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Organic contaminants in sewage sludge (biosolids) and their significance for agricultural recycling

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Organic chemicals discharged in urban wastewater from industrial and domestic sources, or those entering through atmospheric deposition onto paved areas via surface run-off, are predominantly lipophilic in nature and therefore become concentrated in sewage sludge, with potential implications for the agricultural use of sludge as a soil improver. Biodegradation occurs to varying degrees during wastewater and sludge treatment processes. However, residues will probably still be present in the resulting sludge and can vary from trace values of several micrograms per kilogram up to approximately 1 per cent in the dry solids for certain bulk chemicals, such as linear alkylbenzene sulphonate, which is widely used as a surfactant in detergent formulations. However, the review of the scientific literature on the potential environmental and health impacts of organic contaminants (OCs) in sludge indicates that the presence of a compound in sludge, or of seemingly large amounts of certain compounds used in bulk volumes domestically and by industry, does not necessarily constitute a hazard when the material is recycled to farmland. Furthermore, the chemical quality of sludge is continually improving and concentrations of potentially harmful and persistent organic compounds have declined to background values. Thus, recycling sewage sludge on farmland is not constrained by concentrations of OCs found in contemporary sewage sludges. A number of issues, while unlikely to be significant for agricultural utilization, require further investigation and include: (i) the impacts of chlorinated paraffins on the food chain and human health, (ii) the risk assessment of the plasticizer di(2-ethylhexyl)phthalate, a bulk chemical present in large amounts in sludge, (iii) the microbiological risk assessment of antibiotic-resistant micro-organisms in sewage sludge and sludge-amended agricultural soil, and (iv) the potential significance of personal-care products (e.g. triclosan), pharmaceuticals and endocrine-disrupting compounds in sludge on soil quality and human health.

Keywords: human health; soil; agriculture; organic contaminants; regulation; risk assessment

1. Introduction

Recycling sewage sludge to agricultural land (referred to increasingly as biosolids when treated to a level acceptable for land application), to gain benefit from the essential plant nutrients and organic matter it contains, is regarded by most

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scientific and regulatory authorities as the most pragmatic and environmentally sustainable approach to managing the sludge generated from urban wastewater (UWW) treatment. The opinion of the European Commission is that the use of sewage sludge on agricultural soils as a fertilizer is the best environmental option provided that it does not pose any threat to the environment as well as to animal and human health (EC 2003*a*). Indeed, there are no cases (EC 2006) of human, animal or crop contamination due to the use of sludge on agricultural soils following the provisions of Directive 86/278/EEC (CEC 1986). Consequently, the Directive has been effective in preventing pollution from the use of sludge and the European Commission considers that a monitored and well-regulated land spreading of sludge should therefore be encouraged and sustained. The flexible provisions of the Directive have also enabled the effective management of sludge use in agriculture while, at the same time, protecting human health and the environment.

Despite the international support for recycling sludge to land, the acceptance of this practice among different European countries varies considerably and has declined markedly in some cases. Under these circumstances, the decline in agricultural utilization has resulted in the necessary expansion of incineration as the only viable alternative outlet for treating large volumes of sludge, coupled with waste ash disposal in landfill. For example, concerns about the potential consequences for human health and the environment of potentially toxic substances and harmful micro-organisms have led to the banning of the use of sludge in agriculture in Switzerland, despite official recognition that there is no conclusive scientific evidence that the practice is harmful in any way (FOEN 2003). Given the evidence that will be reviewed in this paper for organic contaminants (OCs), this is seemingly an unnecessary and extreme action contravening European policy relating to waste management and the 'waste hierarchy' in particular, which favours recycling above incineration.

In contrast to the consensus view on the specific potentially toxic elements (PTEs) of concern in sludge requiring controls and regulation, there is no consistent approach to the statutory measures introduced on OCs in sludge in different countries that have adopted such controls (table 1). This is mainly because the increasing level of investigation in recent years has not identified the ecotoxicological significance of OCs in the soil–plant–water system and in the food chain (Sauerbeck & Leschber 1992). European regulations on polyhalogenated compounds, for example, have therefore set highly precautionary values that have no toxicological basis (Sauerbeck & Leschber 1992). Some countries, such as the UK, USA and Canada, have therefore argued that there is no technical justification for setting limits on OCs in sludge, on the basis that research has shown that the concentrations present are not hazardous to soil quality, human health or the environment (US EPA 1992*a*,*b*; WEAO 2001; Blackmore *et al.* 2006). The evidence base on the impacts of OCs on human health and the environment is discussed further in the following sections. However, other countries have established limits for different groups of OCs. For example, in Germany, limits are set for the persistent compounds, polychlorinated biphenyls (PCBs) and polychlorinated dibenzodioxins and furans (PCDD/Fs), but not polycyclic aromatic hydrocarbons (PAHs), whereas France regulates PAHs and PCBs, but not PCDD/Fs. Denmark, on the other hand, has established controls for the bulk volume chemicals, including di(2-ethylhexyl)phthalate (DEHP), linear

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Table 1. Standards for maximum concentrations of organic contaminants in sewage sludge (mg kg^{-1} dry solids (DS) except PCDD/F: ng toxic equivalents (TEQ) kg^{-1} DS) (EC 2000, 2003*b*; Smith 2000; Düring & Gäth 2002; US EPA 2003). (Contaminants: AOX, absorbable organic halogen; DEHP, di(2-ethylhexyl)phthalate; LASs, linear alkylbenzene sulphonates; NP/NPEs, nonylphenols and nonylphenol ethoxylates; PAHs, polycyclic aromatic hydrocarbons; PCBs, polychlorinated biphenyls; PCDD/Fs, polychlorinated dibenzo-*p*-dioxins and dibenzo-*p*-furans.)

	AOX	DEHP	LASs	NP/NPEs	PAHs	PCBs	PCDD/Fs
EC (2000)[a]	500	100	2600	50	6[b]	0.8[c]	100
EC (2003*b*)[a]			5000	450	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[c,g]	
USA							300[h]

[a]Proposed but withdrawn and basis subject to review.
[b]Sum of nine 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 seven congeners: PCB 28, 52, 101, 118, 138, 153, 180.
[d]Sum of six congeners.
[e]Each of the six congeners: PCB 28, 52, 101, 138, 153, 180.
[f]Sum of three congeners: fluoranthene, benzo[*b*]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).

alkylbenzene sulphonate (LAS) and nonylphenols and nonylphenol ethoxylates (NPs/NPEs). Even the European Commission has had different opinions about which compounds to regulate and what limit values to adopt in proposals to revise Directive 86/278/EEC (EC 2000, 2003*b*) (table 1). This incoherence has occurred despite the generally consistent chemical composition of sewage sludge produced in different countries (table 2). Consequently, agreement on regulating OCs in sludge is likely to emerge as one of the most controversial aspects of the consultation on the revised Sludge Directive (86/278/EEC).

In this paper, I review the concentration data for OCs in sewage sludge and go on to assess the consequences and significance of OCs for the environment, human health and the food chain when sewage sludge is recycled to farmland as a fertilizer.

2. Organic contaminants in sewage sludge

(*a*) *General categories of organic contaminants*

The range of OCs known to exist in sludge is extensive and diverse, and a recent list of concentration data, compiled by Smith & Riddell-Black (2007) is presented in table 2. For example, Drescher-Kaden *et al.* (1992) reported that 332 organic substances, with the potential to exert a health or environmental hazard, had

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Table 2. Summary of organic compounds found in sewage sludge (mg kg^{-1} DS except where indicated) (see Smith & Riddell-Black (2007) for full inventory of data). (Contaminants: see table 1; HHCB, 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-γ-2-benzopyran; AHTN, 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene; PCNs, polychlorinated naphthalenes; PBDEs, polybrominated diphenyl ethers.)

substance	minimum	maximum	mean
non-halogenated monocyclic aromatics	0.025	22.1	2.29
monocyclic aromatics (chloro- and nitroanilines)	0.0001	192 000	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
∑PAHs	6.4	72	130
∑PCBs	0.054	0.93	0.22
PCDD/Fs	2.4 pg kg^{-1}	80 000 ng kg^{-1}	2178 ng kg^{-1}
TEQ contribution attributable to the PCDD/Fs and PCBs	0.7	680	36.5
Aroclor mixtures	0.00002	23.1	0.023
organochlorine pesticide	0.00001	2.2	0.035
LASs[a]	2100	10 500	5560
DEHP	0.3	1020	110 (median)
NP/NPEs	256	824	351
chlorinated paraffins	0.9	6000	171
polycyclic musks (∑HHCB, AHTN)	2.0	97	32
chlorinated phenols	0.09	52.6	no value
PCNs	0.05	0.19	0.083
polychlorinated *n*-alkanes C_{10}–C_{13}	6.9	200	42
polychlorinated *n*-alkanes C_{14}–C_{17}	30	9700	1800
∑PBDEs (six congeners)[b]	12.5 μg kg^{-1}	288 μg kg^{-1}	108 μg kg^{-1} (median)
triclosan[c]	0.09	16.8	2.3 (median)
triclocarban[d]	36	66	51

[a]Schowanek *et al.* (2007) for anaerobically digested sludge.
[b]Knoth *et al.* (2007).
[c]Ying & Kookana (2007).
[d]Heidler *et al.* (2006).

been identified in German sludges and 42 of these were regularly detected in sludge. Compared with the 10 PTEs of concern in sludge, which are routinely monitored and controlled, regulating this diverse range of OCs would appear to present a much more daunting prospect.

The compounds entering sludge may be generally categorized as follows.

(i) Persistent compounds from incomplete combustion of fossil fuels that enter the UWW collection system through deposition onto paved surfaces via run-off (e.g. PAHs and PCDD/Fs).

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(ii) Persistent compounds that are associated with impurities in wood preservatives such as creosote (PAHs) and pentachlorophenol (PCP) (e.g. PCDD/Fs) and enter UWW in run-off.
(iii) Controlled persistent compounds mobilized by volatilization from soil, deposition and transfer to UWW in run-off (e.g. PAHs, PCBs and PCDD/Fs).
(iv) Persistent compounds generated by cooking food that are discharged from domestic sources (e.g. PAHs).
(v) Persistent compounds that are prohibited from use/manufacture, but domestic sources may exist and can transfer to UWW via run-off (e.g. chlorinated pesticides).
(vi) Compounds discharged to sewer used directly in industrial processes or domestically, including solvents, flame retardants or compounds that leach from plastics and surfaces during end-use and are carried in run-off (e.g. DEHP, PBDEs).
(vii) Detergent residues (e.g. LASs, NPEs).
(viii) Pharmaceuticals, antibiotics, endogenous hormones and synthetic steroids.
(ix) Compounds from the various above groups with endocrine-disrupting potential.

The concentrations of the most important persistent organic pollutants (POPs) in sludge have declined through strict source control measures and these are no longer a significant issue for the quality of sludge for agricultural use (table 3) (Erhardt & Prüeß 2001).

(*b*) *Bulk-volume and industrial compounds*

OCs tend to accumulate in sludge owing to their lipophilic and hydrophobic properties and consequently they sorb onto the sludge organic matter. Readily volatile OCs, such as solvent compounds (e.g. benzene, tetrachloroethane, tetrachloroethylene, toluene and trichloroethane), are lost by volatilization during wastewater and sludge treatment and land spreading and do not present a hazard to the soil or human health (Webber & Goodin 1992). For example, Wilson *et al.* (1994) measured the concentrations of 15 important volatile organic compounds (VOCs) (e.g. chloroform, benzene and toluene) in samples of 12 liquid-digested sewage sludges obtained from rural, urban and industrial treatment works in northwest England. No apparent relationship was found between sludge VOC concentrations and the volume of industrial input to the wastewater treatment plants (WWTPs), influent treatment, population served and sludge dry solids (DS) content. Wilson *et al.* (1994) concluded, therefore, that normal rates of sludge application to agricultural land were unlikely to increase the VOC content of the soil to levels that may cause concern for human health and the environment.

