg) or land area treated >10,000ha) in 2002¹ (CSL, 2003a)

Active substance	Product type	kg used	Area treated (ha)
MCPA	herbicide	217,691	212,720
Atrazine ²	herbicide	134,467	124,913
Mecoprop-P	herbicide	83,619	88,069
Glyphosate	herbicide	69,588	62,210
2,4-DB	herbicide	51,739	62,210
2,4-D	herbicide	50,980	38,509
Triclopyr	herbicide	38,113	121,418
Pendimethalin	herbicide	24,904	22,031
Asulam	herbicide	22,485	11,616
Bromoxynil	herbicide	21,411	70,543
Fluroxypyr	herbicide	20,093	102,418
Trifluralin	herbicide	13,538	13,485
MCPB	herbicide	12,690	10,144
Clopyralid	herbicide	11,187	95,019
Metaldehyde	molluscicide & repellent	10,969	20,053
Chlorpyrifos	insecticide	7,447	11,078
Benazolin	herbicide	6,570	34,845
Dicamba	herbicide	3,817	35,872
Fenpropimorph	seed treatment	4,437	26,138
Epoxiconazole	fungicide	896	17,423
Amidosulfuron	herbicide	721	17,265
Phenmedipham	herbicide	2,733	11,706
Azoxystrobin	fungicide	1,272	10,839

Notes:

- 1 Note that the fifty most widely used arable products are all used in greater quantities and over a larger area than any grassland or fodder crop product.
- 2 Atrazine has been withdrawn from the market since the end of 2003 except for very limited use on sweetcorn and forestry until December 2007.

Table 61 Key products used on arable crops (excluding seed treatments) in terms of amount of active ingredient applied (>10,000 kg) or land area treated >10,000ha) in 2002 (CSL, 2003b)

Active substance	Product type	Tonnes used	Area treated (ha)
Sulphuric acid	desiccant	10,772	72,648
Chlormequat	Growth regulator	2,885	3,017,068
Isoproturan	herbicide	2,254	2,239,215
Glyphosate	herbicide	1,488	1,699,251
Mancozeb	fungicide	1,146	889,253
Pendimethalin	herbicide	1,057	1,078,753
Trifluralin	Herbicide	682	822,491
Mecoprop-P	herbicide	527	1,079,646
Chlorothalonil	fungicide	424	774,434
Tri-allate	herbicide	372	174,936
Chlorotoluron	herbicide	341	118,994
Metaldehyde	molluscicide	334	866,502
Sulphur	fungicide	315	85,490
Fenpropimorph	fungicide	267	1,823,617
1,3-dichloropropene	insecticide	192	Not reported in isolation
Epoxiconazole	fungicide	178	3,665,844
Metamitron	herbicide	174	258,486
Terbutryn	herbicide	163	74,684
Metazachlor	herbicide	161	267,889
Azoxystrobin	fungicide	158	1,654,411
Cyprodinil	fungicide	146	540,847
Simazine	herbicide	135	240,153
Tebuconazole	seed treatment	116	1,134,382
Chloridazon	herbicide	108	99,946

Note: Sulphuric acid is used solely as a desiccant on potatoes.

Two priorities for further research relating to sheep dip disposal are therefore to:

1 Assess the consequences of sheep dip disposal practices on soil biological processes and fertility, develop application recommendations to minimise soil damage and assess recovery rates as a basis for defining application frequencies for treated areas, and

2 Develop land management practices to maximise biodegradation rates and minimise negative impacts of sheep dip chemicals on soil biological processes eg by enhancing microbial activity from inputs of manures and composts.

2.6.3 Measures to reduce pesticide use

Government policy aims to minimise the use of pesticides, and consideration has been given to the introduction of a pesticides tax (<http://www.defra.gov.uk/environment/chemicals/pesticides>). To avoid the potential

introduction of a tax, the crop protection and farming industries have developed a programme of voluntary measures (known as the Voluntary Initiative (VI)) which they believe will achieve the same aim by encouraging standards of best practice. The initiative has been developed in consultation with several environmental bodies and is under continued scrutiny. The House of Commons Environment, Food and Rural Affairs Committee has recently recommended (HoC, 2005) that the VI's current targets for the area of land under Crop Protection Management Plans (CPMPs) and for water quality are insufficiently challenging, and should have been strengthened earlier. The VI steering group's offer to strengthen the target for water quality was welcomed, but the Committee regarded the conditional nature of the offer undermined its credibility. They also recommended that the target for CPMPs be similarly strengthened to reflect the inclusion of the plans in the entry-level stewardship scheme. There was also concern that the VI steering group should be able to show evidence that the CPMPs are leading to real improvements in agricultural practice. The Committee commented that, since the objective of the VI was to minimise the impact of pesticides on the environment, the ability to measure achievements in this respect was fundamental. Data problems and delays to projects have meant that there is little irrefutable evidence of the environmental benefits of the VI, just one year prior to the completion of the programme. The Committee have recommended that Defra, the Environment Agency and the VI steering group move rapidly to put in place the necessary arrangements to allow for a proper assessment of environmental benefits of the VI to be undertaken in 2006. There was concern that Defra is not only unable to provide assurances on the environmental benefits of the VI at this time, but appears to have little confidence in the usefulness of the research it commissioned specifically to provide tools for this assessment. Uncertainty remains about the future of the VI after April 2006 when the programme ends. The Committee criticised Defra for the lengthy delay in launching its national pesticides strategy, the consultation for which closed in June 2005 (<http://www.pesticides.gov.uk/environment.asp?id=1539>). The Committee recommended that the Government publish its final strategy document, as a matter of urgency, to establish a clear policy framework within which the VI, or its successor, can operate. They also expressed frustration with the lack of effort made to devise a means of measuring progress made by the policies intended to control pesticide use. The Government was criticised for struggling to develop an appropriate benchmarking exercise or baseline position against which to judge its pesticide policies.

2.6.4 Plant protection product approval system in UK

Because of public anxiety over the safety of pesticides and the agrochemical industry's concerns over instances of non-conformity with the existing voluntary scheme, in 1986 the controls on pesticides were put on a statutory basis. This was achieved by the introduction of the Control of Pesticide Regulations 1986. The regulations, made under Part III of the Food and Environment Protection Act 1985, apply to Great Britain - separate legislation applies similar controls in Northern Ireland. The legislation gives Ministers broad powers to protect the health of people, creatures and plants, to safeguard the environment, to secure safe, efficient and humane methods of controlling pests and to make publicly available information about pesticides. In particular, the advertisement, sale, supply, storage or use of pesticides is prohibited unless Ministers have approved them.

Pesticides, including plant protection products, are amongst the most strictly regulated of all chemicals. Regulation is necessary to ensure that any risk from using them is within acceptable limits. Before a pesticide can be approved for sale and use, the company must supply extensive information to allow an assessment of risks,

together with evidence that the product is effective. The main components of the data package that typically would be required for a new pesticide/plant protection product are given in Annex H. In 2000 the industry estimated the cost for developing a new pesticide product and bringing it to the market to be in the region of £140 million.

The UK approvals system is gradually being replaced by broadly similar EC requirements under Council Directive 91/414/EEC. The Directive aims to harmonise the authorisation procedures for plant protection products across Member States by setting common health and environmental standards. These provide for an evaluation of active substances at Community level while products containing those active substances are authorised by individual Member States. The key points of the Directive may be summarised as follows:

- based on the precautionary principle by placing protection of human health and the environment above the needs of agricultural production. Data requirements for evaluations of pesticides exceed those required for any other class of substances including pharmaceuticals, food additives and commodity chemicals. A typical dossier is about 50,000 pages long and takes a company four and a half years to prepare.
- laying down provisions on the classification, packaging and labelling of plant protection products to contribute to environmental protection.
- requiring the use of 'integrated use' of plant protection products whereby the use of chemical control is limited to the strictest minimum needed to drive down pest population, and is combined with biological, cultural and plant-breeding methods.
- laying down compliance with regulations of proper use alongside the application of the principles of good plant protection practice and integrated pest control.
- ensuring that a plant protection product will only be authorised if it does not harm human or animal health, pollute groundwater and has no unacceptable effect on plants or plant products.
- requiring compliance with product label directions for dose rate, storage and disposal of plant protection products.
- laying down a requirement on applicants of plant protection products for approval, to include in their dossier, information on the occurrence of the development of pest and disease resistance and appropriate strategies to avoid such occurrences.

The Directive was implemented in Great Britain by the Plant Protection Products Regulations 1995. Again, similar legislation applies in Northern Ireland. For England and Wales the 1995 regulations have recently been replaced by the Plant Protection Products Regulations 2003 (Annex D and G).

Council Directive 91/414/EEC also provides for the review of plant protection products already on the Community market to ensure that they meet modern standards of safety and efficacy. To date approximately 70 active substances out of the 350 (20%) that have UK approvals have been taken off the market (Annex G). Within the EU as a whole approximately 450 out of 970 (46%) active substances have been withdrawn. The Data Packages required for pesticide approval in the UK are outlined in Annex H

2.7 Irrigation water

Irrigation is used to only a limited extent in UK agriculture, on lighter soils and for high value crops. It is more widely used in horticulture, and golf course and landscape maintenance, but this water will normally be sourced from the public mains supply and hence be of drinking water quality. National data are available concerning the use irrigation of outdoor crops in 2001 in England. This survey was carried out by Cranfield University for Defra, and continues a series of similar surveys since 1982 by MAFF. Tables 62 and 63 provide a summary of some of this data. In 2001, 88% of water used was applied to potatoes and vegetables (Table 62). The area of main crop potatoes has increased steadily from 22,810 ha in 1982 to 69,820 ha in 2001. The irrigation of grass, cereals and sugar beet has declined significantly as proportion of the total volume irrigated, the latter dropping from 15% to 6.6% over the same period (Table 62).

An average of 98.3 million m³ of water were used in irrigation annually between 1982 and 2001 during which period the average area irrigated annually was 127,993 ha, giving an average annual application of 729 m³ ha⁻¹ (Table 63). Of this, 57 % was taken from surface water supplies and 36% from groundwater supplies.

Table 62 Selected summary of agricultural crops receiving irrigation between 1982 and 2001 (Weatherhead and Danert, 2002) (m³, '000)

Crop	1982		1990		2001			
	m ³	%	m ³	%	m ³	%	ha	%
Early potatoes	4680	8.5	6770	5.1	5710	4.3	7300	5.0
Main crop potatoes	15280	27.7	51170	38.2	69940	53.3	69820	47.4
Sugar beet	8260	15.0	20320	15.2	4630	3.5	9760	6.6
Orchard Fruit	2180	3.9	2930	2.2	900	0.7	1580	1.1
Small fruit	1890	3.4	3180	2.4	3370	2.6	3770	2.6
Vegetables	6830	12.4	18450	13.8	34120	26.0	39180	26.6
Grass	10030	18.2	13100	9.8	2320	1.8	3970	2.7
Cereals	5040	9.1	11830	8.8	1470	1.1	4620	3.1
Other	1020	1.8	6040	4.5	8840	6.7	7280	4.9
Total	55210		133790		131300		147270	

Data were sourced from the literature for organic compound concentrations in surface and groundwater. This has been used to try to establish the potential scale of OC inputs to soil from crop irrigation. The data are quite limited and variable. Consequently, the whole dataset has been used rather than summary data of minimums, maximums and means. Table 64 provides an indication of potential loadings of some POPs.

Table 63 Water sources used for irrigation between 1982 and 2001¹ and annual average application (Weatherhead and Danert, 2002) (m³, '000)

Source	1982	1984	1987	1990	1992	1995	2001	Mean
Surface water ²	34390	57210	19250	74070	41820	90860	75760	56194
Groundwater ³	16680	32420	11800	50540	28470	61620	47810	35620
Public mains	2040	3840	1100	3860	2620	4390	4300	3164
Rain collected							2050	2050
Reused water							670	670
Other	1830	3540	1470	5330	2130	4880	710	2841
Total	54940	97730	33630	133790	75070	161750	131300	98316
Total area irrigated (ha)	103490	140630	76500	164470	107940	155650	147270	127993
Annual average (m ³ ha ⁻¹)	531	690	439	814	695	1039	892	729

Notes

- 1 Data up to 1992 for England and Wales, data for 1995 and 2001 for England only.
- 2 Surface water includes ponds, lakes, gravel or clay workings, rivers, streams or other water sources.
- 3 Groundwater includes wells, boreholes and springs arising on the holding.

Table 64 Potential loading of OCs through surface water irrigation (Johnson and Jurgens, 2003)

Substance	Concentration (µg l ⁻¹)		Irrigation load	
	Min ¹	Max	Min (mg ha ⁻¹)	Max (g ha ⁻¹)
Nonylphenol	0.01	646	7.3	470.9
Octylphenol	0.005	13	3.6	9.5
Biphenol A	0.0001	1.4	0.07	1.02
Phthalates DEHP DBP, BBP	0.1	98	72.9	71.4

Notes

- 1 All minimums limit of detection

Veterinary medicine data were available only for groundwater as the references examined did not distinguish between fresh and marine surface water. The concentrations for human pharmaceuticals and veterinary medicines are in the same order of magnitude. Hence, the total mass of a particular compound which potentially may enter the soil will be of the same order of magnitude and the broad level of veterinary medicine inputs from surface water might be estimated on that basis.

Table 65 provides a limited picture of the potential scale of veterinary medicine inputs to soil from groundwater irrigation. The figures have been calculated assuming that total mean annual irrigation is 98.316 million m³, 36% of which is supplied from groundwater (Table 63). It is not possible to compare the potential input to soil of a veterinary product found in water with its consumption data, since no compound specific consumption data were obtained.

No UK data have been obtained for groundwater concentrations of human pharmaceuticals. Table 66 provides a limited amount of data from Germany, in which the concentrations are typically an order of magnitude higher than surface water. The reasons for this are unclear and may relate to the depth of sampling and labelling

such that what is described as groundwater is in fact soil water and hence sampled from shallow depth. The mass of compound potentially added to soil in irrigated groundwater is calculated in the same way as the veterinary medicine data for groundwater.

Table 65 Potential loading of a range of veterinary medicines through crop irrigation using groundwater

	Groundwater concentration(ng l^{-1})		Irrigation load (mg ha^{-1})		Total potential input (g y^{-1})		Data origin & Reference	
	Min	Max	Min	Max	Min	Max		
Ectoparasiticides								
Chlorfenvinphos		70		51.0		2478	UK	1
Chlorfenvinphos	15	20	10.0	14.0	531	708	UK	1
Chlortetracycline	170	220	123.9	160.4	6017	7787	Germany	2
Diazinon		216		157.5		7645	UK	1
Diazinon	26	190	19.0	138.5	920	6725	UK	1
Propetamphos		489		356.5		17308	UK	1
Propetamphos	29	110	21.0	80.2	1026	3893	UK	1
Antibiotics								
Sulfamethazine	80	160	58.0	116.6	2832	5663	Germany	2
Chlortetracycline	170	220	123.9	160.4	6017	7787	Germany	2
Oxytetracycline	150	190	109.4	138.5	5309	6725	Germany	2
Tetracycline	110	270	80.0	196.8	3893	9556	Germany	2
Antimicrobials								
Tylosin	130	420	94.0	306.2	4601	14865	Germany	2

Notes

- 1 Boxall *et al.* (2004)
- 2 Hamscher *et al.* (2000a)

There is generally a poor association between the mass of a specific human pharmaceutical used annually and its measured presence in environmental compartments. Many of those used in the greatest quantities are not found in any of the concentration data reported. This may be explained because:

- Reliable analytical techniques may not be available;
- Analysis resources are only focussed on compounds known or suspected to have an negative impact;
- The potential presence of a particular compound in environmental media is influenced by complex processes including its susceptibility to photodegradation, biodegradation and sorption mechanisms.

Where data are available on compound concentrations in media applied to soils, it is questionable whether extrapolation of those values to estimate potential inputs to soil on a national basis bears much relation to the actual inputs in practice, particularly when the parameter is potentially highly variable and representative data are limited, as is the case when estimating the total inputs of pharmaceuticals to soil in irrigation water, for example. In 1995, a total of 1500 kg of the pharmaceutical clofibrate were used in the UK (Table 10). On the basis of measured mean concentrations for surface water data from the UK (Table 67) and assuming 57 % of the total average

water volume irrigated to agricultural land annually is surface water, an estimated 2.24 kg of the drug, equivalent to 0.15 % of the administered quantity, was potentially added to soil in irrigation water.

UK use of erythromycin in 1995 was 67.7 t and in 2000 was 26.5 t (Tables 10 and 11) and 16.2 t of ibuprofen was used in 2000 (Table 11). Using UK concentration data for erythromycin, there is the potential for a range between 560 g and 56.04 kg to be applied to soil *via* irrigation of surface water and soil inputs of ibuprofen nationally from surface water irrigation estimated by this approach were in the range 1121g to 87.1 kg (Table 67).

In conclusion, OC inputs to soil in irrigation are generally unlikely to be toxicologically or ecotoxicologically significant. However, the addition of trace amounts of antibiotic residues through irrigation of surface waters receiving effluents from urban wastewater treatment plant could have implications for the more widespread development and dissemination of antibiotic resistant bacteria in the environment.

Table 66 Potential loading of a range of human pharmaceuticals through irrigation of groundwater

	Concentration ($\mu\text{g l}^{-1}$)		Irrigation load (mg ha^{-1})		Total potential input (kg yr^{-1})		Data origin & Reference	
	Min	Max	Min	Max	Min	Max		
Lipid regulating agents								
Clofibrate	0.0	7.3	51.0	5321.7	2.5	258.4	Germany	1
Fenofibric acid		0.04		32.8		1.6	Germany	1
Antiphlogistics (anti-inflammatory)								
Diclofenac		0.3		218.7		10.6	Germany	1
Ibuprofen		0.2		145.8		7.1	Germany	1
Phenazone	<0.01	1.25	7.1	911.3	0.4	44.2	Germany	1
Antibiotic/antimicrobials								
Sulfamethoxazole		0.47		342.6		16.6	Germany	2
Sulfamethazine		0.16		116.6		5.7	Germany	2

Notes

1 Zwiener *et al.* (2001)

2 Hirsch *et al.* (1999)

Table 67 Potential loading of a range of human pharmaceuticals through irrigation of surface water (mg ha⁻¹)

Substance	Concentration (ug l ⁻¹)			Irrigation load (mg ha ⁻¹)			Data origin & Reference	
	Min	Max	Mean	Min	Max	Mean		
Lipid regulating agents								
Bezafibrate	0.0005	0.38		0.4	277.0		Germany	2
Clofibrate	0.001	0.009		0.7	6.6		Switzerland	1
Clofibrate			0.04			29.2	UK	1
Clofibrate			0.03			21.9	Ireland	1
Clofibrate		0.18			131.2		Germany	1
Clofibrate	0.0005	0.3		0.4	218.7		Germany	2
Fenofibric acid		0.172			125.4		Germany	1
Fenofibric acid	0.0005	0.17		0.4	123.9		Germany	2
Gemfibrozil		0.19			138.5		Germany	1
Gemfibrozil		0.51			371.8		Germany	2
Antiphlogistics (anti-inflammatory)								
Diclofenac	0.005	0.49		3.6	357.2		Germany	2
Ethinylestradiol	0.002	0.005		1.5	3.6		UK	1
Ibuprofen	0.02	1.555	0.423	14.6	1133.6	308.4	UK	3
Ibuprofen		0.139			101.3		Germany	4
Phenazone		0.95			692.6		Germany	2
Antimicrobial								
Chloramphenicol		0.06			43.7		Germany	5
Clarithromycin	0.001	0.037		0.7	27.0		Germany	6
Clarithromycin		0.26			189.5		Germany	5
Erythromycin	0.01	0.057		7.3	41.6		UK	3
Erythromycin	0.004	0.19		2.9	138.5		Germany	6
Erythromycin		1.7	0.15		1239.3	109.4	Germany	5
Erythromycin			1			729.0	UK	1
Roxithromycin	0.004	0.014		2.9	10.2		Germany	6
Roxithromycin		0.56			408.2		Germany	5
Sulfadimidine	0.003	0.007		2.2	5.1		Germany	6
Sulfamethoxazole	0.004	0.052		2.9	37.9		Germany	6
Sulfamethoxazole		0.48	0.03		349.9	21.9	Germany	5
Sulfamethoxazole			1			729.0	UK	1
Tetracycline			1			729.0	UK	1
Trimethoprim		0.2			145.8		Germany	5
Trimethoprim	0.01	0.036		7.3	26.2		UK	3
Trimethoprim	0.003	0.012		2.2	8.7		Germany	6
Betablockers								
Betaxolol		0.028			20.4		Germany	2
Bisoprolol		2.9			2114.1		Germany	2
Metoprolol		2.2			1603.8		Germany	2
Propranolol	0.01	0.115		7.3	83.8		UK	3
Propranolol		0.59			430.1		Germany	2

Table 67 (Continued)

Substance	Concentration (ug l ⁻¹)			Irrigation load (mg ha ⁻¹)			Data origin & Reference
	Min	Max	Mean	Min	Max	Mean	
Others							
Azithromycin	0.001	0.003		0.7	2.2		Germany 6
Ciprofloxacin		0.009			6.6		Germany 6
Clindamycin	0.003	0.024		2.2	17.5		Germany 6
Dextropropoxyphene			1			729.0	UK 1
Diazepam			10			7290.0	UK 1
Fenofibric acid		0.172			125.4		Germany 1
Indomethacin		0.121			88.2		Germany 1
Norethisterone		0.017			12.4		UK 1
Ofloxacin	0.005	0.02		3.6	14.6		Germany 6
Piperacillin		0.048			35.0		Germany 6

Notes

- 1 Zuccato *et al.* (2001)
- 2 Zwiener *et al.* (2001)
- 3 Hilton *et al.* (2003)
- 4 Stumpf *et al.* (2001)
- 5 Hirsch *et al.* (1999)
- 6 Christian *et al.* (2003)

3 POTENTIAL IMPACTS ON SOIL, ENVIRONMENT AND HEALTH

This section of the report examines the published literature on potential impacts on soil, environment and health of principal groups of OC identified as warranting particular attention because they are:

1. of known potential toxicity and persistence;
2. known to have detrimental impacts on soil biological processes;
3. an emerging issue with potential implications for human health;
4. a major bulk chemical group.

The selected compounds considered include:

- Persistent organic pollutants (POPs);
- Approved pesticides;
- Veterinary medicines;
- Plasticiser compounds.

3.1 Persistent organic pollutants

In this section the effects of four groups of POPs are discussed, including:

1. Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzo-*p*-furans (PCDD/Fs);
2. Polychlorinated biphenyls (PCBs);
3. Polyaromatic hydrocarbons (PAHs);
4. Chlorobenzenes (CBs).

All four groups are considered to be persistent and potentially toxic chemicals (Wild *et al.*, 1995).

3.1.1 Fate in soil

PCDD/Fs, PCBs, higher chlorinated CBs and most PAHs are all highly sorbed and persistent in soil (Table 68). Lower chlorinated CBs (mono-, and di-,chlorobenzene) and naphthalene and acenaphthene (types of PAH) are only moderately sorbed. The sorption of these compounds is further enhanced by the land application of sewage sludge (Wild *et al.*, 1995; Zhang *et al.*, 2005). In general, highly sorbed organic compounds are not susceptible to leaching and transport within the environment. They also demonstrate very restricted availability for plant uptake.

The lower chlorinated chlorobenzenes and all PAH congeners (apart from naphthalene, acenaphthene, fluorene, anthracene and phenanthrene) are highly volatile in soil (Wild *et al.*, 1995). For example, Wilson and Meharg (2003) measured volatilisation losses of 85% and 76% of added compound after 5 weeks from soil spiked with 1,2-dichlorobenzene and 1,2,4-trichlorobenzene, respectively.

The lighter congeners of PCBs (18, 28, 44, 52 and 66) are moderately volatile. PCDD/Fs do not tend to volatilise. The exception is 2,3,7,8-TCDD, which is moderately susceptible to volatilisation (Wild *et al.*, 1995). Compounds with greater volatilisation tendencies are more susceptible to foliar absorption by plants.

Table 68 Persistence (as half-life) in soil and sediments of some PCB and PCDD congeners (di Domenico and De Felip 2000 cited Amlinger *et al.*, 2004)

Cogener	Years
PCB (77, 118, 126, 156, 169)	6-10
2,3,7,8-T4CDD	10
1,2,3,7,8-P5CDD	12
1,2,3,4,7,8-, 1,2,3,6,7,8-H6CDD	13

3.1.2 Plant uptake

Due to the strong sorption of most POPs to soil organic matter, the potential for root uptake is very limited. Numerous studies have demonstrated that the soil to plant transfer factors of these contaminants are very low (Fries, 1996; Harms, 1996; Wild *et al.* 1995; Smith, 2000). Even if they enter the root system in significant amounts, most POPs do not efficiently translocate into the above ground plant parts due to their physico-chemical properties (McCraday *et al.*, 1990 cited in Wild *et al.*, 1992).

Volatile compounds are considered to be lost from the soil before they have the opportunity to enter plant tissue via root uptake (Wild *et al.*, 1995; Duarte-Davidson *et al.*, 1996). However, although they may not enter *via* the roots, compounds identified as volatile or moderately volatile can potentially enter plant tissues via foliar absorption (Duarte-Davidson and Jones, 1996). There is substantial evidence to indicate that this pathway is the primary mechanism of plant tissue contamination, and this is discussed further in the following sections.

Polycyclic aromatic hydrocarbons (PAHs)

Wild and Jones (1992) investigated the uptake of PAH compounds by carrots grown on sludge amended soils. 'Worst case' conditions, to maximise the potential transfer to the crop, were provided by using a sandy soil of low organic matter content, which may potentially enhance the bioavailability of PAHs. The sludge was representative of biosolids spread on agricultural land in the UK, and this was mixed with the soil to provide application rates of 0 (control), 18, 55 and 180 t ha⁻¹. The sludge additions represented extreme rates of application compared with operational conditions where inputs are limited by nutrient loading rates. PAHs were detected in the above ground leaf tissues and in the soil (Figure 15). However, the Σ PAH in the soil was in the range of typical of background concentrations.

The mean foliage Σ PAH concentrations were in the range 305 - 370 $\mu\text{g kg}^{-1}$ dw and no statistically significant difference was detected between foliage Σ PAH concentrations of the control and sludge amended soils. Thus, there was no evidence that the sludge-borne PAH compounds in soil increase the PAH concentrations in the foliage. This suggested that atmospheric deposition was the main supply of PAHs to foliage. This was further supported from the profile of individual PAH congeners in the soil and leaf tissue. Thus, the lower molecular weight compounds: acenaphthalene/fluorene and phenanthrene were the most abundant in the carrot foliage. These compounds exist in the vapour phase in the atmosphere and generally dominate the Σ PAH burden of air over the UK (Wild and Jones, 1992). However, the Σ PAH in the peel of carrots grown in the sludge amended soil was significantly larger than the control. Carrot root peel from the control treatment contained 81 $\mu\text{g kg}^{-1}$ Σ PAH dw and in the sludge-amend soil, the

Σ PAH increased to 138, 184 and 203 $\mu\text{g kg}^{-1}$ dw for application rates of 18, 55 and 180 t ha^{-1} , respectively. The transfer of PAHs from the soil into the carrot root was restricted only to the peel with little or no movement detected into the main body of the root. Carrots represent a potentially 'worst case' for absorption of lipophilic compounds into the peel due to their high lipid content. However, this part of the crop is usually removed during food preparation. Also, given that rates of sludge application in practice are much smaller than those used by Wild and Jones (1992), combined with the application restrictions to horticultural crops (due to controls on potential pathogen transmission; ADAS, 2001), the OC content of the peel of carrots produced on sludge-amended soil is likely to be within the normal ranges measured for this crop.

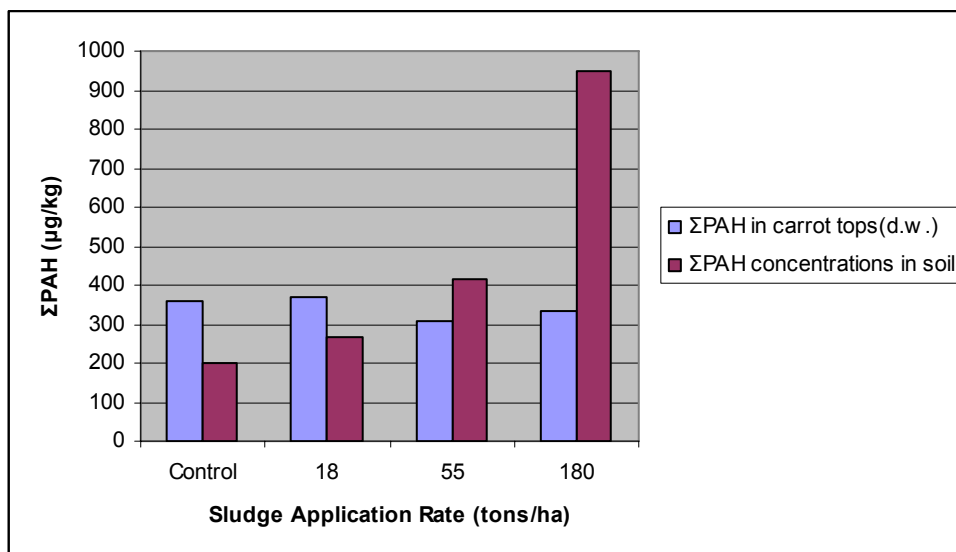


Figure 15 Σ PAH concentrations in soil and carrot foliage (dry weight) for various sludge application rates (Wild and Jones, 1992)

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzo-*p*-furans (PCDD/Fs)

Dietary intake represents over 90% of the human exposure to PCDD/Fs. Meat, milk and fish each contribute approximately 30% of the total exposure, while the intake from consumption of vegetables or fruits is considered to be negligible. Nevertheless, plants are the first link in the food chain and the potential uptake of PCDD/Fs into plant tissues, and its potential significance as a dietary source of this important group of POPs, has received considerable scientific investigation (Hülster *et al.*, 1994).

Various experiments suggest that root uptake of PCDD/Fs is minimal. For example, Müller *et al.* (1994) found no correlation between PCDD/F concentrations in soil and those in above ground plant parts of carrots, peas and lettuce. Hülster *et al.* (1993 cited in Hülster *et al.*, 1994), found that the PCDD/F concentrations in the shoots of various plant species were consistently <1 ng of I-TEq kg^{-1} (dw), even in plants grown on soils contaminated with up to 6000 ng of I-TEq kg^{-1} .

Prinz *et al.* (1990 cited in Wild *et al.*, 1992) found that the concentrations of PCDD/Fs in parts of plants harvested from below ground – such as potatoes and carrots – were significantly lower than concentrations found in above ground plant parts. Above ground, plant tissues are exposed to atmospheric sources of PCDD/Fs, which do not affect the below ground parts of the crop.

Engwall *et al.* (2000) applied anaerobically digested sewage sludges originating from various Swedish cities to a field experiment at rates between 36 and 55 t ha⁻¹ DS and measured the concentrations of PCDD/Fs in plant tissues of different crop types. The sludges were distributed into the top 3 cm of a light clay soil, and three days later, carrot and oil seed rape were sown. The crops were harvested after 82 and 125 days, respectively. The concentrations of dioxin-like compounds in carrots are shown in Figure 16. Oil seed rape seeds were examined because of their high fat content, which may increase the accumulation of lipophilic compounds. However, the concentrations of dioxin like compounds in the seeds were below the analytical limit of detection.

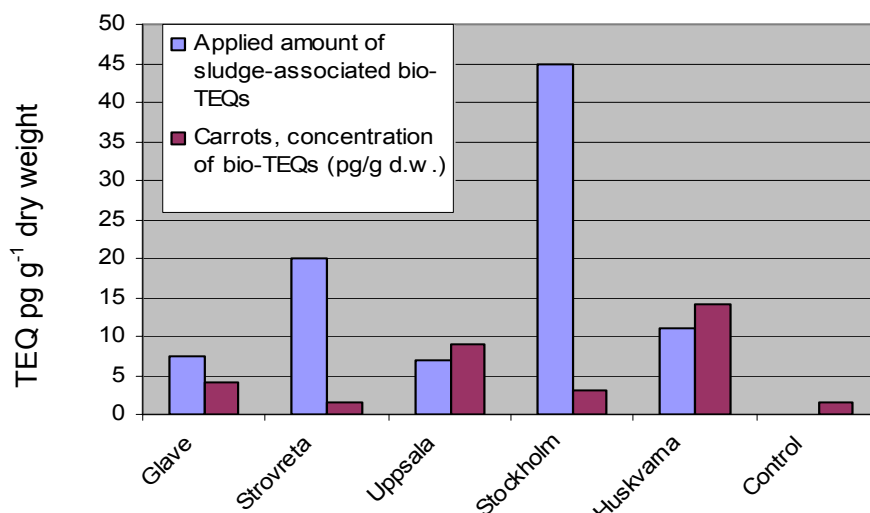


Figure 16 Amounts of dioxin-like compounds applied to soil in sludge and in carrot roots; the sludge application rate was between 36 and 55 t DS ha⁻¹ (Engwall *et al.*, 2002)

The concentrations of dioxin-like substances in carrot roots were in the range 2 - 14 pg bio-TEQs g⁻¹ dw, and were independent of the amounts applied in the different sewage sludges. In the case of sludge from Stockholm for example, which supplied the highest application rate of dioxin-like substances, the resulting concentrations in the carrots were amongst the smallest measured.

In terms of human exposure, the largest carrot concentration from this experiment (14 pg TEQ g⁻¹ dw) gave a total bio-TEQ intake equivalent to 84 pg TEQ if 100 g (fresh weight) of carrots were consumed. The tolerable daily intake (TDI) for dioxins set by the WHO is 1-4 pg TEQ kg⁻¹ of body weight. Using the most conservative estimate for the TDI of 1 pg TEQ kg⁻¹ and a body weight of 70 kg, results in a sum of 70 pg TEQ (Engwall *et al.*, 2000). Thus, the most conservative TDI may be slightly exceeded by normal background variations in the PCDD/F content of carrots. However, the results demonstrated that sewage sludge was not a source of PCDD/Fs entering the human diet through uptake into carrot roots.

Despite the general consensus that there is negligible uptake of PCDD/Fs by crop plants and that atmospheric sources are mainly responsible for crop contamination, there is evidence indicating that, for certain vegetables, eg zucchini and pumpkin, root uptake may be the more dominant pathway. Hülster *et al.* (1994) demonstrated this for zucchini in different experimental conditions shown in Figure 17. The soil had

an organic matter content less than 2%, and the PCDD/F concentration was 148 ng of I-TEQ kg⁻¹.

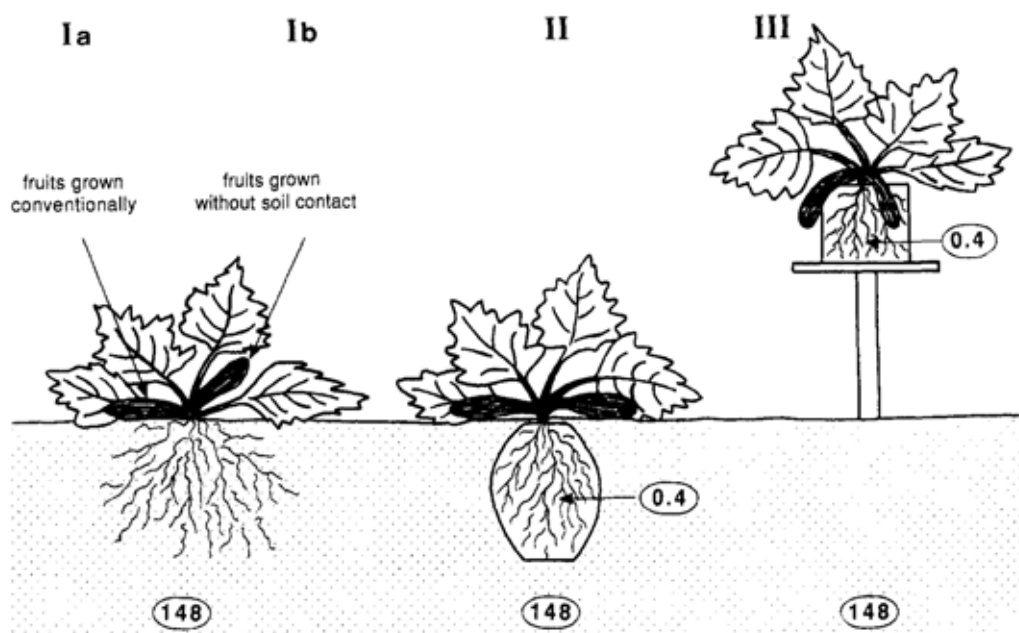


Figure 17 Schematic representation of experimental set up used to evaluate possible PCDD/F pathways into shoots (leaves and fruits) of Zucchini; note values are PCDD/F concentrations in soil in ng I-TEQ kg⁻¹ (Hülster *et al.*, 1994)

Details of each of the treatments shown in Figure 17 are described below:

- **Treatment Ia:** fruits were cultivated 'conventionally' within the soil. This was to allow an evaluation of the influence of direct soil contact on crop contamination.
- **Treatment Ib:** fruits were fixed to a wire frame to avoid soil contact.
- **Treatment II:** Pots containing plants growing in uncontaminated soil (containing 0.4 ng I-TEQ kg⁻¹) were buried into the PCDD/F contaminated soil such that the leaves and fruits were in contact with the contaminated soil, but the contaminated soil was separated from the uncontaminated soil. The purpose of this was to distinguish between root uptake and absorption of volatilised PCDD/F.
- **Treatment III:** Plants were grown in pots in uncontaminated soil (0.4 ng of I-TEQ kg⁻¹ soil) elevated 1.5 m above ground level to assess the contribution of atmospheric deposition.