The principal route of loss of OCs during wastewater and sludge treatment, however, is through microbially mediated biodegradation processes. Destruction during anaerobic or aerobic digestion and composting of sludge significantly reduces the concentrations of many types of OCs in sludge. It is difficult to generalize but destruction rates by anaerobic digestion of sludge may be typically in the range 20–40% (Hijaz 2007). Aerobic treatment processes, including composting, may lead to greater destruction rates compared with

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Table 3. Assessment of the significance of OCs entering UWW and sewage sludge (IC Consultants 2001).

contaminant	content in UWW/sludge[a]	priority hazardous substance?[b]	destruction in treatment[c]		accumulation?		background inputs?	overall significance[d]	
			UWW	sludge	biological	soil		UWW	sludge
LASs	H	N	H	L anaerobic; H aerobic	N	N	N	H	L
NPEs	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

[a]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.
[b]EPCEU (2001): N = no; Y = yes; (Y); substance under review.
[c]Approximate indicative ranges: L < 20%; M = 20–60%; H > 60%.
[d]Significance rating: low, L; moderate, M; high, H.

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anaerobic digestion. This is due to the increased rates of microbial activity at the normally higher operating temperatures of aerobic compared with anaerobic treatment processes, and also because aerobic conditions provide metabolic pathways of destruction for a greater range of organic substrates compared to anaerobic respiration. For example, LAS, an important high-volume usage surfactant compound, is not degraded to any significant extent in anaerobic sludge digesters (AISE-CESIO 1999). LAS concentrations are considerably higher in anaerobically digested sludges (1000–30 000 mg kg^{-1} DS), compared with fresh aerobic sludges (typically <1000 mg kg^{-1} DS), or in aerobically stabilized sludges (100–500 mg kg^{-1} DS) (De Wolf & Feijtel 1998; Ducray & Huyard 2001; HERA 2004; Jensen & Jepsen 2005). There are several reasons for the elevated concentrations of LAS in anaerobically digested sludges: high usage volumes, sorption to primary sludge, precipitation as insoluble Mg/Ca salts in the primary settler, minimal degradation under anaerobic conditions and the solids mass loss effect caused by the digestion process.

Other compounds may be formed during anaerobic digestion of sludge. For example, NPs and NPEs comprise a group of surfactants that were used in large amounts in industry and agriculture. During anaerobic digestion of sewage sludge, mono- and diethoxylates are degraded to 4-NP and this treatment method increases the concentration of 4-NP in sludge. Digested sewage sludge samples collected at two UK WWTPs contained 250–820 mg kg^{-1} DS of NP (Jones & Northcott 2000).

However, both LAS and NP degrade rapidly in soil. Under normal conditions, LAS disappears rapidly from the soil as a result of biodegradation, with half-lives of 10–30 days, depending on microbial adaptation, bioavailability and soil characteristics (Schowanek *et al.* 2007). The half-life of NP in soil is typically 20 days. Thus, neither compound transfers through the food chain or poses a risk to terrestrial organisms at the loadings applied to soils (De Wolf & Feijtel 1998; Sjöström *et al.* 2008). The ecotoxicological risk assessment of LAS is described in more detail later.

In contrast to the low toxicity of LAS, however, NP is an identified endocrine-disrupter compound (EDC) (IC Consultants 2001). Within the EU, the use of NPs and NPEs has been restricted by Directive 2003/52/EC (EPCEU 2003*a*), which stipulates that these compounds may not be placed on the market or used as a substance or constituent of preparations in concentrations equal to or higher than 0.1 per cent by mass for a specified range of purposes. NPs are also classed as a priority hazardous substance under the Water Framework Directive (WFD) (EPCEU 2001) and will therefore be subject to further source controls to ultimately phase out emissions to the environment. In the UK, the Chemical Stakeholders Forum has reached a voluntary agreement within the chemical industry to phase out the use of NPs (DEFRA 2004). Consequently, these measures will ultimately lead to the further reduction of NP in sewage sludge to very low levels in future.

The other major bulk chemical found in sludge is DEHP, which is also unchanged by anaerobic sludge digestion (IC Consultants 2001). Phthalate esters are, however, rapidly destroyed under aerobic conditions and biological wastewater treatment (e.g. activated sludge process) can usually achieve more than 90 per cent removal in 24 h (IC Consultants 2001). In soil, the reported half-life of DEHP is less than 50 days. DEHP is an important chemical constituent

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of plastics and can form up to 50 per cent of plastic products and polyvinyl chloride (PVC). It confers the unique properties and flexibility of plastics and is therefore an essential constituent of plastic products. It is not chemically bound to the polymer and so slowly leaches from the plastic, and hence can be transferred to wastewater. The household contribution of phthalates is reported to be as high as 70 per cent of the total load, emphasizing the ubiquity of DEHP and related compounds in the built environment and the difficulty that would be presented if controls to reduce emissions were required (IC Consultants 2001). Two major sources of domestic releases to wastewater are floor and wall coverings and textiles with PVC prints (IC Consultants 2001). In contrast to LAS and NP, DEHP has received much less attention in terms of the toxicological and ecotoxicological implications of recycling sewage sludge containing DEHP to agricultural land. In many aspects, if controls were imposed on this compound in sludge or to reduce its emission to the environment (for example, DEHP is subject to review for identification as a possible priority hazardous substance under the WFD), it would be much more difficult to manage because of its ubiquitous and widespread use in so many aspects of the built environment.

Polychlorinated *n*-alkanes (PCAs), referred to as chlorinated paraffins, are in active production and widespread use as extreme-pressure lubricant additives, plasticizers, flame retardants and paint additives. Current worldwide production is estimated at 300 000 tonne (Euro Chlor 2005). Therefore, they potentially occur in sludge in much larger concentrations than other related families of POPs, such as PCBs and polychlorinated naphthalenes (PCNs), whose use has been extensively phased out and is therefore no longer a concern for the agricultural use of sludge. PCAs are also persistent and bioaccumulatory. Stevens *et al.* (2003) measured total concentrations of the short-chain and medium-chain PCAs in the range 7–200 and 37–9700 $\mathrm{mg\,kg^{-1}}$ DS, respectively. PCAs are widely used industrial chemicals and the high concentrations found in sludge were indicative of chemicals with numerous and ongoing diffuse sources.

Modern society is dependent on chemicals including plastics and their constituents and detergents, as well as many other types of organic chemical, which may therefore be present in sludge owing to the extent of use and the amounts discharged in wastewater. It is necessary to ensure that the compounds are neither persistent nor pose a toxicological or ecotoxicological risk and further improvements in sludge chemical quality should be expected from the implementation of the EU REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) Regulation 1907/2006 (EPCEU 2006*a*; EC 2007). Nevertheless, the presence of apparently large concentrations of certain chemicals in sewage sludge does not itself constitute a hazard to health or the environment, as this may be perfectly acceptable and safe. The impacts of alternative compounds, introduced as replacements for existing chemicals, should be carefully assessed, as the net advantage of the alternatives may be uncertain.

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 owing to fire regulation requirements and the increased use of plastic material and synthetic fibres. These compounds have properties similar to those of PCDD/Fs; they are persistent and have the potential to

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Table 4. Categories of substances with endocrine-disrupting activities (IC Consultants 2001).

category	examples	uses	modes of action
natural			
phyto-oestrogens	isoflavones, lignans	present in plants	oestrogenic and anti-oestrogenic
female sex hormones	17β-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[a], dieldrin, lindane	insecticides	oestrogenic and anti-oestrogenic
alkylphenols	NP	production of NPE and polymers	oestrogenic
alkylphenol ethoxylates	NPE	surfactant	oestrogenic
phthalates	dibutyl phthalate	plasticizer	oestrogenic
biphenolic compounds	bisphenol A	in polycarbonate plastics and epoxy resins	oestrogenic
synthetic steroids	ethinyl oestradiol	contraceptives	oestrogenic

[a]Dichlorodiphenyltrichloroethane.

bioaccumulate. The consequences of brominated flame retardants for health and the environment have received increasing attention in the scientific literature (De Wit 2002; Letcher 2003). A recent survey of PBDE concentrations in German sewage sludge (Knoth *et al.* 2007) indicated that the total content of the six significant PBDE congeners (28, 47, 99, 153, 154 and 183) was in the range 12.5 and 288 $\mu g\,kg^{-1}$ DS, with a median value of 108 $\mu g\,kg^{-1}$ DS. PentaBDE is on the WFD list of proposed priority hazardous substances, the Chemical Stakeholder Forum list of chemicals of concern (DEFRA 2005) and the EU Pollutant Release and Transfer Registers (PRTR) for water (EPCEU 2006*b*). Action was taken in Europe to significantly restrict the use of pentaBDE and octaBDE and the placing on the market of articles containing one or both of these substances with effect from 15 August 2004 (EPCEU 2003*b*). Therefore, emissions to wastewater and presence in sludge are expected to decrease.

(*c*) *Endocrine disrupters, pharmaceuticals, antibiotics and personal-care products*

Endocrine-disrupting chemicals (EDCs) are synthetic or naturally occurring compounds that affect the balance of normal hormonal functions in animals, potentially resulting in reproductive impairment or disorders. There are at least 100 OCs that are released to the environment that are suspected EDCs (Keith 1998) and most, if not all, are likely to be found in sewage sludge. Some of the main categories of substances with endocrine-disrupting activity are listed in table 4.

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As discussed above, polychlorinated compounds are controlled at source, as are organochlorine pesticides, which are barely detectable in sewage effluents or sludge (Bowen *et al.* 2003), and are therefore no longer a concern for agricultural recycling of sludge. Alkylphenols and ethoxylates are currently being phased out under the WFD as priority hazardous substances and through restrictions imposed on their marketing and use in the EU by other dangerous substances legislation and national measures (EPCEU 2003*b*; DEFRA 2004) and therefore will no longer be significant. Biphenols have very short half-lives in soil of a few days and therefore cannot transfer to the human food chain. Consequently, it is the natural, endogenous hormones, oestrone and 17β-oestradiol, and to a much lesser extent the synthetic hormone ethinyl oestradiol, that are considered primarily responsible for oestrogenic activity observed within treated sewage effluents. Wastewater treatment reduces potential oestrogenic activity (based on 17β-oestradiol equivalence) by 90 per cent and Young *et al.* (1998) estimated that less than 3 per cent may be transferred to the sewage sludge. Oestrogenic compounds partition onto particulates and may be associated with sewage sludge, and more information is necessary on the amounts and biodegradation of endogenous oestrogens and ethinyl oestradiol in sludge. However, this is unlikely to have significant environmental implications for the 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 (Boxall *et al.* 2004) and they are potentially more of a concern for the aquatic environment than for soil (Hotchkiss *et al.* 2008).

Data on pharmaceutical and antibiotic concentrations in sludge applied to land are more limited, but the available evidence indicates that the pharmaceuticals present vary greatly in biodegradability. There is a wide range of removal efficiencies during wastewater treatment and, typically, 60–90% of the compounds in the influent may be removed (Ternes 1998). The most commonly used drugs such as the analgesics, ibuprofen and naxoproxen, are readily biodegradable with removal efficiencies up to 90 and 78 per cent, respectively (IC Consultants 2001). Hilton *et al.* (2003) showed that paracetamol is readily degradable by biological wastewater treatment processes and hence is rarely found in sewage effluents.

Triclosan is a chlorinated phenoxyphenol and is used as an antimicrobial agent in a wide range of medicinal and consumer-care products. European consumption of triclosan is about 350 tonne per annum (Singer *et al.* 2002). The widespread use of triclosan means that it is inevitably discharged to wastewater treatment works. Singer *et al.* (2002) examined the transformation of triclosan through wastewater treatment processes and found that 79 per cent was biologically degraded, 15 per cent was associated with the sludge and 6 per cent was released in final effluent. Degradation in soil is also rapid with reported half-lives in the range 17.4–35.2 days (Samsøe-Petersen *et al.* 2003). Concentrations in activated sludge range from 0.028 to 4.2 mg kg^{-1} DS and values up to 15.6 mg kg^{-1} DS are reported (Singer *et al.* 2002). Concentrations in the range 0.09–16.8 mg kg^{-1} DS with a median value of 2.32 mg kg^{-1} DS were reported in Australian sludge by Ying & Kookana (2007). The range reported in US sludge is 0.53–15.6 mg kg^{-1} DS with a mean of 6.97 mg kg^{-1} DS (McAvoy *et al.* 2002) and German sludge contains 0.4–12 mg kg^{-1} of triclosan (Bester 2003).

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Triclocarban (TCC) is also a widely used topical antiseptic agent that is a common additive in many antimicrobial household consumables, including soaps and other personal-care products. From a mass balance of the compound's behaviour through a typical activated sludge WWTP in the USA, Heidler *et al.* (2006) concluded that approximately 21 per cent of the mass of TCC entering the plant was degraded, 3 per cent was discharged in the effluent and 76 per cent was transferred to the sewage sludge. Anaerobic digestion for 19 days did not promote TCC transformation, resulting in an accumulation of the antiseptic compound in dewatered, digested sludge to $51 \pm 15\,\mathrm{mg\,kg^{-1}}$ DS.

3. Implications for human health

(*a*) *Evidence base and risk assessment*

The toxicological and environmental effects of OCs in sludge and sludge-treated soil have received an increasing level of research attention in the past 20 years and many of the earlier uncertainties and concerns have largely been resolved. Details can be found in a number of recent critical reviews that provide an in-depth analysis and assessment of the literature. For example, IC Consultants (2001) examined the fate and significance of pollutants, including organic compounds, in wastewater and sludge for the European Commission DG Environment. That report provided an exhaustive assessment of concentration data in sludge and fate during sludge treatment processes, and detailed case studies on surfactants, polyacrylamide (used extensively as a polyelectrolyte to aid mechanical dewatering of sludge) and potentially important emerging groups of compounds, such as pharmaceutical and personal-care products. In a related report for DG Environment, Erhardt & Prüeß (2001) examined the occurrence of OCs in sludge, related toxicological data, their persistence in soil and risk assessments for various exposure pathways. In North America, a detailed review for the Water Environment Association of Ontario (WEAO 2001) examined the fate of selected contaminants in sewage biosolids applied to agricultural land based on scientific literature and consultation with stakeholder groups. The compounds considered included:

(i) volatile organic compounds (VOCs), PCBs, PAHs and pesticides,
(ii) LAS surfactants,
(iii) EDCs including alkylphenol surfactants (APs) and oestrogenic hormones, and
(iv) dioxins and furans (PCDD/Fs).

Jones & Northcott (2000) completed a survey of OCs in UK sewage sludge samples and considered their potential significance in a report for the UK Government (also see Stevens *et al.* 2003). More recently, a major review in the UK for DEFRA by Smith & Riddell-Black (2007) considered the evidence relating to OC inputs to soil from all sources, including sludge, and their potential environmental consequences. The behaviour and environmental effects of OCs in sludge-amended soil were examined in detail in a series of papers by international authors published in a special edition of *The Science of the Total Environment* (Jones 1996). In Europe, OCs were also considered by Working Party 2—Chemical Contamination of Sludges and

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Soils of the COST 681 programme on Treatment and Use of Sewage Sludge and Liquid Agricultural Wastes (Davis *et al.* 1983; Hall *et al.* 1992*a*,*b*). These selected examples demonstrate that, while it is always possible to argue that the knowledge base on the diverse range of compounds potentially present in sludge is incomplete (Chaney *et al.* 1996; Harrison *et al.* 2006), a considerable amount is known about the fate and behaviour of the main and most significant compounds, or groups of compounds, identified in sludge to enable their potential significance for human health and the environment to be quantified.

The available research and monitoring of the fate and potential effects of OCs in sewage sludge used on agricultural soil has identified specific pathways of possible transfer of OCs to humans, livestock, plants and other potentially sensitive environmental endpoints (Chaney *et al.* 1996). Transfer coefficients from sludge and sludge-amended soil to plants, animals and humans have been derived for many organic substances and these formed the basis of the first quantitative pathway analysis and risk assessment of OCs in sewage sludge-amended agricultural soil completed by the US EPA (1992*a*,*b*). Fourteen environmental pathways were identified, and the most important for human health were:

Pathway 1: sludge–soil–plant–human (from agricultural application)
(Pathway 2 was also the sludge–soil–plant–human route, but represented the domestic use of sludge by home gardeners)
Pathway 3: sludge–soil–human
Pathway 4: sludge–soil–plant–animal–human
Pathway 5: sludge–soil–animal–human

The US EPA screened 200 pollutants and selected 18 OCs of principal concern for further evaluation by the pathway risk analysis of environmental exposure. The health impact was assessed in relation to the cancer-causing potency of the chemicals in humans from continual exposure of an individual to a specified concentration over a lifetime period of 70 years. The compounds that were evaluated included:

(i) aldrin/dieldrin,
(ii) benzo[*a*]anthracene,
(iii) benzo[*a*]pyrene,
(iv) bis(2-ethylhexyl)phthalate,
(v) chlordane,
(vi) DDD/DDE/DDT,[1]
(vii) heptachlor,
(viii) hexachlorobenzene,
(ix) hexachlorobutadiene,
(x) lindane,
(xi) methyl bis(2-chloroaniline),
(xii) methylene chloride,
(xiii) *n*-nitrosodimethylamine,

[1]DDD (dichlorodiphenyldichloroethane) and DDE (dichlorodiphenyldichloroethylene) are chemicals similar to DDT that contaminate commercial DDT pesticides.

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(xiv) PCP,
(xv) PCBs,
(xvi) toxaphene,
(xvii) trichloroethylene, and
(xviii) tricresyl phosphate.

The US EPA evaluated these contaminants by a pathway risk analysis and decided that their regulation was unnecessary to protect human health and the environment when sewage sludge was used as a soil amendment (US EPA 1992*a*,*b*). Therefore, OCs were deleted from the final Part 503 Standards for the Use or Disposal of Sewage Sludge (US EPA 1993). For an organic pollutant to be deleted from the regulation, one of the following criteria had to be satisfied (Ryan 1993).

(i) The pollutant was banned from use in the USA; its use was restricted or it was no longer manufactured for use in the USA.
(ii) Based on the results of the National Sewage Sludge Survey (NSSS), the pollutant had a low level of detection in sewage sludge.
(iii) Based on the data from the NSSS, the limit for an organic pollutant in the Part 503 exposure assessment (US EPA 1992*b*) was not expected to exceed the concentration in sewage sludge.

In December 1999, the US EPA proposed a limit for PCDD/Fs and certain dioxin-like PCBs of 300 ng TEQ kg^{-1} 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, US 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 in dioxin concentrations in sludge, particularly with more rigorous control on combustion practices. Therefore, the US EPA decided that no numerical limits or specific management practices were required for dioxins in land-applied sewage sludge (US EPA 2003).

Risk assessment procedures for chemicals in sewage sludge will continue to undergo refinement. For example, Schowanek *et al.* (2004) recently presented a conceptual framework for risk assessment of OCs in sludge for potential exposure pathways and environmental endpoints. However, as further data are collected, and concentrations of the most toxic and persistent compounds continue to decline in the environment and in sludge, owing to source control measures, the general trend is for the significance for human health of OCs in sewage sludge to continue to diminish in importance. Furthermore, the exposure to the major groups of high-volume, bulk chemicals found in sludge (e.g. surfactants and plasticizers) from the agricultural use of sludge appear to be no greater than the normal background level. For example, Vikelsøe *et al.* (2002) showed that only small concentrations of a range of phthalates and NPs were detected in soil receiving typical doses of sludge at agronomic rates of application (4.3 tonne DS ha^{-1} yr^{-1}) for at least three consecutive growing seasons and the values were within the normal background ranges measured for other cultivated and uncultivated soils receiving different fertilizer and manure regimes, but without

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sludge input. Consequently, in the practical field situation, using sewage sludge as an agricultural fertilizer does not increase the accumulation of these compounds in soil or their transfer to the human food chain.

(*b*) *Human exposure from uptake into crop plants*

One of the primary concerns associated with the presence of OCs in sludge is the potential for entry into the human food chain from uptake into the edible parts of crop plants. However, despite the increasing amount of scientific investigation into the potential environmental consequences of OCs applied to farmland in sewage sludge, there is no evidence for soil–crop transfer and the risk to human health from consuming food crops grown on soils amended with sludge is negligible (Jacobs *et al.* 1987; Schmitzer *et al.* 1988; Aranda *et al.* 1989; Kampe & Leschber 1989; O'Connor *et al.* 1991; Hembrock-Heger 1992; Offenbacher 1992; Sauerbeck & Leschber 1992; Webber *et al.* 1994; Duarte-Davidson & Jones 1996; NRC 1996; O'Connor 1996; McGrath 2000). This is explained by the behaviour of OCs in soil and the presence of only very small concentrations of some of the more potentially toxic compounds in sludge, e.g. the dioxin, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) (Sauerbeck & Leschber 1992). Thus, organic compounds can be grouped into three broad categories according to their behaviour (Smith 2000):

(i) volatile compounds that are quickly lost to the atmosphere from sludge and sludge-treated soil,
(ii) compounds that are rapidly mineralized by micro-organisms and have little or no persistence, and
(iii) persistent compounds that are strongly adsorbed onto the sludge and soil organic matrix.

Compounds exhibiting some solubility and potential for plant uptake are also usually susceptible to rapid degradation processes in soil or are lost through volatilization or leaching processes (Webber & Goodin 1992; Wilson *et al.* 1994; Duarte-Davidson & Jones 1996; Wilson *et al.* 1996; Wilson & Jones 1999). For example, NP and its precursors, the nonylphenol ethoxylates (NPEs), have caused concern due to their ability to interfere with human and animal endocrine systems and have the potential to transfer to agricultural crops (Sjöström *et al.* 2008). However, their degradation in soil is rapid (half-life 20–60 days for NP) and enhanced by the addition of organic substrates such as biosolids, and uptake by plants is very low (Kirchmann & Tengsved 1991; Roberts *et al.* 2006) so the possibility of any transfer or risk to the human food chain in practice is very limited. Furthermore, NP is identified as a priority hazardous substance under the WFD and is therefore subject to source control measures to phase out discharges, emissions and losses to the water environment (EPCEU 2001). More persistent compounds, on the other hand, usually have very low solubilities, are present in very small concentrations and are strongly adsorbed to the soil matrix in non-bioavailable forms, thus preventing transfer to plant tissues (O'Connor 1996). The evidence suggests that the groups of compounds of emerging interest also follow the same behaviour and are likely to exhibit negligible transfer to crops for the above reasons. For example, Thiele-Bruhn (2003) concluded that uptake into plants even of mobile antibiotic compounds was generally small, although effects on plant growth were apparent for some species and antibiotics.

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EDCs are another emerging concern for human health. However, no link has been identified between environmental sources of EDCs and health effects in humans (Hotchkiss *et al.* 2008). On balance it seems probable that they will have negligible relevance to human health in sludge-amended soil since the most potent forms (e.g. endogenous oestrogens) are present in very small amounts in sludge and/or are likely to degrade very rapidly in soil. Furthermore, humans receive much greater exposures to EDCs through other pathways than are potentially possible from sludge. For example, one of the main identified exposure routes for humans to EDCs is through dietary intake of phyto-oestrogens (Phillips & Harrison 1999). These naturally occurring chemicals are present in many common and staple foodstuffs, have structural similarities to 17β-oestradiol and are more potent oestrogens than many synthetic chemicals. Materials used for food packaging may also contain EDCs, which can migrate into the food in small amounts, for example, bisphenol-A, which is used in the resin linings of food cans.

(*c*) *Human exposure from ingestion by grazing livestock*

The principal concern and theoretical mechanism of entry of OCs to the human food chain from agricultural utilization is by surface spreading liquid sludge to grassland and intake by livestock grazing treated pasture, resulting in the potential accumulation of lipophilic compounds in meat fat and milk (Wild *et al.* 1994; Duarte-Davidson & Jones 1996; Fries 1996). Only lipophilic halogenated hydrocarbons accumulate in animal tissues and products (Fries 1996). Compounds such as phthalate esters, PAHs, acid phenolics, nitrosamines, volatile aromatics and aromatic surfactants are metabolized and do not accumulate (Fries 1996). In practice, there has been no demonstrable link between sludge application and transfer of organics to the human food chain via this pathway (NRC 1996). This theoretical exposure pathway does not operate when surface spreading to pasture is not permitted or when liquid sludge is injected into the soil (Stark & Hall 1992; Wild *et al.* 1994).