PCDD/F concentrations in zucchini after 6 weeks growth are shown in Figure 18.

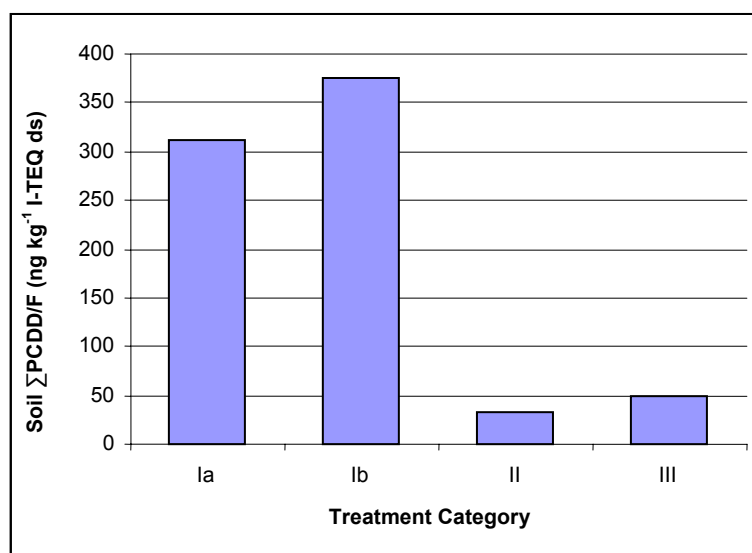


Figure 18 PCDD/F concentrations in zucchini grown in different types of treatment (adapted from Hülster *et al.*, 1994)

PCDD/F concentrations in zucchini fruit were similar with or without contacting the 'contaminated' soil (treatments Ia and Ib) (Figure 18). However, PCDD/F concentrations were much smaller in the fruit for plants grown in uncontaminated soil (treatments II and III). In this case, the presence of PCDD/F was only attributable to atmospheric deposition, and/or volatilisation of PCDD/F from the surrounding soil followed by subsequent redeposition onto the fruit surfaces. The relatively low PCDD/F values associated with treatments II and III indicated that these pathways were relatively minor, and the major pathway of PCDD/F contamination for zucchini fruits was through root uptake and translocation to the shoots.

To further examine the potential for root transfer of PCDD/Fs to zucchini, Hülster *et al.* (1994) grew the crop on another site with a clayey-loam soil with a larger organic matter content (8.1%). The vegetables were grown conventionally on two plots with PCDD/F concentrations of 328 and 2390 ng of I-TEQ kg⁻¹ soil. The resulting ΣPCDD + PCDF concentrations in the fruits were 649 and 2833 ng kg⁻¹ dw, respectively. This provided further evidence that root uptake was the main pathway of entry of PCDD/Fs into zucchini fruits. Therefore, whilst transfers of PCDD/Fs to plant tissues via root uptake are negligible for the majority of crops, a limited range of crop species may exhibit some potential to accumulate PCDD/Fs by this route.

Polychlorinated biphenyls

O'Connor *et al.* (1990) examined the uptake of sludge borne PCBs by fescue, lettuce and carrots. Soil was treated with municipal sewage sludge containing PCBs in amounts ranging from 0.46 to 2.4 mg kg⁻¹ DS. Crops were grown on two different soil types: a Glendale clay loam and a Bluepoint sandy loam.

The soil surface in half the tests were covered with polyurethane to absorb volatilised PCBs to protect plant tops from contamination by PCB vapours. The results for the Bluepoint sandy loam are shown in Table 69 and PCB contamination is expressed in bioconcentration factors (BCFs). The treatments with polyurethane are indicated as 'Protected.'

Table 69 PCB bioconcentration factors (BCF) for plants grown in Bluepoint sandy loam (O'Connor *et al.*, 1990)

BCF = $\mu\text{g PCB kg}^{-1}$ fresh weight / initial soil concentration ($\mu\text{g kg}^{-1}$ ds)

Treatment	PCB loading mg kg^{-1}	Crop or plant part				
		Fescue	Lettuce	Carrot Top	Carrot Root	Carrot Peel
Unprotected	0					-
Protected	0					-
Unprotected	0.46	<0.04 ^a	<0.04	<0.04	<0.04	0.09
Protected	0.46	<0.04	<0.04	<0.04	<0.04	0.08
Unprotected	0.93	<0.02	<0.02	<0.02	<0.02	0.10
Protected	0.93	<0.02	<0.02	<0.02	<0.02	0.06
Unprotected	2.4	<0.008	<0.008	<0.008	<0.008	0.02
Protected	2.4	<0.008	<0.008	<0.008	<0.008	0.04

Notes:

^a All values preceded by < represent plant contents below the detection limit of $20 \mu\text{g kg}^{-1}$

The BCF values were very low in all cases and crop concentrations were less than the detection limit of $20 \mu\text{g kg}^{-1}$ in all plant parts except carrot peels. All the detectable PCB in carrots was located in the peel, which would be removed during food preparation. The results for the Glendale clay loam were smaller than for the sandy loam, reflecting reduced transfer to the crop due to increased sorption in the fine textured soil compared to the sandy soil type.

Chlorobenzenes

Wang and Jones (1994b) grew carrots in soil from a field site not previously treated with sewage sludge or other organic matter amendments. The soil was a sandy soil with an organic matter content of 2.4%. The soil was amended with sewage sludge at two rates of application equivalent to $19.4 \text{ t DS ha}^{-1}$ and 165 t DS ha^{-1} . Another soil sample was spiked with CB and a further treatment remained in an unamended condition and was the experimental control. Carrot seeds were sown and the crop was harvested after 100 days and separated into root and above-ground parts. Substantial losses of CB were measured from the soil during the experimental period (Table 70).

Table 70 Chlorobenzene concentrations in soil before sowing and after harvest ($\mu\text{g kg}^{-1}$ ds) (Wang and Jones, 1994b)

	Control	Spiked with CB	Low rate of sludge	High rate of sludge
Before Sowing	6.3	83	35	150
After harvest	4.4	57	21	110
% Loss	30%	31.0%	41%	27%

The majority of these losses occurred from the dichlorobenzene (DCB) and trichlorobenzene (TCB) congeners. The losses in the tetrachlorobenzene (TeCB), pentachlorobenzene (PeCB) and hexachlorobenzene (HCB) congeners were much smaller.

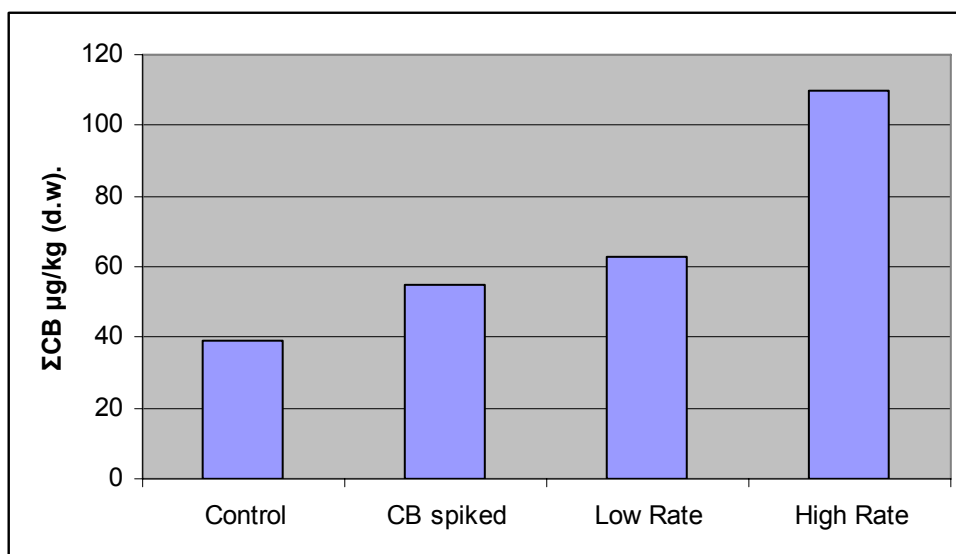
The Σ CB concentrations in carrot foliage and roots are shown in Figure 19.

The order of Σ CB concentration in the carrot foliage was as follows: high rate sludge amendment > low rate sludge amendment > spiked compounds > control. In the carrot cores, the order was: spiked compounds > high rate sludge amendment > control > low rate sludge amendment. The different profiles of CBs in the foliage and roots indicated that CBs occurring in the foliage were not translocated from the roots. Thus, the translocation of CBs from the below ground plant parts to the above-ground plant parts is very restricted. CB contamination in the roots was attributed to root uptake, but the contamination of CBs in the foliage was linked to foliar absorption. Indeed, over the course of the experiment, the concentrations of some trichlorobenzenes in the control plot increased as a result of foliar absorption. However, dichlorobenzenes (DCB), which are also highly volatile, did not increase in the control plants, even though they were lost in large amounts from the sludge-treated plots. A possible explanation for this is that DCB revolatilises from foliar surfaces to the atmosphere. Wilson and Meharg (2003) also proposed this as a mechanism to explain the higher concentrations of the moderately volatile 1,2,4-trichlorobenzene measured in grass grown in spiked soil compared to the more volatile 1,2-dichlorobenzene.

3.1.3 Animal Ingestion

Soil acts as a repository for POPs and, whilst concentrations in soil are declining (see Section 2.1.1), their intake with soil ingested by grazing animals can be anticipated. The amount of soil ingested depends on climatic conditions and the type of livestock. It has been estimated that an average of around 6% of livestock diet is soil (Fries, 1996; Stark and Hall 1992), although ingestion rates may be much higher than this under conditions of drought or over grazing, for example. For example, Stephens *et al.* (1995) suggested that up to 18% of the diet of cattle may be soil. The lipophilic properties of ingested organic compounds may result in their accumulation in animal tissues, milk and dairy products (Fries, 1996; Smith, 2000). Indeed, this pathway is considered to represent the greatest risk of entry of persistent lipophilic organic compounds into the food chain (Fries, 1996; Smith, 2000).

(a) Carrot foliage



(b) Carrot core

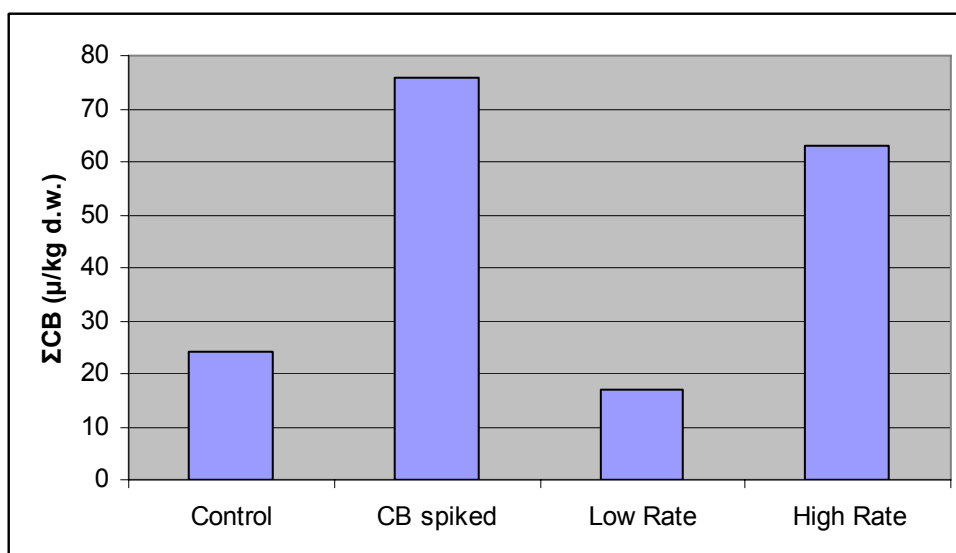


Figure 19 Chlorobenzene concentrations in (a) carrot foliage and (b) carrot core (Wang and Jones, 1994b)

2,3,7,8-TCDD, the lighter congeners of PCBs, higher chlorinated compounds of chlorobenzenes, all PAHs (except for naphthalene, acenaphthene and fluorene) are persistent in soil and have physico-chemical properties giving them a high propensity to bioaccumulate in animal fat. Nevertheless, PAHs do not appear to accumulate in animal tissue. Lusky *et al.* (1992 cited in Fries, 1996) found that the concentrations of PAHs in animal tissues were the same regardless of whether the animals had high or low concentrations of PAHs in their feed. The accumulation of PAHs in the animal tissues did not exceed $0.05 \mu\text{g kg}^{-1}$. This evidence suggests that PAHs are metabolised to soluble compounds and, therefore, do not accumulate significantly in body tissues.

Whilst PCBs, PCDD/Fs and CBs are not metabolised and can accumulate in the food chain, the risks still appear to be extremely low, especially from contaminants that enter soil from sewage sludge applications. Controls outlined in the Safe Sludge Matrix (ADAS, 2001), aimed at reducing the potential risk of infection from enteric pathogens by grazing animals (eg by not permitting the surface spreading of conventionally treated sludge on pasture used for grazing), also indirectly reduce the potential for animal ingestion of contaminants. Soil injection of sludge into grazed pasture is permitted, but this practice also eliminates animal ingestion of OCs (Stark and Hall, 1992). In addition, the risks of grazing animals ingesting OCs from the application of sludge are minimal at current agronomic rates (Stark and Hall, 1992). Detailed analysis of the PCDD/F congeners in sludge (Alcock and Jones, 1997 cited in Smith, 2000) showed that the application of sewage sludge does not cause any significant increase in the concentrations of these compounds in cows milk. Furthermore, the most toxic dioxin, 2,3,7,8 TCDD, is rarely detected in sewage sludge (Suaerbeck and Leschber, 1992).

In December 1999, the US EPA proposed a limit for PCDD/Fs and certain dioxin-like PCBs of 300 ng kg⁻¹ TEQ DS in sludge for agricultural use in the Round Two regulation 40 CFR Part 503 Standards for the Use or Disposal of Sewage Sludge (US EPA, 1999). However, following further evaluation of the pathways of greatest exposure from consumption of crops and meat products by farmers and their families, who were assumed to produce a significant proportion of their own food on sludge-treated land for an entire lifetime, EPA determined that dioxins from this source do not pose a significant risk to human health or the environment. US EPA also noted the continuing decline of dioxin concentrations in sludge, particularly with more rigorous control on combustion practices. Therefore, US EPA decided that no numerical limits or specific management practices were required for dioxins in land-applied sewage sludge (US EPA, 2003). The regulation of PCDD/F emissions has resulted in a significant reduction in the burden of these substances in the human body (Buckler-Golder, 1999).

The risk-based limit for PCBs in sewage sludge derived by US EPA was 6.6 mg kg⁻¹ DS from an evaluation of transfers to the human foodchain via the animal ingestion route (assuming a sludge application rate of 7 t DS y⁻¹; Smith, 2000). Chaney's reevaluation of this pathway (Chaney *et al.*, 1997) gave a risk-based limit for PCBs in sludge of 3.2 mg kg⁻¹ DS (Smith, 2000). However, both of these values are well above the maximum PCB concentrations found in sludge of <1.0 mg kg⁻¹ DS (Table 30 and 32). In a recent survey, Jones and Northcott (2000) reported a maximum Σ PCB content in UK sludge of 0.33 mg kg⁻¹ and mean value of 0.19 mg kg⁻¹ DS. Consequently, the PCB content of sludge is significantly below the safe thresholds indicated by worst-case exposures assumed in risk assessments. Therefore, as with PCDD/Fs, there is also negligible risk to human health and the environment from this group of contaminants when sewage sludge is recycled in agriculture. Since the ban on PCBs in the UK in 1977, the concentrations of this contaminant in soil continue to decline significantly (see Figure 7).

The principal risk from POP accumulation in the food chain comes mainly from atmospheric deposition of contaminants onto soil and crops. However, published information on the changes POP concentrations in soil and plant tissues demonstrate that the environmental controls to reduce emissions of these substances have effectively minimised the potential transfer of POPs to the foodchain.

3.1.4 Soil ecology

TCDD is one of the most toxic known substances. In the past, one of the sources of TCDD entering soil was as a residual by-product in the herbicide 2,4,5-T.

Reinecke and Nash (1984) studied the effects of 2,3,7,8-TCDD on earthworms at concentrations ranging from 0.05 to 5.0 $\mu\text{g g}^{-1}$ soil during an exposure period of 85 days. These concentrations are 1×10^6 and 1×10^8 times greater than the concentrations found in field soil. However, there was no evidence of toxicological effects or mortality from this extent of TCDD exposure. No gross tumours were detected upon dissection and microscopical examination. The lethal concentration of TCDD to earthworms was between 5 – 10 mg kg^{-1} soil. Consequently, TCDD does not represent an acute toxicity risk to earthworms. However, chronic exposure to sublethal concentrations of TCDD may cause an accumulation of TCDD in the body tissues. Reinecke and Nash (1984) concluded that concentrations of TCDD exceeding 2 $\mu\text{g g}^{-1}$ in the body tissues may produce adverse effects in earthworms. Significant bioaccumulation of TCDD in body tissue (0.25 $\mu\text{g g}^{-1}$) was measured equivalent to 5 times the original soil concentration (0.05 $\mu\text{g g}^{-1}$). As earthworms are an important source of food for higher organisms in natural foodchains and the accumulation of TCDD may therefore present a significant ecological risk. Modelling studies also predict the accumulation of chlorobenzenes, chlorophenols and other polychlorodibenzo-p-dioxins in earthworms (eg Belfriod *et al.*, 1995).

Chaudri *et al.* (1996) found that aroclor 1016 (a PCB) and anthracene (a PAH) had no or very little effect on the N fixing bacteria, *Rhizobium leguminosarum* biovar *trifolii*, which is regarded as a sensitive 'sentinel' species for assessing the potential impacts of contaminants on soil ecological systems. Both compounds were added separately to soil samples at rates equivalent to the highest concentrations found in sewage sludge. The absence of any ecotoxicological effects was explained because: (1) the concentrations in sewage sludge are not toxic to *Rhizobium*; (2) the compounds become strongly adsorbed to soil, thus reducing their availability and hence toxicity; and/or (3) *Rhizobium* may be tolerant to the organic compounds and their derivatives.

Aldrich and Daniel (2003) concluded that, for PCDD/Fs, PAHs and PCBs, sufficient data were available to exclude an unacceptable risk to soil organisms by the recycling of compost in agriculture.

In overall assessment, there is no evidence of a direct impact of POPs on soil ecological systems. However, there is the potential for bioaccumulation through natural foodchains and there is a case for a more detailed review and assessment of the potential significance and impacts of POP transfers from soil to wildlife.

3.2 Pesticides

A very large proportion of the pesticides applied for weed, insect and disease control in modern intensive agricultural systems reach the soil where they interact with organic and mineral constituents and are subject to biological and chemical transformation processes (Section 2.6). Some pesticides are applied also directly to the soil. On average, only an estimated 0.3% of an applied pesticide may reach the target organism, and the remaining 99.7% is dispersed into the environment, of this, 85% is assumed to enter the soil (Margni *et al.*, 2002). Microbial degradation is the primary route for loss of pesticide compounds from soil, and hence this is a key process affecting the dynamics of pesticides in the environment, including their

persistence in soil, their susceptibility to leaching and ultimately their entry into surface and groundwater bodies (Aislabie and Lloyd Jones, 1995). Because of the very large number of registered pesticides, only those which are commonly used are reviewed here.

3.2.1 Fate in soil

Pesticides vary in their significance to soil in that some are mobile and readily degradable while others are more persistent and hence have the potential to accumulate and to impact on non-target organisms in soil (HRI, 2002). Those with a 50% decay time (DT50) of less than three months are usually regarded as readily degradable. A number of compounds with a DT50 over 6 months are widely used in the UK, including the triazol fungicides and the herbicide, diflufenican. Diflufenican is the fourth most widely used herbicide in Great Britain, used mainly for controlling broadleaved weeds in winter cereals (CSL, 2003b).

The persistence of different groups of pesticides are shown in Table 71 and measured half-lives from UK field experiments are shown in Table 72.

Table 71 Persistence of different pesticide groups in soil

Type of pesticide	Group	Persistence	Reference
Insecticide	Organophosphate (OP)	Low. Rapid degradation	Merrington <i>et al.</i> , 2002
	Carbamates	Persistent	Merrington <i>et al.</i> , 2002
	Synthetic pyrethroids	Limited persistence	Merrington <i>et al.</i> , 2002
Herbicide	Triazines	Rapid degradation of atrazine. 80% is degraded within one year	Zimdahl <i>et al.</i> , 1970 cited in Voets <i>et al.</i> , 1974
	Phenoxyacetic acids	Rapid degradation upon contact with soil	Merrington <i>et al.</i> , 2002
	Carbamates	Limited persistence, 2-4 weeks. Degraded by soil microflora.	Merrington <i>et al.</i> , 2002

The presence of plant roots increases the rate of pesticide degradation in soil. For example, Sun *et al.* (2004) found that disappearance rates of aldicarb in soil with growing plants was significantly faster ($P < 0.05$) than that in soil without plants. This is explained because exudates and enzymes released by plant roots stimulate both microbial and biochemical activity in the surrounding soil. Degradation rates are also increased by the addition of sewage sludge to soil. Thus, Sanchez *et al.* (2004) showed that fenitrothion and dimethoate both degraded more rapidly in sludge treated soil compared to unamended control soil. Diazinon degrades in soil mainly by chemical processes. However, the availability of this compound was reduced by sludge amendment, presumably due to increased adsorption to the sludge matrix

and organic matter; consequently the residue was more persistent with sludge application compared to the control soil.

The multiple application of pesticide substances may have an enhancing or detrimental effect on soil biological processes. Thus, Williams *et al.* (1996) suggested that, where soils are repeatedly exposed to pesticides, the microbial population becomes acclimated and degrade pesticides more rapidly compared to when pesticides are seldom used. However, Williams *et al.* (1996) do not speculate as to whether this would have any long term influence on the soil microbial community or soil fertility. Other evidence indicates that fungicide applications may impact soil microbial activity and reduce the degradation other pesticide compounds. For example, the fungicide chlorothalonil reduced dehydrogenase activity in soil by up to 45 % over a 3 month period, when applied at typical field rates (HRI, 2002). Significantly, it also reduced the rate of mineralization of subsequent additions of the herbicides isoproturon and bentazone by up to 36 % (HRI, 2002). The fungicide azoxystrobin had no effect on dehydrogenase activity, but inhibited mineralization of a subsequent addition of isoproturon by up to 11 % (HRI, 2002).

Table 72 Summary of pesticide concentrations in soils in Rosemaund field experiments (Williams *et al.*, 1996)

Chemical	First sample ¹		Last sample ²		Half life ³ (days)
	Conc (mg kg ⁻¹)	Days since application	Conc (mg kg ⁻¹)	Days since application	
Mecoprop	0.091	1	<0.001	31	4
2,4-D	0.027	1	<0.004	48	4
Simazine ⁴	0.175	2	0.081	84	84
Lindane ⁴	0.040	5	<0.002	90	28
Isoproturon	0.100	5	<0.01	91	14
Isoproturon	0.030	5	<0.01	75	
Mecoprop	0.058	1	0.002	62	11
Isoproturon	0.200	3	0.056	46	21
Dimethoate	0.031	2	<0.005	41	10
Dimethoate	0.022	2	<0.005	14	
MCPA	0.188	1	<0.001	40	8
Carbofuran	0.350	7	0.087	91	38
Atrazine ⁴	0.097	1	0.017	124	45
Aldicarb	0.030	7	0.020	69	25-50
Trifluralin	0.063	3	0.049	83	
Chlorpyrifos	0.077	5	0.060	33	80

Notes:

1 First samples are mean concentration on first sampling visit after spraying, with time elapsed since spraying.

2 Last samples are mean concentration on last sampling visit, with time since spraying, or detection limit and time of first samples to be below limit.

3 Half lives are estimated from field data assuming first order degradation. No value indicates data too variable to allow calculation.

4 Now withdrawn from general use.

A pesticide may be degraded by both abiotic and biotic processes. The resulting transformation products are generally less toxic than the parent compound, however, there are instances where a transformation product may be more toxic. In addition, differences in the properties and persistence of the breakdown products may be such that that environmental compartments are exposed to the product to a greater extent than to the parent compound, further increasing its potential impact. Sinclair and Boxall (2004) conducted a literature study to determine reported data on pesticide degradation pathways. They obtained data for 60 pesticide active ingredients and 485 transformation products. A comparison of ecotoxicity values for the parent compounds with values for the transformation products indicated that the majority of transformation products had equivalent or reduced toxicity than the parent compound. However, a significant proportion of transformation products (30%) were more toxic than the parent compound (Sinclair and Boxall, 2004).

3.2.2 Soil Ecology

Ammonification

In general, herbicides and insecticides have little effect on ammonification (Yamamoto *et al.*, 1998; Wainwright, 1978). Schreven *et al.* (1970) found that ioxynill, mecoprop, MCPA, picloram and amitrole did not affect ammonification at 10 and 100 times normal rates of application in the field. However, many soil organisms are able to perform this function, therefore, it is regarded as an insensitive measure of the potentially toxic effects of soil additives on fertility. Indeed, Das and Mukherjee (2000) reported the stimulation in the activities of ammonifying bacteria when HCH and phorate were applied to laterite soil samples in a laboratory investigation.

Fungicide treatments are reported to increase ammonification in soils. Wainwright and Pugh (1973) observed such effects after testing captan, thiram and verdesan in field soils. While there were no effects at low concentrations, higher rates of the fungicides increased the rate of ammonification. However, these observations may not be indicative of a beneficial effect of the pesticide, but are likely to be explained due to the release of mineral N resulting from the death of components of the soil microbial community in response to fungicide addition.

Nitrification

At normal rates of field application, the majority of herbicides and insecticides have little effect on nitrification processes (Yamamoto, 1998; Wainwright, 1978). Domsch and Paul (1974) tested the effects of 35 herbicides on nitrification and found that most of them had a negligible effect when applied at field rates. Similar findings are presented by Yamamoto (1998), although bensulfuron methyl caused the temporary inhibition of nitrification. However, a complete recovery was evident 28 days after application.

Older fungicides such as nabam, verdasan and vapam were significant nitrification inhibitors. They are no longer in use, and the new systemic compounds appear to have only a marginal effect on nitrification when used at low concentrations, although some have been found to stimulate nitrate formation (Wainwright, 1978). Thiram, applied at a rate of $10 \mu\text{g g}^{-1}$ soil on a grassland soil caused a marked stimulation in nitrate formation (Wainwright and Pugh, 1973). Das and Mukherjee (2000) also found that the insecticides HCH and phorate stimulated nitrification in soil.

Organic matter decomposition

Respiration, as indicated by oxygen consumption or CO₂ evolution, is an index of the activity of the soil microflora involved in organic matter decomposition (Tu, 1980). Insecticides generally only have a minor influence on the soil respiration rate. Permethrin was found to stimulate oxygen uptake in a loamy sand soil sample in the laboratory (Wainwright, 1978). Lewis *et al.* (1977) applied 25 herbicides at their normal agricultural rates in various combinations to a loamy sand and a silty clay loam. After one week, alfalfa was added as a substrate to test the effects of the agrochemicals on organic matter degradation. However, no changes in CO₂ evolution were recorded compared to the untreated control during a 32 day monitoring period. The tests were repeated with concentrations 100 times those found in the field, but, again, no effects of the pesticides on CO₂ production were observed.

An initial decrease in soil respiration rates has been reported following the addition of fungicide compounds, followed by a marked stimulation of CO₂ production (Domsch, 1970 cited in Wainwright, 1978). The delayed stimulation was attributed to the increased activity of a few resistant microorganisms, rather than the return of the original population.

Smith and Woods (1996) measured the metabolic quotient (specific respiration rate of the microbial biomass) routinely in a programme of arable field trials on a arable loam soil amended with sewage sludge according to normal operational rates of application, and managed following conventional intensive agricultural practice (Figure 20). The microbial biomass responded to changing seasonal environmental conditions, as would be expected, and the quotient increased during periods when the soil moisture content decreased. However, although the purpose of the experimental work was not intended to assess impacts of agrochemical applications on soil microbial processes, this became evident following crop treatment with the herbicide isoproturon, a residual urea herbicide for use in cereals, when metabolic quotients significantly increased in moist soil (Figure 20) - when values are usually at their lowest - indicating a stress response to the applied agrochemical. Others (eg Harden *et al.*, 1993) also report reductions in the microbial biomass content and increased respiration activity in pesticide treated soils.

Population numbers

Das and Mukherjee (2000) tested the effects of four insecticides (hexachlorocyclohexane (a chlorinated hydrocarbon), phorate (an organophosphate), carbofuran (a carbamate) and fenvalerate (a synthetic phrethroid, which has since been withdrawn in the UK)) at their field application rates on the growth and activities of bacteria, actinomycetes and fungi. During a 60 day monitoring period following application, no negative effects were observed on the organisms and numbers increased, with bacteria showing the largest rise in population. The population increase was attributed to two factors: (1) the ability of the microorganisms to make use of the insecticides as substrates to derive energy, and (2) the death of a proportion of the soil microbial biomass, which was utilised as a nutrient source by bacteria, actinomycetes and fungi insensitive to the insecticides thus increasing the population of these organisms. The death and subsequent mineralization of microbial biomass also increased the available mineral N and P content in the soil.

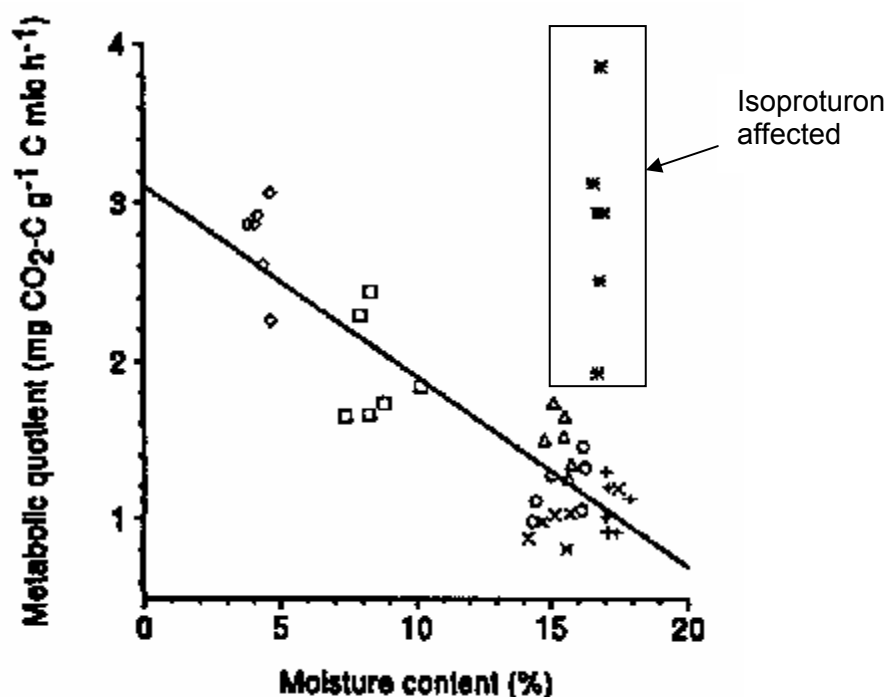


Figure 20 Effect of seasonal variations in soil moisture content, and the herbicide isoproturon, on the specific respiration activity of the soil microbial biomass under arable cultivation (Smith and Woods, 1996)

Kale *et al.* (1989) applied the insecticides carbofuran and carbaryl to soil samples in liquid cultures at normal and 10 times their normal field application rates. The metabolites of these pesticides are known to effect some biological processes more than the parent compounds. Carbofuran is metabolised to 3-hydroxycarbofuran and 3-keto-carbofuran. Carbaryl is metabolised to 1-naphthol. However, neither of the parent compounds or their metabolites affected the growth of *Rhizobium* sp. However, the growth of *Azotobacter chroococcum* was inhibited by the insecticides and their metabolites at field application rates (Table 73). The impact of the metabolites on the activities of *Azotobacter* depended on the extent of transformation of the parent compounds in soil, which may be interfere with the nitrogen fixing mechanisms of the bacterium.

Chaudri *et al.* (1996) applied 200 mg kg⁻¹ of pentachlorophenol (PCP) (the maximum concentration of PCP found in sewage sludge) to a sandy loam soil. After 5 weeks, a 99% reduction was observed in the population of *Rhizobium leguminosarum* bv *trifolii*, without any evidence of a recovery. Further tests revealed that the lowest observed adverse effect concentration (LOAEC) in soil was 75 mg kg⁻¹. PCP is no longer manufactured in the UK.

The Danish National Environmental Research Institute investigated the sub-lethal effects of pesticides on invertebrates such as protozoa, enchytraeidae, collembola, predaceous mites and on microbial respiration (DK EPA, 1995). A semi-field test system was developed involving collembola and predacious mites. The organophosphate (OP) insecticide, dimethoate, caused a significant reduction in collembola populations in the laboratory and field tests. Pirimicarb (an insecticide) and fenpropimorph (a fungicide) showed effects at single sampling dates in the field, but not in laboratory incubation tests.

Table 73 Effect of carbofuran, carbaryl and their metabolites on the growth of *Azotobacter chroococcum* in nitrogen free culture medium (adapted from Kale *et al.*, 1989)

<i>Treatment</i>	<i>Concentration in soil (mg kg⁻¹)</i>	<i>Population after 48 hours of incubation</i>
Untreated (Control)	-	4.40
Carbofuran^a	0.5	0.72
	5	0.44
3-hydroxycarbofuran^a	0.5	0.55
	5	0.37
3-ketocarbofuran^a	0.5	0.64
	5	0.22
Carbaryl^b	2.5	1.00
	25	0.45
1-napthol^b	2.5	2.45
	25	1.00

^a 0.5 mg kg⁻¹ represents the normal application rate for carbofuran and both its metabolites.

^b 2.5 mg kg⁻¹ represents the normal application rate for carbaryl and its metabolites.

Bromilow *et al.* (1996) analysed the soil from a field that had received annual applications of the insecticide aldicarb over a period of 20 years. No negative effects on crop productivity were measured when yields at the start and end of the 20 year period were considered. Microbial processes were also unaffected.

The effects of phenoxyalkanoic acid herbicides (eg 2,4-D, mecoprop and MCPB) on soil microorganisms and microbial processes have been intensively investigated since the early 1950s. No significant effects have been found on soil fertility. 2,4-D and other phenoxies have been applied repeatedly for many successive years on the same soil in many areas of the world without any negative impacts being recorded on soil ecology. For example, McCurdy and Molbery (1974 cited in Voets *et al.*, 1974), showed that field applications of 2,4-D for 18 years did not affect the numbers of bacteria, actinomycetes or fungi in soil. Similarly, Biederbeck *et al.* (1987) reported that 35 years of annual 2,4-D field applications had no effects on the microbial biomass or N mineralization. Small reductions in nitrification were measured immediately after the application of 2,4-D, but these were only temporary and did not cause a loss in soil fertility.

The influence of triazine herbicides (eg simazine, atrazine) on soil microflora have also been thoroughly investigated. Significant reductions of sporeformers (Audus, 1970), and nitrifying bacteria (Farmer *et al.*, 1965; Chunderova and Zubets, 1971 cited in Voets *et al.*, 1974) have been observed in soils treated with these herbicides. Voets *et al.* (1974) examined the effects of annual applications of atrazine over a 14 year period on a field soil and observed long term reductions in the numbers of anaerobic bacteria, sporeformers and cellulolytic organisms. The long term application of atrazine also caused large and persistent depression of phosphatase

and urease enzyme activities, which were reduced by 42% and 36% compared to untreated control soil, respectively (Voets *et al.*, 1974).

Recent investigations (HRI, 2002) have examined the soil microbial community structure 3 months after treatment with the fungicides: chlorothalonil, azoxytrobin and tebuconazole. None of the pesticides affected the structure of the soil bacterial community. However, as may be expected, they inhibited members of the eukaryote community, and, in particular had a negative impact on the soil protozoa population (HRI, 2002).

3.2.3 Implications for Human Health

Humans are exposed to pesticides through drinking water, food, inhalation of air and contact with skin. Food contamination is considered to be the main source of exposure, and intakes are approximately 10^3 to 10^5 times larger from this route compared to drinking water or by inhalation (Margni *et al.*, 2002). Pesticides can potentially enter the food chain through plant uptake from soil or in animal products resulting from the ingestion of contaminated soil by grazing animals. Direct application of pesticides onto food is the main source of pesticide entry into the food chain. This section reviews the possible risks to human health from pesticide exposure *via* food.

Understanding of the intensity and duration of exposure to pesticides is a critical prerequisite for assessing the potential health risks. Unfortunately, despite advances in analytical chemistry, there remains considerable uncertainty regarding human exposure to pesticides and evaluating toxicological effects. A large volume of data on the acute toxicity of pesticides to humans is available (based on tests with other mammals) for nearly all pesticides. Data on chronic toxicity, however, is scarce.

Public concern over the potential adverse health effects of pesticides has focused on chronic end points including cancer, developmental, reproductive, immunological and mutagenic effects (van der Werf, 1996). Experimentalists and epidemiologists have devoted considerable attention to assessing the potential for these effects from pesticide exposure. There are, however, inconsistencies in the results obtained from these two approaches (Baker and Wilkinson, 1990). In contrast to experimental studies, where the effects of specific pesticides can be evaluated, epidemiologic studies are difficult to design and interpret because humans are rarely exposed to only one pesticide. As a result, few reliable epidemiological studies into chronic adverse health effects of pesticides are available (Baker and Wilkinson, 1990).

The immune system plays a critical role in resistance to infectious disease. Some research has examined the potential for pesticide induced immune dysfunction in animals. Olson *et al.* (1987) found that mice exposed to levels of aldicarb at $1 \mu\text{g kg}^{-1}$ in the diet for 34 days had suppressed antibody responses.

Due to similarities between the vertebrate and invertebrate nervous systems, insecticides designed to affect the insect nervous system are potentially capable of producing acute and chronic neurotoxic effects in humans. Both acute and chronic alterations in sensory motor, autonomic, cognitive and behavioural functions have been observed in people exposed occupationally to relatively high levels of insecticides (Branch and Jacqz, 1986).

A number of pesticides have also been shown to cause reproductive toxicity in animal species. Carbaryl reduced male reproduction following occupational

exposures (Baker and Wilkinson, 1990). Epidemiologic studies of occupational groups exposed mainly to some of the organochlorine pesticides have noted small, but consistent excesses of lung cancer. Blar *et al.* (1985) observed elevated risks for cancer among farmers.

Pesticides undergo an extensive toxicological evaluation prior to receiving approval for commercial use (see Annex H). To safeguard consumers, maximum residue limits (MRLs) for some pesticides found in foodstuffs have been set (Pesticides Safety Directorate, 2005). MRLs are set for each pesticide on a wide range of fruit and vegetables, cereals and animal products. The Independent Pesticides Residues Committee (PRC) monitors residues in foodstuffs in the UK. The law prohibits suppliers from marketing produce containing more than a specified amount of residue. MRLs are set below safety limits. The safety limit depends on a number of factors such as the properties of the pesticide, the amount of residue, amount of food being consumed, whether this is being consumed in a single meal or over a longer period, and bodyweight. As a result of these measures, it must be concluded that human dietary exposure to pesticide residues in the UK is consistently well within established safety standards (Pesticides Safety Directorate, 2005).

3.3 Veterinary medicines

Antibiotics are biologically active substances, designed with the intent to effect microorganisms. They are usually mobile as their water solubility is high relative to the molecular weight. Many medical substances have similar properties to other harmful xenobiotics: they are lipophilic (in order to be able to pass membranes) and are persistent. Thus, they have a high potential to bioaccumulate and impact the environment.

The spread of antibiotic resistant human pathogens has been directly linked to the use of antibiotics in animal husbandry (Haller *et al.*, 2002). Haller *et al.* (2002) suggested that, rather than due to direct food contamination, this is as a result of antibiotics entering the water environment following manure application to land, given that large quantities of antibiotics and antibiotic resistant genes are excreted in manure. The possible environmentally relevant modes of action of selected groups of medicines and potentially sensitive species are shown in Table 74.

3.3.1 Fate in soil

A significant portion of a drug is excreted in the faeces or urine after administration, depending on the pharmacokinetics of the compound, either as the parent substance or more water-soluble metabolites, which frequently transfer to the manure. Knowledge about the distribution coefficients, K_d , of the drugs in the specific matrix, for example, between the solid phase ie manure particles, and the aqueous phase ie the liquid portion of manure, can help provide an estimation of the bioavailability of the compounds (Jørgensen and Halling-Sørensen, 2000). K_d may be estimated from K_{ow} and f_{oc} , however, Loke *et al.* (2002) suggested that, whilst these physico-chemical parameters may be useful for estimating distribution co-efficients in soil, they provide only a limited indication of the likely partitioning in manures.

Olaquinox (log K_{ow} = -2.3) and metronidazole (log K_{ow} = - 0.1) both have low tendencies to sorb to particles in manure. This corresponds with the negative log K_{ow} values of these antibiotics. Compounds with K_{ow} values in the range 1.5 – 2.0. on the other hand, sorp relatively strongly to manure particles, eg, tylosin (log K_{ow} = 1.63). The relative tendency of these four antibiotics to bind to manure is the same as their

sorption to soil. Sorption of oxytetracycline to manure is much higher than would be expected from the negative log K_{ow} value of this compound. Loke *et al.* (2002) suggested that sorption of oxytetracycline to manure is influenced by ionic binding to divalent metal ions as such Mg and Ca as well as other charged compounds in the matrix. In contrast, the relatively strong sorption of tylosin A to manure corresponds with data found for soil sorption of tylosin.

Table 74 Possible environmentally relevant modes of action for selected groups of medicines and potential sensitive species (RIVM, 2003)

Major Group	Class	Mode of action	Possible sensitive organisms
Antimicrobials	tetracycline	block bacterial translation by binding to the 30S subunit of ribosomes	soil and sediment, bacteria
	sulphonamides	analogues of p-aminobenzoic acid and competitively inhibit formation of dihydropteroic acid structurally similar to sulphonylureas which have herbicidal activity	soil and sediment bacteria, possible effects on macrophytes
	macrolides	inhibit translocation	gram-positive bacteria in soil and sediment
	β -lactams	inhibits transpeptidase enzyme, critical in the production of bacterial cell walls	gram-positive bacteria in soil and sediment
	quinolones	bind to A sub-unit of DNA gyrase and inhibit DNA synthesis	gram-positive bacteria in soil and sediment
Fungicides	imidazoles	inhibit action of fungal cytochrome P450	soil fungi and aquatic hyphomycetes
Sex hormones	estrogens	mimic estrogen, the female sex hormone	Fish, birds
Parasiticides	macrolide endectins	stimulation of γ -amino butyric acid, an inhibitory neurotransmitter	dung beetles and flies, other arthropods
	benzimidazoles	interfere with energy metabolism by inhibition of polymerisation of microtubules. Also effect fungi	dung beetles and flies, soil fungi and aquatic hyphomycetes
	tetrahydropyrimidines	cholinergic inhibitors	dung beetles and flies, and other arthropods
	organophosphates	inhibitors of cholinesterase	arthropods, fish, birds
Cytotoxics		cytotoxicity	fish, invertebrates

The persistence of veterinary medicines in a soil or manure depends on its photostability, its binding and adsorption capability, its biodegradation rate, and leaching in water (Kümpel *et al.*, 2001). Some compounds, such as ivermectin, chlorotetracycline and amprolium, persist for several months, while others, such as tylosin in pig slurry, penicillin and ncarbazin in poultry manure, degrade within a few

days. The antibiotic, sulfadimidine was detected in environmentally significant concentrations 7 months after liquid pig manure application indicating the high stability of some antibiotics in manure and soil (Christian *et al.*, 2003). The type of manure in which the compound is in may also affect degradation rates: sulfachloropyridazine rapidly degraded in broiler faeces, for example, but persists in faeces of laying hen (Boxall *et al.*, 2004). On livestock farms that house many animals, large quantities of manure or slurry are produced. The manure is usually stored for varying lengths of time before it is applied to land as fertilizer. During the storage period, veterinary medicines and their degradation products may potentially degrade further. This may reduce the potency of the antibiotics. Degradation rates in manure are generally faster than degradation in soil (Loke *et al.*, 2000; Boxall *et al.*, 2004). The persistence classes of different veterinary medicines in manure are listed in Table 50.

A number of different mechanisms are involved in drug sorption. The most important being sorption to organic matter, surface adsorption to mineral constituents, ion exchange, and complex formation with metal ions such as Ca^{2+} , Mg^{2+} , Fe^{3+} , or Al^{3+} (e.g. tetracyclines) (RIVM, 2003). Antibiotics are capable of binding to soil, or forming complexes with ions present in the soil. On contact with soil, a veterinary medicine may partition to the soil particles, leach to groundwater and/or be degraded. The extent to which veterinary medicines may adsorb to particulates varies widely and, consequently, so does their mobility and availability for uptake by soil organisms. This variation is due to the chemistry of the specific compound, which is influenced by soil chemistry including organic carbon content, clay content, pH of the soil solution and ion-exchange capacity. In general, increasing sorption of an antibiotic to the manure or soil matrix reduces the antimicrobial activity. Desorption, on the other hand, tends to reactivate antimicrobial potency (Lunestad and Goksøyr, 1990).

The main route for degradation of veterinary medicines in soil is *via* aerobic biodegradation (Boxall *et al.*, 2004). Degradation rates in soil vary with half-lives ranging from days to years (Ingerslev and Halling-Sørensen, 2001). The persistence of major classes of veterinary medicine in soil are listed in Table 75. As for other xenobiotics, if the manure or sludge contains high numbers of microorganisms, biodegradation is increased in soil.

Environmental conditions also affect degradation rates: temperature, soil moisture and the presence of specific degrading bacteria, some of which will have developed the ability to degrade specific group veterinary products, also have a role. Gavalchin and Katz (1994) studied the degradability of seven faecal-borne antibiotics in soil. Five of the seven antibiotics disappeared at 30°C, while only two were eliminated at 4°C. Ivermectin degraded 6 times faster in summer than in winter (Boxall *et al.*, 2003a). Thus, the timing of manure application to land may be a significant factor in determining the subsequent degradation rate of a compound (Boxall *et al.*, 2003a). As well as temperature, soil texture and type are also important. For example, ivermectin degraded faster in a sandy soil than in a sandy loam (Boxall *et al.*, 2003a). Weerasinghe and Towner (1997) found that an antimicrobial agent had half lives varying from 87 to 173 days depending on the soil type.

Metabolites, in general, are less potent than the parent compounds, but may still be highly toxic. Studies on tetracyclines have shown that some metabolites have similar potencies on bacteria as their parent compounds (Halling-Sørensen *et al.*, 2002). A decline in concentration of tetracyclines in soil, for example, was not found to cause a decline in microbial toxicity (Halling-Sørensen *et al.*, 1998). Indeed, 5a,6-anhydrotetracycline and 5a,6-anhydrochlortetracycline had potency on tetracycline-resistant bacteria indicating a different mode of action than that of the parent

compounds (Halling-Sørensen *et al.*, 2002). Thus, any risk assessment based on the parent compound may underestimate real effects in the environment. Also, some metabolites behave differently from the parent compound. For example, 5a,6-anhydrotetracycline hydrochloride (ATC) is more mobile than its parent, tetracycline, and is therefore more readily transported into groundwater and surface water.

Overall, despite their varying levels of degradability, most antibiotics are considered to be relatively persistent. Several antibiotic compounds are not transformed by wastewater treatment processes or by the aeration of manure, even at increased ambient temperatures (Jørgensen, 2000). Several studies have detected a variety of antibiotics in surface and tap water at concentrations up to $1 \mu\text{g l}^{-1}$ (Stan *et al.*, 1994; Stan and Linkerhägner, 1992 cited Halling-Sørensen *et al.*, 1998). The presence of these chemicals in surface and tap waters indicates that little or no degradation of the substances took place during sewage treatment, thus confirming their persistence (Kümpel *et al.*, 2001). Furthermore, residues of antibiotic measured in soil and sediment were shown to be associated with the most persistent compounds in laboratory and field degradation studies (Kümpel *et al.*, 2001).

The most widely used groups of animal husbandry antibiotics in the European Union are tetracyclines, macrolides, penicillins, aminoglycosides, sulfonamides and trimethoprim (Haller *et al.*, 2002). Tetracyclines sorb strongly to soil organic matter and mineral particles, largely through formation of complexes with double-charged cations, like calcium and therefore are rarely to be found in the free form in surface waters (Hirsch *et al.*, 1999; Hamscher *et al.*, 2002; Tolls, 2001). Consequently, they can be expected to remain in the soil or to be transported into surface waters *via* particles. Penicillins, macrolides and aminoglycosides are moderately degradable with half lives of 30 days or less (Table 75). However, sulfonamides appear to have a high potential to resist degradation and are hydrophilic enough to be transferred into the aquatic environment (Haller *et al.*, 2002; Christian *et al.*, 2003).

3.3.2 Food chain transfer

There are very few examples reported of the detection of drug residues in food for human consumption arising from environmental contamination. The majority of these examine incidents of contamination from commercial fish farming, where veterinary medicines given as feed additives accumulate in sediments and are ingested by aquatic life in the vicinity of the farms. The effects on human health from this pathway are not addressed here. The potential for drug residues to enter the food chain via transfers from contaminated soil to food crops or grazing animals has so far received little attention, but given the general behaviour of OC in soil, is unlikely to be a significant mechanism. The risk of human ingestion from animal products is likely to be greater from the direct administration of veterinary medicines rather than through the indirect soil transfer pathway.

Migliore *et al.* (1996) examined the bioaccumulation of sulphamethoxine in barley grown in soil supplied with a solution containing 300 mg l^{-1} of the antibiotic and detected 70 mg kg^{-1} and 18.22 mg kg^{-1} of the compound after 45 days in the roots and foliage, respectively. Increasing the humus content of the soil decreased the amount of accumulation, suggesting that sulphamethoxine became less available due to increased sorption. However, Thiele-Bruhn (2003) concluded from a recent review that uptake into plants even of mobile antibiotics was generally small, although effects on plant growth were apparent for some species and antibiotics.

**Table 75 Persistence of major classes of veterinary medicines in soil
(Boxall *et al.*, 2004)**

Chemical group	Compound	t _{1/2} (d)	Persistence class
azoles	metronidazole	9.7-26.9	slightly-moderately persistent
bambermycins	flavomycin	<30*	-
cephalosporin derivatives	ceftiofur	22.2-49	moderately persistent
fluoroquinolones/quinolones	danofloxacin	87-143	very persistent
	olaquinox	5.8-8.8	slightly persistent
	sarafloxacin	>65 <80	very persistent
Macrolides	tylosin	<5*	impersistent
		3.3-8.1	impersistent-slightly impersistent
macrolide endectins	emamectin benzoate	174-427	very persistent
	ivermectin	7-217*	slightly- very persistent
		14-56	slightly-moderately
organophosphorous compounds	chlorfenvinphos	4-30 weeks	moderately-very persistent
	coumaphos	200-300	very persistent
	diazinon	1.7-112	impersistent-very persistent
	dichlorvos	<1	impersistent
penicillins	procaine benzyl penicillin	<3 h*	impersistent
synthetic pyrethroids	deltamethrin	<23	-
tetracyclines	chlortetracycline	>30*	-
others	bacitracin	12-22.5*	slightly-moderately persistent
	virginamycin	>64	very persistent

Notes:

Classification of persistence (DT₅₀ is the time (days) taken for 50 % of a compound to decay – half-life):

impersistent: DT₅₀ < 5 d

slightly persistent: DT₅₀ 5-21 d

moderately persistent: DT₅₀ 22-60 d

very persistent: DT₅₀ > 60 d

* mixture of soil and manure/faeces

There is as yet no evidence about whether the bioaccumulation of some therapeutic compounds poses any significant health hazard. Antibiotics are persistent and lipophilic and therefore have the potential to bioaccumulate (Halling-Sørensen *et al.*, 1998). However, in 2003, a WHO workshop on antimicrobial resistance concluded that residues of antimicrobials in foods, under present regulatory regimes, represent a significantly less important human health risk than the risk related to antimicrobial resistant bacteria in food (WHO, 2003).

3.3.3 Antimicrobial Resistance

The view expressed by WHO (2003), regarding the risk to health from the presence of antibiotic resistant bacteria in food, is in agreement with other researchers in the field. Jørgensen and Halling-Sørensen (2000) identified the potential for widespread antibiotic resistant microorganisms as the most important effect on human health from veterinary and pharmaceutical medicines. Nwosu (2001) concluded that the selective pressure for the spread of resistance genes correlated strongly with the clinical and agricultural overuse of antibiotics. Subtherapeutic use of antibiotics was linked to increased numbers and types of antibiotic-resistant bacteria in nearby agricultural soil (Onan and LaPara, 2003). Evidence of increasing resistance to antibiotics in soil and other environmental bacterial isolates highlights the importance of horizontal transfer of resistance genes in facilitating gene flux in bacteria (Nwosu, 2001). Horizontal gene transfer in bacteria is favoured by the presence of mobile genetic elements and by the organisation of bacterial genomes into operons allowing for cooperative transfer of genes with related functions (Nwosu, 2001).

The increased use of antibiotics since the 1950s has caused a genetic selection of more drug resistant bacteria. When medicated livestock excrete drug metabolites, bacteria in the manure reconvert the metabolites into active compounds. The application of manure onto agricultural soils can therefore provoke pathogens and bacteria into developing resistance to drugs (Thiel-Bruhn, 2003). Administration of antibiotics also causes the formation of resistant microorganisms within the treated animal and resistant organisms are transferred to the soil directly in the excreta. Only trace concentrations of active substances are required to provoke resistance development (Halling-Sørensen *et al.*, 1998). Because human and animal microbial ecosystems are closely related, microbial antibiotic resistance readily crosses boundaries (Witte, 1998). In this way, multiple-resistant strains of microorganisms have found their way into the food chain (Berger *et al.*, 1996 cited in Halling-Sørensen *et al.*, 1998).

Several papers have documented the spread of antimicrobial resistance. Two notable studies are reported here to demonstrate the impacts of resistance transfer across and spatial boundaries, and from microorganisms in soil, to microorganisms in animals and humans.

1. Nourseothricin was used as a growth promoter from 1983 to 1990 in the former East Germany. Resistance to nourseothricin in *Enterobacteriaceae* from humans and animals was negligible in 1983. Two years later, resistance was found in *E. coli* from the gut of pigs and in meat products. By 1990, resistance to nourseothricin had spread to *E. coli* from the gut flora of pig farmers, their families, citizens from municipal communities, and patients suffering from urinary tract infections. In 1987, the same resistance determinant was detected in other enteric pathogens, including *Shigella*, an organism found only in humans (Tschäpe, 1994 cited in Witte 1998).
2. In an early study, Levy *et al.* (1976 cited in Shea, 2003) examined the effects of chlorotetracycline in feed on the intestinal flora of chickens and farm dwellers. Chickens were divided into two groups: the experimental group received feed that contained subtherapeutic doses of oxytetracycline. The control group received feed without the drug. After 2 weeks, 90% of the experimental chickens excreted 100% resistant organisms. By the 12th week, almost two thirds of the experimental chickens excreted organisms that were resistant to other drugs besides tetracycline. In the fourth month, chickens in the control group, despite isolation in different pens excreted >50% resistant organisms. Resistance also

transferred to humans. Within 6 months, over 30% of the faecal samples from farm dwellers contained 80% tetracycline resistant bacteria, compared with 7% in neighbourhood control subjects.

The ability of antibiotics to exert these effects at very low concentrations appears to be a unique characteristic of antibiotic compounds and is not known to be true for any other chemical (Jørgensen and Halling-Sørensen, 2000).

As microbes become increasingly resistant to antibiotics, drugs that were previously effective against disease in humans and animals, become redundant. This is a particular concern as multidrug-resistant organisms are being increasingly documented.

The widespread dissemination of antibiotic resistant organisms in the environment, associated with their extensive use of antibiotic medicines in livestock production, and their application to soil, is a major concern for human health. However, the development of resistance characteristics in soil bacterial populations appears to be a transient phenomena. Recent studies show that, once the selection pressure from inputs of antibiotic compounds in livestock manures is removed, the resistance profiles of the soil community returns to pre-treatment values, or equivalent to untreated control soil. For example, Sengeløv *et al.* (2003) measured resistance to tetracycline, macrolides and streptomycin for a period of 8 months in soil bacteria isolated from farmland treated with pig slurry. Soil samples were collected from four different farms where slurry had been applied and from another farm where no slurry had been spread as the control treatment. Tetracycline-resistant bacteria were elevated after pig manure application, but declined throughout the sampling period following cessation of manure inputs to a level equivalent to the control. Resistance was increased at higher rates of slurry application, but, nevertheless resistance levels returned to the control value. These effects occurred at very low concentrations of the antibiotic in soil as the compound could not be detected at any time in the soil samples, although it was measured in the slurry. The slurries applied to the field sites contained 42, 81 and 698 $\mu\text{g l}^{-1}$ of tetracycline. For streptomycin and macrolides, only minor variations in resistance levels were observed.

In other work, also with the antibiotic tetracycline, Rysz and Alvarez (2004) measured a decline in heterotrophic bacteria overall, but increased numbers of resistant soil bacteria in effluents from a soil column flow-through experiments treated with the compound. This indicated that antibiotic release to the environment from farm animals contributes to the development and amplification of resistance, with soil bacteria serving as reservoirs for antibiotic resistance continuance. After 300 days, exposure to tetracycline was removed and the proportion of resistant heterotrophic bacteria enumerated decreased from 25 % to the control value of 1 % within 1 month. This was due to a significant rebound in the total heterotrophic population and also to a significant decrease in the concentration of resistant forms. Thus, discontinuing exposure to antibiotics, or curtailing use should enhance natural attenuation mechanisms that mitigate the spread of resistance vectors.

The resistance characteristics are rapidly lost because, once the selective advantage of maintaining antibiotic resistant genes is removed, the maintenance requirements set the resistant organisms at a disadvantage to the general population, so the acquired resistance is depleted from the population.

A long-term priority is to reduce reliance on routine veterinary administration of antibiotic drugs in livestock production. The potential health consequences of not addressing this issue could be very serious for the human population. In the short-to-

medium term, however, a practical option would be to adapt manure storage and composting practices to maximise degradation of antibiotic compounds prior to spreading, and modify spreading frequency and rates of application to enable sufficient time for microbial populations to recover to avoid supporting a permanent reservoir of resistant bacteria in soil.

Manure applications to agricultural land are restricted to limit inputs of nitrogen within Nitrate Vulnerable Zones (CEC, 1991) and as required by the Code of Good Agricultural Practice for the Protection of Water (Defra, 1998) and these measures could also provide a degree of indirect control to minimise the extent of antibiotic resistance and allow natural attenuation of antibiotic resistant soil bacterial populations to take place. Further work is necessary to determine the potential impacts of manure application practices within current nutrient controls and guidelines on the development of antibiotic resistance in manure treated agricultural soil. Also, fundamental work is necessary to determine the potential risk and implications of disseminating antibiotic resistance from agricultural soil to livestock and the human population.

3.3.4 Effects on soil ecology

As antibiotics are designed with the intention to exert an effect on bacteria, they are naturally a potential hazard to microorganisms in the environment. However, published information on their effects on soil organisms and processes appears to be inconsistent (Thiele-Bruhn, 2003).

Some studies report that antibiotics inhibit microorganisms. For example, Colinas *et al.* (1994) observed strong inhibitory effects when antibiotics were added to soil in concentrations of 10 mg kg⁻¹. Elvers and Wright (1995) showed that ibuprofen (an analgesic drug) inhibited growth of Gram positive bacteria, but two Gram negative species were unaffected. Growth of *Staphylococcus aureus* was suppressed by ibuprofen at concentrations greater than 150 µg ml⁻¹ at pH 7. Other studies have reported enhanced microbial growth and activity when exposed to pharmaceuticals (Höper *et al.*, 2002).

Thiele-Bruhn and Beck (2005) tested the effects of sulfapyridine (SPY) and oxytetracycline (OTC) on a sandy Cambisol and loamy Luvisol. Both antibiotics are commonly used for the medication of livestock. The level of microbial activity was examined by a substrate induced respiration (SIR) test. The test involved the addition of a nutrient substrate to the soil, together with the antibiotic under consideration. This method was considered as environmentally relevant since antibiotics mostly reach soils *via* manure, sludge and excreta from grazing livestock.

No effects were observed when the sample was incubated for four hours, even at concentrations as high as 1000 µg g⁻¹. When the incubation time was extended to 24 hours, however, SPY and OTC were found to cause strong inhibitory effects on respiration rates of microorganisms in the sandy Cambisol. This showed that short term incubation tests may be misleading because microorganisms can maintain respiration rates by oxidising internal energy sources and active transport from the external environment into the microbial cell is required before the antibiotic can take effect. These processes allow the maintenance of microbial cells for a period of time, and thus, effects may only become evident after a sufficient period of time of exposure has elapsed.

When the incubation period in the sandy Cambisol was extended for a further 24 hours, the effects on SIR were much less significant. There was clear evidence of a

recovery in soil respiration during the second 24 h incubation. This may be linked to a decrease in the bioavailable antibiotic fraction, or an increasing adaptation and resistance of the microorganisms. The adaptation and development of resistance in soil microorganisms in antibiotic spiked soil samples has been increasingly documented (Thiele-Bruhn, 2003; Schmitt *et al.*, 2005). The decrease in bioavailability of sulphonamides and tetracyclines is mostly due to sorption and fixation processes, rather than biodegradation.

In contrast to the sandy Cambisol, the antibiotics did not produce any change in respiration rates during the first 24 hours in the loamy Luvisol. This can be explained by the increased sorption of the antibiotics in the loamy Luvisol compared to the sandy soil. Adsorption coefficients of SPY in the loamy Luvisol were three times larger relative to those in the sandy Cambisol. The concentrations of soil organic matter, pedogenic oxides and clay minerals were also two to three times larger in the loamy Luvisol. These soil components provide sorption sites for sulphonamide and tetracycline compounds. During the second 24 h incubation in the loamy Luvisol, however, a significant effect on the SIR was observed from SPY and OTC. The reason for this delayed effect was unclear. Similarly, the effects of the antibiotics neomycin and thiostrepton on soil organisms are fundamentally influenced by their sorption and bioavailability, and by the availability of nutrients (Herron *et al.*, 1998).

The results of Thiele-Bruhn and Beck (2005) suggested that reduced adsorption and hence greater bioavailability of SPY and OTC increased their toxicity to microorganisms in the sandy Cambisol compared to the loamy soil. Stronger adsorption, on the other hand, produced a smaller and delayed response in the loamy Luvisol. The antibiotics significantly ($P < 0.05$) reduced numbers of soil bacteria causing dose related shifts in the fungal:bacterial ratio. It was concluded that pharmaceutical antibiotics can exert a temporary acute toxicity selective pressure on soil microorganisms at environmentally relevant concentrations.

Boleas *et al.* (2005) tested the effects of OTC on soil microbial respiration by measuring the glucose induced CO_2 production rate. Soil samples were spiked with 1, 10 and 1000 mg OTC kg^{-1} soil and incubated at 30°C. CO_2 production was measured after 0, 7, 14, 21 and 28 days. At the 1 mg OTC kg^{-1} soil concentration, respiration rates were unaffected. At 10 mg OTC kg^{-1} soil, respiration rates were initially inhibited by 25% compared to the control, but by day 21 the inhibition was reduced to 21%. At 1000 mg kg^{-1} OTC, respiration inhibition was 28% at day 0, and increased to 38% by day 28. Thus, the sensitivity of carbon respiration to OTC was very low. As previously indicated, the concentrations of OTC in soil are at least an order of magnitude below this.

Baguer *et al.* (2000) investigated the effects of two widely used antibiotics – oxytetracycline and tylosin – on earthworm, springtails and enchytraeids in a laboratory culture. No toxic effects on the soil fauna were observed when the antibiotics were applied at environmentally relevant concentrations. The lowest observed effect concentration was 3000 mg kg^{-1} and in most cases no effect was observed at the highest test concentrations adopted of 5000 mg kg^{-1} . The growth and fertility of the organisms were found to be the most sensitive end points. This was also in agreement with experimental work by Boleas *et al.* (2005). No earthworm (*Eisenia foetida* S.) mortality was observed during a 21 day test period, in which the earthworms were exposed to OTC concentrations up to 1000 mg kg^{-1} soil in a multi species soil system (MS 3). Using an identical multispecies soil system (MS 3), Fernández *et al.* (2004) observed no effects on earthworms of doxycycline (a structural isomer of tetracycline with a broad-spectrum antimicrobial activity) in aged spiked pig manure. Soil phosphatase activity was reduced at the highest exposure

dose ($>1 \text{ mg kg}^{-1}$ in soil) in all layers of soil spiked with a doxycycline solution, but only in the top soil layer in the spiked pig manure system, suggesting application with manure attenuated the toxicity response.

Antibacterial agents (tiamulin, olanquinox and metronidazole) were not toxic to adults springtails or enchytraeids and effects on reproduction occurred generally above concentrations normally found in soil or dung in studies reported by Jensen *et al.* (2003). The threshold values for toxicity (10 % reduced reproduction or EC_{10}) were in the range $61\text{--}111 \text{ mg kg}^{-1} \text{ ds}$ for springtails and $83\text{--}722 \text{ mg kg}^{-1} \text{ ds}$ for enchytraeids. Thus, indirect effects of antibacterial agents are very unlikely to occur at environmentally realistic concentrations in soil, although impacts due to changes in the food web could not be ruled out.

Significant effects of pharmaceutical compounds on soil have generally only been observed for anthelmintic (deworming) compounds (Thiel-Bruhn, 2003) and specifically those products that control both internal and external parasites, eg ivermectin.

Insects are important in soil because of their involvement in processes of dung degradation and nutrient recycling. The drugs coumaphos, dichlorvos and phenothiazine were found to adversely effect their survival and reproduction for at least 4 to 5 days after treatment (Blume *et al.*, 1976). Wall and Strong (1987) showed that ivermectin, an antiparasitic (endoparasiticide or endectocide) drug for cattle treatment, was toxic to dung degrading insects and caused a significant delay in the degradation of pats from treated cattle. Not only is this significant for pasture hygiene, but there is also concern that it may impact natural food chains that depend on dung organisms as a food source (Davis *et al.*, 1999). Ivermectin is also significantly more toxic than antimicrobial agents to springtails and enchytraeids and Jensen *et al.* (2003) reported EC_{10} values for these groups of organisms of $0.26 \text{ mg kg}^{-1} \text{ ds}$ and $14 \text{ mg kg}^{-1} \text{ ds}$, respectively. Thus, there is a potential risk of toxicity to these non-target organisms from ivermectin at environmentally relevant concentrations of this compound. However, alternative endectocides are available (eg moxidectin), which are less toxic to dung inhabiting insects than ivermectin (Strong and Wall, 1994).

Figure 21 shows a comparison of the concentrations of some veterinary medicines found in soil with EC_{50} values for standard test organisms (Boxall *et al.*, 2003a). For the veterinary medicines considered, EC_{50} values are orders of magnitude above concentrations found in the environment. The exception is monensin, where measured concentrations in the environment ($1080 \text{ } \mu\text{g kg}^{-1}$) are 7 fold greater than the EC_{50} . Therefore, in general, acute ecotoxicological effects of medicines are unlikely when mixed in soil except in specific cases. The main ecotoxicological risks, however, are associated with concentrations present in dung itself (Boxall *et al.*, 2003a).

3.3.5 Effects on plants

Controlled laboratory experiments have shown that certain veterinary medicines are potentially phytotoxic. Bradel *et al.* (2000 cited in Jjemba, 2002) applied a bioassay technique and treated poinsettia scions with a solution containing 400 mg l^{-1} of tetracycline. Free-branching was suppressed in the treated plants. Whilst significant, however, the concentration used in the experiments was several fold greater than the amounts measured in soils treated with manure.

Migilore *et al.* (1996) found that 300 mg l⁻¹ of sulphamethoxine significantly ($P < 0.005$) depressed the growth of *Amaranthus retroflexus*, *Plantago major*, *Rumex acetosella*, and *Zea mays*, but again this concentration is in excess of environmentally relevant values.

Table 76 shows some of the therapeutic compounds that have been reported to be phytotoxic under laboratory conditions. The majority of the compounds have been assayed in vitro rather than under soil conditions and the concentrations used are significantly larger than what may be present under field soil conditions. Based on similar data, Thiele-Bruhn (2003) concluded that effects of pharmaceutical antibiotic compounds on plant growth were possible for some species and antibiotics. Fernández *et al.* (2004) detected no effects on plants of the antibiotic doxycycline.

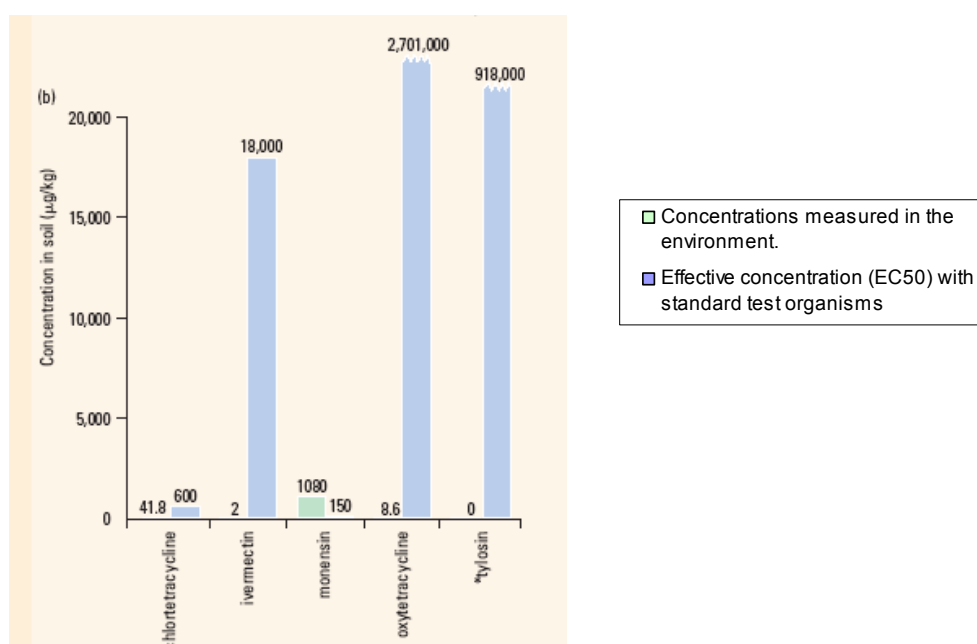


Figure 21 Concentrations of selected veterinary medicines in soil samples; *Tylosin was not detected in soil. EC₅₀ for oxytetracycline and tylosin are off scale (Boxall *et al.*, 2003a)

3.4 Di(2-ethylhexyl)phthalate (DEHP) and other phthalates

Phthalates are ubiquitous chemicals in the built environment and transfer to the environment. They are regulated in sewage sludge for agricultural recycling in Denmark and are under review with regard to the WFD. It is surprising, therefore, that their significance in the environment has not been more fully considered, compared to surfactant compounds for example. This section presents a summary assessment of the impacts of DEHP and other phthalates used as plasticizers on soil quality and human health.

Phthalates enter soil through the land application of sludge, artificial fertilizers, manure, and atmospheric deposition (Staples *et al.*, 1997). There are also significant releases during phthalate and PVC product manufacture. All large volume plasticizer phthalates are ubiquitous in the environment (Lim, 2003).

DEHP has a high octanol/water partition coefficient ($\log K_{ow} = 4.89$) and therefore has the potential to bioaccumulate. The bioconcentration factor (BCF) for DEHP is

reported as 120. However, bioaccumulation of DEHP is limited because the compound readily biodegrades and is metabolised. Therefore, biomagnification of DEHP in the food chain is not expected (Staples *et al.*, 1997).

3.4.1 Fate in Soil

Biodegradation is the dominant loss mechanism of phthalates from soils. Microorganisms, particularly, bacteria and actinomycetes, degrade phthalate esters and their metabolites. Various methods of testing the biodegradability of phthalate esters have shown that they are not persistent and undergo relatively rapid degradation in soils (Staples *et al.*, 1997).