Recent studies in the UK (Erhard & Rhind 2004; Rhind 2004; Paul *et al.* 2005) with sheep grazing sludge-amended pasture soils have suggested that there is a relationship between the apparent exposure of the animals to environmental contaminants in sludge and their behavioural and reproductive development, and that this could indicate potential implications for human health from exposures to these chemicals in sludge. Careful scrutiny of the basic design of the grazing trials, however, shows that they were not sufficiently critically controlled to be able to draw such a profound conclusion. For example, there were major differences in the amounts and characteristics of the diets fed to the animals owing to variations in fertilizer nitrogen supply and this could be a major factor influencing animal performance and development. In the published reports (Erhard & Rhind 2004; Paul *et al.* 2005), no supporting chemical analysis of the applied sludge, soil or herbage or measurement of direct ingestion of soil or sludge by the experimental animals is presented, making conclusive interpretation impossible. In the unpublished report (Rhind 2004), DEHP concentrations in soil were affected by seasonal factors, but not by sludge application and, furthermore, sludge application did not increase the body burden of DEHP above the control animals. The fact that EDC concentrations (DEHP and alkyl phenols) did not accumulate in soil following repeated applications of sludge supports the view

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that they are rapidly degraded in the soil by microbial activity and that the soil environment is very efficient at destroying these compounds through natural attenuation processes.

Attempting to understand and quantify the impacts of subtle physiological responses to trace amounts of organic substances in the diet of grazing animals in a complex field grazing environment is very difficult in practice. The only practicable and quantitatively robust way to do this would be through controlled feeding experiments where animals are managed under identical conditions and receive exactly the same diet with the only variable being the addition or absence of the target compound.

(*d*) *Phthalates*

Plasticizers have been identified in this review as deserving special mention because there is apparent misunderstanding regarding their potential impacts on human health, and consequently also their significance in sewage sludge-amended agricultural soil.

Plasticizers are added to plastic polymers to give plastics useful properties such as colour, resistance to fire, strength and flexibility. Over 90 per cent of plasticizers used are phthalate-based compounds and in Western Europe about one million tonnes of phthalates are produced each year, of which approximately 90 per cent are used to plasticize PVC (CSTEE 1999). The annual global production of DEHP has been estimated to be approximately two million tonnes (Koch *et al.* 2003*a*,*b*). Concentrations of phthalates in PVC range from 15 to 50 per cent. There are five phthalate plasticizers: DEHP (sometimes also referred to as DOP), diisodecyl phthalate and diisononyl phthalate, butyl benzyl phthalate (BBP) and di-*n*-butyl phthalate (DBP). DEHP is one of the most commonly used plasticizers and accounts for approximately 20 per cent of all plasticizer usage in Western Europe (ECPI 2007). DEHP is a priority substance under review within the WFD (EPCEU 2001) and an EU draft limit was proposed for sludge (EC 2000), although DEHP was not included in the Draft Directive for agricultural use of sludge later proposed by the European Commission (EC 2003*b*). DEHP is also regulated under Danish legislation for agricultural use of sludge (table 1). DEHP is listed as a pollutant with a maximum threshold value for release to land under the new European Regulation on PRTRs (E-PRTR Regulation) (EPCEU 2006*b*). A further reason for giving DEHP special consideration here is that it is one of the most frequently detected, high-concentration compounds found in municipal sludges. Mattson *et al.* (1991) (cited in Paxéus 1996) estimated that the household contribution of phthalates to municipal wastewater was 70 per cent of the total load, emphasizing the ubiquity of the compounds and difficulty of control. Concentrations in US sludge are reported to range from 0.3 to 1020 $\mathrm{mg\,kg^{-1}}$ DS with a weighted average value of 110 $\mathrm{mg\,kg^{-1}}$ DS (US EPA 1992*c*). Given the ubiquitous use of phthalates and their potential to transfer to the environment, and the fact that 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 with surfactant compounds, for example.

Initial concerns that DEHP may be potentially carcinogenic to humans were based on animal testing with rodents, which developed liver tumours when exposed to the compound. However, the mechanisms by which DEHP increases

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the incidence of hepatocellular tumours in rats and mice are 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), and the latter 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 that shows that DEHP is a developmental and reproductive toxicant (ATSDR 2002; Fisher 2004). However, from a comprehensive toxicological profile of the compound, the US Agency for Toxic Substances and Disease Registry (ATSDR 2002) concluded that there was no evidence that DEHP was an endocrine disrupter in humans at the levels found in the environment. While research in this area has advanced significantly, the link between environmental sources of DEHP and human male reproductive health remains unanswered (Fisher 2004; Hotchkiss *et al.* 2008). A key area of current investigation is the study of multi-component EDC mixtures and this could be important in future for human environmental risk assessment strategies.

Humans are exposed to phthalates in numerous ways, such as migration of phthalates into foodstuff from packaging materials, by dermal contact of cosmetics and inhalation, and young children can also be exposed through mouthing of soft PVC toys, for example (Koch *et al.* 2003*a*,*b*; Fisher 2004). Nevertheless, exposure of the general population to DEHP is considered to be significantly below (at least 280 times) levels that may place human health at risk (ECPI 2007). Furthermore, large exposures to DEHP occur through medical procedures as a result of leaching of DEHP out of plastic medical devices into solutions that come in contact with the plastic, and this can result in an aggregate exposure when multiple devices are used (US FDA 2001). However, there is no evidence of health abnormalities in these highly exposed and sensitive groups (US FDA 2001), despite the widespread use of PVC plasticized with DEHP in medical situations. In contrast to these possible pathways of exposure to DEHP, the risk to human health arising from diffuse environmental sources, such as from DEHP inputs to soil from recycling sewage sludge, would appear to be very minor indeed. This is reinforced by the degradability and biotransformation of DEHP in aerobic soil and also the absence or minimal transfer of DEHP to crops and the food chain (Schmitzer *et al.* 1988; Aranda *et al.* 1989; Staples *et al.* 1997; Madsen *et al.* 1999; Van Wezel *et al.* 2000; Yin *et al.* 2003). Thus, the link between environmental sources of phthalates and endocrine-disrupting effects in humans has yet to be proved (Fisher 2004; Hotchkiss *et al.* 2008). Overall it would appear highly unlikely that the agricultural use of sewage sludge would contribute significantly to the accumulative human exposure from multiple sources of DEHP.

(*e*) *Antibiotics and pharmaceuticals*

Many pharmaceutical compounds have similar physico-chemical characteristics to other organic compounds, such as persistence and lipophilicity with the potential to bioaccumulate, but much less is known about their entry into the environment and subsequent fate (Alcock *et al.* 1999;

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Smith & Riddell-Black 2007). However, based on the general models of behaviour identified for OCs described earlier, pharmaceuticals are also likely to follow the same general fate and behaviour as the other OCs with these properties, which have already been reasonably well characterized in sludge-treated soils. Thus, it is unlikely for antibiotics (and indeed, other pharmaceutical compounds) to have a direct toxicological impact on humans from agricultural use of sludge owing to the very small concentrations present in sludge, but more importantly because environmental transfer pathways to humans do not operate (e.g. crop plant uptake).

Of considerably greater potential importance than direct toxicological impacts of environmental sources of antibiotics on human health is the potential spread of antibiotic-resistant human pathogens from emissions of these compounds to the environment (Jørgensen & Halling-Sørensen 2000). The development of antibiotic-resistant populations of bacteria in soil, in particular, has been directly linked to the use of antibiotics in animal husbandry and from spreading livestock manures on land (Jørgensen & Halling-Sørensen 2000; Nwosu 2001; Haller *et al.* 2002; Onan & LaPara 2003; Thiele-Bruhn 2003) and is also potentially a concern for the agricultural use of sewage sludge since residues of these compounds may also be expected to occur in sludge (Kinney *et al.* 2006).

Only trace concentrations of active antibiotic substances in soil and other environmental media 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 species boundaries (Witte 1998). In this way, multiple-resistant strains of micro-organisms have found their way into the food chain (Berger *et al.* 1996, cited in Halling-Sørensen *et al.* 1998). The ability of antibiotics to exert these effects at very low concentrations appears to be a unique characteristic of antibiotic compounds, as this type of behaviour is not apparent for any other chemical (Jørgensen & Halling-Sørensen 2000).

However, the development of resistance characteristics in soil bacterial populations appears to be only a short-lived, transient response to the presence of antibiotics in soil. 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 or are equivalent to untreated control soil (Sengeløv *et al.* 2003; Rysz & Alvarez 2004). Thus, resistance characteristics are rapidly lost because, once the selective advantage of maintaining antibiotic-resistant genes is removed, the acquired resistance is depleted from the population since the maintenance requirements set the resistant organisms at a disadvantage to the general population. Consequently, natural attenuation mechanisms operate in the soil microbial community that mitigate the spread of resistance vectors.

4. Ecotoxicological and environmental effects

(*a*) *General impacts on soil ecology*

Toxic effects of OCs to plants can be induced under artificial laboratory culture, using *in vitro* and hydroponic test conditions (e.g. Harms & Kottutz 1992; Sweetman *et al.* 1992; Harms 1996; Bradel *et al.* 2000 cited in Jjemba 2002).

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However, this does not reflect the actual behaviour and interactions that occur in sludge-amended soil systems, which significantly reduce bioavailability of OCs to soil organisms. Consequently, there is no evidence that OCs are phytotoxic at concentrations that are likely to occur in operationally sludge-treated agricultural soil (e.g. Shea *et al.* 1982; Overcash 1983; De Wolf & Feijtel 1998; Jensen 1999; Roberts *et al.* 2006; Smith & Riddell-Black 2007). For example, a recent 3-year programme of field and glasshouse investigations in Denmark (Petersen *et al.* 2003) examined the effects of sludge and other organic residuals on soil properties and soil biota, the fate of selected OCs (which included four principal groups or types of OC present in sludge: PAHs, DEHP, NP + NPE and LAS), and their potential for plant uptake. No accumulation of the OCs in soil or plant uptake were detected and no adverse effects of waste application on soil biota or crop growth were found (Petersen *et al.* 2003).

There are very few reports of toxicity of OCs to soil micro-organisms at representative environmental concentrations. For example, Chaudri *et al.* (1996) selected 10 OCs (LAS, NP, toluene, Aroclor 1016, 2,4-dichlorophenol, ethylbenzene, phenol, anthracene, trichloroethylene and PCP) representing a wide range of chemical classes, including those that potentially present the highest risk to soil micro-organisms, and added them directly to soil without sludge. Numbers of the N_2-fixing bacterium, *Rhizobium leguminosarum* bv. *trifolii*, free-living in the soil were measured after an incubation period, and of the different compounds tested, only PCP was toxic and significantly reduced the indigenous soil population. The conditions of the test were designed to represent a worse case, and for PCP, for example, the amount of compound added to the potentially vulnerable sandy loam soil was $200\,\mathrm{mg\,kg^{-1}}$, which is the maximum concentration of PCP found in sewage sludge. However, PCP was not detected in any influent samples in a screening study of UK sewage treatment works with a detection limit of $2\,\mu\mathrm{g\,l^{-1}}$ (Bowen *et al.* 2003); therefore, its presence in sludge in significant or potentially toxic concentrations is unlikely. PCP has been principally used for timber treatment and as a textile preservative; however, its production in the EC was banned in 1992 and its use as a chemical intermediate in the chemical industry was banned in 2000 (Bowen *et al.* 2003). PCP is also a WFD priority substance under review (EPCEU 2001).

There is no evidence of a direct impact of POPs on soil ecological systems (Smith & Riddell-Black 2007). Roberts *et al.* (2006) reported no effects of NP on soil respiration except at exceptionally high soil concentrations (greater than $10\,000\,\mathrm{mg\,kg^{-1}}$). After reviewing the available scientific literature, De Wolf & Feijtel (1998) and Jensen (1999) concluded that LAS was not toxic to terrestrial biota. No ecotoxicological impacts of antibiotics or pharmaceutical compounds are expected at the small concentrations likely to occur in sewage sludge-amended agricultural soil (Smith & Riddell-Black 2007). Therefore, overall the available evidence indicates that OCs do not present an ecotoxicological risk to soil micro-organisms or fauna from agricultural recycling of sewage sludge (McGrath 2000; Smith & Riddell-Black 2007). This contrasts with the marked biocidal effects on soil micro-organisms reported for a range of pesticide compounds licensed for use in agriculture (Smith & Riddell-Black 2007).