Biodegradation studies using a standardised modified Sturm test procedure (OECD 1993), which is specifically designed for testing substances of low water solubility, demonstrate the rapid biodegradability of DEHP. Under aerobic conditions, DEHP undergoes significant biodegradation (>95%) after gradual acclimation of the microbial population over a period of about 3 weeks under the conditions of static-flask and shake-flask screening tests (Sugatt *et al.*, 1984; Tabak *et al.*, 1981). In the shake flask study, using an acclimated inoculum, the biodegradation was initially low on days 2 and 3. However, the rate increased by 5-10 folds by days 6 and 7. After 28 days, 87% of DEHP was biodegraded to carbon dioxide. Standardized aerobic biodegradation tests with sewage sludge inocula show that phthalate esters undergo approximately 50% ultimate degradation within 28 days (Staples *et al.*, 1997). Fairbanks *et al.* (1985) reported the half-life of DEHP was 8 to 72 days depending on the experimental conditions. The reported half-life of DEHP due to microbial activity in river water is about 1 month.

Roslev *et al.* (1998) examined the microbial degradation of DEHP in an agricultural soil amended with sewage sludge. The soil was a sandy loam with a pH of 5.9 and an organic matter content of 2.5%. The sludge contained 82.9 $\mu\text{g g}^{-1}$ DS of DEHP. In the first 28 days of incubation, DEHP was mineralised at an exponential rate, and had a half life of 58 days during this phase. After 28 days of incubation, however, the rate of mineralization decreased and the corresponding half life was 147 days. A possible explanation for this is that time-dependent immobilization of DEHP may occur in the soil-sludge matrix. By extrapolating these results, approximately 40% of DEHP would have remained after 1 year of incubation. In another assay containing only sludge, the degradation of DEHP followed a similar pattern, but was significantly faster. The DEHP half life during the first 28 day incubation period was 39 days, after which it increased to 51 days. From these results, it was concluded that DEHP became increasingly less bioavailable during incubation. Fairbanks *et al.* (1985) observed greater degradation of DEHP in sandy loam soil compared to clay soil and this was associated with increased adsorption of the compound in the fine textured soil type. DEHP persistence was also reduced by previous exposure of the soil to sludge. However, fresh sludge additions increased persistence, or had no effect.

Shanker *et al.* (1985) incorporated di-n-methyl phthalate (DMP), di-n-butyl phthalate (DBP) and DEHP in soil (alluvial, pH=8.2) to give a concentration of 500 mg phthalate kg^{-1} of soil. The amended soils were incubated at 30°C for 30 days under aerobic and anaerobic conditions (by flooding with sterile water). The biodegradation profile of DEHP is shown in Figure 22.

Table 76 Some therapeutic compounds reported to be potentially phytotoxic to vegetation under laboratory conditions (Jjemba, 2002)

Compound	Type of Vegetation	Matrix	Concentration	Reference
Chlorotetracycline	<i>Phaseolus vulgaris</i> L.	Liquid Soil	10 mg l ⁻¹ 160 mg kg ⁻¹	Batchelder (1981, 1982)
Chloroquine	Soybean (<i>Glycine max</i>)	Soil	8 mg g ⁻¹	Jjemba (2002)
Estrogen	<i>Medicago sativa</i>	Water	50–500 µg l ⁻¹	Shore <i>et al.</i> (1992)
Metronidazole	Algae (<i>Chlorella</i> sp.)	Water	EC ₅₀ ^a of 12.5 mg l ⁻¹	Lanzky & Halling-Sørensen (1997)
	Soybean (<i>Glycine max</i>)	Soil	0.5 mg g ⁻¹	Jjemba (2002)
Oxytetracycline	<i>Phaseolus vulgaris</i> L.	Liquid Soil	10 mg l ⁻¹ 160 mg kg ⁻¹	Batchelder (1981, 1982)
Quinacrine	Soybean (<i>Glycine max</i>)	Soil	10.6 mg g ⁻¹	Jjemba (2002)
Tetracycline	Poinsettia	Liquid/soil ^b	400 ppm	Bradel <i>et al.</i> (2000)
Sulphadimethoxine	<i>Amaranthus retroflexus</i>	Agar	300 mg l ⁻¹	Migliore <i>et al.</i> (1997)
	<i>Plantago major</i>	Agar	300 mg l ⁻¹	Migliore <i>et al.</i> (1997)
	<i>Rumex acetosella</i>	Agar	300 mg l ⁻¹	Migliore <i>et al.</i> (1997)
	<i>Panicum miliaceum</i>	Agar	300 mg l ⁻¹	Migliore <i>et al.</i> (1995)
	<i>Zea mays</i>	Agar	300 mg l ⁻¹	Migliore <i>et al.</i> (1995)
	<i>Pisum sativum</i>	Agar	300 mg l ⁻¹	Migliore <i>et al.</i> (1995)
Sulphamethoxine	<i>Amarantus retroflexus</i>	Agar	300 mg l ⁻¹	Migliore <i>et al.</i> (1998)
	<i>Plantago major</i>	Agar	300 mg l ⁻¹	Migliore <i>et al.</i> (1998)
	<i>Zea mays</i>	Agar	300 mg l ⁻¹	Migliore <i>et al.</i> (1998)
Sulphamethoxine	<i>Rumex acetosella</i>	Agar	300 mg l ⁻¹	Migliore <i>et al.</i> (1998)
	<i>Hordeum disthicum</i>	Liquid Soil	300 mg l ⁻¹ 0.1 mg g ⁻¹	Migliore <i>et al.</i> (1998)
Flumequine	<i>Lythrum salicaria</i>	Agar	100 mg l ⁻¹	Migliore <i>et al.</i> (2000)

Notes:

^a EC₅₀ is the effective concentration of the compound that causes toxicity to 50% of the test population.

^b Poinsettia scions were immersed in a solution containing 400 ppm tetracycline, grafted and then grown in soil (Bradel *et al.*, 2000).

Phthalates were degraded rapidly under aerobic conditions. Shorter chain compounds (DMP and DBP) were degraded at a faster rate than the longer chain DEHP. However, no significant degradation was observed under anaerobic conditions. Johnson *et al.* (1984) also reported that DEHP was not easily broken down in anaerobic conditions, such as deep in the soil profile or in sediments of lakes or rivers. The degradation half-life of DEHP was approximately 15 days in aerobic soil, and was approximately 7 days for the other phthalate compounds. This is significantly shorter than the 58 days reported by Roslev *et al.* (1998). However, Roslev's experiments were conducted using sludge amended soil, whereas Shanker *et al.* (1985) spiked soil with phthalate compounds directly, without sludge addition. A probable explanation is that the larger organic matter content from sludge application increased the sorption of DEHP and thus reduced its bioavailability and degradation.

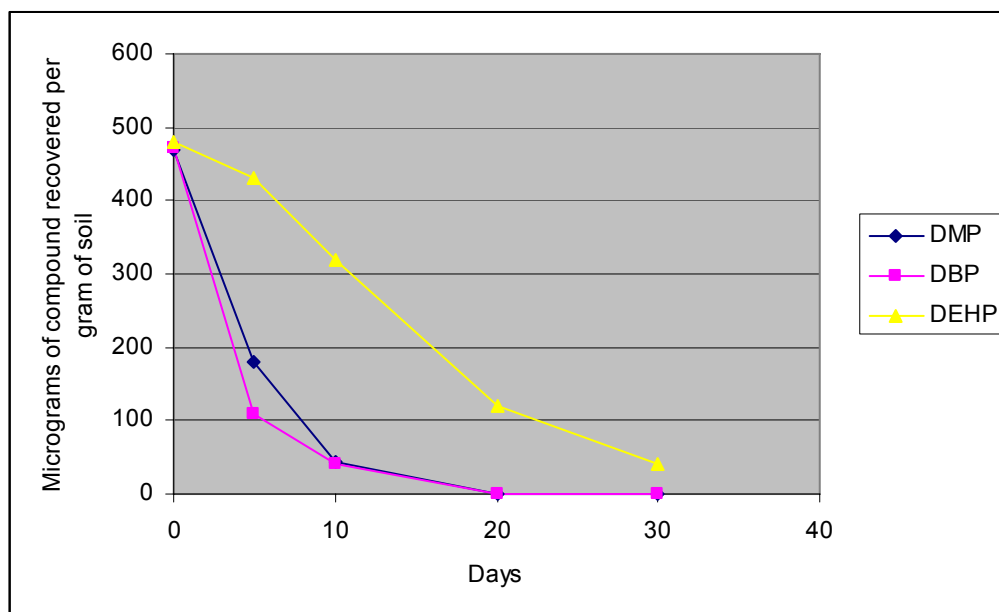


Figure 22 Biodegradation of DMP, DBP and DEHP in alluvial soil (pH 8.2) under aerobic conditions (adapted from Shanker *et al.*, 1985)

Thus, in overall assessment, DEHP is considered to be readily biodegraded in soil. However, the strong adsorption of DEHP onto soil organic matter reduces its availability for degradation. The sorption of phthalate esters to soil is partially governed by the relative hydrophobicity of the chemical. Higher molecular weight phthalate esters are highly hydrophobic and adsorb to organic matter. Consequently, the rate of biodegradation of DEHP in soil is at much a slower rate than that in water (Cartwright *et al.*, 2000). However, the presence of soluble humic material in soils is reported to increase the water solubility of phthalates and may reduce the degree of sorption (Carlberg and Martinsen, 1982 cited in Staples *et al.*, 1997). Other important environmental factors also influence the rate of biodegradation of DEHP. Optimum biodegradation occurs at high concentration, warm temperature and in nutrient-rich conditions.

The potential for volatilisation of phthalates is difficult to predict. Measured values obtained in different studies often vary by more than an order of magnitude (Staples *et al.*, 1997). In general, however, phthalate esters are considered to have low volatility (Smith, 2000).

3.4.2 Effects on human health

Humans are exposed to phthalates in numerous ways, such as migration of phthalates into foodstuff, by dermal contact of cosmetics and inhalation. Young children can also be exposed through mouthing of soft PVC toys (Koch *et al.*, 2003ab). The widespread use of PVC plasticised with DEHP in medical products is also controversial. Leaching of DEHP out of plastic medical devices into solutions that come in contact with the plastic results in an aggregate exposure from multiple devices and is time, temperature and agitation dependent. The FDA Safety Assessment states that aggregate exposure to DEHP from multiple devices can result in doses that exceed the Tolerable Intake (US FDA, 2001) and seriously ill individuals may require more than one of these procedures leading to higher levels of exposure to DEHP.

In vitro and animal studies indicate several mechanisms of DEHP toxicity. The main target organs for DEHP toxicity are the liver, kidney and testes, but of greatest concern are effects on the development of the male reproductive system and production of normal sperm in young animals (Feigal, 2002). However, The Scientific Committee on Medicinal Products and Medical Devices of the Health and Consumer Protection DG (EC, 2002) recently concluded that there are no reports concerning any adverse effects in humans following exposure to DEHP-PVC, even in neonates or other groups of relatively high exposure. So far, for example, there are no indications that neonates of high DEHP exposure have any altered long-term fertility patterns. There are also other groups of patients or individuals who experience prolonged periods of elevated DEHP exposure, including patients on haemodialysis or in receipt of repeated blood product transfusions. At present there is no evidence that any of these groups experience DEHP related adverse effects. In view of the lack of a full analysis of all risks associated with potential alternative materials, the Committee concluded that no specific recommendations can be made to limit the use of DEHP in any particular patient group.

Initial concerns that DEHP was carcinogenic to humans were based on animal testing with rodents which developed liver tumours when exposed to DEHP. However, the mechanisms by which DEHP increases the incidence of hepatocellular tumours in rats and mice is not relevant to humans. Apparently, primate species do not absorb DEHP as efficiently as rodents, nor do they convert it to mono (ethylhexyl) phthalate (MEHP) as readily as rats or mice (Huber *et al.*, 1996), which is the chemical thought to initiate the process leading to liver cancer in rodents. Taking due regard of this scientific evidence, the International Agency for Research on Cancer (IARC) downgraded the carcinogenicity classification of DEHP from Group 2B, *as possibly carcinogenic to humans* to Group 3, *not classifiable as to carcinogenicity in humans* (IARC, 2000).

There is a wealth of information in animals administered DEHP for periods ranging from a few days to lifetime studies that show DEHP is a developmental and reproductive toxicant by mechanisms not yet completely understood (ATSDR, 2002). However, the reproductive effects observed in some rodents exposed to DEHP during fetal development and as adults are not thought to be caused by DEHP docking to an oestrogen receptor. Rather, as with carcinogenicity, these effects are apparently related to unique mechanisms and sensitivity in susceptible rodents (Davis *et al.*, 1994). Indeed, results from *in vivo* and *in vitro* studies indicate that DEHP has negligible estrogenic potency relative to the endogenous hormone, 17 β -estradiol. From a comprehensive toxicological profile of the compound, the US Agency for Toxic Substances and Disease Registry (2002) concluded that there is no evidence that DEHP is an endocrine disruptor in humans at the levels found in the environment.

There appears to be uncertainty and controversy about the potential impacts on human health from high exposures of DEHP. However, exposures received through medical procedures are significantly larger than they are likely to be through environmental routes. In the absence of any actual evidence of carcinogenic or reproductive abnormalities in these highly exposed and sensitive groups, given the widespread use of PVC plasticized with DEHP in medical situations, and also the direct ingestion of DEHP, for instance, by the general population transferred to food from plastic packaging materials, it would appear that the risk to human health from diffuse environmental sources, such as from DEHP inputs to soil from recycling sewage sludge, is very minor. This is reinforced by the rapid degradability of DEHP in soil (Section 3.4.1) and also the absence of significant transfers of DEHP to food crops (Section 3.4.3).

3.4.3 Plant uptake

In general, plant growth studies show there is little uptake of DEHP via the roots.

Aranda *et al.* (1989) grew lettuce, carrot, chilli peppers and tall fescue in sludge amended soil contaminated with DEHP at concentrations ranging from 2.6 to 14.1 mg kg⁻¹ ds. The soil was a Glendale clay, with a pH of 7.6 and an organic carbon content of 1% and the applied sludge was secondary anaerobically digested. Soil was treated in 5 different ways. Indigenous DEHP was supplied in sludge added at two rates, an agronomic rate (34 t DS ha⁻¹) and at three times that rate (102 t DS ha⁻¹) to increase the DEHP loading. Reagent grade DEHP was added at two concentrations (4.58 and 11.45 mg kg⁻¹) to the lower sludge rate. Details of the experimental conditions are listed in Table 77.

Bioconcentration factors (BCFs) were in the range 0.01 - 0.03 suggesting minimal uptake of DEHP by the crop species examined (Figure 23). The BCFs were also overestimated by this method because DEHP was biodegraded in the soil and metabolised by plants. However, BCFs were greater for T4 than for T2 for all crops except carrot roots. Both these treatments received the same total loading of DEHP (7.23 mg kg⁻¹). However, DEHP was indigenous to the sludge in T2, whereas T4 received sludge spiked artificially with 4.58 mg kg⁻¹ of DEHP. Therefore, the indigenous compound was sorbed more strongly to the sludge-soil matrix compared to the artificially spiked system, reducing the bioavailability of the compound for plant uptake.

Table 77 Sludge and DEHP treatment rates applied to soil by Aranda *et al.* (1989)

Treatment	Sludge rate		DEHP as mg kg ⁻¹			
	t ha ⁻¹	g kg ⁻¹	Indigenous	Reagent	¹⁴ C	Sum
T1	34	29.75	2.29	0	0.362	2.65
T2	102	89.25	6.87	0	0.362	7.23
T3	0	0	0	0	0	0
T4	34	29.75	2.29	4.58	0.362	7.23
T5	34	29.75	2.29	11.45	0.362	14.02

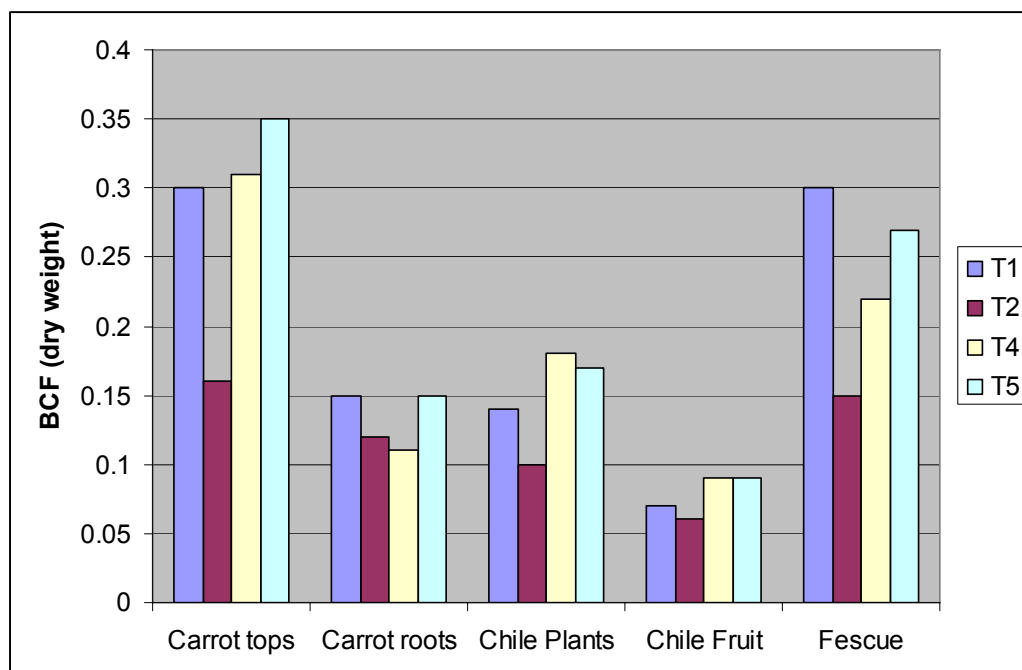


Figure 23 Relationship between crop bioconcentration factors and initial DEHP soil concentration – see Table 77 for the different soil treatments (T) (Aranda *et al.*, 1989)

Although the high sludge rate condition, T2, contained more DEHP than T1, a smaller BCF value was measured for treatment T2 for all plant species. Thus, increasing the organic matter content of soil by the larger rate of sludge addition (T2) also reduced DEHP bioavailability.

DEHP is lipophilic and, therefore, accumulation in carrot roots may be anticipated due to their high lipid content. However, carrot roots contained less DEHP than carrot tops. The translocation of DEHP from the carrot roots into aboveground tissue was suggested as a possible mechanism to explain this.

Other studies confirm the minimal transfer of DEHP to plant tissues. For example, Schmitzer *et al.* (1989) grew barley and potatoes in soils containing 0.2 to 3.3 mg kg⁻¹ of DEHP, but detected no DEHP in either crop. Kirchmann and Tengsved (1991) investigated the uptake of DBP and DEHP in barley grown on soil amended with sludge at a rate of 5 t ha⁻¹. The sludge contained 37 mg kg⁻¹ DS of DBP and 116 mg kg⁻¹ DS of DEHP. Uptake of the added phthalates into grain was very low and equivalent to 0.1-0.2 % of the amount added to the soil.

No DEHP was detected in the roots, shoots or fruit of capsicum grown on a yellow brown soil with an organic matter content of 2.5% and contaminated with up to 83.7 mg kg⁻¹ of DEHP (Yin *et al.*, 2003). However, di-n-butyl phthalate (DBP) was detected in capsicum fruits. The soil amendment treatments with DnBP and DEHP by Yin *et al.* (2003) are shown in Table 78. No effect of DEHP or DBP on the yield of the fruits was detected in the experiments.

Table 78 DBP and DEHP concentrations (mg kg⁻¹ dry soil) in test plots used by Yin *et al.* (2003)

Concentrations		Treatments (mg kg ⁻¹ dry soil)						
		Control	T2	T3	T4	T5	T6	T7
DBP	Indigenous	2.3	2.3	2.3	2.3	2.3	2.3	2.3
	Applied	0	2.5	5.0	10.0	20.0	40.0	80.0
DEHP	Indigenous	3.7	3.7	3.7	3.7	3.7	3.7	3.7
	Applied	0	2.5	5.0	10.0	20.0	40.0	80.0
DBP + DEHP		6.0	11.0	16.0	26.0	46.0	86.0	166.0

The concentrations of DBP detected in capsicum fruits and roots are shown in Figure 24. The DBP concentrations in the capsicum fruits and roots showed a dose response and were raised with increasing DBP concentration in the soil. Differences in fruit and root DBP concentrations were statistically significant when soil was supplemented with 10, 20, 40 and 80 mg kg⁻¹ DBP (Treatments 4, 5, 6 and 7), compared to the control.

The differences in plant absorption observed for the two phthalate compounds may be associated with their contrasting soil binding properties. The soil adsorption coefficient for DBP was 2144 whereas the value for DEHP was considerably larger, 67,040, indicating much stronger adsorption of this compound and, therefore, lower bioavailability compared to DBP.

Vitamin C is abundant in capsicum fruit and represents one of its main nutritional properties. However, analysis of capsicum fruits showed that DBP transfer to plants reduced the formation of vitamin C, which decreased with increasing DBP/DEHP content (Figure 25). The reduction in vitamin C was only statistically significant when the DBP/DEHP concentration was greater than 40 mg kg⁻¹ of soil (Treatments 5,6 and 7). However, since only DBP was detected in the capsicum fruits and roots, DBP rather than DEHP was considered to be responsible for the decrease in vitamin C content.

DBP uptake is also reported by Shea *et al.* (1982) for corn (*Zea Mays*) grown under glasshouse conditions in pots spiked with DBP at concentrations of 0, 200, 2000, and 20,000 mg kg⁻¹ ds. The soil was a Lakeland sand, with 1% organic matter content and pH of 4.0. The shoot material was harvested after three weeks and analysed for DBP concentration. Plant growth parameters and DBP content are shown in Table 79.

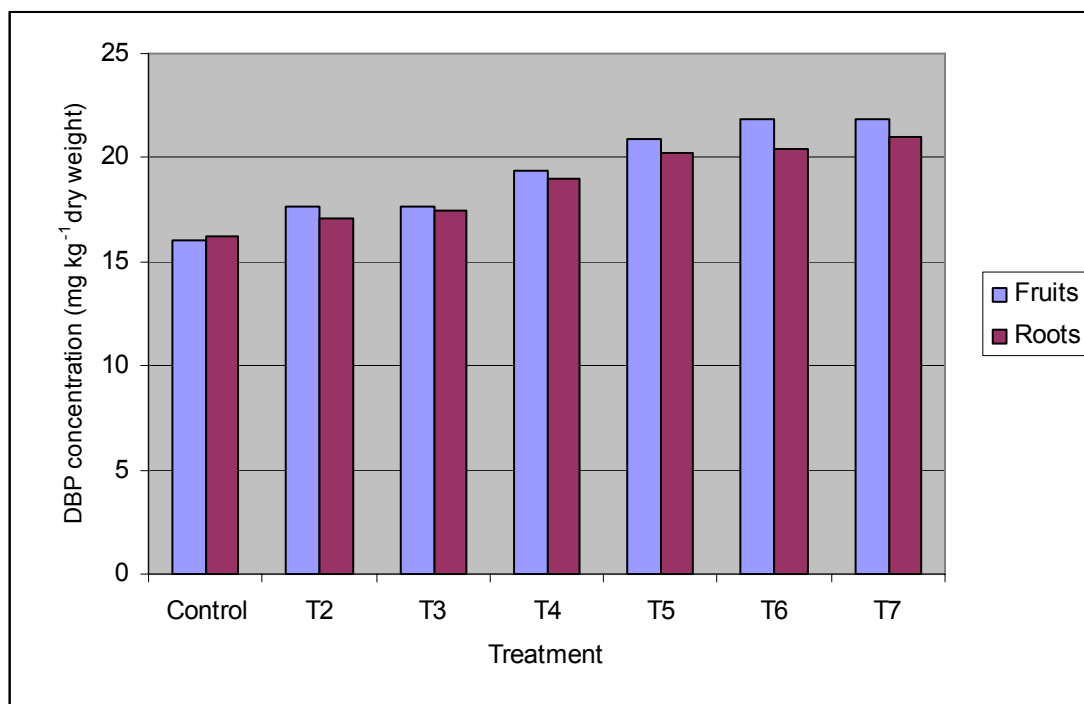


Figure 24 DBP concentrations in capsicum fruits and roots (mg kg⁻¹ dry weight) – see Table 78 for DBP concentrations in the soil treatments (T) (adapted from Yin *et al.*, 2003)

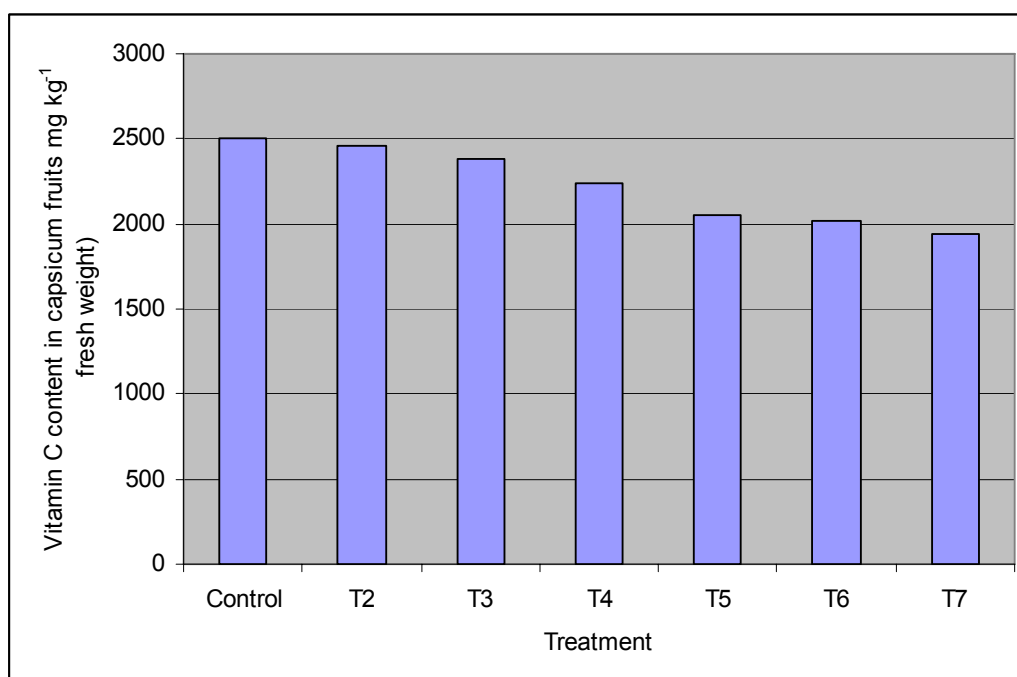


Figure 25 Vitamin C content in capsicum fruits grown under different treatments – see Table 78 for DBP concentrations in soil (Yin *et al.*, 2003)

Table 79 Plant height, shoot fresh weight and DBP concentrations in corn after 3 weeks growth on soil containing DBP (Shea *et al.*, 1982)

Soil DBP concentration (mg kg ⁻¹)	Plant height (cm)	Reduction relative to control (%)	Shoot fresh weight (g)	Reduction relative to control	DBP concentration (mg kg ⁻¹ FW)
0 (Control)	50.2	0	18.49	0	0
200	51.0	-2	17.46	6	0.32
2000	41.9	17	13.94	25	1.24
20000	27.7	45	5.12	72	13.8

There was no significant effect of 200 mg kg⁻¹ DBP in soil on plant development, but higher concentrations significantly reduced plant growth. The DBP concentration in plant tissue increased with the amount of DBP in the soil and reached a maximum value of 13.8 mg kg⁻¹ (fresh weight). The small concentration of DBP (1.24 mg kg⁻¹) measured in plants grown in soil containing up to 2000 mg kg⁻¹ indicated that there was only limited transfers of the compound to plant tissues.

After this initial experiment, new seeds of corn were replanted in the same pots and grown for a further three weeks. However, in this case, plant height and shoot fresh weights were not significantly different from the controls at DBP concentrations less than or equal to 2000 mg kg⁻¹. This suggested the bioavailability of DBP had decreased, either due to sorption to the soil matrix or by microbial decomposition.

Phthalates have low volatility from soil (Fairbanks *et al.*, 1985). Consequently, the uptake of DEHP by plants from the atmosphere is limited (Lokke and Bro-Rasmussen, 1981; Lokke and Rasmussen, 1983 both cited in Staples *et al.*, 1997).

3.4.4 Animal Ingestion

Phthalates can potentially be ingested by grazing animals. However, they are metabolised and do not appear to bioaccumulate (Fries, 1996; Smith, 2000). DEHP is rapidly metabolised by livestock and there is no significant transfer of phthalate esters from sludge to food products (UKWIR, 1995).

Lowenbach *et al.* (1995 cited in Staples *et al.*, 1997) estimated the bioconcentration factor of DEHP in cattle was 0.008. This estimate was based on the empirical correlation between measured BCFs in rodents and BCFs in cattle for a large set of chemicals. This contrasts with an earlier prediction by Travis and Arms (1988 cited in Staples *et al.*, 1997), which suggested the bioconcentration factor of DEHP in cattle was three orders of magnitude higher. However, Travis and Arms (1988) based their model on data for persistent organic pollutants, but these are not representative of the behaviour of phthalates, which are degraded much more rapidly. The model also over estimated the accumulation of phthalates in animals by not taking into account metabolism (Lowenbach *et al.*, 1995 cited in Staples *et al.*, 1997). Consequently, the occurrence of phthalates in animals and dairy products is uncommon. Surveys of market milk for example, indicate that the occurrence of phthalate esters is rare and can be attributed to exposure of the milk to phthalate containing plastic products (Peterson, 1991).

More recently, Erhardt and Rhind (2004) assessed the behavioural characteristics of lambs produced by ewes grazing sludge-treated pasture and related this to apparent exposures to environmental pollutants present in sewage sludge. The authors studied the behaviour of two groups of 5 month old lambs with respect to their emotional reactivity and exploratory behaviour. One group (T) were the offspring of ewes that had been grazed on pasture to which sewage sludge had been applied at rates used in normal practice. The other group of lambs (C) represented the control group and were grazed on pasture which had received inorganic fertiliser at a rate to supply a comparable total N concentration to that applied in the sewage sludge. Behavioural tests demonstrated that T lambs were less emotionally reactive than C lambs, but vocalised more. The C group exhibited typical behaviour where female lambs explored more than male lambs, however, in the T group, both sexes exhibited similar levels of exploration. It was suggested that these behavioural differences were due to the demasculinisation of the males in the T group as a result of exposure to the environmental pollutants present in sludge. Decreased body weight of fetuses and significant reduction in testis weight and numbers of specific cell types have also been reported (Paul *et al.*, 2005). Further studies of the same trial also suggested that sheep grazing in pastures treated with sludge had significant hepatic bioaccumulation of a phthalate endocrine disruptor (Rhind, 2004), however, both control and treated soils contained similar, small amounts of phthalate and thus both groups were apparently exposed to the same intake of the soil contaminant. Also DEHP concentrations that were considered biologically significant were recorded in both treated and control animals. It was suggested that the presence of phthalate in the control was due to atmospheric deposition, so both sets of treatments would have been equally affected. However, atmospheric deposition is not widely regarded as an important source of phthalate entry to soil, and the absence of any accumulation of phthalate in sludge-amended soil was consistent with the rapid biodegradation of the compound in soil.

The experimental approach adopted in the grazing studies reported by Erhardt and Rhind (2004) did not permit a rigorous and critical appraisal of the effects of potential endocrine disrupting substances on livestock grazing pasture treated with sewage sludge. The experiments were not strictly controlled to provide any information about the effects of sewage sludge on the physiological development of animals. For example, differences in N supply between the sludge and N fertilised control plots resulted in lower herbage yields on the sludge-amended plots and this more restrictive diet would explain the lighter weights of the ewes and fetuses grazing the pasture fertilised only by the biosolids. No data relating to sward characteristics and dietary composition were reported so it was not possible to determine which dietary factors influenced the animals. The behavioural testing completed was limited and the absence of supporting chemical analysis of the sludge applied, soil or herbage, or measurement of direct ingestion of soil or sludge by grazing animals makes conclusive interpretation impossible. This was a general grazing study; however, to elucidate the effects of endocrine disrupting compounds (EDC), controlled feeding experiments would be required where animals receive the same diet with the only variable being the addition or withdrawal of the target compound. This type of procedure is routinely carried out in animal testing of foodstuffs, drugs and supplements. Given the current uncertainty about the potential oestrogenic effects of phthalate compounds, for example, *in vivo* and *in vitro* studies indicate that DEHP has negligible estrogenic potency (ATSDR, 2002), it is arguably premature to suggest that exposure to phthalates in the grazing trial was the cause of the physiological and behavioural differences of animals reared on the sludge-treated pasture. More likely it was associated with a basic aspect of animal husbandry and feeding different diet qualities and amounts rather than any effect of a factor as subtle as endocrine disruption caused by sewage sludge.

It would be more reasonable to suggest that the principal route of exposure to phthalates by the general human population is from other sources such as food packaging and that transfer of phthalate to the foodchain via animals grazing sewage sludge treated soil is of negligible concern.

3.4.5 Effects on soil ecology

Phthalates have not been found to cause any significant adverse effects on soil microbial processes or on soil fertility.

Kirchmann *et al.* (1991) reported that important soil microbial parameters including respiration, N mineralization and nitrification were not influenced by DEHP in soil. Drewes *et al.* (1984) detected no sublethal neurophysiological effects on earthworms in a solution lethality contact exposure test following treatment with dimethyl phthalate (48h, LC₅₀ was 10,900 mg l⁻¹).

Hu *et al.* (2005) detected DBP and DEHP in earthworms exposed to soil artificially spiked with 5 mg kg⁻¹ of the compounds. Phthalate concentrations increased rapidly from 0 to 10 days and then remained constant for the following 20 day period of the experiment. Thus, DBP and DEHP may accumulate in mesofauna and represent a potential risk to these organisms. However, Lokke (1988 cited in Staples *et al.*, 1997) studied woodlice feeding on fallen *Acer* leaves that had been contaminated with DEHP. No bioconcentration of DEHP in adult woodlice or offspring was detected following exposure for a period of 6 months indicating the compound is degraded and metabolised in the terrestrial food chain.

Lethal and sublethal effects of di(2-ethylhexyl) phthalate (DEHP) and dibutyl phthalate (DBP) on adult individuals of the collembolan *Folsomia fimetaria* were investigated by Jensen *et al.* (2001b) in small-scale laboratory microcosms. Effects of DEHP and DBP were also tested on newly hatched collembolans in a multidish system. The endpoints were juvenile mortality, growth, and development. When exposed to DEHP, adults and juveniles were unaffected at all test concentrations up to 5,000 mg kg⁻¹. However, DBP caused increased adult mortality at 250 mg kg⁻¹ and juvenile mortality at 25 mg kg⁻¹. For DBP, adult reproduction was a more sensitive endpoint than survival, with an EC10 and EC50 of 14 and 68 mg kg⁻¹, respectively. Juvenile molting frequency was also a sensitive parameter and numbers of cuticles produced by young springtails was reduced at 1 mg kg⁻¹. Toxicity was reduced when soil spiked with DBP was stored at 20°C for a period of up to 28 d before adding the animals. Reduction in toxicity of DBP may be due a combination of degradation, evaporation, and adsorption of DBP to soil material. This was confirmed by chemical analyses, which showed a rapid initial disappearance followed by a much slower disappearance. Jensen *et al.* (2001b) therefore concluded that significant adverse effects of phthalates on collembolans were unlikely to occur in sewage sludge amended agricultural soil under normal conditions.

4 SUMMARY AND CONCLUSIONS

4.1 Introduction

Soil is potentially the recipient of inputs of a very large number of organic contaminants (OC). In the past effort has concentrated on examining the fate of OC in the aquatic environment and the potential for direct impact on human health *via* the food chain. Only more recently has attention focused on the impacts of OC on soil. For the purposes of this report, OC inputs to soils were divided into seven broad groups:

- Persistent organic pollutants (POPs);
- Bulk chemicals used in industry and domestically;
- Pesticides;
- Human pharmaceuticals;
- Veterinary medicines;
- Biocides and personal care products (PeCPs);
- Endocrine disrupting chemical (EDCs)

4.2 Sources of OC inputs to soil

Potential sources of OC inputs to soil include: atmospheric deposition, sewage sludge, livestock manure, compost, other 'wastes', pesticides and irrigation water. A brief summary is provided below.

Atmospheric deposition Information on atmospheric emissions and concentrations of POPs, provides an indirect indication of POP inputs to soils. National emissions data is collected annually in accordance with international treaties to monitor and limit POP emissions. Inevitably, the UK is both a recipient of POPs from overseas and an exporter of emissions. Modelling of long-range transport and deposition of POPs (MSC-E, 2004) has provided reasonable predictions of actual and relative POP concentrations in UK air, soil and vegetation. In general, concentrations have decreased over time and illustrate the effectiveness of action taken during the 1980s and 1990s to curb emissions and reduce the environmental burden of some principal POPs (PCDD/Fs, PCBs and PAHs).

There are a variety of routes through which pesticides may enter the atmosphere including spray drift and volatilisation. Since the loss of spray means that chemicals are not being effective it is in the farmers' interest to minimise losses through appropriate operating practices. The use of aerial application of pesticides has declined substantially in the last 20 years, with applications in 2002 estimated to be equivalent of 0.01% of the total area of pesticide application (CSL, 2003c). Wet deposition is generally the most significant route for pesticide redeposition to soils (Dubus *et al.*, 2000).

Sewage sludge. Quality standards for various OC in sewage sludge for agricultural use have been established in a number of European countries. The range of OC with potential health or environmental implications is much greater than the number of PTEs in sludge which are routinely monitored and controlled. Indeed, 42 organic compounds are regularly detected in sludge (IC Consultants, 2001).

Many OC will adsorb to the sludge matrix, although a proportion of the volatile OC may be lost by volatilisation during wastewater and sludge treatment. Biodegradation during anaerobic digestion may also eliminate certain OC from sewage sludge, but in general destruction is typically only 15 – 35 %. Aerobic composting and thermophilic digestion processes are generally more effective at OC degradation than mesophilic

anaerobic digestion, particularly for industrial bulk chemicals such as the surfactants LAS and NPE. Thermal hydrolysis prior to conventional anaerobic stabilisation may have a significant influence on the removal of OCs from sludge, but the effects have yet to be investigated for this comparatively new treatment process.

Controls on POPs introduced between 1980-90 have been relatively effective and there have been significant reductions in the primary sources of PAHs, PCBs and PCDD/Fs (Smith, 2000). This has also lowered inputs to the urban wastewater (UWW) system and reduced concentrations in sewage sludge. Inputs of POPs to sewage sludge now principally reflect:

- Background inputs to the sewer from normal dietary sources;
- Background inputs by atmospheric deposition due to remobilisation/volatilisation from soil and cycling in the environment (e.g. PCBs, PCDD/Fs and PAHs);
- Atmospheric deposition from waste incineration (eg PCDD/Fs);
- Atmospheric deposition from domestic combustion of coal;
- Biodegradation during sludge treatment;
- Volatile solids destruction during sludge treatment.

PAHs are Water Framework Directive (WFD) priority hazardous substances and the aim is to cease emissions, discharges and losses of these compounds by 2020 (CEC, 2001). However, curbing the emissions of PAHs and PCDD/Fs from domestic coal burning would be technically difficult and incinerators are already subject to stringent air quality emission standards (EPCEU, 2000a). Consequently, there is probably little opportunity to further reduce the inputs and concentrations of PAHs, PCDD/Fs as well as PCBs in UWW and sewage sludge.

POPs generally strongly bind to the sludge solids and the body of scientific evidence suggests that there are no significant environmental consequences from PAHs, PCBs or PCDD/Fs when sludge is applied to agricultural land. In the light of these developments, it may be argued that these substances are no longer as environmentally important as they were. However, soil is a major repository for POPs and further investigations are necessary to improve understanding of the remobilisation and cycling processes that control diffuse inputs of these organic compounds to UWW.

Data on the concentrations of pharmaceuticals in materials applied to land is very limited for the UK. In general, studies suggest that the pharmaceuticals vary greatly in biodegradability and are present in sewage influents and effluents to various extents. Typically, 60 % of the compounds in the influent may be removed during wastewater treatment although there is a wide range of removal efficiencies from 7-99% (Ternes, 1998).

Recent investigations show that approximately 90% of potential oestrogenic activity in UWW is reduced by sewage treatment and that <3 % is transferred to the sewage sludge. Oestrogenic substances excreted in farm livestock manures are likely to represent a much greater loading onto soil compared to recycling sewage sludge in agriculture (IC Consultants, 2001).

There is concern over persistent pesticide compounds (particularly organochlorines) in sewage sludge due to potential soil accumulation and long-term impacts on the environment (Bowen *et al.*, 2003). Modern pesticides have been developed with improved biodegradabilities in wastewater treatment and in the environment in general, so their presence is less of a concern than in the past. Varying persistences and ecotoxicities have been reported (Boxall *et al.*, 2004). However, the implications for soil quality arise more from direct applications of pesticides to crops and soils,

and from the application of livestock manures rather from inputs *via* agricultural application of sewage sludge. Indeed, the withdrawal of persistent pesticides from agricultural means they are unlikely be detected in influents to urban wastewater treatment plants (Bowen *et al.*, 2003) or sludge.

Livestock manures. POPs are not considered to be a concern in livestock manures applied to land (e.g. Stevens and Jones, 2003).

Veterinary medicines are used extensively in livestock production and consequently are present in livestock excreta. Direct deposition or application of manures to land provides a direct route of entry to the soil. In the UK, approximately 40-45% of the 459t of therapeutic-use antimicrobials are administered to pigs, implying that areas of pig production will be most susceptible to impacts from manure antimicrobial compounds (Burch, 2003).

Excreta deposited directly in the field may contain much higher concentrations of antibiotics than manure from housed stock because there is no dilution with material from medication-free time periods or degradation during storage (Boxall *et al.*, 2004). De Liguoro *et al.* (2003) and Boxall *et al.* (2004) have demonstrated that processes occurring between excretion and manure application to the soil were very effective in reducing the load of a number of antibiotics. In contrast, ivermectin (an endectocide), tetracyclines and quinolones (both antibiotics) are highly persistent with half-life values of 100 days in manure.

Manure and slurry management practices designed to reduce the risks from microbial pathogens by ensuring adequate storage and composting (FSA, 2002) are also likely to reduce the concentrations of veterinary medicines in livestock manures, however, further work is recommended to fully assess their effectiveness.

Compost. A recent review (Amlinger *et al.*, 2004) has concluded that concentrations of PCBs, PCDD/F and PAHs in source separated biowaste and green waste composts were similar to background concentrations in soils, and that regular measurements of these compounds and the establishment of limit values were not required. However, due to the higher concentrations in mixed waste compost the authors recommended that these compounds should be monitored and their use limited to non-food areas. This would appear to be an overly precautionary measure given the absence of environmental effects of POPs, their accumulation in compost amended soil is negligible and the concentrations present in mixed waste compost are below conservative and risk-derived limits for POPs in sewage sludge intended for agricultural use. Groeneveld and Hébert (2005) also concluded that the inclusion of dioxins/furans, PCBs, or PAHs in compost quality criteria was not justified.

A number of chlorinated pesticides have been found in compost, but generally only in very small amounts, with biowaste composts having higher concentrations than green compost (Amlinger *et al.*, 2004; Brändli *et al.*, 2005). Comparisons of pesticide concentrations in feedstock with the composted end products showed that composting substantially decreases the concentrations of most compounds. Consequently, there is no need for regular analyses of adsorbable organohalogenes (AOX) or specific pesticides in composts. However, given the high persistence/toxicity of wood preservatives, a precautionary measure would be to exclude pesticide treated wood from the production of marketable compost products or for recycling in agriculture.

LAS, NPE, DEHP, PBDE are rapidly degraded under aerobic composting conditions and extremely low concentrations have been reported in the literature (Amlinger *et*

al., 2004). Thus there is no evidence of a need for general threshold or limit values in composts.

Fungicides, disinfectants and insecticides are used in mushroom production. The use of spent mushroom compost (SMC) in agriculture, gardening and landscaping means that any pesticide residues will be added to soil. However, the range and quantities of chemicals applied have diminished in recent years and mushroom production has declined to an extent in the UK. Nevertheless, the estimated production of mushroom compost applied to land remains a significant volume, equivalent to approximately 400,000 t y (fresh weight) and, given the uncertainty about the extent of its contamination with pesticide residues, a chemical survey of the material is warranted.

Other waste materials. Davis and Rudd (1997) reported that a large number of compounds (and their degradation products) could be associated with waste materials applied to land and considered that such wastes should be subject to a detailed evaluation and risk assessment.

Information on OC concentrations in industrial wastes spread to land was compiled from data from EU Member States by Gendebien (2001). With the exception of waterways dredgings, POPs were within the ranges measured in sewage sludge and greenwaste composts and would not be considered limiting to land spreading. However, only a limited range of compounds was examined and a broader survey of wastes from sources where OC contamination may arise is required.

A recent survey of land spreading practices for paper waste (Gibbs *et al.*, 2005) concluded that there was no evidence of any significant risks to the environment from OC in paper waste materials applied to land. This was confirmed by field investigations which demonstrated significant agronomic benefit from the application of paper sludge and concluded that detrimental effects on soil microbial activity were not important in the medium-to-long-term after application (Aitken *et al.*, 2002).

Pesticides. The Pesticide Safety Directorate commissions regular surveys of pesticide use across the agricultural and horticultural industry. In this study, only arable crops, and grassland and fodder crops have been examined in detail because of the area of land they encompass and the amount of plant protection products which are used.

Agrochemicals are applied at different times of year depending on the crop to be protected. The extent to which a pesticide will be washed into soil will in part be dependant on weather conditions and hence will vary through the seasons. Likewise, the amount of leaf on a crop will vary through the year further influencing the extent to which a pesticide will fall directly onto the soil.

Drift can occur to a greater or lesser extent with both spray and granular products, depending on the equipment used. This will both reduce the concentration reaching the soil at the point of application and increase the area of soil which may be affected by plant protection products (CSL, 2004).

Pesticide and veterinary medicine residue disposal. Farm operations are a significant source of pesticides to surface and groundwaters, although soil may also be at risk of contamination from pesticide residues during, for example, spray equipment washing and cleaning. Managed soil-bioreactor systems or reedbeds may have potential for treating pesticide residues from tanks and equipment washing for example and require further evaluation to develop an engineered design specification

for effective remediation of pesticide wastes to protect soil and the water environment.

Land treatment is the principal approach for disposing of sheep dip chemicals, with 116,454 t disposed annually in the UK (EA, 2003). The primary focus of current environmental control measures is to protect water resources from contamination by sheep dip chemicals (Defra, 2001), with disposal to land requiring authorisation from the Environment Agency (EA). However, land treatment should also account for the potential impacts on soil fauna and flora. For instance, diazinon, one of the main organophosphate pesticides used in sheep dip, is acutely toxic to earthworms and other invertebrates (Boxall *et al.*, 2004), although other soil biological compartments may be less sensitive to sheep dip chemicals. Further research is needed to assess the consequences of sheep dip disposal on soil biological processes and fertility, and to develop recommendations to minimise soil damage and assess recovery.

Irrigation water. Irrigation is used to only a limited extent in UK agriculture, on lighter soils and for high value crops. It is more widely used in horticulture, and golf course and landscape maintenance, but this water will normally be from the mains supply. Because river water is often polluted with pharmaceutical compounds from WWT discharges, irrigation water abstracted from rivers is a potential source of pharmaceutical inputs to soil.

Limited data on OC concentrations in surface and groundwater were used to try to establish the potential scale of OC inputs to soil from crop irrigation. These are unlikely to have significant toxicological or ecotoxicological impacts in the main. However, the addition of trace quantities of antibiotic residues through irrigation of surface waters receiving effluents from urban wastewater treatment could have implications for the wider development and dissemination of antibiotic resistant bacteria in the environment. However, the implications of OC inputs for soil quality arise more from direct application of pesticides to crops and soils, and in managed applications of organic sludges and livestock manures rather than from inputs *via* irrigation waters.

4.3 Effects of OC inputs on soil quality and function

Soil is an effective scavenger and sorptive medium for OC and acts as a long-term and major repository, although biodegradation will also take place. The behaviour of OC in soil depends on their physical and chemical properties and on the nature of the soil. The persistence of OC in the environment is one of the key properties used to determine its potential significance and long-term impact. Those that are highly resistant to breakdown are described as refractory or recalcitrant (Walker, 2001). Many are not photochemically stable and may be transformed when exposed to sunlight. Some, such as carbamates and pyrethroids are susceptible to hydrolysis especially at high pH. Highly halogenated compounds (e.g. some PCBs and dioxins) are resistant to oxidation and chemical degradation.

Some OC bind to soil organic matter (OM) or minerals and tend to be immobile and persistent. Metabolism is limited and they are therefore not freely accessible to soil enzymes (Walker, 2001). Heavy soils, high in OM and/or clay adsorb hydrophobic compounds that would be more mobile or bioavailable in light sandy soils, low in OM. In contrast, hydrophilic or polar compounds are less adsorbed to soil colloids and are both more rapidly degraded by soil enzymes and more readily lost in soil drainage.

Persistent organic pollutants. PCDD/Fs, PCBs, higher chlorinated CBs and most PAHs are highly persistent in soil, whereas lower chlorinated CBs and some types of

PAH are only moderately sorbed. Soil sorption of these compounds is enhanced by sewage sludge applications (e.g. Zhang *et al.*, 2005). In general, highly sorbed POPs are less susceptible to leaching and transport. The lower chlorinated chlorobenzenes and most PAH congeners are highly volatile in soil (Wild *et al.*, 1995). The lighter PCB congeners are moderately volatile, whilst PCDD/Fs do not tend to volatilise.

Due to the strong soil sorption of most POPs, the potential for root uptake is limited (e.g. Fries, 1996; Smith, 2000). Moreover, most POPs are not efficiently translocated into the above ground plant parts (McCrary *et al.*, 1990 cited in Wild *et al.*, 1992). Volatile compounds are thought to be lost from the soil before having the opportunity to enter plant tissue *via* the roots (Wild *et al.*, 1995; Duarte-Davidson and Jones, 1996). However they can potentially enter plant tissues *via* foliar absorption (Duarte-Davidson and Jones, 1996) and there is substantial evidence to indicate that this is the primary mechanism of plant contamination. POPs have no reported detrimental effects on plant growth and the scientific literature consistently shows that there is effectively no crop uptake.

POP ingestion by grazing animals could be expected and their lipophilic properties may result in their accumulation in animal tissues and food products (Fries, 1996; Smith, 2000). Indeed this pathway is considered to represent the greatest risk for POP entry into the food chain from agricultural sources (Fries, 1996; Smith, 2000). However, PAHs do not appear to accumulate in animal tissue. Lusky *et al.* (1992 cited in Fries, 1996) found that the concentrations of PAHs in animal tissues were the same regardless of whether the animals had received high or low feed PAH concentrations. Whilst PCBs, PCDD/Fs and CBs are not metabolised and can accumulate in the food chain, the risks still appear to be extremely low, especially from contaminants in sewage sludge applications since measures in the Safe Sludge Matrix designed to further limit potential infections from pathogenic organisms that may be present in sludge, at the same time, also reduce the potential for animal ingestion of OC (eg grazing restrictions on sludge-treated pasture). Thus, the main route for POP accumulation in the food chain is via atmospheric deposition onto the soil. Since the 1977 UK ban on PCBs, the amount of these contaminants in soil has been greatly reduced and is now similar to values prior to the production of PCBs. Thus, the risks of transfer into the human food chain are minimal.

Reinecke and Nash (1984) found that acute exposure to TCDD at concentrations currently found in the environment did not present a risk to earthworms. However, chronic exposure to sublethal TCDD concentrations could cause accumulation in earthworms, and as earthworms are a major source of food for higher organisms, this could present significant ecological risks. Other studies have reported the accumulation of chlorobenzenes, chlorophenols and other PCDDs in earthworms (Belfroid *et al.*, 1995).

In terms of soil microorganisms, Chaudri *et al.* (1996) found that Aroclor 1016 (a mixture of PCB congeners) and anthracene (a PAH) had little or no effect on the soil rhizobial population. Aldrich and Daniel (2003) concluded that, for PCDD, PAH and PCB there was sufficient data to exclude an unacceptable risk to soil organisms from agricultural recycling of compost.

Pesticides. Approximately 85% of an applied pesticide may reach the soil where it is subject to biological or chemical transformation (Margni *et al.*, 2002). Some pesticides are mobile and readily degradable, while others are persistent and may accumulate and impact non-target soil organisms (HRI, 2002). Microbial degradation is the key process affecting pesticide persistence in soil, susceptibility to leaching and entry into surface and ground waters (Aislabie and Lloyd Jones, 1995). Plant

roots release substances that stimulate soil microbial and biochemical activity, enhancing pesticide degradation. Sludge application has also been shown to increase the degradation of some pesticides (Sanchez *et al.*, 2004). Sinclair and Boxall (2004) found that 30% of pesticide breakdown products were more toxic than the parent compound. In addition, the properties and persistence of the breakdown products may be such that environmental compartments are exposed to them to a greater extent than the parent compound, further increasing the potential impact.

Multiple pesticide applications may have an enhancing or deleterious effect on soil biological processes. Williams *et al.* (1996) suggested that in soils repeatedly exposed to pesticides, the microbial population becomes acclimated to more rapidly degrade them. However, multiple pesticide applications may also impair the soils ability to metabolise subsequent applications (HRI, 2002).

At normal application rates, herbicides and insecticides generally have little effect on soil ammonification or nitrification processes (Yamaoto, 1998; Wainwright, 1978). Fungicides have been reported to increase ammonification in soils (Wainwright and Pugh, 1973) and some older fungicides were significant nitrification inhibitors. However, newer compounds appear to have only marginal effects on nitrification (Wainwright, 1978). Insecticides generally have a minor influence on soil respiration (e.g. Lewis *et al.*, 1977). In contrast, fungicides have been found to initially decrease soil respiration rates, followed by a marked stimulation attributed to the increased activity of a few resistant microorganisms (Domsch, 1970 cited in Wainwright, 1978). Others (e.g. Smith and Woods, 1996) have reported reductions in the microbial biomass and increased respiration in pesticide treated soils.

The effects of insecticides on the growth and activities of soil organisms are not consistent. No negative effects of insecticides on soil organisms, microbial processes or crop productivity were found by Bromilow *et al.* (1996) or Das and Mukherjee (2000). In contrast, Kale *et al.* (1989) found that, whilst neither insecticides nor their metabolites had negative effects on *Rhizobium* sp. growth, *Azotobacter chroococcum* growth was inhibited, indicating that the chemicals may interfere with nitrogen fixing mechanisms. Moreover, after PCP was applied in sewage sludge, Chaudri *et al.* (1996) found a 99% reduction in soil rhizobia, with no evidence of recovery. However, production and use of PCP has been restricted in Europe since the 1980s. The compound was not detected in a contemporary survey of sewage influents in the UK (Bowen *et al.*, 2003).

Phenoxyalkanoic acid herbicides have been applied repeatedly on the same soil in many areas of the world with no negative impacts on soil fertility or ecology. Similarly, 35 years of annual 2,4-D field applications had no apparent effects on biomass N or N mineralization (Biederbeck *et al.*, 1987). Triazines have been found not to alter soil bacterial and fungal populations (Voets *et al.*, 1974). However, reductions in sporeformers (Audus, 1970), and nitrifying bacteria (e.g. Farmer *et al.*, 1965 cited in Voets *et al.*, 1974) have been observed. Voets *et al.* (1974) also studied the long term effects of atrazine and found reductions in the numbers of various soil organisms, and a large and persistent depression of certain soil enzymes.

Veterinary medicines. A significant portion of most drugs are excreted after administration to livestock, either as the parent substance or metabolites. Antibiotics are biologically active substances designed to affect microorganisms. They are usually mobile as their water solubility is high relative to the molecular weight. Many medicines are lipophilic and persistent, with a high potential to bioaccumulate in the soil environment.

Most research on the health effects arising from the presence of antibiotics in the environment has focussed on the development of antibiotic resistant bacteria. When medicated livestock excrete drug metabolites, bacteria in the manure reconvert the metabolites into active compounds. Thus, manure application to agricultural soils can provoke pathogens and bacteria into developing drug resistance (Thiel-Bruhn, 2003). Antibiotic treatment also causes the formation of resistant microorganisms within the animal which can be transferred to the soil in the excreta. Even trace concentrations of active substances are sufficient to provoke resistance (Halling-Sørensen *et al.*, 1998). Microbial antibiotic resistance readily crosses species boundaries (Witte, 1998), allowing multiple-resistant strains of microorganisms to find their way into the food chain (Berger *et al.*, 1996 cited in Halling-Sørensen *et al.*, 1998). Indeed, the spread of antibiotic resistant human pathogens has been directly linked to the use of antibiotics in animal husbandry which have entered the water environment following manure application (Haller *et al.*, 2002). However, the development of resistance in soil bacterial populations appears to be a transient phenomenon. Recent studies show that, once the selection pressure from inputs of antibiotic compounds in livestock manures is removed, the resistance profiles of the soil community return to pre-treatment values (e.g. Sengeløv *et al.*, 2003).

The mobility and availability of veterinary medicines for uptake by soil organisms depends on the chemistry of the compounds and soil properties. In general, an antibiotic sorbed to soil demonstrates reduced antimicrobial activity. Desorption on the other hand reactivates antimicrobial potency (Lunestad and Goksøyr, 1990).

Antibiotics and other veterinary medicines and their metabolites vary in persistence (Kümpel *et al.*, 2001). Some compounds, such as ivermectin (an endoparasiticide), chlorotetracycline and amprolium (both antibiotics) persist for months, while others like tylosin, penicillin (both antibiotics) and nicarbazin (an endoparasiticide), degrade after a few days. Manure type also affects degradation, although breakdown rates in manure are generally faster than in soil (Loke *et al.*, 2000; Boxall *et al.*, 2004). Soil type and manure application timing may also affect the degradation rate of a compound (Boxall *et al.*, 2003a). Metabolites in general are less potent than the parent compounds, but may still be toxic. Thus, risk assessments based on the parent compound alone may underestimate actual potential effects on the soil environment.

There are very few reports of the detection of drug residues in food for human consumption arising from environmental contamination. Thiele-Bruhn (2003) concluded that plant uptake even of mobile antibiotics was small, although some effects on plant growth were apparent. There is as yet no evidence that bioaccumulation of some therapeutic compounds poses any significant health hazard to consumers.

A long-term priority is to reduce reliance on routine veterinary administration of antibiotics in livestock production. A more immediate practical option would be to adapt manure storage and composting practices to maximise antibiotic degradation. Spreading frequency and rates of application could also be modified to allow time for microbial populations to recover and avoid supporting a permanent reservoir of resistant bacteria in soil. Manure applications to agricultural land are restricted to limit inputs of nitrogen within Nitrate Vulnerable Zones (CEC, 1991). These measures could also provide a degree of indirect control to minimise the extent of antibiotic resistance and allow natural attenuation of antibiotic resistant soil bacterial populations to take place. Further work is necessary to determine the potential impacts of current manure application practices on the development of antibiotic

resistance in manure treated soil. Also, fundamental work is necessary to establish the risks and implications of disseminating antibiotic resistance from agricultural soil to livestock and the human population.

As antibiotics are designed to affect bacteria, they are naturally a potential hazard to soil microorganisms. However, published information on their effects on soil organisms and processes is inconsistent (Thiele-Bruhn, 2003). Some studies have reported that antibiotics inhibit microorganisms (e.g. Colinas *et al.*, 1994; Elvers and Wright, 1995) whilst others have reported enhanced microbial growth and activity (Höper *et al.*, 2002). Significant effects of pharmaceutical compounds on soil have generally only been observed for anthelmintic (deworming) compounds (Thiel-Bruhn, 2003) and anti-parasitic agents e.g. ivermectin.

In general, acute ecotoxicological effects of medicines are unlikely when mixed in soil (Boxall *et al.*, 2004). Some drugs (e.g. ivermectin) have been found to adversely effect insect (e.g. springtail and enchytraeid) survival and reproduction (Blume *et al.*, 1976; Wall and Strong, 1987). This is important because of potential effects on food chains that depend on these organisms (Davis *et al.*, 1999). Laboratory experiments have shown that certain compounds are potentially phytotoxic, although the concentrations used were often much larger than those in field soils (Thiele-Bruhn, 2003).

Phthalates. A large number of chemicals are used in industrial manufacturing processes and domestic products and potentially transfer to soil. However, plasticizers deserve special mention because they are ubiquitous in the built environment. They leach from plastic materials and can transfer to soil by the water and sludge application route. Di(2-ethylhexyl)phthalate (DEHP) is a WFD priority substance under review and there is a degree of controversy regarding its potential carcinogenicity and oestrogenic properties. However, the available evidence indicates that the risk to human health from diffuse environmental sources of DEHP is negligible. Biodegradation is the dominant loss mechanism of phthalates in soils. Microorganisms, particularly, bacteria and actinomycetes degrade phthalate esters and their metabolites. Various studies have shown that phthalate esters are not persistent and undergo relatively rapid degradation in soils (e.g. UKWIR, 1995). In general, phthalate esters are considered to be nonvolatile (Smith, 2000).

Plant growth studies show there is little uptake of DEHP via the roots (e.g. Schmitzer *et al.*, 1989), with the increased organic matter associated with sludge applications thought to reduce DEHP bioavailability. The low volatility of phthalates also restricts their potential for redeposition onto above-ground plant parts.

Phthalates are usually rapidly metabolised by livestock and there is no significant transfer from soil or sludge to food products (UKWIR, 1995; Fries, 1996; Smith, 2000). The principal route of human exposure to phthalates is probably from other sources such as food packaging. DEHP is widely used as a plasticizer of PVC and the most critical human exposure route to DEHP is from medical equipment. Phthalates have not been found to cause any significant adverse effects on soil microbial processes or on soil fertility. However, some authors have found that DBP and DEHP may accumulate in some mesofauna and represent a potential risk to these organisms (e.g. Hu *et al.*, 2005). If DEHP use were to be restricted in future, the implications for soil quality of alternative plasticizers should be assessed as much less is known about these potential replacement compounds compared to DEHP.

5 RESEARCH RECOMMENDATIONS AND PRIORITIES FOR ORGANIC CONTAMINANTS

Actions on specific chemicals

1. Bulk chemicals used in industrial and manufacturing processes, and domestically, may be discharged directly as a waste product or leach from the built environment into the urban wastewater collection system. They may undergo varying degrees of biodegradation during wastewater treatment and partition to the sewage sludge. They potentially transfer to soil in sewage sludge, or in irrigation from surface water sources receiving treated effluent from wastewater treatment plant. Action to ban or restrict the use of a chemical (eg this is currently relevant in the case of the plasticizer DEHP, surfactants including NPE and LAS, and flame retardants: PentaBDE and OctaBDE) may lead to its substitution with an alternative compound or compounds. Often much less is known about the fate and behaviour of substitute compounds in the environment and soil. The European Commission's White Paper (COM(2001)88 final) proposes that in the future new and existing substances should be regulated under the same procedures and within a single system called REACH (**R**egistration, **E**valuation, **A**uthorisation of **C**hemicals) to ensure a high level of protection for human health and the environment. Therefore, a priority will be to assess the consequences, implications and potential impacts on soil of alternative plasticizers, surfactants and flame retardants and other substituted industrial bulk chemicals.
2. A list of 'chemicals of concern' has been developed by the UK Chemical Stakeholder Forum for compounds produced and used in large volumes of $>1000 \text{ t y}^{-1}$ in the EU, based on their persistence, toxicity and/or potential to bioaccumulate. Many of these compounds have not been considered previously in terms of their potential to transfer to soil and the consequences for soil quality. Therefore, a review of the behaviour and fate of these compounds in the environment and soil is recommended to determine their significance for soil quality, microbial processes, soil invertebrates, foodchains, plant growth and quality and human health.
3. Triclosan is an antibacterial agent and is used in cosmetics, household goods and personal care products. It is also used in plastics (children's toys) and textiles (kitchen and table goods) for antibacterial activity purposes. Triclosan may be transferred to soil by sewage sludge application. A recent terrestrial risk assessment by the Danish EPA indicated that impacts on the soil ecosystem may be apparent at contemporary concentrations and applications rates in sludge, but the database of information on which this conclusion was reached was limited. Therefore, further research on the acute and chronic toxicity of this compound is required and data on concentrations in UK sewage sludge are also necessary to assess the potential significance of triclosan inputs in sludge on soil quality.

Environmental processes

4. Contemporary inputs of POPs to soil arise largely from mobilisation through volatilisation of contaminants from soil and redeposition to soil. Further research is recommended to quantify the processes controlling the soil fluxes of POPs, their influence on the redistribution of POPs within the environment and the potential consequences for human health.

Pesticides

5. Sprayer tank and equipment washing operations are a potential source of incidental pesticide contamination of soil, as well as the water environment. Engineered modular soil based or reed bed treatment systems have potential for the remediation of pesticide washing residues. Further field evaluation of treatment option designs is required and a specification for a simple modular system should be developed suitable for on-farm construction and operation.
6. Direct application to soil is a permitted method for the managed disposal of sheep dip compounds. Rapid attenuation by soil of disposed pesticide residues is therefore desirable to minimise environmental problems. Current recommendations and guidance available to farmers on the disposal of sheep dip residues on land are aimed at protecting the water environment and do not consider degradation and attenuation by the soil. Soil conditions have a significant influence on attenuation rates and research is required to develop soil management practices that optimise the degradation of pesticide residues disposed on land. This information would provide additional, complimentary advice on techniques to further reduce potential impacts on the environment from land disposal practices.
7. Linked to 6 above, no consideration in the guidance on land disposal of sheep dip compounds is given to the potential damage or impacts of this practice on soil quality. For instance, the pesticide diazinon, which is commonly used as a sheep dip chemical, is acutely toxic to soil invertebrates. Therefore, research is necessary to determine the impacts of managed agrochemical disposal on soil ecological processes and to assess the significance of acute short-term and potentially long-term chronic impacts on the soil ecosystem. In particular, the ability of soil to recover following sheep dip disposal, and the rate of recovery should be determined. On the basis of this work, land-based pesticide waste management regimes could be developed that would also account for the recovery of the soil ecosystem following pesticide addition.
8. The environmental risk assessment for approval of a pesticide focuses upon possible effects of the product on various populations of non-target organisms including: birds, wild mammals, fish, aquatic invertebrates and plants, insects (including bees) and other arthropods, earthworms and soil micro-organisms. The risk to non-target organisms is generally assessed by the use of standard laboratory tests that give an indication of the toxicity of a particular active ingredient or formulation. These are used to derive LD50/LC50s (the doses/concentrations at which 50% mortality occurs in acute toxicity studies) and NOEL/NOECs (the levels or concentrations at which no effect is observed in longer-term studies). Current risk assessment procedures for chemicals in the environment and soil adopt a multiple species approach to derive a Predicted No Effect Concentration. Pesticides undergo rigorous environmental testing before approval, but a review of these procedures, laboratory tests and risk assessment methodologies is required to determine if they are sufficiently robust to minimise impacts on the soil ecosystem, particularly in the light of recent developments in testing and evaluating the ecotoxicity of environmental contaminants.

Composted residuals

9. Overall, the concentrations of OC in compost products derived from green and woody waste are not a concern. However, contamination of compost with

pesticide treated wood is identified as a particular potential problem. A small investigation is therefore warranted to assess the extent that woody wastes treated with preservation chemicals may enter compost production systems and to determine whether this is likely to have a significant impact on the quality of compost for use on soil.

10. Mechanical sorting of mixed municipal solid waste (MSW), to recover recyclable materials, including the production of 'compost like output' from the biodegradable fraction, that may ultimately be applied to land, is likely to expand in the UK with the introduction of mechanical biological treatment (MBT) of MSW. Mixed household waste contains potentially hazardous liquid and solid organic chemical wastes (household hazardous waste, HHW; eg solvents, paint, pesticides etc). The potential contamination with HHW of the biodegradable fraction used for compost production from mixed collected MSW by mechanical sorting processes requires further study.
11. Pesticides are used intensively by the mushroom production industry. The use of pesticides in mushroom cultivation has declined recently owing to the withdrawal of a number of active ingredients that have not been replaced and the industry has also contracted to some extent in the UK. Nevertheless, significant quantities of mushroom compost are recycled to land and there is uncertainty about the extent of the contamination of this material with pesticide residues. Therefore, an analytical survey of mushroom compost samples is required to determine the pesticide contents and whether these are significant for soil quality.

Veterinary medicines

12. A link has been identified between the therapeutic use of antibiotic drugs in intensive livestock production and the potential consequences for human health of the dissemination of antibiotic resistant bacteria within the environment. Most of the published work in this area has focussed on identifying the hazards to health associated with this practice. However, the actual risks to human health have not been fully quantified. Therefore, a microbiological risk assessment of the potential consequences for human health of antibiotic resistant bacteria in soil amended with livestock manures is required so that the significance of this and the urgency for policy action to address the issue can be determined.
13. Intensive livestock production relies on the therapeutic use of veterinary medicines. Therefore, livestock manures and slurries from intensive animal husbandry systems are routinely contaminated with these compounds and their metabolites. These residues are significant because they may have a direct ecotoxicological effect on soil or, more seriously, the presence of trace amounts of antibiotics in livestock wastes applied to land promote the development of communities of antibiotic resistant bacteria in soil with potentially important consequences for human health by reducing the effectiveness of medically administered antibiotic drugs. However, manure and slurry may be managed to achieve varying degrees of attenuation of veterinary medicines prior to application on land. Indeed, practices recommended for the reduction of enteric pathogens in livestock wastes by storing slurry or composting management of solid manures may have such additional benefits by increasing the degradation of veterinary medicines. The effects of manure management practices on removal of veterinary medicines require further investigation and the results of this work could be incorporated into the advice on appropriate handling

procedures to also mitigate environmental and health problems arising from the application of these contaminants to soil in livestock waste.

14. A complementary recommendation to 13 is the need to develop land management practices for antibiotic contaminated livestock wastes to enable the natural attenuation of antibiotic resistant bacteria in amended soil. The development of antibiotic resistance within the soil bacterial community is influenced by the rate of waste application and antibiotic addition and increases with increasing loading rate. However, this is a transient effect and antibiotic resistance within the bacterial community decays with time after application. Nutrient control measures for N dictate rates and frequency of application of livestock wastes to soils. These may also indirectly benefit the attenuation of antibiotic resistance in soil. Research is required to investigate the effects of antibiotic inputs to soil in livestock wastes on resistance profiles of the soil microbial community under operationally realistic farming conditions, taking account of the nutrient and other restrictions and controls influencing the spreading of livestock manures on land. These measures could be further refined and adapted to provide adequate attenuation periods to minimise the development and maintenance of antibiotic resistant bacteria in manure-amended soil.

Livestock and agricultural production systems

15. In the long-term, moving away from intensive livestock production practices, that rely on heavy therapeutic use of veterinary medicines, to more extensive, less drug dependent production methods, may be the most sustainable solution to reduce potential impacts of veterinary medicines on soil quality and human health. Therefore, the broader potential environmental and health benefits of farming systems that reduce reliance on routine use of veterinary medicines should be reviewed to inform long-term decisions about the development of farming practices in the future. The review should also consider and identify potential alternative pesticides to substitute for compounds that are known to have significant ecotoxicological impacts on soil.