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(*b*) *Linear alkylbenzene sulphonate*

The total consumption of surfactant chemicals for industrial and domestic purposes was 1.7 million tonnes in 2000, 85 per cent of which were used in domestic products. The chemical LAS is a low to moderately toxic, non-bioaccumulative, high-production-volume anionic surfactant employed in detergents and cleaning products. It was introduced in 1964 as the readily biodegradable replacement for highly branched alkylbenzene sulphonates (www.lasinfo.org). It is presently used at rates of 350 000–400 000 tonne yr^{-1} in Western Europe. Potentially large concentrations of LAS can occur in sludge due to: high usage per capita, sorption and precipitation of the compound onto sludge solids and low degradability during anaerobic digestion. However, LAS biodegrades rapidly in aerobic soil (table 5) with primary and ultimate half-lives of up to 7 and 30 days, respectively (Figge & Schöberl 1989; Holt *et al.* 1998; Jensen 1999; Prats *et al.* 1999, 2006; HERA 2004). LAS is not generally regarded as toxic; it is not on the 'list of priority substances in the field of water policy' of the WFD (EPCEU 2001), or the European PRTR (EPCEU 2006*b*), or recognized as a chemical of concern by the UK Chemical Stakeholder Forum (DEFRA 2005).

Early uncertainties over the potential environmental impacts of LAS in sludge-treated soil prompted the Danish EPA to introduce a quality standard for agricultural application (2600 mg LAS kg^{-1} DS from 1997, which was reduced to 1300 mg LAS kg^{-1} DS in 2000) based on a risk assessment using the ecotoxicological data available at the time and a $PNEC_{soil}$ (predicted no-effect concentration is the chronic HC_5 hazardous concentration protecting 95 per cent of soil species) of 5.2 mg LAS kg^{-1} DS (SPT 1999, also see Jensen *et al.* 2001*a*). This was a controversial decision in the light of an apparently substantial amount of evidence demonstrating that there were no tangible ecotoxicological effects of LAS (e.g. De Wolf & Feijtel 1998). Another reason for the apparently conservative limit value estimated for LAS was that the rapid biodegradation of the compound was not considered in the initial risk assessment (Erhardt & Prüeß 2001). Nevertheless, the European Commission proposed to include the upper limit for LAS adopted in Danish regulations in a revision of Directive 86/278/EEC for agricultural use of sludge (CEC 1986; EC 2000) (table 1). However, a revised risk assessment on the compound has been recently published 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 (Schowanek *et al.* 2007), based on the conceptual framework for risk assessment for organic chemicals in sewage sludge for agricultural use proposed by Schowanek *et al.* (2004). Fundamental to this is that the species-sensitivity distribution for LAS has been more comprehensively profiled, which has led to a new $PNEC_{soil}$ value of 35 mg LAS kg^{-1} DS. Risk analysis procedures in Europe have also been refined and standardized (EC 2003*c*), and these recommendations, including, for example, taking account of the biodegradability of a compound in soil, have been incorporated into the revised risk assessment for LAS (table 5). A Monte Carlo procedure was used to deal with multiple sources of variability and the sludge limit value derived from these calculations was approximately 50 000 mg LAS kg^{-1} DS. This value is significantly higher than the European average concentration for LAS in anaerobically digested sludges of 5564 mg kg^{-1} DS (table 2) and the maximum value reported recently for LAS in UK sludge of 10 500 mg kg^{-1} DS

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Table 5. Summary of key risk assessment parameter values in the EU Technical Guidance Document (TGD) (EC 2003*c*), the initial agricultural soil risk assessment of LAS by the Danish EPA and the recently revised calculation by ILSI[a] (the potential variability across the EU is also shown) (Jensen *et al.* 2007; Schowanek *et al.* 2007).

parameter	TGD parameters	Danish EPA	ILSI[a]: distribution of parameters for sensitivity analysis
$PNEC_{soil}$ LAS	value determined by experimental investigation and soil testing	$5.2\,mg\,kg^{-1}$	$35\,mg\,kg^{-1}$
sludge application rate	$5\,tonne\ DS\ ha^{-1}\ yr^{-1}$	$6\,tonne\ DS\ ha^{-1}\ yr^{-1}$	triangular distribution (trigen)[b] with 4000 as mode, 2500 as 5th percentile and $10\,000\,kg\,ha^{-1}$ as 95th percentile (truncated at 1500 and $13\,000\,kg\,ha^{-1}$)
soil bulk density	$1500\,kg\,m^{-3}$		lognormal distribution with mean $= 1350\,kg\,m^{-3}$, s.d. 150 (truncated at 1000 and $1700\,kg\,m^{-3}$)
soil depth	0.2 m (0.1 for grassland) (assumes homogeneous mixing)	0.1 m	0.15–0.25 m: trigen distribution with mean = 0.2 m (truncated at 0.15 and 0.25 m)
sludge/soil dilution factor	600	250	calculated as dependent variable
averaging time to calculate initial exposure	30 days	not considered	30 days
biodegradation half-life in soil	primary biodegradation[c]: $T_{0.5} =$ 10 d ($k = 0.069\ d^{-1}$); mineralization: $T_{0.5} = 30$ d ($k = 0.023\ d^{-1}$)	not considered	primary biodegradation: lognormal distribution of half-life with mean = 10 days and s.d. = 5 days; mineralization: lognormal distribution with mean = 30 days, s.d. = 15 days (for information, data not presently used in the simulations)
sludge quality standard		$1300\,mg\,kg^{-1}$DS	$50\,000\,mg\,kg^{-1}$ DS

[a]International Life Sciences Institute–Europe (see Schowanek *et al.* 2007).
[b]Trigen is a type of triangular distribution in the @RISK software.
[c]The TGD (EC 2003*c*) uses a half-life of 30 days as a default value, which was adjusted to 10 days here based on field monitoring data.

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(Bowen *et al.* 2003). Therefore, this revised assessment emphasizes that there is no risk identified for LAS in sludge. Indeed, based on further examination of the ecotoxicity of LAS, Jensen *et al.* (2007) concluded that LAS does not represent an ecological risk in Western Europe when applied to soil in sewage sludge under normal practice.

Other comprehensive risk assessments of LAS have also been completed or updated recently (HERA 2004; OECD 2005). These independent studies also concluded that the ecotoxicological parameters of LAS have been adequately and sufficiently characterized and that the ecological risk of LAS is low. Policies or controls that would ultimately limit the use of LAS would inevitably lead to its substitution with alternative surfactant compounds that are potentially less well characterized or understood in terms of their possible impacts on soil.

(*c*) *Phthalates*

Phthalates enter sludge by leaching from plastic materials in the built environment and are present in relatively high concentrations (table 2). In the environment, phthalates are degraded by a wide range of bacteria and actinomycetes under both aerobic and anaerobic conditions (Staples *et al.* 1997) and they degrade relatively rapidly in soil (Shanker *et al.* 1985). Kirchmann *et al.* (1991) reported that there were no effects of DEHP in soil on important soil microbial parameters including respiration, nitrogen mineralization and nitrification. Cartwright *et al.* (2000) showed that, even at concentrations as high as $100\,\mathrm{g\,kg^{-1}}$ in soil, DEHP had no effect on the structural diversity (bacterial number and fatty acid methyl ester analysis) and functional diversity (BIOLOG) of the soil microbial community or on cell membrane integrity, and concluded therefore that DEHP would have no impact on soil micro-organisms. Diethyl phthalate (DEP) had no impact on soil microbes at a soil concentration of $0.1\,\mathrm{g\,kg^{-1}}$, but did cause perturbation at concentrations more than $1\,\mathrm{g\,kg^{-1}}$ soil. However, DEP was biodegraded very rapidly in soil with a half-life of 0.75 days at 20°C, and, in sludge-treated soil, phthalate concentrations would not be increased to this extent in practice (Vikelsøe *et al.* 2002). Accumulation of DBP and DEHP has been reported in some mesofauna, suggesting a potential risk to these organisms (e.g. Hu *et al.* 2005) and the bioaccumulation through natural food chains, although the compounds were artificially introduced into soil by direct spiking without sludge, which may exaggerate their apparent bioavailability. However, no significant adverse effects of DEHP or DBP were observed by Jensen *et al.* (2001*b*) on soil collembolans.

Phthalates are suspected EDCs and, while emissions of chemicals exhibiting this behaviour on surface water habitats have potentially important consequences for aquatic life (EA 1998; Hotchkiss *et al.* 2008), the significance of endocrine disruption for soil ecology has not been identified and is likely to be much less important. Van Wezel *et al.* (2000) considered how effects on the endocrine/reproductive system should be incorporated into environmental risk limits (ERLs) for phthalates and performed *in vitro* and *in vivo* tests with these endpoints for a range of phthalate compounds (ERLs are concentrations of a substance in water, air, sediment and soil that are expected to be protective of the environment). However, for those compounds that demonstrated endocrine-disruptive effects (DBP, DEP, BBP, DEHP, MEHP, dihexyl phthalate and

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diisobutyl phthalate), the relative potency compared with that of the natural oestrogen, 17β-estradiol, was very low (10^{-4}–10^{-8}). Van Wezel *et al.* (2000) concluded, therefore, that dose–response relationships obtained from conventional ecotoxicity tests give sufficient protection against endocrine-disruptive effects. The ERLs obtained for DBP and DEHP in soil/sediment were 0.7 and 1.0 mg kg^{-1} soil (fresh weight). The ERL for DEHP, for example, is more than 25 times greater than the concentration measured by Vikelsøe *et al.* (2002) in soil regularly receiving applications of sludge at typical agronomic rates.

In conclusion, phthalates are one of the main groups of OCs present in sewage sludge. However, research into their potential impacts on soil micro-organisms and macrofauna has shown that, as with other groups of OCs present in sludge, they are unlikely to have ecotoxic effects at the concentrations found in contemporary, operationally produced sewage sludges.

(*d*) *Triclosan and other personal-care products*

Triclosan is a chlorophenol compound and is used for its antibacterial properties as an ingredient in many detergents, dish-washing liquids, soaps, deodorants, cosmetics, lotions, antimicrobial creams and toothpastes and as an additive in plastics and textiles. Consequently, it can be found in low-to-moderate concentrations in sewage sludge. For example, Ying & Kookana (2007) reported that the maximum concentration of triclosan in Australian sewage sludges was 17 mg kg^{-1} DS with a median content of 2.3 mg kg^{-1} DS. The safety of triclosan has been questioned in regard to environmental and human health, and a terrestrial risk assessment of triclosan recently completed by the Danish EPA (Samsøe-Petersen *et al.* 2003) indicated that the concentrations measured in sewage sludge could have negative effects on soil organisms immediately after application. Other antimicrobial agents are also extensively used in personal-care products and may also have potential implications for soil health when applied in sewage sludge. Consequently, these would seem to be an environmentally undesirable group of substances and there appear to be strong grounds to question the purpose and rationale for their use in domestic and other products and the possible need for source control measures to be implemented. Nevertheless, a recent laboratory investigation (Pipe 2007) showed no significant effects of triclosan and two other important biocidal personal-care compounds (butylparaben and methylchloroisothiazolinone) on the microbial biomass content of a sensitive sandy loam soil after the first week of application at concentrations 100 and 1000 times greater than the highest recorded amounts of triclosan measured in sludge, and assuming an application rate of 10 tonne DS ha^{-1} and incorporation depth of 10 cm (figure 1). No significant effects of the personal-care chemicals on soil microbial biomass were detected in a sandy silt loam soil. A possible explanation for the apparent low toxicity of triclosan and the other personal-care products in soil may be related to their strong adsorption to the soil organic and mineral phases and the rapid biodegradation of the compounds in the soil environment. Considering the 'averaging' times (30 days) accepted for environmental risk assessment of chemicals (EC 2003*c*) and the high concentrations used in this study, there would appear to be little cause for concern from personal-care products applied to soil in sewage sludge under normal operational conditions. However, further work is necessary to examine

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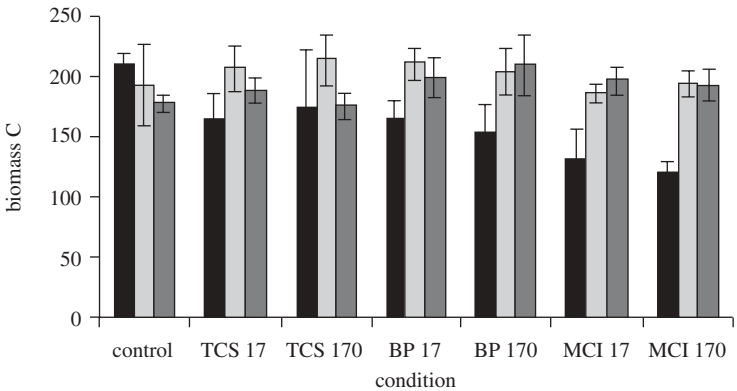

Figure 1. Microbial biomass C concentration in sandy loam soil (mg C kg^{-1} DS) after incubation for one, two and four weeks with three antimicrobial personal-care products (TCS, triclosan; BP, butylparaben; MCI, methylchloroisothiazolinone) applied at rates of 17 and 170 mg kg^{-1} DS (Pipe 2007). Black bar, week 1; light grey bar, week 2; dark grey bar, week 4.

the impacts of antimicrobial personal-care products on soil health, such as the common antiseptic agent TCC. Heidler *et al.* (2006) found that the average concentration of TCC in sludge from a large representative sewage treatment works in the USA was 51 ± 15 mg kg^{-1}; approximately 75 per cent of the mass of TCC disposed of by consumers in the catchment of the plant was ultimately released into the environment by application of sewage sludge on land, including for agricultural use.