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ANNEX A Categories of different organic compound

Non-chlorinated phenols	2,4-Dimethylphenol, 2,4-dinitrophenol, 2-methyl 4,6-dinitrophenol, nitrophenols (2-,4-), phenol, o-cresol, m- cresol, p-cresol
Chlorinated phenols	Chlorophenols, dichlorophenols, trichlorophenols, tetrachlorophenols and pentachlorophenol
Chlorinated hydrocarbons	Dichlorobenzenes, trichlorobenzenes, tetrachlorobenzenes, pentachlorobenzene, hexachlorobenzene, and hexachlorocyclohexane
Polycyclic aromatic Hydrocarbons (PAHs; unsubstituted)	Acenaphthylene, acenaphthene, anthracene, benzo[a]pyrene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[g,h,i]perylene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene, dibenzo[a,h]pyrene, fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, naphthalene, phenanthrene, and pyrene
Phthalate esters	Benzyl butyl phthalate, bis(2-ethylexyl) phthalate, di-n-butyl phthalate, di-n-octyl phthalate, diethyl phthalate and dimethyl phthalate
Volatile organic compounds (VOCs)	BTEX, tetrachloroethylene, trichloroethylene, chloroform, dichloroethanes, dichloroethenes, dichloromethane, 1,2-dichloropropane, dichloropropenes, 1,1,2,2-tetrachloroethane, carbon tetrachloride, and trichloroethanes
Halogenated volatiles	1,4-Dichlorobenzene, cis-1,2-Dichloroethylene, Dichloromethane, Tetrachloroethylene
Non-halogenated volatiles	Toluene, Meta- and para-xylene, Ortho-xylene, Total xylenes, Volatile petroleum hydrocarbons
Base-neutral extractables	Benzyl butyl phthalate Bis(2-ethylhexyl) phthalate Di-n-butyl phthalate Diethyl phthalate Dimethyl phthalate
Polycyclic aromatic hydrocarbons	Acenaphthene Acenaphthylene Anthracene Benz(a)anthracene Benzo(a)pyrene Benzo(b)fluoranthene Benzo(g,h,i)perylene Benzo(k)fluoranthene Chrysene Dibenz(a,h)anthracene Fluoranthene Fluorene Indeno(1,2,3-c,d)pyrene

	Naphthalene Phenanthrene Pyrene
Chlorinated and nonchlor. phenolics	4-Chloro-3-methylphenol 2,4 and 2,5 Dichlorophenol 3,4,5-Trichlorophenol 2,3,4,5-Tetrachlorophenol 2,3,4,6-Tetrachlorophenol Pentachlorophenol m-Cresol o-Cresol p-Cresol 2,4-Dimethylphenol 2-Nitrophenol 4-Nitrophenol Phenol
Extractables	Light extractable petroleum Hydrocarbons (LEPHs) Heavy extractable petroleum Hydrocarbons (HEPHs)
Dioxins	2,3,7,8-TCDD TCDD—Total 1,2,3,7,8-PCDD PCDD—Total 1,2,3,4,7,8-HexCDD 1,2,3,6,7,8- HexCDD 1,2,3,7,8,9- HexCDD HexCDD—Total 1,2,3,4,6,7,8-HCDD HCDD—Total OCDD—Total
Furans	2,3,7,8-TCDF TCDF—Total 1,2,3,7,8-PCDF 2,3,4,7,8-PCDF PCDF—Total 1,2,3,4,7,8-HexCDF 1,2,3,6,7,8-HexCDF 2,3,4,6,7,8-HexCDF 1,2,3,7,8,9-HexCDF HexCDF—Total 1,2,3,4,6,7,8-HCDF 1,2,3,4,7,8,9-HCDF HCDF—Total OCDF—Total

Annex B **Summary of data held on detection of pharmaceuticals in different types of water samples**

	Sewage influent	River water	Final effluent	River water down stream of STW	Groundwater
Atenolol	✓				
Azithromycin		✓			
Betaxolol		✓	✓		
Bezafibrate	✓	✓	✓		
Bisoprolol	✓	✓			
Carbamazepine	✓				
Chloramphenicol	✓	✓			
Ciprofloxacin		✓			
Clarithromycin	✓	✓	✓		
Clindamycin		✓			
Clofibrate		✓	✓		✓
Dextropropoxyphene		✓	✓	✓	
Diazepam		✓			
Diclofenac	✓	✓	✓	✓	✓
Erythromycin	✓	✓	✓	✓	
Ethinylestradiol	✓	✓			
Fenofibric acid		✓	✓		✓
Gemfibrozil	✓	✓	✓		
Ibuprofen	✓	✓	✓	✓	✓
Indomethacine	✓	✓			
Mefenamic acid			✓	✓	
Metoprolol	✓	✓	✓		
Naproxen	✓				
Norethisterone		✓			
Ofloxacin		✓			
Phenazone	✓	✓			✓
Piperacillin		✓			
Propranolol	✓	✓	✓	✓	
Propyphenazone	✓				
Roxithromycin	✓	✓			
Sotalol	✓				
Sulfadimidine		✓			
Sulfamethazine	✓	✓			✓
Sulfamethoxazole	✓	✓	✓	✓	✓
Tetracycline		✓			
Trimethoprim	✓	✓	✓	✓	

ANNEX C Inventory of concentration data of organic contaminants in different environmental media

Means (cal) = means calculated from the min and max data in the table. Mean (meas) = means provided in the original reference

Manure

Substance	Material	Min	unit	Max	unit	Mean (cal)	unit	Mean (meas)	unit	sample number	Sample year	Country of data origin	Ref	Ref year
POPs														
polycyclic aromatic hydrocarbons (PAH)	pig manure							0.51	mg/kg dw		1998-2000	Denmark	Petersen et al	2003
di(2-ethylhexyl) phthalate (DEHP)	pig manure							0.4	mg/kg dw		1998-2000	Denmark	Petersen et al	2003
nonylphenol (NP)	pig manure							<0.5	mg/kg dw		1998-2000	Denmark	Petersen et al	2003
linear alkylbenzene sulfonates (LAS)	pig manure							<10	mg/kg dw		1998-2000	Denmark	Petersen et al	2003
VETERINARY MEDICINES														
Antibiotics														
Oxytetracycline	Calf faeces							871 700	ug/kg	3		Italy	De Liguoro et al	2003
Oxytetracycline	Bedding							366 820	ug/kg	3		Italy	De Liguoro et al	2003
Oxytetracycline	Bedding							160 830	ug/kg	3		Italy	De Liguoro et al	2003
Oxytetracycline	Calf manure							19 000	ug/kg	3		Italy	De Liguoro et al	2003
Oxytetracycline	Calf manure							8780	ug/kg	3		Italy	De Liguoro et al	2003
Oxytetracycline	Calf manure							7930	ug/kg	3		Italy	De Liguoro et al	2003
Oxytetracycline	Calf manure							11 910	ug/kg	3		Italy	De Liguoro et al	2003
Oxytetracycline	Calf manure							6360	ug/kg	3		Italy	De Liguoro et al	2003
Oxytetracycline	Calf manure							2110	ug/kg	3		Italy	De Liguoro et al	2003
Oxytetracycline	Calf manure							820	ug/kg	3		Italy	De Liguoro et al	2003
Tylosin	Calf faeces							115 500	ug/kg	3		Italy	De Liguoro et al	2003
Tylosin	Bedding							32 800	ug/kg	3		Italy	De Liguoro et al	2003
Tylosin	Bedding							5400	ug/kg	3		Italy	De Liguoro et al	2003
Tylosin	Calf manure							110	ug/kg	3		Italy	De Liguoro et al	2003
Tylosin	Calf manure							<100	ug/kg	3		Italy	De Liguoro et al	2003

sulfadimidine	Cattle manure					<0.1	mg/kg		2001	Germany	Christian et al	2003
[14C]Ceftiofur	Cattle manure	11.3	mg/kg	216.1	mg/kg	113.7	mg/kg		1990	USA	Boxall	2004
Chlortetracycline	Cattle manure						7.6	ug/kg		Germany	Hamscher et al c	2000
Tetracycline	Cattle manure						2.5	µg/kg		Germany	Hamscher et al c	2000
Chlortetracycline	Pig manure	3.4	µg/kg	1001.6	µg/kg	502.5	µg/kg			Germany	Hamscher et al c	2000
sulfadimidine	Stored pig manure						1.1	mg/kg	2001	Germany	Christian et al	2003
sulfadimidine	Stored pig manure						1	mg/kg	2001	Germany	Christian et al	2003
Tetracycline	Pig manure	44.4	µg/kg	132.4	µg/kg	88.4	µg/kg			Germany	Hamscher et al c	2000
Chlortetracycline	Poultry manure						22.5	ug/g	1981	Canada	Boxall	2004
[14C]Narasin	Poultry manure	1	µg/kg	725	µg/kg	363	µg/kg		1991	USA	Boxall	2004
Endectocides												
Ivermectin	Cattle manure	12	µg/kg	75	µg/kg	43.5	µg/kg		1989	USA	Boxall	2004
Ivermectin	Cattle manure	0.3	mg/kg	9	mg/kg	4.65	mg/kg		1993	Denmark	Boxall	2004
Ivermectin	Cattle manure	0.2	mg/kg dw	3.8	mg/kg dw	2	mg/kg dw		1992	Tanzania	Boxall	2004
Ivermectin	Cattle manure	0.07	mg/kg ww	0.36	mg/kg ww	0.215	mg/kg dw		1996	Australia	Boxall	2004
Ivermectin	Cattle manure						0.353	mg/kg	1983	USA	Boxall	2004
Ivermectin	Cattle manure	13	µg/kg	80	µg/kg	46.5	µg/kg		1986	USA	Boxall	2004
Ivermectin	Cattle manure	0.24	ng/l	0.27	ng/l	0.255	ng/l		1989	USA	Boxall	2004
Ivermectin	Cattle manure			3.9	mg/kg dw				1993		Montsfort	2001
Ivermectin	Pig manure	0.22	mg/kg	0.24	mg/kg	0.23	mg/kg		1989	USA	Boxall	2004
Ivermectin	Sheep manure	0.63	mg/kg	0.714	mg/kg	0.672	mg/kg		1989	USA	Boxall	2004
Ivermectin	Horse manure			8.5	mg/kg dw				1995		Montfort	2001
Ivermectin	Horse manure	0.05	ug/g	8.47	ug/g	4.26	ug/g		1990	USA	Boxall	2004
Coccidiostat												
Monensin	Cattle manure	0.7	ng/l	4.7	ng/l	2.7	ng/l		1984	Canada	Boxall	2004
Antimicrobial												
Sulfadimethoxine	Cattle manure	300	mg/kg	900	mg/kg	600	mg/kg		1993	Italy	Boxall	2004
Oxytetracycline	broiler litter	5.5	mg/kg dw	29.1	mg/kg dw		10.9	mg/kg dw	12	1975	Muller	1980
Chlortetracycline	broiler litter	0.8	mg/kg dw	26.3	mg/kg dw		12.5	mg/kg dw	26	1975	Muller	1980
Chlortetracycline	broiler litter	0.1	mg/kg dw	2.8	mg/kg dw		0.75	mg/kg dw	19	1975	Muller	1980
Penicillin	broiler litter	0	units/g dw	25	units/g dw		12.5	units/g dw	2	1975	Muller	1980
Zinc bacitracin	broiler litter	0.8	units/g	36	units/g		7.2	units/g	6	1975	Muller	1980

Zinc bacitracin	broiler litter	0.16 units/g dw	36 units/g dw	12.3	units/g dw	5	1975	Muller	1980
Amprolium	broiler litter	0 mg/kg dw	77 mg/kg dw	27.3	mg/kg dw	29	1975	Muller	1980
Nicarbazin	broiler litter	35.1 mg/kg dw	152.1 mg/kg dw	81.2	mg/kg dw	25	1975	Muller	1980

Water and wastewater (Note: ds = downstream of a sewage treatment works discharge point)

Substance	Material	Min	unit	Max	unit	Mean (cal)	unit	Mean (meas)	unit	sample number	Sample year	Country of data origin	Ref	Ref year
Nonylphenol	domestic effluent	<0.02	µg/l	69	µg/l						1993- 2002	various	Various sources cited Johnson & Jürgens	2003
Octylphenol	domestic effluent	0.005	µg/l	1.7	µg/l						1993- 2002	various	Various sources cited Johnson & Jürgens	2003
Biphenol A	domestic effluent	<0.0001	µg/l	4.5	µg/l						1993- 2002	various	Various sources cited Johnson & Jürgens	2003
Phthalates DEHP ^b DBP ^c , BBP ^d	domestic effluent	<0.1	µg/l	30.5	µg/l						1993- 2002	various	Various sources cited Johnson & Jürgens	2003
Nonylphenol	industrially impacted effluent	142	µg/l	330	µg/l						1993- 2002	various	Various sources cited Johnson & Jürgens	2003
Octylphenol	industrially impacted effluent	0.26	µg/l	9	µg/l						1993- 2002	various	Various sources cited Johnson & Jürgens	2003
Biphenol A	industrially impacted effluent	<0.01	µg/l	8	µg/l						1993- 2002	various	Various sources cited Johnson & Jürgens	2003
Phthalates DEHP ^b DBP ^c , BBP ^d	industrially impacted effluent	<0.1	µg/l	80.5	µg/l						1993- 2002	various	Various sources cited Johnson & Jürgens	2003
Nonylphenol	surface water	<0.01	µg/l	646	µg/l						1993- 2002	various	Various sources cited Johnson & Jürgens	2003
Octylphenol	surface water	<0.005	µg/l	13	µg/l						1993- 2002	various	Various sources cited Johnson & Jürgens	2003
Biphenol A	surface water	<0.0001	µg/l	1.4	µg/l						1993- 2002	various	Various sources cited Johnson & Jürgens	2003
Phthalates DEHP ^b DBP ^c , BBP ^d	surface water	<0.1	µg/l	98	µg/l						1993- 2002	various	Various sources cited Johnson & Jürgens	2003
PHARMACEUTICALS														
Lipid regulating agents														
Bezafibrate	sewage influent			4.6	ug/l			2.2	ug/l	49		Germany	Ternes	1998
Bezafibrate	sewage influent	0.1	ug/l	1.75	ug/l							Germany	Huschek	2004

Gemfibrozil	sewage influent			1.5	ug/l		0.4	ug/l		Germany	Ternes	1998
Gemfibrozil	sewage influent						0.28	ug/l		Germany	Huschek	2004
Bezafibrate	final effluent	0.25	ug/l	4.56	ug/l				1996-99	Germany	Zwiener et al	2001
Clofibrate	final effluent	0.46	ug/l	1.56	ug/l				1996-99	Germany	Zwiener et al	2001
Fenofibric acid	final effluent	0.05	ug/l	1.19	ug/l				1996-99	Germany	Zwiener et al	2001
Gemfibrozil	final effluent			1.5	ug/l				1996-99	Germany	Zwiener et al	2001
Bezafibrate	lake			380	ng/l				1996	Germany	Zuccato et al	2001
Clofibrate	lake	1	ng/l	9	ng/l				1998	Switzerland	Zuccato et al	2001
Bezafibrate	river water	0.0005	ug/l	0.38	ug/l				1996-99	Germany	Zwiener et al	2001
Gemfibrozil	river water			0.19	ug/l				1996	Germany	Zuccato et al	2001
Gemfibrozil	river water			0.51	ug/l				1996-99	Germany	Zwiener et al	2001
Clofibrate	river water						40	ng/l	1985	UK	Zuccato et al	2001
Clofibrate	river water						30	ng/l	1997	Ireland	Zuccato et al	2001
Clofibrate	river water			180	ng/l				1998	Germany	Zuccato et al	2001
Clofibrate	river water	0.0005	ug/l	0.3	ug/l				1996-98	Germany	Zwiener et al	2001
Fenofibric acid	river water			172	ng/l				1996	Germany	Zuccato et al	2001
Fenofibric acid	river water	0.0005	ug/l	0.17	ug/l				1996-98	Germany	Zwiener et al	2001
Clofibrate	groundwater	0.07	ug/l	7.3	ug/l				1997	Germany	Zwiener et al	2001
Fenofibric acid	groundwater			0.05	ug/l				1997	Germany	Zwiener et al	2001
Antiphlogistics (anti-inflammatory)												
Atenolol	sewage influent	0.19	ug/l	0.27	ug/l					Germany	Huschek	2004
Carbamazepine	sewage influent			6.3	ug/l		2.1	ug/l		Germany	Ternes	1998
Carbamazepine	sewage influent	0.9	ug/l	1.2	ug/l					Germany	Huschek	2004
Diclofenac	sewage influent			2.1	ug/l		0.81	ug/l	49	Germany	Ternes	1998
Diclofenac	sewage influent	1.47	ug/l	2.1	ug/l					Germany	Huschek	2004
Ethinylestradiol	sewage influent			0.02	ug/l		0.001	ug/l		various	Ternes	1999
Ibuprofen	sewage influent			3.4	ug/l		0.37	ug/l		Germany	Ternes	1998
Ibuprofen	sewage influent			1.9	ug/l		0.34	ug/l		Germany	Stumpf et al	1998
Ibuprofen	sewage influent	0.054	ug/l	0.35	ug/l					Germany	Huschek	2004
Ibuprofen-OH	sewage influent			5.96	ug/l		0.92	ug/l		Germany	Stumpf et al	1998
Indomethacin	sewage influent			0.6	ug/l		0.27	ug/l		Germany	Ternes	1998
Indomethacin	sewage influent						0.14	ug/l		Germany	Huschek	2004

Naproxen	sewage influent			0.52	ug/l					0.3	ug/l			Germany	Ternes	1998
Naproxen	sewage influent				ug/l					0.1	ug/l			Germany	Huschek	2004
Propyphenazone	sewage influent									0.11	ug/l			Germany	Huschek	2004
Phenazone	sewage influent			0.41	ug/l					0.16	ug/l			Germany	Ternes	1998
Phenazone	sewage influent									0.09	ug/l			Germany	Huschek	2004
Sotalol	sewage influent	0.57	ug/l	0.68	ug/l									Germany	Huschek	2004
Diclofenac	final effluent	<20	ng/l	2349	ng/l					599	ng/l	45	2002	UK	Hilton et al	2003
Ibuprofen	final effluent	<20	ng/l	####	ng/l					4201	ng/l	45	2002	UK	Hilton et al	2003
Diclofenac	river water (ds)	<20	ng/l	568	ng/l					154	ng/l	45	2002	UK	Hilton et al	2003
Ibuprofen	river water (ds)	<20	ng/l	5044	ng/l					1105	ng/l	45	2002	UK	Hilton et al	2003
Diclofenac	river water			489	ng/l								1996	Germany	Zuccato et al	2001
Diclofenac	river water	0.005	ug/l	0.49	ug/l								1996-99	Germany	Zwiener et al	2001
Ethinylestradiol	river water	2	ng/l	5	ng/l								1989	UK	Zuccato et al	2001
Ibuprofen	river water	<20	ng/l	1555	ng/l					423	ng/l	45	2002	UK	Hilton et al	2003
Ibuprofen	river water			139	ng/l								1996	Germany	Stumpf et al	1996
Phenazone	river water			0.95	ug/l								1996-99	Germany	Zwiener et al	2001
Diclofenac	groundwater			0.3	ug/l								1997	Germany	Zwiener et al	2001
Ibuprofen	groundwater			0.2	ug/l								1997	Germany	Zwiener et al	2001
Phenazone	groundwater	<0.01	ug/l	1.25	ug/l								1997	Germany	Zwiener et al	2001
Antibiotics																
Clarithromycin	sewage influent			0.24	ug/l							1	1998		Hirsch	1999
Clarithromycin	sewage influent									0.071	ug/l			Germany	Huschek	2004
Chloramphenicol	sewage influent			0.56	ug/l							10	1998	Germany	Hirsch et al	1999
Erythromycin	sewage influent	0.15	ug/l	0.43	ug/l									Germany	Huschek	2004
Erythromycin	sewage influent			6	ug/l					2.5	ug/l	10	1998	Germany	Hirsch et al	1999
Roxithromycin	sewage influent			1	ug/l					0.68	ug/l	10	1998	Germany	Hirsch et al	1999
Roxithromycin	sewage influent	0.11	ug/l	0.52	ug/l									Germany	Huschek	2004
Trimethoprim	sewage influent			0.66	ug/l					0.32	ug/l	10		Germany	Hirsch et al	1999
Trimethoprim	sewage influent	0.16	ug/l	0.42	ug/l									Germany	Huschek	2004
Sulfamethoxazole	sewage influent			2	ug/l					0.4	ug/l	10	1998	Germany	Hirsch et al	1999
Clarithromycin	final effluent			0.24	ug/l								1996-99	Germany	Zwiener et al	2001
Erythromycin	final effluent	<10	ng/l	1842	ng/l					109	ng/l	45	2002	UK	Hilton et al	2003

Sulfamethoxazole-acetate	final effluent	0	ng/l	2235	ng/l			161	ng/l	45	2002	UK	Hilton et al	2003
Trimethoprim	final effluent	<10	ng/l	1228	ng/l			128	ng/l	45	2002	UK	Hilton et al	2003
Chloramphenicol	river water			0.06	ug/l					52	1998	Germany	Hirsch <i>et al</i>	1999
Clarithromycin	river water			0.26	ug/l						1996-99	Germany	Zwiener et al	2001
Clarithromycin	river water	1	ng/l	37	ng/l	9.33	ng/l			8	2002	Germany	Christian et al	2003
Clarithromycin	river water			0.26	ug/l					33	1998	Germany	Hirsch <i>et al</i>	1999
Erythromycin	river water	<10	ng/l	57	ng/l			<10	ng/l	45	2002	UK	Hilton et al	2003
Erythromycin	river water	4	ng/l	190	ng/l	72.75	ng/l			8	2002	Germany	Christian et al	2003
Erythromycin	river water			1.7	ug/l			0.15	ug/l	52	1998	Germany	Hirsch <i>et al</i>	1999
Erythromycin	river water							1	ug/l		1985	UK	Zuccato et al	2001
Erythromycin	river water (ds)	<10	ng/l	1022	ng/l			159	ng/l	45	2002	UK	Hilton et al	2003
Roxithromycin	river water	4	ng/l	14	ng/l	8.50	ng/l			8	2002	Germany	Christian et al	2003
Roxithromycin	river water			0.56	ug/l					52	1998	Germany	Hirsch <i>et al</i>	1999
Sulfadimidine	river water	3	ng/l	7	ng/l	4.33	ng/l			8	2002	Germany	Christian et al	2003
Sulfamethoxazole	river water	4	ng/l	52	ng/l	24.43	ng/l			8	2002	Germany	Christian et al	2003
Sulfamethoxazole	river water			0.48	ug/l			0.03	ug/l	52	1998	Germany	Hirsch <i>et al</i>	1999
Sulfamethoxazole	river water							1	ug/l		1985	UK	Zuccato et al	2001
Sulfamethoxazole-acetate	river water (ds)	0	ng/l	239	ng/l			70	ng/l		2002	UK	Hilton et al	2003
Tetracycline	river water							1	ug/l		1985	UK	Zuccato et al	2001
Trimethoprim	river water			0.2	ug/l					52	1998	Germany	Hirsch <i>et al</i>	1999
Trimethoprim	river water	<10	ng/l	36	ng/l			<10	ng/l	45	2002	UK	Hilton et al	2003
Trimethoprim	river water (ds)	<10	ng/l	42	ng/l			12	ng/l	45	2002	UK	Hilton et al	2003
Trimethoprim	river water	3	ng/l	12	ng/l	6.75	ng/l			8	2002	Germany	Christian et al	2003
Sulfamethoxazole	groundwater			0.47	ug/l					59	1998	Germany	Hirsch <i>et al</i>	1999
Betablockers														
Bisoprolol	sewage influent			0.37	ug/l			0.06	ug/l			Germany	Ternes	1998
Bisoprolol	sewage influent							0.13	ug/l			Germany	Hushek	2004
Propranolol	sewage influent			0.29	ug/l			0.17	ug/l			Germany	Ternes	1998
Propranolol	sewage influent	0.056	ug/l	0.09	ug/l							Germany	Hushek	2004
Metoprolol	sewage effluent			2.2	ug/l			0.73	ug/l			Germany	Ternes	1998

Metoprolol	sewage effluent	0.99	ug/l	1.18	ug/l						Germany	Huschek	2004	
Betaxolol	final effluent			0.19	ug/l					1996-99	Germany	Zwiener et al	2001	
Metoprolol	final effluent			2.2	ug/l					1996-99	Germany	Zwiener et al	2001	
Propranolol	final effluent	16	ng/l	284	ng/l		93	ng/l	45	2002	UK	Hilton et al	2003	
Betaxolol	river water			0.03	ug/l					1996-99	Germany	Zwiener et al	2001	
Bisoprolol	river water			2.9	ug/l					1996-99	Germany	Zwiener et al	2001	
Metoprolol	river water			2.2	ug/l					1996-99	Germany	Zwiener et al	2001	
Propranolol	river water	<10	ng/l	115	ng/l		10	ng/l	45	2002	UK	Hilton et al	2003	
Propranolol	river water			0.59	ug/l					1996-99	Germany	Zwiener et al	2001	
Propranolol	river water (ds)	<10	ng/l	215	ng/l		41	ng/l	45	2002	UK	Hilton et al	2003	
Others														
Azithromycin	river water	1	ng/l	3	ng/l	1.75	ng/l		8	2002	Germany	Christian et al	2003	
Ciprofloxacin	river water	lod	ng/l	9	ng/l		ng/l		8	2002	Germany	Christian et al	2003	
Clindamycin	river water	3	ng/l	24	ng/l	8.20	ng/l		8	2002	Germany	Christian et al	2003	
Dextropropoxyphene	river water (ds)	<20	ng/l	682	ng/l			147	ng/l	45	2002	UK	Hilton et al	2003
Dextropropoxyphene	river water							1	ug/l		1985	UK	Zuccato et al	2001
Diazapam	river water							10	ng/l		1985	UK	Zuccato et al	2001
Fenofibric acid	river water			172	ng/l					1996	Germany	Zuccato et al	2001	
Indomethacin	river water			121	ng/l					1996	Germany	Zuccato et al	2001	
Mefenamic acid	river water (ds)	<50	ng/l	366	ng/l			86	ng/l	45	2002	UK	Hilton et al	2003
Norethisterone	river water			17	ng/l					1985	UK	Zuccato et al	2001	
Ofloxain	river water	5	ng/l	20	ng/l	12.50	ng/l		8	2002	Germany	Christian et al	2003	
Piperacillin	river water	lod	ng/l	48	ng/l				8	2002	Germany	Christian et al	2003	
Sulfamethazine	groundwater			0.16	ug/l				59	1998	Germany	Hirsch <i>et al</i>	1999	
Mefenamic acid	final effluent	<50	ng/l	1440	ng/l			273	ng/l	45	2002	UK	Hilton et al	2003
Dextropropoxyphene	final effluent	<20	ng/l	585	ng/l			199	ng/l	45	2002	UK	Hilton et al	2003
VETERINARY MEDICINES														
Ectoparasiticides														
Chlorfenvinphos	groundwater			70	ng/l					1997	UK	Boxall et al		
Chlorfenvinphos	groundwater	15	ng/l	20	ng/l					2001	UK	Boxall et al		
Chlortetracycline	groundwater	0.17	ug/l	0.22	ug/l						Germany	Hamscher et al (a)		

Diazinon	groundwater			216	ug/l	1997	UK	Boxall et al
Diazinon	groundwater	26	ng/l	190	ng/l	2001	UK	Boxall et al
Propetamphos	groundwater			489	ng/l	1997	UK	Boxall et al
Propetamphos	groundwater	29	ng/l	110	ng/l	2001	UK	Boxall et al
Antibiotics								
Sulfamethazine	groundwater	0.08	ug/l	0.16	ug/l	1999	Germany	Boxall et al
Chlortetracycline	groundwater	0.17	ug/l	0.22	ug/l		Germany	Hamscher et al (a)
Oxytetracycline	groundwater	0.15	ug/l	0.19	ug/l		Germany	Hamscher et al (a)
Tetracycline	groundwater	0.11	ug/l	0.27	ug/l		Germany	Hamscher et al (a)
Antimicrobials								
Tylosin	groundwater	0.13	ug/l	0.42	ug/l		Germany	Hamscher et al (a)

River sediment

Substance	Material	Min	unit	Max	unit	Mean (cal)	unit	Mean (meas)	unit	Sample number	Sample year	Country of data origin	Ref	Ref year
Brominated Flame Retardants														
2,2',4,4'-TeBDE	river sediment	<0.3ug/kg dw		368ug/kg dw		45.06ug/kg dw				29	1996	UK	Allchin et al	1999
2,2',4,4',5-PeBDE	river sediment	<0.6ug/kg dw		898ug/kg dw		86.39ug/kg dw				29	1996	UK	Allchin et al	1999
2,2',3,4,4'-PeBDE	river sediment	<0.4ug/kg dw		72ug/kg dw		9.36ug/kg dw				29	1996	UK	Allchin et al	1999
Tetra+penta-BDEs	river sediment	21	ug/kg	59	ug/kg	40	ug/kg				1995	Japan	Eljarrat & Barcelo	2003
BDE-47	river sediment			490	ug/kg						1995	Sweden	Eljarrat & Barcelo	2003
BDE-99	river sediment			750	ug/kg						1995	Sweden	Eljarrat & Barcelo	2003
BDE-100	river sediment			170	ug/kg						1995	Sweden	Eljarrat & Barcelo	2003
BDE-47+99+100	river sediment			9.6	ug/kg						1998	Sweden	Eljarrat & Barcelo	2003
BDE-209	river sediment			360	ug/kg						1998	Sweden	Eljarrat & Barcelo	2003
BDE-47	river sediment	<0.17	ug/kg	6.2	ug/kg	3.2	ug/kg				1997	Europe	Eljarrat & Barcelo	2003
BDE-99	river sediment	<0.19	ug/kg	7	ug/kg	3.6	ug/kg				1997	Europe	Eljarrat & Barcelo	2003
POPs														
PCDD/F	river sediment	0.1pg TEQ/g dw		15.6pg TEQ/g dw						11	1996	USA	Eljarrat & Barcelo	2004
PCDD/F	river sediment	0.4pg TEQ/g dw		12pg TEQ/g dw							1993	Austria	Eljarrat & Barcelo	2004
PCDD/F	river sediment	0.1pg TEQ/g dw		17.5pg TEQ/g dw							1997	Germany	Eljarrat & Barcelo	2004
PCDD/F	river sediment	0.08pg TEQ/g dw		9.4pg TEQ/g dw							2000	Russia	Eljarrat & Barcelo	2004
PCDD/F	river sediment	0.4pg TEQ/g dw		3.7pg TEQ/g dw							2001	Spain	Eljarrat & Barcelo	2004
PCDD/F	river sediment	1.8pg TEQ/g dw		7.7pg TEQ/g dw							2001	Spain	Eljarrat & Barcelo	2004
PCDD/F	river sediment	0.02pg TEQ/g dw		24pg TEQ/g dw						12	1998	Japan	Eljarrat & Barcelo	2004
PCDD/F	river sediment	0.04pg TEQ/g dw		4.4pg TEQ/g dw							2000	Korea	Eljarrat & Barcelo	2004
PCDD/F	polluted area sediment	223pg TEQ/g dw		250pg TEQ/g dw							1989	USA	Eljarrat & Barcelo	2004
PCDD/F	polluted area sediment	10pg TEQ/g dw		761pg TEQ/g dw							1989	USA	Eljarrat & Barcelo	2004
PCDD/F	polluted area sediment	20pg TEQ/g dw		230pg TEQ/g dw							1990	Finland	Eljarrat & Barcelo	2004
PCDD/F	polluted area sediment	100pg TEQ/g dw		59,000pg TEQ/g dw							1995	Finland	Eljarrat & Barcelo	2004
PCDD/F	polluted area sediment	434pg TEQ/g dw		923pg TEQ/g dw							1989	Netherlands	Eljarrat & Barcelo	2004
PCDD/F	polluted area sediment	352pg TEQ/g dw		1849pg TEQ/g dw							1989	Netherlands	Eljarrat & Barcelo	2004
PCDD/F	polluted area sediment	1.1pg TEQ/g dw		150pg TEQ/g dw							1989	Norway	Eljarrat & Barcelo	2004

Soil

Substance	Material	Min	unit	Max	unit	Mean (cal)	unit	Mean (meas)	unit	Sample number	Sample year	Country of data origin	Ref	Ref year
POPS														
PCDD/Fs	soil	0.0356	pg TEQ/g	1.68	pg TEQ/g			0.8	pg TEQ/g		2004	UK	http://www.emep.int/index_pollutants.html	2005
HBC	soil	0.0087	ug/kg	1.31	ug/kg	0.66	ug/kg	0.38	ng/g		2004	UK	http://www.emep.int/index_pollutants.html	2005
PCBS	soil	0.33	ug/kg	61.7	ug/kg	31.03	ug/kg	33.22	ng/g		2004	UK	http://www.emep.int/index_pollutants.html	2005
PAH - B[b]F	soil	0.32	ug/kg	7.64	ug/kg	3.98	ug/kg	3.92	ng/g		2004	UK	http://www.emep.int/index_pollutants.html	2005
PAH - B[k]F	soil	0.15	ug/kg	4.75	ug/kg	2.45	ug/kg	2.43	ng/g		2004	UK	http://www.emep.int/index_pollutants.html	2005
VETERINARY MEDICINES														
Antibiotics														
sulfadimidine	Pig slurry treated soil					15	ug/l	1			2001	Germany	Christian et al	2003
Chlortetracycline	soil	0.7	ug/kg	2.8	ug/kg							Germany	Hamscher et al (a)	2000
Chlortetracycline	soil	<1	ug/kg	26.4	ug/kg							Germany	Hamscher et al (b)	2000
Chlortetracycline	soil	1.2	ug/kg	41.8	ug/kg							Germany	Hamscher et al (c)	2000
Oxytetracycline	soil	0.9	ug/kg	8.6	ug/kg							Germany	Hamscher et al (a)	2000
Tetracycline	soil	1.2	ug/kg	12.3	ug/kg							Germany	Hamscher et al (a)	2000
Tetracycline	soil	<1	ug/kg	32.2	ug/kg							Germany	Hamscher et al (b)	2000
Tetracycline	soil	1.1	ug/kg	39.6	ug/kg							Germany	Hamscher et al (c)	2000
Endectocides														
Ivermectin	soil	0.1	ug/kg	2	ug/kg						1989	USA	Boxall et al	2004
Coccidiostats														
Monensin	soil	0.8	mg/kg	1.08	mg/kg						1984	Canada	Boxall et al	2004

Compost

Substance	Material	Min	unit	Max	unit	Mean (cal)	unit	Mean (meas)	unit	Sample number	Sample year	Country of data origin	Ref	Ref year
POPs														
polycyclic aromatic hydrocarbons (PAH)	household compost							0.65	mg/kg dw		1998-2000	Denmark	Petersen et al	2003
di(2-ethylhexyl) phthalate (DEHP)	household compost							18	mg/kg dw		1998-2000	Denmark	Petersen et al	2003
nonylphenol (NP)	household compost							2.7	mg/kg dw		1998-2000	Denmark	Petersen et al	2003
linear alkylbenzene sulfonates (LAS)	household compost							<10	mg/kg dw		1998-2000	Denmark	Petersen et al	2003
PCB (sum 6 congeners)	green waste compost							0.24	mg/kg dw	5	1992	EU	Amlinger et al	2004
PCB (sum 6 congeners)	green waste compost	0.03	mg/kg dw	0.48	mg/kg dw					9	1992	EU	Amlinger et al	2004
PCB (sum 6 congeners)	green waste compost							0.045	mg/kg dw		1992	EU	Amlinger et al	2004
PCB (sum 6 congeners)	green waste compost							0.178	mg/kg dw		1993	EU	Amlinger et al	2004
PCB (sum 6 congeners)	MSW compost							1.493	mg/kg dw		1993	EU	Amlinger et al	2004
PCB (sum 6 congeners)	biowaste							0.03	mg/kg dw	6	1997	EU	Amlinger et al	2004
PCB (sum 6 congeners)	green waste compost							0.03	mg/kg dw	3	1997	EU	Amlinger et al	2004
PCB (sum 6 congeners)	biowaste							0.077	mg/kg dw	15	2001	EU	Amlinger et al	2004
PCB (sum 6 congeners)	green waste compost							0.036	mg/kg dw	5	2001	EU	Amlinger et al	2004
PCB (sum 6 congeners)	biowaste							0.00979	mg/kg dw	20	2002	EU	Amlinger et al	2004
PCB (sum 6 congeners)	green waste compost							0.01108	mg/kg dw	5	2002	EU	Amlinger et al	2004
PCB (sum 6 congeners)	biowaste	0.034	mg/kg dw	0.104	mg/kg dw					4	2003	EU	Amlinger et al	2004
PCB (sum 6 congeners)	green waste compost	0.019	mg/kg dw	0.066	mg/kg dw					2	2003	EU	Amlinger et al	2004
PCB (sum 6 congeners)	biowaste							0.44	mg/kg dw	3	1992	EU	Amlinger et al	2004
PCB (sum 6 congeners)	biowaste	0.15	mg/kg dw	0.86	mg/kg dw				mg/kg dw	6	1992	EU	Amlinger et al	2004
PCB (sum 6 congeners)	biowaste							0.104	mg/kg dw		1992	EU	Amlinger et al	2004
PCB (sum 6 congeners)	biowaste							0.26	mg/kg dw		1993	EU	Amlinger et al	2004

Sewage Sludge (1)

Substance	Material	Min	unit	Max	unit	Mean (cal)	unit	Mean (meas)	unit	Sample number	Sample year	Country of data origin	Ref	Ref year
POPs and surfactants														
Polychlorinated n-alkanes (PCS)	digested sludge	1.8 mg/kg dw		93.1 mg/kg dw		19.6 mg/kg dw				9	1999	UK	Nicholls et al	2001
polycyclic aromatic hydrocarbons (PAH)	sewage sludge							9.15 mg/kg dw			1998-2000	Denmark	Petersen et al	2003
polycyclic aromatic hydrocarbons (PAH)	sewage sludge							3.38 mg/kg dw			1998-2000	Denmark	Petersen et al	2003
di(2-ethylhexyl) phthalate (DEHP)	sewage sludge							55 mg/kg dw			1998-2000	Denmark	Petersen et al	2003
di(2-ethylhexyl) phthalate (DEHP)	sewage sludge							27 mg/kg dw			1998-2000	Denmark	Petersen et al	2003
nonylphenol (NP)	sewage sludge							60 mg/kg dw			1998-2000	Denmark	Petersen et al	2003
nonylphenol (NP)	sewage sludge							12.5 mg/kg dw			1998-2000	Denmark	Petersen et al	2003
linear alkylbenzene sulfonates (LAS)	sewage sludge							2870 mg/kg dw			1998-2000	Denmark	Petersen et al	2003
linear alkylbenzene sulfonates (LAS)	sewage sludge							110 mg/kg dw			1998-2000	Denmark	Petersen et al	2003
Nonylphenol (NP)	sewage sludge	8 mg/kg dw		4000 mg/kg dw		2004 mg/kg dw					1993-2002	various	Various sources cited Johnson & Jürgens	2003
Octylphenol	sewage sludge	<0.01 mg/kg dw		20 mg/kg dw		10.01 mg/kg dw					1993-2002	various	Various sources cited Johnson & Jürgens	2003
Biphenol A	sewage sludge	<0.004 mg/kg dw		1.36 mg/kg dw		0.68 mg/kg dw					1993-2002	various	Various sources cited Johnson & Jürgens	2003
Phthalates DEHP ^b DBP ^c , BBP ^d	sewage sludge	0.19 mg/kg dw		154 mg/kg dw		77 mg/kg dw					1993-2002	various	Various sources cited Johnson & Jürgens	2003
FLAME RETARDANTS														
polybrominated diphenyl ethers (PBDE)	sewage sludge	11 ng/kg dw		270 ng/kg dw		97.5 ng/kg dw				12	1998	Sweden	de Wit	2002
hexabromocyclododecane (HBCD)	sewage sludge	19 ng/kg dw		54 ng/kg dw		31.3 ng/kg dw				3	1998	Sweden	de Wit	2002
tetrabromobisphenol A (TBBPA)	sewage sludge	3.6 ng/kg dw		45 ng/kg dw		19 ng/kg dw				3	1998	Sweden	de Wit	2002

Sum PBDE	sludge digested	20 ug/kg	30 ug/kg	25 ug/kg	1992	Sweden	Eljarrat & Barcelo	2003
Sum PBDE	sludge sewage	0.4 ug/kg	15 ug/kg	7.7 ug/kg	1992	Germany	Eljarrat & Barcelo	2003
BDE-47	digested sludge	39 ug/kg	91 ug/kg	65 ug/kg	1999	Sweden	Eljarrat & Barcelo	2003
BDE-99	digested sludge	48 ug/kg	120 ug/kg	84 ug/kg	1999	Sweden	Eljarrat & Barcelo	2003
BDE-100	digested sludge	11 ug/kg	28 ug/kg	19.5 ug/kg	1999	Sweden	Eljarrat & Barcelo	2003
BDE-209	digested sludge	140 ug/kg	350 ug/kg	245 ug/kg	1999	Sweden	Eljarrat & Barcelo	2003
BDE-47+ BDE-99+ BDE-100	sewage sludge	15 ug/kg dw	120 mg/kg dw	67.5 ug/kg dw	1993- 2002	Various sources cited various	Johnson & Jürgens	2003

Sewage sludge (2) – Data specific to the UK

Substance	Sludge Type		Min		Max		Mean		Median		Sample year	Reference	Ref year
			mg/kg	µg/kg	mg/kg	µg/kg	mg/kg	µg/kg	mg/kg	µg/kg			
Non-halogenated monocyclic aromatics													
Benzene	anaerobically digested		0.114	N/A	0.246	N/A						Rogers et al	2001
Benzene	activated anaerobically digested	dry wt	0.126	N/A	0.317	N/A						Rogers et al	2001
Benzene			0.084		0.317						1994	Bowen et al	2003
Benzene				4.6		483					1996	Bowen et al	2003
Benzene		dry wt	0.11		0.317		0.084		0.211		1994	UKWIR	1995
m+p xylene	anaerobically digested			nd		73						Rogers et al	2001
m+p xylene		dry wt	0.276		22.1							Rogers et al	2001
m+p xylene		dry wt	0.276		22.1		5.05		3.79		1994	UKWIR	1995
o-xylene	anaerobically digested			nd		16						Rogers et al	2001
o-xylene	anaerobically digested	dry wt	0.22		7.18							Rogers et al	2001
	activated anaerobically digested												
o-xylene	digested	dry wt	0.54		2.64							Rogers et al	2001
o-xylene		dry wt	0.22		7.18		1.73		1.46		1994	UKWIR	1995
xylenes	anaerobically digested		0.025	25	0.103	103						Rogers et al	2001
Monocyclic aromatic (chloro- and nitro-anilines)													
Monochlorobenzene		dry wt	35100		192000		108875		101050		1994	UKWIR	1995
1,2-Dichlorobenzene		dry wt	71.3		4110		877		237.5		1994	UKWIR	1995
1,2-Dichlorobenzene		dry wt	1.5		13.6		7.5		8.5		1994	UKWIR	1995
1,3-Dichlorobenzene		dry wt	13		467		110		47.2		1994	UKWIR	1995
1,3-Dichlorobenzene		dry wt	0.6		40.2		5.3		2		1989	UKWIR	1995
1,4-Dichlorobenzene		dry wt	561		2320		1310		1250		1994	UKWIR	1995
1,4-Dichlorobenzene		dry wt	1.6		33.9		14.3		12.65		1998	UKWIR	1995
1,2,3-trichlorobenzene	anaerobically digested	dry wt	0.04		2.33							Rogers et al	2001
1,2,3-trichlorobenzene	anaerobically digested			<0.3		0.85						Rogers et al	2001
1,2,3-trichlorobenzene		dry wt	2.35		484		107		9.11		1994	UKWIR	1995
1,2,3-trichlorobenzene		dry wt	0.04		1.23		0.31		0.16		1989	UKWIR	1995
1,2,4-trichlorobenzene	anaerobically digested	dry wt	<0.02		8.1							Rogers et al	2001

1,2,4-trichlorobenzene	anaerobically digested			<0.5	9.36				Rogers et al	2001
1,2,4-trichlorobenzene		dry wt	14.7		1070	264	51.1	1994	UKWIR	1995
1,2,4-trichlorobenzene		dry wt	0.02		4.8	0.92	0.36	1989	UKWIR	1995
1,3,5-trichlorobenzene	anaerobically digested	dry wt	<0.02		2.33				Rogers et al	2001
1,3,5-trichlorobenzene	Anaerobically digested		<0.3		3.14				Rogers et al	2001
1,3,5-trichlorobenzene		dry wt	0.005		39.7		0.06	1994	UKWIR	1995
1,3,5-trichlorobenzene		dry wt	0.11		0.65	0.34	0.27	1989	UKWIR	1995
1,2,3,4-Tetrachlorobenzene		dry wt	0.22		45.4	11	4.41	1994	UKWIR	1995
1,2,3,4-Tetrachlorobenzene		dry wt	0.01		0.22	0.13	0.13	1989	UKWIR	1995
1,2,3,5 - Tetrachlorobenzene		dry wt	0.43		101	13	2.48	1994	UKWIR	1995
1,2,4,5 - Tetrachlorobenzene		dry wt	2.19		38.2	11.4	5.76	1994	UKWIR	1995
1,2,3,5 - & 1,2,4,5-TeCB		dry wt	0.01		0.21	0.11	0.1	1989	UKWIR	1995
Pentachlorobenzene		dry wt	2.16		37.36	9.8	4.85	1994	UKWIR	1995
hexachlorobenzene	anaerobically digested	dry wt	<0.01	0.72	0.35	6.89			Rogers et al	2001
hexachlorobenzene						LOD		1996	Bowen et al	2003
hexachlorobenzene		dry wt	8.03		90.1	26.1	17.2	1994	UKWIR	1995
hexachlorobenzene		dry wt	0.0001		0.055	0.013	0.002		UKWIR	1995
hexachlorobenzene		dry wt				0.017			UKWIR	1995
hexachlorobenzene		dry wt	0.0002		0.32	0.023	0.009		UKWIR	1995
hexachlorobenzene		dry wt	0.01		0.42	0.09	0.09	1989	UKWIR	1995
Monocyclic aromatics										
2,3-DCP		dry wt	0.0004		0.072	0.024	0.005	1993	UKWIR	1995
2,4-DCP		dry wt	0.35		2.6	1.36	1.25	1993	UKWIR	1995
2,5-DCP		dry wt	0.018		0.4	0.1	0.059	1993	UKWIR	1995
2,6-DCP		dry wt	0.002		0.036	0.015	0.0135	1993	UKWIR	1995
3,4-DCP		dry wt	0.025		0.18	0.065	0.054	1993	UKWIR	1995
2,4,6-TCP		dry wt	0.008		0.254	0.058	0.026	1993	UKWIR	1995
2,3,5-TCP		dry wt	0.002		0.052	0.013	0.0115	1993	UKWIR	1995
2,4,5-TCP		dry wt	0.002		0.067	0.026	0.023	1993	UKWIR	1995

2,3,6-TCP	dry wt	0.002	0.005	0.003	0.003	1993 UKWIR	1995
3,4,5-TCP	dry wt	0.004	0.007	0.025	0.017	1993 UKWIR	1995
2,3,4-TCP	dry wt	0.013	0.013	0.013	0.013	1993 UKWIR	1995
2,3,5,6-TeCP	dry wt	0.002	0.018	0.009	0.011	1993 UKWIR	1995
2,3,4,6-TeCP	dry wt	0.004	0.031	0.016	0.015	1993 UKWIR	1995
2,3,4,5-TeCP	dry wt	0.002	0.036	0.013	0.009	1993 UKWIR	1995
PCP	dry wt	0.005	0.101	0.043	0.0305	1993 UKWIR	1995
PCP	dry wt			0.5		1992 UKWIR	1995
Alkyl and aromatic amines/imines							
Ethylene-diamine-tetraacetic acid (EDTA)	dry wt	2.2	3.8	2.32	1.2	1992 UKWIR	1995
Organotin							
Σorganotins	dry wt	0.01	1.3	0.36	0.2	1989 UKWIR	1995
Halogenated aliphatics							
Carbon tetrachloride (CCl ₄)	anaerobically digested	dry wt	0.003	0.042		Rogers et al	2001
Carbon tetrachloride (CCl ₄)	anaerobically digested		<0.1µg/l	0.2µg/l		Rogers et al	2001
	activated anaerobically						
Carbon tetrachloride (CCl ₄)	digested	dry wt	0.005	0.1		Rogers et al	2001
Carbon tetrachloride (CCl ₄)		dry wt	0.003	0.1	0.019	0.007	1994 UKWIR 1995
1,1,2,2-tetrachloroethane (PCA)		dry wt	0.027	0.084	0.012	0.032	1994 UKWIR 1995
1,1-Dichloroethane (DCE)		dry wt	1.92	16.6	7.97	7.11	1994 UKWIR 1995
Trichloroethane (TCE)		dry wt	0.011	0.119	0.038	0.029	1994 UKWIR 1995
Trichloroethane (TCE)		dry wt	2.00E-05	8.00E-04	4.00E-04	0.7	UKWIR 1995
Trichloroethane (TCE)		dry wt	1.00E-04	0.028	0.007	0.006	UKWIR 1995
Trichloroethane (TCE)		dry wt			0.003		UKWIR 1995
Tetrachloroethene (PCE)		dry wt	0.004	0.515	0.093	0.047	1994 UKWIR 1995
Non halogenated aliphatics							
n-alkanes (C17-C32)	dry wt		436	265		1994 UKWIR	1995
n-alkanes (C12-C25, pristine & phytane)	dry wt		826	540		1994 UKWIR	1995

Substance	Sludge type		Min mg/kg	µg/kg	Max mg/kg	µg/kg	Mean mg/kg	µg/kg	Median mg/kg	µg/kg	Sample date	Ref	Ref date
Carbonyl													
Nitroacetic acid (NTA)		dry wt	1.4		23		10.1		8.5		1992UKWIR		1995
Polynuclear aromatic hydrocarbons													
naphtalene	anaerobically digested		0.21		106							Rogers et al	2001
naphtalene		dry wt	0.15		19		3.63		1.4			Jones & Northcott	2000
naphtalene		dry wt	0.8		3		1.8		1.9		1991UKWIR		1995
naphtalene	industrial	dry wt	0.5		14.9		7.4		5.9		1991UKWIR		1995
Acenaphthylene	mesophilic anaerobically digested	dry wt	0.03		0.1		0.06		0.05			Jones & Northcott	2000
Acenaphthylene	domestic	dry wt	<0.38		1		0.45		0.3		1991UKWIR		1995
Acenaphthylene	industrial	dry wt	<0.38		7.83		8.9		7.8		1991UKWIR		1995
acenapthene	domestic	dry wt	0.9		2.1		1.45		1.46		1991UKWIR		1995
acenapthene	industrial	dry wt	<0.3		6.3		2.2		1.3		1991UKWIR		1995
Fluorene	mesophilic anaerobically digested	dry wt	3.6		8.1		5.69		5.7			Jones & Northcott	2000
Fluorene	domestic	dry wt	1.26		2.54		1.95		1.81		1991UKWIR		1995
Fluorene	industrial	dry wt	3.4		15.8		6.1		5.85		1991UKWIR		1995
phenanthrene	anaerobically digested		<0.3		39.52							Rogers et al	2001
phenanthrene	mesophilic anaerobically digested	dry wt	3.2		16		6.94		6.35			Jones & Northcott	2000
phenanthrene	domestic	dry wt	2.4		6.1		3.9		3.3		1991UKWIR		1995
phenanthrene	industrial	dry wt	<0.3		32.4		10.6		6.47		1991UKWIR		1995
anthracene	anaerobically digested		<0.3		16.11							Rogers et al	2001
anthracene	mesophilic anaerobically digested	dry wt	0.38		1.8		0.72		0.65			Jones & Northcott	2000
anthracene		dry wt	0.003		1.71		0.23				1996Bowen et al		2003
anthracene	domestic	dry wt	<0.3		1.25		0.8		0.8		1991UKWIR		1995
anthracene	industrial	dry wt	<0.3		10.6		3.7		3.02		1991UKWIR		1995
fluoranthene	anaerobically digested	dry wt	<0.311		3.5							Rogers et al	2001
fluoranthene	mesophilic anaerobically digested	dry wt	1.4		7.4		4.89		5.35			Jones & Northcott	2000

fluoranthene			1.1	4	2.30		2002Bowen et al	2003
fluoranthene					1.04		1996Bowen et al	2003
fluoranthene	domestic	dry wt	1.1	4	2.3	2.5	1991UKWIR	1995
fluoranthene	industrial	dry wt	0.3	7.2	4.5	5.6	1991UKWIR	1995
fluoranthene		dry wt	0.34	11.4		2.06	1987UKWIR	1995
pyrene	anaerobically digested	dry wt	<0.3	9.65			Rogers et al	2001
pyrene	mesophilic anaerobically digested	dry wt	2.1	35	6.42	4.6	Jones & Northcott	2000
pyrene	domestic	dry wt	0.8	2.15	1.5	1.66	1991UKWIR	1995
pyrene	industrial	dry wt	<0.3	7.1	3.4	3.5	1991UKWIR	1995
chrysene	anaerobically digested	dry wt	<0.3	2.82			Rogers et al	2001
chrysene	mesophilic anaerobically digested	dry wt	0.96	5.9	2.57	2.3	Jones & Northcott	2000
chrysene	domestic	dry wt	<0.3	1.5	0.34	<0.3	1991UKWIR	1995
chrysene	industrial	dry wt	<0.3	1.18	0.6	0.79	1991UKWIR	1995
2-methylnaphthalene	mesophilic anaerobically digested	dry wt	5.9	93	24.53	13.5	Jones & Northcott	2000
1-methylnaphthalene	mesophilic anaerobically digested	dry wt	2.4	39	9.84	4.95	Jones & Northcott	2000
2,6-dimethylnaphthalene	mesophilic anaerobically digested	dry wt	5	110	29.82	17.5	Jones & Northcott	2000
2,3,6-trimethylnaphthalene	mesophilic anaerobically digested	dry wt	0.96	14.5	6.95	5.65	Jones & Northcott	2000
1-methylphenanthrene	mesophilic anaerobically digested	dry wt	0.46	8.1	3.88	3.45	Jones & Northcott	2000
benzo a anthracene	anaerobically digested	dry wt	<0.3	2.65			Rogers et al	2001
	mesophilic anaerobically digested	dry wt	0.63	2.8	1.74	1.75	Jones & Northcott	2000
benzo b fluoranthene	anaerobically digested		0.51	2.16			Rogers et al	2001
	mesophilic anaerobically digested	dry wt	1	7.1	2.96	2.9	Jones & Northcott	2000
benzo k fluoranthene	anaerobically digested		0.36	0.67			Rogers et al	2001
	mesophilic anaerobically digested	dry wt	0.71	4.5	2.16	1.95	Jones & Northcott	2000
Benzo(e)pyrene	mesophilic anaerobically digested	dry wt	0.82	4.4	2.16	1.95	Jones & Northcott	2000
Perylene	mesophilic anaerobically	dry wt	0.12	0.61	0.36	0.345	Jones & Northcott	2000

Indeno(123-cd)pyrene	digested mesophilic anaerobically digested	dry wt	0.39	2.7	1.33	1.14	Jones & Northcott	2000
Dibenz(ah)anthracene	mesophilic anaerobically digested	dry wt	0.06	0.38	0.20	0.195	Jones & Northcott	2000
Benzo(ghi)perylene	digested	dry wt	0.47	2.3	1.24	1.055	Jones & Northcott	2000
PAHs		dry wt	67	246			2000Gawlik & Bidoglio	2004
PAHs		dry wt	18	46		34	2003Gawlik & Bidoglio	2004
ΣPAHs *	treated	dry wt	6.0	83.8	27.8		1997IC Consultants Ltd	2001
biphenyl	anaerobically digested mesophilic anaerobically digested					0.68	Rogers et al	2001
		dry wt	1.7	28	6.31	4	Jones & Northcott	2000
benzo a pyrene	anaerobically digested mesophilic anaerobically digested		0.63	0.66			Rogers et al	2001
		dry wt	0.69	4	2.09	2.05	Jones & Northcott	2000

Polychlorinated biphenyls

Congener specific data

polychlorinated biphenyls	activated anaerobically digested				6.6			Rogers et al	2001
ΣPCB	anaerobically digested				1.2			Rogers et al	2001
ΣPCB			0.05	0.5				2001Bowen et al	2003
ΣPCB			0.08	0.33	0.19			2000Jones & Northcott	2000
6		dry wt	0.008	0.7	0.019			1993UKWIR	1995
8		dry wt	0.002	0.021	0.009			1993UKWIR	1995
18	mesophilic anaerobically digested	dry wt		1.14	10.31	4.90	4.61	Jones & Northcott	2000
		dry wt	0.001	0.018	0.009			1993UKWIR	1995
22	mesophilic anaerobically digested	dry wt		2.84	2.84	2.84	2.84	Jones & Northcott	2000
28	mesophilic anaerobically digested	dry wt		4.38	23.18	10.98	10.08	Jones & Northcott	2000
28		dry wt	0.001	0.021	0.01			1993UKWIR	1995
28		dry wt	0.0005	1.626	0.142	0.007		UKWIR	1995
31	mesophilic anaerobically digested	dry wt		2.55	45.89	11.21	7.32	Jones & Northcott	2000

41/64	mesophilic anaerobically digested	dry wt		0.79	5.31	2.69	2.47	Jones & Northcott	2000
44	mesophilic anaerobically digested	dry wt		0.63	4.72	2.55	2.16	Jones & Northcott	2000
49	mesophilic anaerobically digested	dry wt		1.41	9.43	3.32	2.625	Jones & Northcott	2000
52	mesophilic anaerobically digested	dry wt		2.48	21.09	8.75	6.48	Jones & Northcott	2000
52		dry wt	0.003		0.041	0.011		1993UKWIR	1995
54	mesophilic anaerobically digested	dry wt		nd	nd	nd	nd	Jones & Northcott	2000
60/56	mesophilic anaerobically digested	dry wt		0.73	5.11	2.28	2.29	Jones & Northcott	2000
70	mesophilic anaerobically digested	dry wt		2.24	29.79	7.51	4.94	Jones & Northcott	2000
74	mesophilic anaerobically digested	dry wt		1.63	6.4	2.98	2.86	Jones & Northcott	2000
104	mesophilic anaerobically digested	dry wt		0.09	0.09	0.09	0.09	Jones & Northcott	2000
104		dry wt	0.001		0.02	0.011		1993UKWIR	1995
61		dry wt	0.001		0.032	0.002		1993UKWIR	1995
61/74		dry wt	0.0004		0.456	0.042	0.005	1993UKWIR	1995
66		dry wt	0.001		0.009	0.007		1993UKWIR	1995
101		dry wt	0.001		0.047	0.016		1993UKWIR	1995
87	mesophilic anaerobically digested	dry wt		0.99	4.16	2.48	2.15	Jones & Northcott	2000
95	mesophilic anaerobically digested	dry wt		1.92	20.36	5.90	4.29	Jones & Northcott	2000
99	mesophilic anaerobically digested	dry wt		1.27	4.52	2.45	2.19	Jones & Northcott	2000
99		dry wt	0.001		0.02	0.006		1993UKWIR	1995
110	mesophilic anaerobically digested	dry wt		1.38	7.46	4.11	3.95	UKWIR	2000
110		dry wt	0.001		0.043	0.014		1993UKWIR	1995
82/151		dry wt	0.001		0.028	0.012		1993UKWIR	1995
149		dry wt	0.002		0.065	0.019		1993UKWIR	1995
118	mesophilic anaerobically digested	dry wt		0.06	7.9	4.54	3.87	Jones & Northcott	2000

118		dry wt	0.0007	0.091	0.017	0.002	1993UKWIR	1995
123	mesophilic anaerobically digested	dry wt		0.52	0.76	0.64	Jones & Northcott	2000
153		dry wt	0.001	0.049	0.012		1993UKWIR	1995
105	mesophilic anaerobically digested	dry wt		0.18	2.15	1.21	Jones & Northcott	2000
		dry wt	0.002	0.026	0.012	1993	UKWIR	1995
138		dry wt	0.002	0.047			UKWIR	1995
155	mesophilic anaerobically digested	dry wt		0.18	1.89	1.04	Jones & Northcott	2000
187		dry wt	0.001	0.018	0.005		1993UKWIR	1995
180		dry wt	0.002	0.043	0.013		1993UKWIR	1995
170		dry wt	0.001	0.061	0.021		1993UKWIR	1995
201		dry wt	0.001	0.013	0.006		1993UKWIR	1995
208		dry wt	0.001	0.021	0.006		1993UKWIR	1995
194/205		dry wt	0.002	0.035	0.01		1993UKWIR	1995
206		dry wt	0.001	0.02	0.008		1993UKWIR	1995

Annex D Legislation relating to organic contaminants

United Nations Environment Programme (UNEP) 'dirty dozen' which are the subject of the Stockholm Convention on Persistent Organic Pollutants (POPs) signed May 2001

http://www.worldwildlife.org/toxics/pubs/stockholm_convention.pdf

Organic Pollutant	Primary application	Pesticide	Industrial chemical product	By-product
Aldrin	Insecticide used against soil pests (primarily termites) on corn, cotton and potatoes	✓		
Chlordane	Insecticide now used primarily for termite control	✓		
DDT	Insecticide now used mainly against mosquitoes.	✓		
Dieldrin	Insecticide used on fruit, soil and seed crops, including corn, cotton and potatoes.	✓		
Endrin	Rodenticide and insecticide used on cotton, rice and corn	✓		
Heptachlor	Insecticide used against soil insects, especially termites. Also used against fire ants and mosquitoes.	✓		
Hexachlorobenzene (HCB)	Fungicide. Also a byproduct of pesticide manufacturing and a contaminant of other pesticide products.	✓	✓	✓
Mirex	Insecticide used on ants and termites. One of the most stable and persistent pesticides. Also a fire retardant.	✓		
Toxaphene	Insecticide used especially against ticks and mites. A mixture of up to 670 chemicals. Not used in UK	✓		
PCBs	Used primarily in capacitors and transformers, and in hydraulic and heat transfer systems. Also used in weatherproofing, carbon less copy paper, paint, adhesives and plasticizers in synthetic resins.		✓	✓
Dioxins	By-products of combustion (especially of plastics) and of chlorine product manufacturing and paper bleaching.			✓
Furans	By-products, especially of PCB manufacturing, often with dioxins.			✓

Notes: 1 HCB also falls into the categories of industrial chemical products and unwanted by-products.

Compounds considered as Candidate POPs by United Nations Economic Commission for Europe (UNECE)

http://www.es.lanacs.ac.uk/ecerg/kcjgroup/new_chemicals.htm

- Dicofol
- Endosulfan
- Short-chain chlorinated paraffins (SCCPs)
- Pentachlorobenzene
- Polychlorinated Naphthalenes (PCNs)
- Hexachlorobutadiene (HCBD)
- Pentabromodiphenylether (PeBDE)
- Perfluoro octane sulphonate (PFOS)

Legislation and voluntary measures relating to organic contaminants

A summary of legislation and voluntary measures relating to organic contaminants can be found in Appendix 6

Veterinary Medicines

Primary legislative controls of veterinary medicines relate to their manufacture and sale and to the periods required post dosing to ensure that any remaining in animal products to be used as human food stuffs are below maximum permitted residual levels (MRL).

From Veterinary Medicine Directorate website <http://www.vmd.gov.uk/>

Antimicrobial growth promoters are currently permitted for use under EC Directive 70/524, of 23 November 1970 concerning additives in feeding-stuffs which allows their authorisation across the European Union. With the emergence of concerns about antimicrobial resistance in both human and veterinary medicines and, in particular, the impact of resistance on the ability to treat humans, it was decided in 1999 to ban some antimicrobial growth promoters. The products that were banned were those that contained antimicrobials that were also used in the treatment of humans.

The European Union has now decided to ban the use of the remaining antimicrobial growth promoters from 1 January 2006 on a precautionary basis. There is currently no evidence that these antimicrobial growth promoters have led to any antimicrobial resistance problems in humans but it is to be prudent to remove any risk that such problems may occur from the use of these products.

EC (2003) Regulation (EC) No 1831/2003 of the European Parliament and of the Council of 22 September 2003 on additives for use in animal nutrition OJ L 268/29 18/10/2003 applies to coccidiostats and histomonostats used as feed additives from 2012 and to all other antibiotics from January 2006.

Following a major review of EU medicines legislation (Review 2001), new legislation was published by the European Commission on 30 April 2004. This comprised:

1. Regulation (EC) No 726/2004, revoking and replacing Regulation 2309/93 setting out procedures for EU centralised authorisations of human and veterinary medicines and establishing a European Agency for the evaluation of Medicinal Products (EMA);
2. Directive 2004/28/EC amending Directive 2001/82/EC on the Community code relating to veterinary medicinal products.

The VMD intend to replace the existing UK legislation with The Veterinary Medicines Regulations 2005, which will contain all the provisions in a single legislative instrument and will simplify and streamline the law where possible. The exercise will also implement recommendations from the Marsh and Competition Commission reports on aspects of supply of veterinary medicines in the UK.

On 1 July 1999 an EU-wide ban of the use of four growth promoting antimicrobial ingredients came into effect. This meant that spiramycin, bacitracin zinc, tylosin and virginiamycin could no longer be used for growth promotion in livestock production. A similar EU-wide ban will come into effect from 1 January 2006 for the remaining antimicrobial growth promoting ingredients (monensin, avilamycin, salinomycin and flavophospholipol).

ANNEX E

CHEMICAL STAKEHOLDER FORUM LIST OF CHEMICALS OF CONCERN

Last updated – July 2005

This list must not be circulated without the accompanying text which can be found at:

<http://www.defra.gov.uk/environment/chemicals/csf/index.htm>

Name	Chemical Abstract Service Number (CAS)	PBT Data available (D) PBT Properties predicted by QSAR (Q)	Use	Regulatory/Voluntary Activity	Other Research/Further testing underway
* On OSPAR Priority list of Chemicals					
Chemicals meeting Forum Highest Concern Criteria for PBT					
Bis(tributyltin) oxide (TBTO)*	56-35-9	D	It is still produced or used in the UK and exposure is expected to be widespread, although marketing and use restrictions exist.	OES for tin compounds (organic) under COSHH Regulations 1999 (HSE). OSPAR Priority List Chemical.	Environmental Quality Standard failures have been reported for this substance in the UK. OSPAR monitoring strategy agreed in June 2004
6,6'-di-tert-butyl-2,2'-methylenedi-p-cresol	119-47-1	D	Polymers and Adhesives	Prioritised for action by the Chemical Stakeholder Forum in October 2004.	OECD Screening Information Assessment Report available indicating a BCF <500. This would mean that it is not B/vB if confirmed
Anthracene, pure*	120-12-7	D	Isolated anthracene is used as a chemical intermediate and has some minor uses (e.g. as a plasticiser in thermosetting resins). Other sources are creosote and coal tar derivatives, and fuel combustion.	Thorough assessment performed under ESR priority list (risk assessment in preparation) (rapporteur is Greece). Judged to be screening PBT. Is listed under the Water Framework Directive as a	Is included in the PAHs TDS and was analysed in olive-pomace oil samples by the Food Standards Agency. OSPAR monitoring strategy agreed in June 2004

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Name	Chemical Abstract Service Number (CAS)	PBT Data available (D) PBT Properties predicted by QSAR (Q)	Use	Regulatory/Voluntary Activity	Other Research/Further testing underway
* On OSPAR Priority list of Chemicals				priority substance and a possible 'priority hazardous substance' subject to review by the Commission. OSPAR Priority List Chemical.	
Octamethylcyclotetrasiloxane	556-67-2	D Confirmed PBT		In US HPV Challenge Programme	
Triphenylphosphine*	603-35-0	D	It is still produced or used in the UK, and exposure is expected to be widespread.	Undergoing hazard assessment via ICCA (sponsor country unknown). OSPAR Priority List Chemical.	OSPAR monitoring strategy agreed in June 2004
2-Ethylhexyl 10-ethyl-4,4-dioctyl-7-oxo-8-oxa-3,5-dithia-4-stannatetradecanoate	15571-58-1	D	Plastic additive approved for food contact	Undergoing hazard assessment via ICCA (USA is the sponsor company). Currently it has completed ESR risk assessment minus the worker exposure section carried out by RPA under contract to DG Enterprise. This exercise was completed	Industry has conducted further testing which they feel demonstrates that this chemical does not meet the criteria. This was discussed at an ACHS meeting in February 2003 who agreed the chemical should remain on the list

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Name	Chemical Abstract Service Number (CAS)	PBT Data available (D) PBT Properties predicted by QSAR (Q)	Use	Regulatory/Voluntary Activity	Other Research/Further testing underway
* On OSPAR Priority list of Chemicals				<p>in 7 months in active co-operation with industry and is awaiting a CSTEE opinion.</p> <p>Covered by the Food Contact Plastics Directive – Specific Migration Limit = 0.04mg/kg (expressed as tin) (FSA)</p>	<p>and this was ratified by the Forum in March. Industry has actively worked in conjunction with ACHS and the EU working group, where the UK Environment Agency are rapporteur on this substance.</p> <p>There is also a Japanese government report on a related compound which the EU has yet to consider. Industry has also undertaken its own risk assessment and has been proactive in suggesting a strategy for investigating further the bioaccumulation potential of this chemical.</p>
Nonylphenol* & Phenol, 4-nonyl-, branched	25154-52-3 & 84852-15-3	D	Used to make nonylphenol ethoxylates, resins and plastic stabilisers.	UK Chemicals Stakeholder Forum has advised Government to reach a voluntary agreement with industry to phase this out for	OSPAR monitoring strategy agreed in June 2004

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Name	Chemical Abstract Service Number (CAS)	PBT Data available (D) PBT Properties predicted by QSAR (Q)	Use	Regulatory/Voluntary Activity	Other Research/Further testing underway
* On OSPAR Priority list of Chemicals				<p>most uses. OSPAR Priority List of Substances. Marketing and Use restriction proposals have been published for negotiation with EU member states.</p> <p>Thorough assessment performed under ESR (risk assessment and risk reduction strategy, involving marketing and use restrictions) (rapporteur is the UK). Restrictions on certain uses entered into force in the EU on 17 January, 2005. The Working Party on Organic Environmental Contaminants in Food prioritization of this chemical has been completed. Nonylphenol was afforded low priority. Nonylphenol is a Priority Hazardous Substance under Annex X (the priority list) of</p>	

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Name	Chemical Abstract Service Number (CAS)	PBT Data available (D) PBT Properties predicted by QSAR (Q)	Use	Regulatory/Voluntary Activity	Other Research/Further testing underway
* On OSPAR Priority list of Chemicals				the Water Framework Directive (EU).	
Hexabromocyclododecane*	25637-99-4	D	Flame retardant for plastics (mainly rigid polystyrene insulation panels for building construction) and textiles.	Risk assessment in progress under ESR (rapporteur is Sweden). Industry data suggest not P – Sweden are reviewing. Due for completion in 2005. Ongoing consideration by the UK Chemicals Stakeholder Forum. Emissions reduction programme underway in the UK. Industry have developed Best Practice Guidelines for users of HBCD.	Will be analysed in the Food Standards Agency 2001 TDS samples.
1,2,5,6,9,10-hexabromocyclododecane	3194-55-6				
2-Ethylhexyl 10-ethyl-4-[[2-[(2-ethylhexyl)oxy]-2-oxoethyl]thio]-4-octyl-7-oxo-8-oxa-3,5-dithia-4-stannatetradecanoate	27107-89-7	D	Plastic additive approved for food contact. It is still produced or used in the UK, and exposure is expected to widespread.	Undergoing hazard assessment via ICCA (USA is the sponsor country). Currently it has completed risk assessment minus the worker exposure section carried out by RPA under contract to DG Enterprise.	Industry has also undertaken its own risk assessment and has been proactive in suggesting a strategy for investigating further the bioaccumulation potential of this chemical.