Nitro musks (chloronitrobenzenes), a group of synthetic dinitro- or trinitro-substituted benzene derivatives, and polycyclic musks are used as synthetic fragrance ingredients in perfume and personal-care products, washing agents, etc., and therefore have obvious routes into the wastewater stream. Tas *et al.* (1997) completed an environmental risk assessment of the nitro musks, musk ketone and musk xylene, following EU Technical Guidance Document guidelines. For soil organisms, the predicted environmental concentration/predicted no-effect concentration (PEC/PNEC) ratio (i.e. the risk quotient (RQ)) was 0.5 for musk ketone, indicating no adverse effect of the compound on soil biota. However, the RQ value for musk xylene was greater than 1 and equivalent to 1.3, indicating that this compound may have adverse effects on soil organisms. However, nitro musks have largely been replaced in Europe because of concerns about safety and bioaccumulation (Gatermann *et al.* 1999) and consequently this is reflected in the concentrations of these compounds measured in contemporary sewage sludges. Thus, Jones & Northcott (2000) and Stevens *et al.* (2003) did not detect any of the major nitro musk compounds (musk xylene, musk ketone, musk ambrette, musk moskene and musk tibetene) in UK sewage sludge samples. The two main compounds currently used as fragrance ingredients are the polycyclic musks: 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (AHTN) and 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-γ-2-benzopyran (HHCB). Consequently, Stevens *et al.* (2003) found that HHCB and AHTN were the most abundant synthetic musks in sludge, with concentrations in the range 1.9–81 and 0.12–16 mg kg^{-1} DS,

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respectively, and mean values of 27 and 4.7 mg kg^{-1} DS, respectively. This was consistent with the use patterns, as together these compounds share more than 95 per cent of the market for polycyclic musks (Rimkus 1999). Relatively little biodegradation and destruction of HHCB or AHTN occurs during wastewater treatment or anaerobic digestion of sewage sludge (Kupper *et al.* 2004; Yang & Metcalfe 2006). However, Yang & Metcalfe (2006) reported that the initial amounts of HHCB and AHTN in field soil immediately after sludge application were 1.0 and 1.3 μg kg^{-1}, respectively, but found that concentrations declined relatively rapidly over the next six weeks and AHTN was not detectable in the sludge-amended field soil after six months. Polycyclic musks are hydrophobic and sorb strongly to organic matter and sludge solids; therefore, it is unlikely that they were lost from the soil by leaching or some other transport mechanism and a possible explanantion is that they were biodegraded by soil microbial activity. In the field study of Yang & Metcalfe (2006), sludge was applied just before the onset of winter, and it is plausible, therefore, that the rate of removal would be increased when warmer soil conditions support faster rates of microbial activity. The potential risks of human toxicity to synthetic musks from the use of sewage sludge on farmland is obviously a very minor consideration compared with the general exposure received from these compounds in body-care and washing products. In relation to their potential ecotoxicological significance in soil, Balk & Ford (1999) estimated an adjusted PNEC value for AHTN and HHCB in soil of 0.32 mg kg^{-1} DS using a risk assessment factor of 50. However, the above observations, coupled with the soil ecotoxicological data and no-observed-effect concentrations for earthworms and springtails of 45 mg kg^{-1} or more for both HHCB and AHTN (Balk & Ford 1999), suggest that there is likely to be a minimal impact of polycyclic musks in practice under normal operational field conditions when sewage sludge is used as an agricultural fertilizer.

5. Conclusions

(*a*) *Environmental assessment*

An overall assessment of the potential environmental impacts associated with OCs in sewage sludge recycled to agricultural land is presented in table 6 by ascribing a qualitative description of the apparent risk, based on the scientific information discussed in this paper, for important environmental endpoints. It has been assumed in this analysis that sludge is applied according to the regulations (CEC 1986; UK SI 1989) and codes of practice and other guidance (e.g. DoE 1996; ADAS 2001).

(*b*) *Trends in OC concentrations in sludge*

Concentrations of POPs in sludge have declined in response to source controls and improved industrial practices and are no longer relevant to human health or the environment when sludge is used in agriculture. The chemical quality of sludge is currently at the highest level it has ever been and this further ensures the sustainability of the agricultural recycling of sewage sludge.

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Table 6. Assessment of risks to health and the environment from recycling sewage sludge to agricultural land (L, low risk[a]; P, possible risk[b]).

environmental parameter	risk attributed
human health	P[c]
crop yields	L
animal health	L
groundwater quality	L
surface water quality	L
air quality	L
soil fertility	P[c,d]

[a]Risk is designated as 'low' (L) where environmental effects are minimized by current operational practice.
[b]Risk is designated as 'possible' (P) where there is some reported evidence that current operational practice may result in a potential impact on the environment on the basis that one or more of the following conditions apply:
[c]there is uncertainty about the environmental implications of particular sludge components;
[d]effects may occur under certain extreme 'worst-case' conditions, given the current regulations and codes of practice.

(c) *Human health*

OCs present minimal risk to the human food chain from land application of sewage sludge. The most toxic compounds (e.g. TCDD) cannot be detected in sludge, and they are also influenced by a variety of physico-chemical and biological attenuation mechanisms that prevent transfer to crop tissues and the human food chain, including:

(i) rapid volatilization and loss to the atmosphere;
(ii) rapid biodegradation and minimal or no persistence, or
(iii) strong adsorption of persistent compounds.

The risk to human health via dietary intake of OCs from crops grown on sludge-treated soils is minimal owing to the absence of crop uptake.

The potential impacts on the food chain of persistent OCs in sludge, including PAHs, PCDD/Fs or PCBs, have been a key concern for agricultural utlilization. However, international emission controls on the main point sources of these priority-persistent compounds have significantly reduced their entry into the environment and consequently also into the UWW collection system. Thus, atmospheric deposition and environmental cycling are the main sources of PCBs in sludge, and consequently the concentrations of this historically used chemical in sludge generally represent background environmental levels. The potential transfer to the human food chain of certain groups of OCs contained in sludge has been predicted based on known physico-chemical properties of the compounds. However, ongoing research has not identified any toxicological (or ecotoxicological) link with these compounds in sludge. Therefore, on balance, the importance of these contaminants has significantly diminished and there is no quantitative, scientific evidence to support the need

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for limits or controls on PAHs, PCBs or PCDD/Fs in sewage sludge. The EC Joint Research Centre (Erhardt & Prüeß 2001) concluded that 'OCs in sludge are not expected to pose major health problems to the human population when sludge is re-used for agricultural purposes'. They also have stated that 'it does not make much sense to include PCDD/Fs, PCBs and PAHs in routine monitoring programmes'.

Brominated flame retardants are also an important group of persistent, lipophilic and bioaccumulative compounds potentially found in sludge. However, the use of the main types (pentaBDE and octaBDE) has been restricted in the EU; therefore, they are also expected to diminish in importance as contaminants in sewage sludge.

In contrast to other POPs, PCAs, also known as chlorinated paraffins, are in active production and occur in sludge in much larger concentrations than PCBs and PCNs, for example. Consequently, further work is recommended to assess the potential transfer to the food chain and significance for human health of PCAs in sewage sludge-amended agricultural soil. Therefore, because of this uncertainty, the risk to human health from OCs has been designated as 'possible' in table 6.

Because they are lipophilic, POPs characteristically show a high potential propensity to transfer and accumulate in animal fat tissue and milk fat from livestock ingesting surface-applied sludge adhering to herbage, which is theoretically the principal route of human exposure to potentially toxic OCs in sewage sludge. In practice, however, there is no evidence that organic pollutants transfer to the food chain by this route, owing to the low concentrations of POPs present and management factors (e.g. injecting sludge) avoiding surface application to grazed pastures for pathogen control.

The significance of the phthalate plasticizer compound, DEHP, in sewage sludge for human health and the environment requires careful and appropriate interpretation. DEHP has been recently downgraded as a carcinogen by IARC, and the US ATSDR concluded that there was no evidence to indicate that DEHP was an endocrine disrupter in humans at the levels found in the environment. Exposures received through medical procedures by the use of DEHP in PVC 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 highly exposed, sensitive medical situations, and also the direct ingestion by the general population of DEHP, for instance, transferred to food from plastic packaging materials and other dietary intakes, 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 relatively rapid degradability of DEHP in soil and also the absence of significant transfers of DEHP to food crops. The risk assessment of DEHP in sludge-treated agricultural soil is recommended, following the protocol developed by Schowanek *et al.* (2004), to clarify the impact of this plasticizer compound on human health, soil quality and the environment.

(*d*) *Antibiotic resistance*

The possibility that sludge may contain populations of antibiotic-resistant bacteria and also trace concentrations of antibiotic compounds causing antibiotic resistance to develop in soil bacteria has raised concerns that this could

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have important consequences for human health. However, antibiotic resistance is a transient characteristic and elevated resistance levels in soil relatively quickly return to normal background values. This is because high maintenance requirements place the resistant organisms at a disadvantage; therefore, natural attenuation occurs when the selection pressure is removed. Application of sludge at normal agronomic rates, the relatively infrequent application of sludge to land and extended return periods are likely to permit natural attenuation of antibiotic-resistant bacteria populations in soil. However, a microbiological risk assessment should be completed to confirm that antibiotic-resistant micro-organisms in sludge-treated soil represent a negligible risk to human health. This is also the basis for designating the risk to human health from OCs as 'possible' in table 6.

(*e*) *Crop yields*

OCs have no phytotoxic activity at the concentrations found in sludge-treated soils.

(*f*) *Soil fertility*

There is no evidence that the vast majority of sludge-borne OCs have a detrimental impact on soil microbial processes. Earlier concerns about the potential impact of LAS, a detergent surfactant present in large concentrations in sludge, on soil ecological processes have been further elucidated and shown to be unfounded. While the presence of large concentrations of certain high-volume bulk chemicals, such as LAS, warrants careful investigation and assessment of the risks to the environment when sludge is used as an agricultural soil amendment, this does not necessarily represent a hazard to the soil ecological environment. However, if compounds such as LAS were to be banned or their use restricted in future, this would lead to product substitution, but there is uncertainty about the potential environmental consequences of the alternatives. Phthalates have not been found to cause any significant adverse effects on soil microbial processes or on soil fertility. In general, high-volume usage compounds have very low toxicity and degrade rapidly in soil. A number of emerging compounds have been identified in this review as having a potential impact on soil microbes and these belong to the group of chemicals described as body-care products, e.g. triclosan, and the significance of these warrants further investigation. Consequently, the risk to soil fertility of OCs in sewage sludge spread on farmland has been designated as 'possible' in table 6.