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Name	Chemical Abstract Service Number (CAS)	PBT Data available (D) PBT Properties predicted by QSAR (Q)	Use	Regulatory/Voluntary Activity	Other Research/Further testing underway
* On OSPAR Priority list of Chemicals				This exercise was completed in 7 months in active co-operation with industry and is awaiting a CSTEE opinion. Covered by the Food Contact Plastics Directive – Specific Migration Limit = 1.2 mg/kg (expressed as tin)	
Di(tert-dodecyl) pentasulphide	31565-23-8	D	It is still produced or used in the UK, and exposure is expected to be widespread.	VPvB based on screening data; a further testing programme to be agreed with industry. UK lead in the EU.	
Diphenyl ether, pentabromo derivative* [pentabromodiphenyl ether, Penta BDE]	32534-81-9	D	Flame retardant for polyurethane.	Thorough assessment performed under ESR (risk assessment and risk reduction strategy, involving marketing and use restrictions) (rapporteur is the UK). Pentabromodiphenylether is a priority hazardous substance under Annex X (the priority list) of the Water Framework Directive (EU). OSPAR Priority List of Chemicals.	Will be analysed in the Food Standards Agency 2001 TDS samples. OSPAR monitoring strategy for brominated flame retardants agreed in June 2004

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Name	Chemical Abstract Service Number (CAS)	PBT Data available (D) PBT Properties predicted by QSAR (Q)	Use	Regulatory/Voluntary Activity	Other Research/Further testing underway
* On OSPAR Priority list of Chemicals					
Vinyl neodecanoate*	51000-52-3	D		Considered by the UK Chemicals Stakeholder Forum in 2002/03. Manufacturer prepared to undertake testing to refine understanding of PBT properties. Testing strategy under discussion including OECD ICCA submission and possible UK lead on OSPAR background document. OSPAR Priority List Chemical. Ongoing consideration by the UK Chemicals Stakeholder.	
1,4-Benzenediamine, N,N'-mixed phenyl and tolyl derivatives	68953-84-4	D			
Alkanes, C10-13, chloro* [short chain chlorinated paraffins (SCCPs)]	85535-84-8	D	Extreme pressure additive in metal working fluids, flame retardant in rubbers and textiles, plasticiser/ flame retardant in paints, coatings and sealants/adhesives, and fat liquoring agent in leather processing.	Thorough assessment performed under ESR (risk assessment and risk reduction strategy, involving marketing and use restrictions) (rapporteur is the UK). EU commission further review in 2003.	OSPAR monitoring strategy agreed for SCCPs in June 2004

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Name	Chemical Abstract Service Number (CAS)	PBT Data available (D) PBT Properties predicted by QSAR (Q)	Use	Regulatory/Voluntary Activity	Other Research/Further testing underway
* On OSPAR Priority list of Chemicals				Priority Hazardous Substances under Annex X (the Priority list) of the Water Framework Directive (EU).	
Dodecylphenol, mixed isomers (branched)	121158-58-5	D	Used to make oil and lubricant additives, with a small amount used to produce phenol/formaldehyde resins, latex for rubber tyres, printing inks and other niche applications. Minor use for ethoxylate surfactants	Undergoing ICCA assessment. UK is sponsor. UK national risk assessment in progress sponsored by the Environment Agency. PBT based on screening data; voluntary testing strategy being developed with industry. UK lead on PBT properties. Ongoing consideration by the UK Chemicals Stakeholder Forum	Draft environment risk assessment available (Environment Agency).
Chemicals meeting the Forum's criteria for vPvB					
2,4-di-tert-butylphenol	96-76-4	D	Intermediate. Polymers? (It is not clear if this is an actual use)	Prioritised for action at the Chemical Stakeholder Forum in October 2004.	
N,N'-ethylenedi(stearamide)	110-30-5	D			

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Name	Chemical Abstract Service Number (CAS)	PBT Data available (D) PBT Properties predicted by QSAR (Q)	Use	Regulatory/Voluntary Activity	Other Research/Further testing underway
* On OSPAR Priority list of Chemicals 2,2',6,6'-tetra-tert-butyl-4,4'-methylenediphenol	118-82-1	D	Automotive and industrial lubricants	Prioritised for action at the Chemical Stakeholder Forum in October 2004.	
Cyclododecane*	294-62-2	Q		Undergoing hazard assessment under ICCA (sponsor country unknown). OSPAR Priority List Chemical.	
4,6-di-tert-butyl-m-cresol*	497-39-2	D	It is unclear whether this substance is still produced or used in the UK. Exposure is probably not widespread, but this needs checking. (IUCILID indicates it is an intermediate)	OSPAR Priority List Chemical. Prioritised for action at the Chemical Stakeholder Forum – October 2004.	
N,N'-ethylenebis(3,4,5,6-tetrabromophthalimide)	32588-76-4	Q			
Phenol, styrenated	61788-44-1	D	It is still produced or used in the UK, but it is unclear if exposure is widespread.	Prioritised for action by the Chemicals Stakeholder Forum – October 2004.	Industry to undertake a voluntary bioaccumulation study
Tallow, hydrogenated, reaction products with 2-[(2-aminoethyl)amino]ethanol	68308-55-4	Q			
1,2-Benzenedicarboxylic acid, mixed cetyl and stearyl esters	68442-70-6	Q			
Benzoic acid, 2-hydroxy-, mon-C ₁₃ -alkyl derives., calcium salts (2:1)	83846-43-9	Q		Under consideration by the EU PBT working group.	
Magnesium, bis(2-hydroxybenzoato-O1,O2)-,	84929-98-6	D	It is unclear whether this substance is still		

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* On OSPAR Priority list of Chemicals ar,ar'-di-C>13-alkyl derivatives			produced or used in the UK. Exposure is expected to be widespread if it is.		
Fatty acids, C10-20-neo-	85116-96-7	Q			
1,2-Benzenedicarboxylic acid, mixed decyl and lauryl and myristyl diesters	90193-92-3	Q			
1,2,4-Benzenetricarboxylic acid, mixed decyl and octyl triesters	90218-76-1	Q			
Resin acids and Rosin acids, tall oil, fumarated, compds. with triethanolamine	91081-30-0	Q			
Sulfonic acids, C10-21-alkane, phenyl esters	91082-17-6	D	It is unclear whether this substance is still produced or used in the UK. Exposure is expected to be widespread if it is.		Industry testing currently in progress.
Benzenesulfonic acid, C ₁₄₋₁₈ -branched and linear alkyl derives., calcium salts	91696-73-0	Q			Industry testing currently in progress.
Glycerides, C16-18 and C18-unsatd. mono- and di-, 2,3-bis(acetyloxy)butanedioates	91744-16-0	Q			
Amines, bis(hydrogenated tallow alkyl), 2-[[bis(hydrogenated tallow alkyl)amino]carbonyl]benzoates	91745-35-6	Q			

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Name	Chemical Abstract Service Number (CAS)	PBT Data available (D) PBT Properties predicted by QSAR (Q)	Use	Regulatory/Voluntary Activity	Other Research/Further testing underway
* On OSPAR Priority list of Chemicals Hydrocarbons, C4, 1,3-butadiene-free, polymd., triisobutylene fraction, hydrogenated	93685-81-5	D	It is unclear whether this substance is still produced or used in the UK. Exposure is expected to widespread if it is.		
Alkenes, C20-24 alpha-	93924-10-8	Q			
Glycerides, C8-21 and C8-21-unsatd. mono- and di-, 2-(acetyloxy)-3-hydroxybutanedioates 2,3-bis(acetyloxy)butanedioates	100085-39-0	D		Prioritised for action at the Chemical Stakeholder Forum – October 2004.	
Chemicals meeting the Forum's criteria for PBT					
Hexachlorocyclopentadiene*	77-47-4	Q		4 th priority list ESR substance (EU). OSPAR Priority List Chemical	
2,2',6,6'-tetrabromo-4,4'-isopropylidenediphenol (tetrabromobisphenol A)*	79-94-7	D	Primary use is as a reactive flame retardant in the manufacture of flame-retarded epoxy resin printed circuit boards. Secondary use is as an additive flame retardant in ABS plastics used in electronic housings. Also used in the synthesis of TBBPA derivative flame retardants. It may also be used as an additive flame retardant in the manufacture of acrylonitrile-butadiene-styrene (ABS) resins, high impact polystyrene (HIPS) and phenolic resins. It is also used to make derivatives with niche flame retardant applications.	Thorough assessment under ESR in preparation. (rapporteur is the UK). Due for completion in 2005. OSPAR Priority List Chemical. Ongoing consideration by Chemicals Stakeholder Forum.	

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Name	Chemical Abstract Service Number (CAS)	PBT Data available (D) PBT Properties predicted by QSAR (Q)	Use	Regulatory/Voluntary Activity	Other Research/Further testing underway
* On OSPAR Priority list of Chemicals Hexamethyldisiloxane (HMDS)*	107-46-0	D	Mostly used as an intermediate. Small use in personal care products e.g. cosmetics and household care products. 1000-4999 tonnes.	OSPAR (sponsor country is France) risk assessment completed 2004. Considered by Chemicals Stakeholder Forum in 2002/03/04	Monitoring by industry of a small number of point discharges, wastewater treatment plants, estuarine locations etc. indicates HMDS is below the detection limit in the aqueous phase. Trace concentrations are detected in sediment in the vicinity of identified local sources and are of the order predicted by models.
2,6-di-tert-butyl-p-cresol [butylated hydroxytoluene (BHT)]	128-37-0	D	Used as an antioxidant for food products, animal feed, cosmetics, and packaging material. It is also used in petroleum products, synthetic rubbers, plastics, elastomers, oils, waxes, soaps, paints, and inks.	A hazard assessment was recently agreed at the OECD (ICCA substance, sponsored by Germany). The conclusion was that there is a need for an environmental exposure assessment of the substance and its primary degradation products. Occupational Exposure Standard under COSHH Regulations 2002 (HSE) Prioritised for action at the	

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* On OSPAR Priority list of Chemicals				Chemical Stakeholder Forum – October 2004.	
2,6-di-tert-butylphenol	128-39-2	D		Prioritised for action at the Chemical Stakeholder Forum – October 2004.	
4-(1,1,3,3-tetramethylbutyl)phenol [octylphenol]*	140-66-9	D	Used to make phenolic/formaldehyde resins (e.g. for use in tyres) and octylphenol ethoxylates and derivatives (used as emulsifiers for polymerisation, for textile and leather treatment, in pesticide formulations and in water-based paints).	UK Chemicals Stakeholder Forum has advised Government to reach a voluntary agreement to control this substance and its ethoxylate. Targeted risk assessment being carried out for presentation to the EU. Priority hazardous substance based on proposal from the European Commission. OSPAR Priority List Chemical. OSPAR monitoring strategy agreed in June 2004. Environment risk assessment being carried out by the Environment Agency. The Working Party on Organic Environmental Contaminants in Food	OSPAR monitoring strategy agreed in June 2004

CHEMICAL STAKEHOLDER FORUM LIST OF CHEMICALS OF CONCERN

Last updated – July 2005

This list must not be circulated without the accompanying text which can be found at:

<http://www.defra.gov.uk/environment/chemicals/csf/index.htm>

Name	Chemical Abstract Service Number (CAS)	PBT Data available (D) PBT Properties predicted by QSAR (Q)	Use	Regulatory/Voluntary Activity	Other Research/Further testing underway
* On OSPAR Priority list of Chemicals				prioritization of this chemical has been completed. Octylphenol was afforded low priority. Octylphenol is a possible Priority Hazardous Substance under Annex X (the Priority List) of the Water Framework Directive.	
3,4-dichloro- α,α,α -trifluorotoluene	328-84-7	Q			
2,6,6-trimethylbicyclo[3.1.1]heptane	473-55-2	Q			
Diocetyl-3,3'-thiodipropionate	693-36-7	D	Not produced or used in the UK or at very low tonnage		
Barium bis[2-[(2-hydroxynaphthyl)azo]naphthalenesulphonate]	1103-38-4	Q			
1,1,2,3,3-pentamethylindan	1203-17-4	Q			
Beta, 1,1,2,3,3-hexamethylindan-5-ethanol	1217-08-9	Q			
1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylindino[5,6-c]pyran	1222-05-5	Q			
1-(5,6,7,8-tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthyl)ethan-1-one	1506-02-1	Q			
Zinc bis[bis(tetrapropylene-phenyl)] bis(hydrogen dithiophosphate)	11059-65-7	Q		OSPAR list of chemicals of possible concern.	
Triethyldialuminium trichloride	12075-68-2	Q			

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Name	Chemical Abstract Service Number (CAS)	PBT Data available (D) PBT Properties predicted by QSAR (Q)	Use	Regulatory/Voluntary Activity	Other Research/Further testing underway
* On OSPAR Priority list of Chemicals 4-(2,4-dichlorophenoxy)aniline	14861-17-7	D	Exposure is not likely to be widespread based on IUCLID information (intermediate).		
Tert-dodecanethiol	25103-58-6	D	Main use is in the production of lattices and other polymers used in paper coating, the car industry, tyre production, appliance manufacture, carpet backing and rubber articles manufacture. 1000 to 4999 tonnes in UK.	Undergoing hazard assessment via ICCA (sponsor country unknown). Ongoing consideration by the Chemicals Stakeholder Forum. Environment Agency Risk Assessment has identified risks to the environment. Some further data required to fine tune the risk assessment.	
Terphenyl*	26140-60-3	Q		OSPAR Priority List of Chemicals	OSPAR monitoring strategy agreed in June 2004
5-chloro-2-(2,4-dichlorophenoxy)aniline	56966-52-0	Q			
Amines, bis(hydrogenated tallow alkyl)	61789-79-5	D	It is still produced or used in the UK, but the tonnage is decreasing and exposure is not likely to be widespread	Undergoing hazard assessment via ICCA . Prioritised for action at the Chemical Stakeholder Forum – October 2004. Under consideration by the EU PBT working group.	
Paraffin waxes and Hydrocarbon waxes,	63449-39-8	D	Used as a secondary plasticiser in PVC, flame retardant in rubber and textiles, as a plasticiser/flame retardant in	Undergoing hazard assessment via ICCA (sponsored by the UK).	

CHEMICAL STAKEHOLDER FORUM LIST OF CHEMICALS OF CONCERN

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Name	Chemical Abstract Service Number (CAS)	PBT Data available (D) PBT Properties predicted by QSAR (Q)	Use	Regulatory/Voluntary Activity	Other Research/Further testing underway
* On OSPAR Priority list of Chemicals chloro* and Paraffin oils, chloro [long chain length chlorinated paraffins (LCCPs)]	85422-92-0		sealants/adhesives and paints, as an extreme pressure additive to metal cutting/working fluids and as a component of leather fat liquoring treatments.	Environment risk assessment available (Environment Agency). OSPAR List of Chemicals of Possible concern.	
Benzenamine, N-phenyl-, styrenated	68442-68-2	Q			
Hydrocarbons, C14-30, olefin-rich	68514-35-2	Q	May have some minor uses in veterinary medicines		
Alkenes, C12-24, chloro [Chlorinated alphaolefins]	68527-02-6	D	It is unclear whether this substance is still produced or used in the UK. Exposure is expected to be widespread if it is.		
Phenol, C12-and C18-30-alkyl derivs., sulfurized, calcium salts, overbased	73758-62-0	Q		Prioritised for action by the Chemicals Stakeholder Forum – October 2004.	
Alkanes, C14-17, chloro [medium chain length chlorinated paraffins* (MCCPs)]	85535-85-9	D	Used as secondary plasticiser in PVC, extreme pressure additive in metal working fluids, plasticiser in paints, additive to adhesives and sealants, in fat liquors used in leather processing and as flame retardant plasticiser in rubber.	The UK Chemicals Stakeholder Forum have issued a statement of their concerns about this chemical and asked industry to take voluntary action to reduce risks to the environment.. Thorough assessment performed under ESR – a risk reduction strategy is being developed by DEFRA/HSE) (rapporteur is the UK).	

CHEMICAL STAKEHOLDER FORUM LIST OF CHEMICALS OF CONCERN

Last updated – July 2005

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<http://www.defra.gov.uk/environment/chemicals/csf/index.htm>

Name	Chemical Abstract Service Number (CAS)	PBT Data available (D) PBT Properties predicted by QSAR (Q)	Use	Regulatory/Voluntary Activity	Other Research/Further testing underway
* On OSPAR Priority list of Chemicals				Is listed on the Existing Substances Regulation priority lists. Is being prioritized by The Working Party on Organic Environmental Contaminants in Food prioritisation of this chemical has been completed. MCCPs were considered a high priority.	
Resin acids and Rosin acids, tall-oil, fumarated, ammonium salts	91081-29-7	Q			
Fatty acids, tallow, hydrogenated, 2-[4,5-dihydro-2-(hydrogenated nortallow alkyl)-1H-imidazol-1-yl]ethyl esters	91697-81-3	Q			
Amines, C12-14-alkyl, reaction products with hexanol, phosphorus oxide (P2O5), phosphorus sulfide (P2S5) and propylene oxide	91745-46-9	D	It is unclear whether this substance is still produced or used in the UK. Exposure is expected to be widespread if it is.		
Zinc bis[O-(6-methylheptyl)] bis[O-(sec-butyl)]	93819-94-4	Q			

CHEMICAL STAKEHOLDER FORUM LIST OF CHEMICALS OF CONCERN

Last updated – July 2005

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Name	Chemical Abstract Service Number (CAS)	PBT Data available (D) PBT Properties predicted by QSAR (Q)	Use	Regulatory/Voluntary Activity	Other Research/Further testing underway
* On OSPAR Priority list of Chemicals bis(dithiophosphate)					

ANNEX F List of WFD priority substances

33 substances or group of substances are on the list of priority substances including selected existing chemicals, plant protection products, biocides, metals and other groups like Polyaromatic Hydrocarbons (PAH) that are mainly incineration by-products and Polybrominated Biphenylethers (PBDE) that are used as flame retardants.

http://europa.eu.int/comm/environment/water/water-framework/priority_substances.htm

List of priority substances in the field of water policy (*)

	CAS number	EU number	Name of priority substance	Identified as priority hazardous substance
(1)	15972-60-8	240-110-8	Alachlor	
(2)	120-12-7	204-371-1	Anthracene	(X)***
(3)	1912-24-9	217-617-8	Atrazine	(X)***
(4)	71-43-2	200-753-7	Benzene	
(5)	n.a.	n.a.	Brominated diphenylethers (**)	X****
(6)	7440-43-9	231-152-8	Cadmium and its compounds	X
(7)	85535-84-8	287-476-5	C ₁₀₋₁₃ -chloroalkanes (**)	X
(8)	470-90-6	207-432-0	Chlorfenvinphos	
(9)	2921-88-2	220-864-4	Chlorpyrifos	(X)***
(10)	107-06-2	203-458-1	1,2-Dichloroethane	
(11)	75-09-2	200-838-9	Dichloromethane	
(12)	117-81-7	204-211-0	Di(2-ethylhexyl)phthalate (DEHP)	(X)***
(13)	330-54-1	206-354-4	Diuron	(X)***
(14)	115-29-7	204-079-4	Endosulfan	(X)***
	959-98-8	n.a.	(alpha-endosulfan)	
(15)	206-44-0	205-912-4	Fluoranthene (****)	
(16)	118-74-1	204-273-9	Hexachlorobenzene	X
(17)	87-68-3	201-765-5	Hexachlorobutadiene	X
(18)	608-73-1	210-158-9	Hexachlorocyclohexane	X
	58-89-9	200-401-2	(gamma-isomer, Lindane)	
(19)	34123-59-6	251-835-4	Isoproturon	(X)***
(20)	7439-92-1	231-100-4	Lead and its compounds	(X)***
(21)	7439-97-6	231-106-7	Mercury and its compounds	X
(22)	91-20-3	202-049-5	Naphthalene	(X)***
(23)	7440-02-0	231-111-4	Nickel and its compounds	
(24)	25154-52-3	246-672-0	Nonylphenols	X
	104-40-5	203-199-4	(4-(para)-nonylphenol)	
(25)	1806-26-4	217-302-5	Octylphenols	(X)***
	140-66-9	n.a.	(para-tert-octylphenol)	
(26)	608-93-5	210-172-5	Pentachlorobenzene	X
(27)	87-86-5	201-778-6	Pentachlorophenol	(X)***

(28)	n.a.	n.a.	Polyaromatic hydrocarbons	X
	50-32-8	200-028-5	(Benzo(a)pyrene),	
	205-99-2	205-911-9	(Benzo(b)fluoroanthene),	
	191-24-2	205-883-8	(Benzo(g,h,i)perylene),	
	207-08-9	205-916-6	(Benzo(k)fluoroanthene),	
	193-39-5	205-893-2	(Indeno(1,2,3-cd)pyrene)	
(29)	122-34-9	204-535-2	Simazine	(X)***
(30)	688-73-3	211-704-4	Tributyltin compounds	X
	36643-28-4	n.a.	(Tributyltin-cation)	
(31)	12002-48-1	234-413-4	Trichlorobenzenes	(X)***
	120-82-1	204-428-0	(1,2,4-Trichlorobenzene)	
(32)	67-66-3	200-663-8	Trichloromethane (Chloroform)	
(33)	1582-09-8	216-428-8	Trifluralin	(X)***

* Where groups of substances have been selected, typical individual representatives are listed as indicative parameters (in brackets and without number). The establishment of controls will be targeted to these individual substances, without prejudicing the inclusion of other individual representatives, where appropriate.

** These groups of substances normally include a considerable number of individual compounds. At present, appropriate indicative parameters cannot be given.

*** This priority substance is subject to a review for identification as possible "priority hazardous substance". The Commission will make a proposal to the European Parliament and Council for its final classification not later than 12 months after adoption of this list. The timetable laid down in Article 16 of Directive 2000/60/EC for the Commission's proposals of controls is not affected by this review.

**** Only Pentabromobiphenylether (CAS number 32534-81-9)

***** Fluoranthene is on the list as an indicator of other, more dangerous Polyaromatic Hydrocarbons

ANNEX G Pesticides (legislation and banned substances)

In the UK HSE acts as the regulatory authority for non-agricultural pesticides and biocides by administering the regulatory schemes. Legislation which limits the amount of pesticide residue which is permissible in food crops will have an indirect influence on the use of plant protection products since residue levels will in part be a function of application rate and frequency.

The Plant Protection Products Directive (91/414/EEC), 'The Authorisations Directive', came into force on 26 July 1993 (EU 1991) and is implemented in the UK by the Plant Protection Products Regulations 2003. The Directive provides for the establishment of a positive list of active substances (Annex I), that have been shown to be without unacceptable risk to people or the environment. Active substances are added to Annex I of the Directive as existing active substances are reviewed, under the European Commission (EC) Review Programme and new ones authorised. Member States can only authorise the marketing and use of plant protection products after an active substance is listed in Annex I, except where transitional arrangements apply.

The European Plant Protection Products Directive 91/414/EEC and its subsequent amendments (Directive 96/12/EC) stipulate that plant protection products should be evaluated for their possible effects on organic matter breakdown. This requirement poses a number of problems, not least of which is determining how to measure the effects of plant protection products on this highly complex set of organisms, interactions and processes.

EU Pesticide Review Programme

The purpose of the EC review programme is to ensure that the safety of all pesticides used throughout Europe is evaluated to modern standards. The basis of the EC review programme is set out in Article 8.2 of Council Directive 91/414/EEC. (implemented in the UK by the Plant Protection Products Regulations 1995 as amended).

All pesticides used in products for plant protection purposes that were on the market within the EC on or before 26 July 1993 (or, in Austria, Finland, Iceland, Norway, Sweden or Liechtenstein, on or before 1 July 1994) are subject to review.

The Review programme has been set out in four stages each consisting of lists of active substances to be reviewed, these are detailed in several Commission Regulations. EC Member States have been allocated certain active substances for which they are responsible (known as the rapporteur Member State).

The rapporteur Member State is responsible for the evaluation of the submitted data package (dossier) and the production of an evaluation and report (known as a Draft Assessment Report (DAR)). These reports are considered by other Member States, the Commission and now also by the European Food Safety Authority (EFSA), before a decision is taken by the Commission whether or not to include the active substance in Annex I to the Directive 91/414/EEC.

Individual Member States are responsible for the national approval of plant protection products containing active substances on Annex I. For substances in the UK this will be done by a process known as re-registration, this will apply once all the active substances present in a product are included on Annex I. PSD will write to

affected approval holders detailing the steps to be taken and deadlines to be met for re-registration of their products.

Because the EC review programme has resulted in the withdrawal of many pesticides from the market certain uses have been identified where the lack of alternative products could lead to particular problems for certain sectors. These uses have been given an extended period for withdrawal from the market to allow time for the development of alternatives. These essential uses are detailed in Commission Regulation (EC) No 2076/2002 and a PSD letter dated 12 August 2002.

Further information on the EC review programme and the EC pesticide programmes can be found on the Commissions website in their State of works document.

Details of the active substances in stages 1-4 of the review programme, are available in a consolidated list for stage 1-3 (pdf, 15 pages) (latest version October 2003) and a separate list of active substances in stage 4 (pdf, 15 pages) (first version December 2004). These lists were prepared by PSD and indicate which actives have been supported or not supported/withdrawn together with their UK approval status.

EU (1991) Plant Protection Products Directive (91/414/EEC), 19 August 1991 OJ L230, ISSN 0378 6978

The Biocidal Products Directive 98/8/EC

The Biocidal Products Directive 98/8/EC (BPD) seeks to establish a high level of human and the environmental protection, and to eliminate barriers to trade by harmonising the processes involved in placing biocidal products on the European market. The Directive describes biocides as chemical preparations containing one or more active substances that are intended to control harmful organisms by either chemical or biological means. The formal definition of a biocidal product is given as:

"Active substances and preparations containing one or more active substances, put up in the form in which they are supplied to the user, intended to destroy, deter, render harmless, prevent the action of, or otherwise exert a controlling effect on any harmful organism by chemical or biological means." (EC 1998)

The Directive has a very wide scope, with 23 product types (see Table below). This covers non-agricultural pesticides currently approved under the Control of Pesticides Regulations 1986 (as amended). These include wood preservatives, public hygiene insecticides, rodenticides, surface biocides and antifouling paints, as well as a wide range of biocidal products not currently requiring authorisation under other legislation such as disinfectants, preservatives and a number of other specialist products. The Directive does not apply to certain products already subject to European legislation including plant protection products, human medicines, veterinary medicines, medical devices or cosmetics. The legislation also excludes the non-biocidal uses of products and active substances.

The Directive requires that only those biocidal products containing active substances listed in "positive lists", that is, Annexes I, IA and IB of the Directive 98/8/EC, will be authorised for use. Once an active substance has been included in Annex I, national Competent Authorities can authorise products containing it in individual Member States, providing that any necessary data have been supplied and any conditions put on Annex I inclusion are met.

Existing active substances are substances which have been on the EU market for biocidal purposes before the 14th May 2000. A substance which was not on the market before the 14th May 2000 is regarded as a new active substances and has to be approved by Member States before it will be entered on the "positive lists".

The review of existing active substances is expected to last 10 years and is being controlled by a series of Commission Regulations. The notification procedure of existing active substances is described in the Regulations (EC) No 1896/2000 (First Review Regulation) and No 1687/2002. This required that producers, formulators or associations either Identified active substances that were used in biocidal products, or Notified their intention of supporting the active substance in specific product types in the review programme. After evaluation, authorisation for the continuous marketing of the active substance is granted only in those product types, for which the substance is notified and approved. Once a substance is notified, it may be marketed freely for the product types specified in the notification until such time as authorities require a full dossier for approval and inclusion in the positive list of the Biocides Directive.

Those actives substance for which applications have not been specified in the notification may no longer marketed after 27 March 2002. Marketing of the substance for this application will only be authorised when a new dossier is accepted by the authorities and the substance is listed in the Biocide Directive for this particular product type.

The notification procedure of existing active substances started in 2000 and was finalised at the 31st January 2003 after the additional period for notification of certain active substances. Those which were successfully notified were published in the Official Journal of the European Communities in the Second Review Regulation on the Annexes I, II, III and V.

The Commission Regulation No 2032/2003 (Second Review Regulation) entered into force on 14 December 2003, gives the outcomes of the notification and identification procedures as exhaustive lists of substances and the product types in which they have been supported. Where an active substance has been neither Identified nor Notified, i.e. it is on neither list, then products containing that active substance can no longer be legally placed on the EU market. If an active substance has been Identified but not Notified, or Notified but not for the product types in which products are marketed, such products can only continue to be placed on the market, subject to any existing national rules, until 1 September 2006 (HSE 2004).

The system of approval requires two regulatory submissions before a biocidal product can be marketed: the first on the active substances, and the second on the formulated biocidal products. Each requires a dossier per product type that contains information on its biocidal efficacy, toxicological and ecotoxicological properties, and so on. The procedure is most advanced for biocidal active substances which have been notified for wood preservatives and rodenticides (product types 08 and 14) as there is already a considerable amount of the relevant data available for these product types.

The Directive and the Regulations is progressively replacing the UK national approval scheme for non-agricultural pesticides under the Control of Pesticides Regulations 1986 (as amended). Over time, there will be a substantial increase in the number of products subject to approval by including many which are currently controlled as general chemicals, such as disinfectants. Ultimately only those biocidal

products which contain an active substance which is included in Annex I of the Directive will be authorised for use.

EU (2000) First Review Regulation 1896/2000/EC, 8 September 2000, Official Journal of the European Communities, 8 September 2000 (L228 Vol 43, P6)

EU (2003) Second Review Regulation 2032/2003/EC, Official Journal of the European Union 24 November 2003 (L307, vol. 46)

HSE (2004) Health & Safety Executive
<http://www.hse.gov.uk/biocides/background.htm#2>

The 23 product types of the Biocidal Products Directive

Number	Product Type	Description
Main Group 1	Disinfectants & General Biocidal Products	
1	Human hygiene biocidal products	Used for human hygiene purposes
2	Private and public health area disinfectants and other biocidal products	Used for the disinfection of air, surfaces, materials, equipment and furniture which are not used for direct food or feed contact in private, public or industrial areas, including hospitals, as well as products used as algacides. Usage areas include swimming pools, aquariums, bathing and other waters; air-conditioning units; walls and floors in health and other institutions; chemical toilets, waste water, hospital waste, soil and other substrates (in playgrounds).
3	Veterinary hygiene biocidal products	Includes products used in areas in which animals are housed, kept or transported.
4	Food and feed area disinfectants	Used for the disinfection of equipment, containers, consumption utensils, surfaces or pipework associated with the production, transport, storage, or consumption of food, feed or drink (including drink water) for humans and animals.
5	Drinking water disinfectants	For both humans and animals.
Main Group 2	Preservatives	
6	In-can preservatives	Used for the preservation of manufactured products, other than foodstuffs or feeding stuffs, in containers by the control of microbial deterioration to ensure their shelf life
7	Film preservatives	Used for the preservation of films or coatings by the control of microbial deterioration in order to protect the initial properties of the surface of materials or objects such as paints, plastics, sealants, wall adhesives, binders, papers, art works etc.
8	Wood preservatives	For wood from and including saw-mill stage, and wood products (including preventative and curative products).
9	Fibre, leather, rubber and polymerised materials preservatives	Includes the preservation of fibrous materials, such as paper or textile products.
10	Masonry preservatives	Used for the preservation and remedial treatment of masonry or other construction materials other than

		wood by the control of microbiological algal attack.
11	Preservatives for liquid-cooling and processing systems	Use for the preservation of water and other liquids used in cooling and processing systems by the control of harmful organisms such as microbes, algae and mussels (not drinking water preservation products).
12	Slimicides	Used for the prevention or control of slime growth on materials, equipment and structures, used in industrial processes, e.g. on wood and paper pulp, and porous sand strata in oil extraction.
13	Metalworking-fluids preservatives	Products used for the preservation of metalworking fluids by the control of microbial deterioration
Main Group 3	Pest Control	
14	Rodenticides	Control of mice, rats or other rodents
15	Avicides	Control of birds
16	Molluscicides	Control of molluscs, e.g. snails that may clog pipes
17	Piscicides	Control of fish; excludes products for the treatment of fish diseases.
18	Insecticides, acaricides and to control other arthropods	e.g. insects arachnids and crustaceans
19	Repellents or attractants	Used to control, harmful organisms (invertebrates such as fleas, vertebrates such as birds), by repelling or attracting, including those that are used for human or veterinary hygiene either directly or indirectly.
Main Group 4	Other Biocidal Products	
20	Preservatives for food and feedstocks	Used for the preservation of food or feedstuffs by the control of harmful organisms.
21	Antifouling products	Used to control growth and settlement of fouling organisms (microbes and higher forms of plant and animal species) on vessels, aquaculture equipment or other structures used in water
22	Embalming or taxidermist fluids	Used for the disinfection and preservation of human or animal corpses, or parts thereof.
23	Control of vertebrates	i.e. vermin

Banned and non-authorised pesticides in the UK

Many pesticides which were once widely used have been banned or withdrawn from sale in recent years. Consequently, while these products have been detected in different environmental media in the past they should not be present in the future. Pesticides Safety Directorate website <http://www.pesticides.gov.uk/print.asp?id=55>

Active substances banned in the European Union under Council Directive 79/117/EEC

Council Directive 79/117/EEC dated 21 December 1978 prohibits the placing on the market and the use of plant protection products containing certain active substances which, even if applied in an approved manner, could give rise to harmful effects on human health or the environment. Some of these active substances had already been banned in the UK prior to inclusion in Directive 79/117/EEC.

Directive 79/117/EEC was published in the Official Journal of the European Communities L33 of 8 February 1979. It has been amended by Council Directives:

- 83/131/EEC 14 March 1983
- 85/298/EEC 22 May 1985
- 86/214/EEC 26 May 1986
- 86/355/EEC 21 July 1986
- 87/181/EEC 09 March 1987
- 87/477/EEC 09 September 1987
- 89/365/EEC 30 May 1989
- 90/335/EEC 07 June 1990
- 90/533/EEC 15 October 1990
- 91/188/EEC 19 March 1991

Banned substances:

Active Substance	Effective Date Of Ban
Mercury Compounds	
Mercuric oxide (mercury oxide)	1992
Mercurous chloride (calomel)	1992
Other inorganic mercury compounds	1981
Alkyl mercury compounds	1991
Alkoxyalkyl and aryl mercury compounds	1992
Persistent Organo-chlorine Compounds	
Aldrin	1991
Chlordane	1981
Dieldrin	1981
DDT	1986
Endrin	1991
HCH containing less than 99% of gamma isomer	1981
Heptachlor	1984
Camphechlor	1984
Hexachlorobenzene	1981
Other compounds	
Ethylene oxide	1991
Nitrofen	1988
1,2 Dibromoethane (Ethylene dibromide)	1988
1,2 Dichloroethane (Ethylene dichloride)	1989
Dinoseb, its acetate and salts	1991
Binapacryl	1991
Captafol	1991
Dicofol containing less than 78% of pp ¹ – dicofol or more than 1g/kg DDT and DDT related compounds	1991
(a) Maleic hydrazide and its salts, other than its choline, potassium and sodium salts	1991
(b) Choline, potassium and sodium salts of maleic hydrazide containing more than 1mg/kg of free hydrazine expressed on the	1991

basis of the acid equivalent	
Quintozene containing more than 1g/kg of HCB or more than 10g/kg pentachlorobenzene	1991

Active substances banned in the UK

In addition to the substances listed as being banned in the European Union under Council Directive 79/117/EEC, above, the UK has also banned the following substances. Various other active substances not listed below were effectively banned pre-1986 by being withdrawn under the non-statutory scheme that was in place before Control of Pesticides Regulations (COPR).

Banned substances:

Active substance	Effective date of ban	Reason for ban
Antu (thiourea)	1966	Evidence of carcinogenicity
Azobenzene	1975	Evidence of carcinogenicity
Cadmium compounds	1965	Evidence of carcinogenicity
Calcium arsenate	1968	High acute toxicity; persistence in soil; evidence of carcinogenicity
Chlordecone	1977	Evidence of carcinogenicity
Cyhexatin	1988	Evidence of teratogenicity
Methyl mercury	1971	Environmental hazard (accumulation in the food chain)
Phenylmercury salicylate	1972	Acute toxicity; accumulation in the environment
Potassium arsenite	1961	Acute toxicity to wildlife and livestock
Selenium compounds e.g. sodium selenate	1962	Acute toxicity to humans and livestock
Sodium arsenite	1961	Acute toxicity to wildlife and livestock
1,1,2,2-tetrachloroethane	1969	Acute and chronic toxicity to humans

ANNEX H Data packages required for pesticide approval

(http://www.pesticides.gov.uk/uploadedfiles/Web_Assets/PSD/National_Pesticides_Strategy_%2005.pdf)

1. Before a new plant protection product can be approved for sale and use, evidence is required of its efficacy and that it will not pose an unacceptable risk to human health or to wildlife. To this end, companies seeking provisional or full approval for a new product are required to submit an extensive package of scientific data. The components of the package vary according to the nature of the product and the uses to which it will be put, but as far as possible they are standardised. Such standardisation helps to ensure that important aspects of risk assessment are not overlooked, and also that products are assessed consistently and equitably.

2. The main components of the data package that typically would be required for a new plant protection product fall into the following seven areas.

Physico-chemical properties

3. The applicant is required to specify the chemical composition of the product, its active ingredient, and any significant impurities that it may contain. Information must also be supplied on the physico-chemical properties of the active ingredient, and on methods by which it can be detected and measured, e.g. in foodstuffs and water.

Potential toxicity in humans

4. Data on potential toxicity are required for the active ingredient, the product as a whole, and also any important metabolites of the active ingredient to which humans might be exposed. These data are derived largely from tests in laboratory animals, but care is taken to ensure that all use of laboratory animals is the minimum strictly necessary. Reliable information obtained by other means are used in preference.

Dietary Intake

5. One of the ways by which a plant protection product might cause harm to humans is through its presence as a residue in food. A particular concern is the potential for residues in the food derived directly from any crops to which it is applied or that might arise in the meat of animals that have fed on a treated crop. In assessing the risks from residues of a plant protection product in foods, therefore, it is necessary to identify and take account of all foodstuffs in which significant residues might occur, including those resulting from the use of other products that contain the same active ingredient. Additionally if the use of a plant protection product produces significant concentrations of toxic metabolites in food (i.e. substances formed by its chemical degradation in plants or animals), the acceptability of exposure to each of these metabolites is also assessed.

Exposures to operators, other workers and bystanders

6. The other circumstance in which human exposure to plant protection products commonly occurs is in the course of their application or through contact with crops or other materials that have been treated with them. Estimating the profile of exposure in operators, other workers and bystanders is complex and takes into account many factors including the physical form of the plant protection product (e.g. liquid or granules) and the way (including frequency and duration) it is used.

Environmental fate and behaviour

7. In order to assess the potential impact of a plant protection product on the environment, it is necessary to establish what happens to it once it has been applied - where it gets to; how fast it is degraded and by what mechanisms; and whether any

of its degradation products might occur at levels sufficient to pose a risk. In particular, information is needed about the concentrations of the product and any relevant breakdown products that will occur in soil, water and air, and the persistence of such pollution. Predicted environmental concentrations are derived, and are used to assess the exposure of non-target species in soil and water; the possible contamination of drinking water supplies; the possible contamination of groundwater; and the potential for effects on, or residues in, following crops.

Ecotoxicology

8. The other major determinant of a plant protection product's environmental impact is its toxicity to wildlife. The environmental risk assessment focuses upon possible effects of the product on various populations of non-target organisms including: birds, wild mammals, fish, aquatic invertebrates and plants, insects (including bees) and other arthropods, earthworms and soil micro-organisms.

9. The risk to non-target organisms is generally assessed by the use of standard laboratory tests that give an indication of the toxicity of a particular active ingredient or formulation. These are used to derive LD50/LC50s (the doses/concentrations at which 50% mortality occurs in an acute toxicity study) and NOEL/NOECs (the levels or concentrations at which no effect is observed in longer-term studies).

Efficacy and risk to following crops

10. Consideration of product efficacy is an integral part of the risk assessment process. If there are no discernible benefits from the application of the plant protection product, there is no acceptable level of exposure. Data must be available to demonstrate the efficacy of the plant protection product against target organisms when it is used in accordance with the label instructions. In addition, the application of plant protection products (especially herbicides) to a crop may pose a risk to the crop itself or to adjacent or following crops. This risk is assessed through the evaluation of both laboratory and field trial data.