(*g*) *Implications for regulating organic contaminants in sludge*

Despite the extensive range of organic chemicals that can be present in sewage sludge, the expanding experimental evidence base indicates that these are not a significant limitation to the agricultural use of sewage sludge. This view is based on a technical evaluation of the situation, which acknowledges that the presence of effective source control measures and small concentrations of persistent contaminants in sludge, biodegradation and behaviour in soil, absence of crop uptake and sludge application practices minimize the potential impacts of OCs in sludge on soil quality, human health and the environment. The consensus

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view therefore is that there appears to be no scientific rationale for including numerical limits on OCs in quality assurance systems for the agricultural use of sewage sludge. Nevertheless, new issues and compounds of concern, including endocrine-disrupting, pharmaceutical and personal-care products, require an ongoing and proactive approach to research and vigilant monitoring and rational assessment of the significance of new developments as they arise.

There has been much debate about the relevance of quality standards for OCs in sludge. 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 among other issues included standards for organic chemicals (table 1), 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 PCDD/Fs, 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, owing to concerns about their solubility and potential to impact aquatic systems (Erhardt & Prüeß 2001). However, the consensus of scientific opinion is that detergent residues in sludge do not pose a significant environmental or health risk. Thus, limit values for OCs in sludge previously considered by the European Commission (Leschber 2004) are not supported by the available scientific evidence on the effects of OCs in sludge-amended agricultural soils on human health, soil quality and the environment.

References

ADAS (Agricultural Development and Advisory Service). 2001 The safe sludge matrix. Guidelines for the application of sewage sludge to agricultural land. See www.adas.co.uk/publications/document_store/index.html.

AISE-CESIO. 1999 Anaerobic degradation of surfactants. Review of scientific information. AISE-CESIO Report, Brussels.

Alcock, R. E., Sweetman, A. & Jones, K. C. 1999 Assessment of organic contaminant fate in wastewater treatment plants. I: selected compounds and physicochemical properties. *Chemosphere* **38**, 2247–2262. (doi:10.1016/S0045-6535(98)00444-5)

Aranda, J. M., O'Connor, G. A. & Eiceman, G. A. 1989 Effects of sewage sludge on di-(2-ethylhexyl) phthalate uptake by plants. *J. Environ. Qual.* **18**, 45–50.

ATSDR (Agency for Toxic Substances and Disease Registry). 2002 Toxicological profile for di(2-ethylhexyl)phthalate. US Department of Health and Human Services. See http://www.atsdr.cdc.gov/toxprofiles/tp9.pdf.

Balk, F. & Ford, R. A. 1999 Environmental risk assessment for the polycyclic musks, AHTN and HHCB. II. Effect assessment and risk characterisation. *Toxicol. Lett.* **111**, 81–94. (doi:10.1016/S0378-4274(99)00170-8)

Bester, K. 2003 Triclosan in a sewage treatment process—balances and monitoring data. *Water Res.* **37**, 3891–3896. (doi:10.1016/S0043-1354(03)00335-X)

Blackmore, K., Davis, L., Davis, M., Davis, R. & Gendebien, A. 2006 Accommodating the implications of the Revised EU Sludge Directive. Final Report to UKWIR, UKWIR, London.

Bowen, E., Comber, S., Makropoulos, C., Rautiu, R., Ross, D., Rule, K. & Thornton, A. 2003 Priority hazardous substances, trace organics and diffuse pollution (Water Framework Directive): screening study and literature review of quantities in sewage, sludge and effluent. Report Ref. No. 03/WW/17/2, UKWIR, London.

Boxall, A. B. A., Fogg, L. A., Blackwell, P. A., Kay, P., Pemberton, E. J. & Croxford, A. 2004 Veterinary medicines in the environment. *Rev. Environ. Contam. Toxicol.* **180**, 1–91. (doi:10.1007/0-387-21729-0_1)

Downloaded from rsta.royalsocietypublishing.org on August 26, 2013

Cartwright, C. D., Thompson, I. P. & Burns, R. G. 2000 Degradation and impact of phthalate plasticizers on soil microbial communities. *Environ. Toxicol. Chem.* **19**, 1253–1261. (doi:10.1897/1551-5028(2000)019<1253:DAIOPP>2.3.CO;2)

CEC (Council of the European Communities). 1986 Council Directive of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture (86/278/EEC). *Off. J. Eur. Comm.* **L181**, 6–12.

Chaney, R. L., Ryan, J. A. & O'Connor, G. A. 1996 Organic contaminants in municipal biosolids: risk assessment, quantitative pathways analysis, and current research priorities. *Sci. Total Environ.* **185**, 187–216. (doi:10.1016/0048-9697(96)05051-6)

Chaudri, A. M., McGrath, S. P., Knight, B. P., Johnson, D. L. & Jones, K. C. 1996 Toxicity of organic compounds to the indigenous population of *Rhizobium leguminosarum* biovar *trifolii* in soil. *Soil Biol. Biochem.* **28**, 1483–1487. (doi:10.1016/S0038-0717(96)00156-3)

CSTEE (Scientific Committee on Toxicity, Ecotoxicity and the Environment). 1999 Opinion on the toxicological characteristic and risks of certain citrates and adipates used as a substitute for phthalates as plasticisers in certain soft PVC products. B2/JCD/csteeop/cit28999.D(99), DG Health and Consumer Protection, European Commission, Brussels.

Davis, R. D., Hucker, G. & L'Hermite, P. 1983 *Environmental effects of organic and inorganic contaminants in sewage sludge*. Dordrecht, The Netherlands: Reidel.

DEFRA (Department for Environment, Food and Rural Affairs). 2004 Voluntary agreement—risk reduction for nonylphenol, nonylphenol ethoxylates, octylphenol and octylphenol ethoxylates by chemical supply industry and downstream users. DEFRA, London, UK.

DEFRA (Department for Environment, Food and Rural Affairs). 2005 Chemical stakeholder forum list of chemicals of concern. July 2005. See http://www.defra.gov.uk/environment/chemicals/csf/criteria/index.htm.

De Wit, C. A. 2002 An overview of brominated flame retardants in the environment. *Chemosphere* **46**, 583–624. (doi:10.1016/S0045-6535(01)00225-9)

De Wolf, W. & Feijtel, T. 1998 Terrestrial risk assessment for linear alkylbenzene sulfonate (LAS) in sludge-amended soils. *Chemosphere* **36**, 1319–1343. (doi:10.1016/S0045-6535(97)10021-2)

DoE (Department of the Environment). 1996 Code of practice for agricultural use of sewage sludge. HMSO, London, UK.

Drescher-Kaden, U., Brüggeman, R., Matthes, B. & Matthies, M. 1992 Contents of organic pollutants in German sewage sludges. In *Effects of organic contaminants in sewage sludge on soil fertility, plants and animals* (eds J. E. Hall, D. R. Sauerbeck & P. L'Hermite), pp. 14–34. Luxembourg: Commission of the European Communities.

Duarte-Davidson, R. & Jones, K. C. 1996 Screening the environmental fate of organic contaminants in sewage sludge applied to agricultural soils: II The potential for transfers to plants and grazing animals. *Sci. Total Environ.* **185**, 59–70. (doi:10.1016/0048-9697(96)05042-5)

Ducray, F. & Huyard, A. 2001 Impact du futur projet Européen sur la valorisation des boues en agriculture. Campagne d'analyse sur des boues STEP. Rapport Final, Anjou Recherche–CIRSEE, France.

Düring, R.-A. & Gäth, S. 2002 Utilization of municipal organic wastes in agriculture: where do we stand, where will we go? *J. Plant Nutr. Soil Sci.* **165**, 544–556. (doi:10.1002/1522-2624(200208)165:4<544::AID-JPLN544>3.0.CO;2-#)

EA (Environment Agency). 1998 Endocrine-disrupting substances in wildlife: a review of the scientific evidence and strategic response. Environment Agency, Bristol, UK.

EC (European Commission). 2000 Working document on sludge. 3rd draft. 27 April. Brussels, Belgium: DG Environment, European Commission.

EC (European Commission). 2003*a* Report from the Commission to the Council and the European Parliament on the implementation of community waste legislation ... for the period 1998–2000. COM(2003) 250 final/3. Brussels, Belgium: EC. See http://eur-lex.europa.eu/en/index.htm.

EC (European Commission). 2003*b* Proposal for a Directive of the European Parliament and of the Council on spreading of sludge on land. 30 April 2003. Brussels, Belgium: European Commission.

EC (European Commission). 2003*c* *Technical guidance document on risk assessment ... for new notified substances, ... for existing substances, and ... concerning the placing of biocidal products*

Downloaded from rsta.royalsocietypublishing.org on August 26, 2013

on the market, 2nd edn. April 2003. European Chemicals Bureau (ECB), JRC-ISPRA, Italy. See http://ecb.jrc.ec.europa.eu/tgdoc.

EC (European Commission). 2006 Report from the Commission to the Council and the European Parliament on the implementation of community waste legislation for the period 2001–2003. COM(2006) 406 final, European Commission, Brussels.

EC (European Commission). 2007 REACH in brief. October 2007. Environment Directorate General, European Commission, Brussels.

ECPI (European Council for Plasticisers and Intermediates). 2007 DEHP Information Centre. ECPI, Brussels. See http://www.dehp-facts.com/.

EPCEU (The European Parliament and the Council of the European Union). 2001 Decision No. 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC. *Off. J. Eur. Comm.* **L331**, 1–5.

EPCEU (The European Parliament and the Council of the European Union). 2003*a* Directive 2003/53/EC of the European Parliament and of the Council of 18 June 2003 amending for the 26th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (nonylphenol, nonylphenol ethoxylate and cement). *Off. J. Eur. Union* **L178**, 24–27.

EPCEU (The European Parliament and the Council of the European Union). 2003*b* Directive 2003/11/EC of the European Parliament and of the Council of 6 February 2003 amending for the 24th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (pentabromodiphenyl ether, octabromodiphenyl ether). *Off. J. Eur. Union* **L42**, 45–46.

EPCEU (The European Parliament and the Council of the European Union). 2006*a* Regulation (EC) No. 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No. 793/93 and Commission Regulation (EC) No. 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC. *Off. J. Eur. Union* **L396**, 1–849.

EPCEU (The European Parliament and the Council of the European Union). 2006*b* Regulation (EC) No. 166/2006 of the European Parliament and of the Council of 18 January 2006 concerning the establishment of a European Pollutant Release and Transfer Register amending Council Directives 91/689/EEC and 96/61/EC. *Off. J. Eur. Union* **L33**, 1–17.

Erhard, H. W. & Rhind, S. M. 2004 Prenatal and postnatal exposure to environmental pollutants in sewage sludge alters emotional reactivity and exploratory behaviour in sheep. *Sci. Total Environ.* **332**, 101–108. (doi:10.1016/j.scitotenv.2004.04.012)

Erhardt, W. & Prüeß, A. 2001 Organic contaminants in sewage sludge for agricultural use. See http://ec.europa.eu/environment/waste/sludge/pdf/organics_in_sludge.pdf.

Euro Chlor. 2005 About chlorinated paraffins. See http://www.eurochlor.org/aboutparaffins.

Figge, K. & Schöberl, P. 1989 LAS and the application of sewage sludge in agriculture. *Tenside Surfact. Deterg.* **26**, 122–128.

Fisher, J. S. 2004 Environmental anti-androgens and male reproductive health: focus on phthalates and testicular dysgenesis syndrome. *Reproduction* **127**, 305–315. (doi:10.1530/rep.1.00025)

FOEN (Swiss Federal Office for the Environment). 2003 Ban on the use of sludge as a fertiliser. FOEN, Switzerland. See http://www.bafu.admin.ch/dokumentation/medieninformation/00962/index.html?lang=en&msg-id=1673.

Fries, G. F. 1996 Ingestion of sludge applied organic chemicals by animals. *Sci. Total Environ.* **185**, 93–108. (doi:10.1016/0048-9697(96)05045-0)

Gatermann, R., Hellou, J., Huhnerfuss, H., Rimkus, G. & Zitko, V. 1999 Polycyclic and nitro musks in the environment: a comparison between Canadian and European aquatic biota. *Chemosphere* **38**, 3431–3441. (doi:10.1016/S0045-6535(98)00564-5)

Downloaded from rsta.royalsocietypublishing.org on August 26, 2013

Hall, J. E., L'Hermite, P. & Newman, P. J. 1992*a* *Treatment and use of sewage sludge and liquid agricultural wastes. Review of the COST 68/681 Programme, 1972–90.* Luxembourg: Commission of the European Communities.

Hall, J. E., Sauerbeck, D. R. & L'Hermite, P. (eds) 1992*b* *Effects of organic contaminants in sewage sludge on soil fertility, plants and animals.* Luxembourg: Commission of the European Communities.

Haller, M. Y., Muller, S. R., McArdell, C. S., Alder, A. C. & Suter, M. J.-F. 2002 Quantification of veterinary antibiotics (sulfonamides and trimethoprim) in animal manure by liquid chromatography–mass spectrometry. *J. Chromatogr. A*, **952**, 111–120. (doi:10.1016/S0021-9673(02)00083-3)

Halling-Sørensen, B., Nors Nielsen, S., Lanzky, P. F., Ingerslev, F., Holten Lützhøft, H. C. & Jørgensen, S. E. 1998 Occurrence, fate and effects of pharmaceutical substances in the environment—a review. *Chemosphere* **36**, 357–393. (doi:10.1016/S0045-6535(97)00354-8)

Harms, H. H. 1996 Bioaccumulation and metabolic fate of sewage sludge derived organic xenobiotics in plants. *Sci. Total Environ.* **185**, 83–92. (doi:10.1016/0048-9697(96)05044-9)

Harms, H. & Kottutz, E. 1992 Uptake, fate and persistence of organic contaminants in different plant systems—cell suspension cultures, root cultures and intact plants. In *Effects of organic contaminants in sewage sludge on soil fertility, plants and animals* (eds J. E. Hall, D. R. Sauerbeck & P. L'Hermite), pp. 125–133. Luxembourg: Commission of the European Communities.

Harrison, E. Z., Oakes, S. R., Hysell, M. & Hay, A. 2006 Review: organic chemicals in sewage sludges. *Sci. Total Environ.* **367**, 481–497. (doi:10.1016/j.scitotenv.2006.04.002)

Heidler, J., Sapkota, A. & Halden, R. 2006 Partitioning, persistence, and accumulation in digested sludge of the topical antiseptic triclocarban during wastewater treatment. *Environ. Sci. Technol.* **40**, 3634–3639. (doi:10.1021/es052245n)

Hembrock-Heger, A. 1992 Persistent organic contaminants in soils, plants and food. In *Effects of organic contaminants in sewage sludge on soil fertility, plants and animals* (eds J. E. Hall, D. R. Sauerbeck & P. L'Hermite), pp. 78–89. Luxembourg: Commission of the European Communities.

HERA (Human and Environmental Risk Assessment on ingredients of household cleaning products). 2004 LAS linear alkylbenzene sulphonate (CAS No. 68411-30-3) Version 2.0. Brussels, Belgium: HERA. See http://www.heraproject.com.

Hijaz, M. 2007 The fate of organic chemicals in wastewater and sewage sludge. MSc thesis, Department of Civil and Environmental Engineering, Imperial College London.

Hilton, M. J., Thomas, K. V. & Ashton, D. 2003 Targeted monitoring programme for pharmaceuticals in the aquatic environment. EA R&D Technical Report P6-012/06/TR, Environment Agency, Bristol, UK.

Holt, M. S., Fox, K. K., Burford, M. D. M. & Buckland, H. 1998 UK monitoring study on the removal of linear alkylbenzene sulfonate in trickling filter type sewage treatment plants. Contribution to GREAT-ER Project No. 2. *Sci. Total Environ.* **210/211**, 255–269. (doi:10.1016/S0048-9697(98)00016-3)

Hotchkiss, A. K., Rider, C. V., Blystone, C. R., Wilson, V. S., Hartig, P. C., Ankley, G. T., Foster, P. M., Gray, C. L. & Gray, L. E. 2008 Fifteen years after 'Wingspread'—environmental endocrine disrupters and human and wildlife health: where we are today and where we need to go. *Toxicol. Sci.* **105**, 235–259. (doi:10.1093/toxsci/kfn030)

Hu, X., Wen, B., Zhang, S. & Shan, X. 2005 Bioavailability of phthalate congeners to earthworms (*Eisenia fetida*) in artificially contaminated soils. *Ecotoxicol. Environ. Safety* **62**, 26–34. (doi:10.1016/j.ecoenv.2005.02.012)

Huber, W. W., Grasl-Kraupp, B. & Schulte-Hermann, R. 1996 Hepatocarcinogenic potential of di(2-ethylhexyl) phthalate in rodents and its implication on human risk. *Crit. Rev. Toxicol.* **26**, 365–481. (doi:10.3109/10408449609048302)

IARC (International Agency for Research on Cancer). 2000 Di(2-ethylhexyl) phthalate (Group 3). *IARC monographs on the evaluation of carcinogenic risks to humans,* vol. 77, *Some industrial chemicals*, p. 41. Lyons, France: IARC. See http://monographs.iarc.fr/ENG/Monographs/vol77/index.php.

Downloaded from rsta.royalsocietypublishing.org on August 26, 2013

IC Consultants. 2001 Pollutants in urban wastewater and sewage sludge. Final Report to Directorate General Environment, European Commission. See http://ec.europa.eu/environment/waste/ sludge/pdf/sludge_pollutants.pdf.

Jacobs, L. W., O'Connor, G. A., Overcash, M. A., Zabik, M. J., Rygiewicz, P., Machno, P., Munger, S. & Elseavi, A. A. 1987 Effects of trace organics in sewage sludges on soil–plant systems and assessing their risk to humans. In *Land application of sludge: food chain implications* (eds A. L. Page, T. J. Logan & J. A. Ryan), pp. 101–143. Chelsea, MI: Lewis.

Jensen, J. 1999 Fate and effects of linear alkylbenzene sulphonates (LAS) in the terrestrial environment—a review. *Sci. Total Environ.* **226**, 93–111. (doi:10.1016/S0048-9697(98)00395-7)

Jensen, J. & Jepsen, S. E. 2005 The production, use and quality of sewage sludge in Denmark. *Waste Manage.* **25**, 239–247. (doi:10.1016/j.wasman.2004.08.011)

Jensen, J., Lokke, H., Holmstrup, M., Krogh, P. H. & Elsgaard, I. 2001*a* Effects and risk assessment of linear alkylbenzene sulfonates in agricultural soil. 5. Probabilistic risk assessment of linear alkylbenzene sulfonates in sludge-amended soils. *Environ. Toxicol. Chem.* **20**, 1690–1697. (doi:10.1897/1551-5028(2001)020<1690:EARAOL>2.0.CO;2)

Jensen, J., van Langevelde, J., Pritzl, G. & Krogh, P. H. 2001*b* Effects of di(2-ethylhexyl) phthalate and dibutyl phthalate on the collembolan *Folsomia fimetaria*. *Environ. Toxicol. Chem.* **20**, 1085–1091. (doi:10.1897/1551-5028(2001)020<1085:EODEPA>2.0.CO;2)

Jensen, J., Smith, S. R., Krogh, P. H., Versteeg, D. J. & Temara, A. 2007 European risk assessment of LAS in agricultural soil revisited: species sensitivity distribution and risk estimates. *Chemosphere* **69**, 880–892. (doi:10.1016/j.chemosphere.2007.07.029)

Jjemba, P. K. 2002 The potential impact of veterinary and human therapeutic agents in manure and biosolids on plants grown on arable land: a review. *Agric. Ecosyst. Environ.* **93**, 267–278. (doi:10.1016/S0167-8809(01)00350-4)

Jones, K. C. 1996 Introduction. *Sci. Total Environ.* **185**, 1. (doi:10.1016/S0048-9697(96)90028-5)

Jones, K. C. & Northcott, G. L 2000 Organic contaminants in sewage sludges: a survey of UK samples and a consideration of their significance. Final Report to the Department of the Environment, Transport and the Regions, Water Quality Division.

Jørgensen, S. E. & Halling-Sørensen, B. 2000 Editorial. Drugs in the environment. *Chemosphere* **40**, 691–699.

Kampe, W. & Leschber, R. 1989 Occurrence of organic pollutants in soil and plants after intensive sewage sludge application. In *Organic contaminants in waste water, sludge and sediment: occurrence, fate and disposal* (eds D. Quaghebeur, I. Temmerman & G. Angeletti), pp. 35–41. Barking, UK: Elsevier Applied Science.

Keith, L. H. 1998 Environmental endocrine disruptors. *Pure Appl. Chem.* **70**, 2319–2326. (doi:10.1351/pac199870122319)

Kinney, C. A., Furlong, E. T., Zaugg, S. D., Burkhardt, M. R., Werner, S. L., Cahill, J. D. & Jorgensen, G. R. 2006 Survey of organic wastewater contaminants in biosolids destined for land application. *Environ. Sci. Technol.* **40**, 7207–7215. (doi:10.1021/es0603406)

Kirchmann, H. & Tengsved, A. 1991 Organic pollutants in sewage sludge. 2. Analysis of barley grains on sludge-fertilized soil. *Swed. J. Agric. Res.* **21**, 115–119.

Kirchmann, H. A., Astrum, G. & Jonsall, G. 1991 Organic pollutants in organic sewage sludge. 1. Effect of toluene, naphthalene, 2-methylnaphthalene, 4-nonylphenol, and di-2-ethylhexyl phthalate on soil biological processes and their decomposition in soil. *Swed. J. Agric. Res.* **21**, 107–113.

Knoth, W., Mann, W. Meyer, R. & Nebhuth, J. 2007 Polybrominated diphenyl ether in sewage sludge in Germany. *Chemosphere* **67**, 1831–1837. (doi:10.1016/j.chemosphere.2006.05.113)

Koch, H. M., Drexler, H. & Angerer, J. 2003*a* An estimation of the daily intake of di(2-ethylhexyl) phthalate (DEHP) and other phthalates in the general population. *Int. J. Hyg. Environ. Health* **206**, 77–83. (doi:10.1078/1438-4639-00205)

Koch, H. M., Rossbach, B., Drexler, H. & Angerer, J. 2003*b* Internal exposure of the general population to DEHP and other phthalates—determination of secondary and primary phthalate monoester metabolites in urine. *Environ. Res.* **93**, 177–185. (doi:10.1016/S0013-9351(03)00083-5)

Downloaded from rsta.royalsocietypublishing.org on August 26, 2013

Kupper, T., Berset, J. D., Etter-Holzer, R., Furrer, R. & Tarradellas, J. 2004 Concentrations and specific loads of polycyclic musks in sewage sludge originating from a monitoring network in Switzerland. *Chemosphere* **54**, 1111–1120. (doi:10.1016/j.chemosphere.2003.09.023)

Leschber, R. 2004 Evaluation of organic micro-pollutants in sewage sludge. Provisional Report for Commenting. Results of a JRC-coordinated survey on background values. European Commission, Directorate General, Joint Research Centre.

Letcher, R. J. 2003 The state-of-the-science and trends of brominated flame retardants in the environment: present knowledge and future directions. *Environ. Int.* **29**, 663–664. (doi:10.1016/S0160-4120(03)00122-3)

Madsen, P. L., Thyme, J. P., Henriksen, K., Møldrup, P. & Roslev, P. 1999 Kinetics of di-(2-ethylhexyl)phthalate mineralization in sludge-amended soil. *Environ. Sci. Technol.* **33**, 2601–2606. (doi:10.1021/es981015o)

McAvoy, D. C., Schatowitz, B., Jacob, M., Hauk, A. & Eckhoff, W. S. 2002 Measurement of triclosan in wastewater treatment systems. *Environ. Toxicol. Chem.* **21**, 1323–1329. (doi:10.1897/1551-5028(2002)021<1323:MOTIWT>2.0.CO;2)

McGrath, S. P. 2000 Persistent organic pollutants and metals from sewage sludges: their effects on soil, plants and the foodchain. In *Workshop on Problems Around Sludge*, *Proc., Stresa, Italy, 18–19 November 1999* (eds H. Langenkamp & L. Marmo).

NRC (National Research Council). 1996 *Use of reclaimed water and sludge in food crop production.* Washington, DC: National Academy Press.

Nwosu, V. C. 2001 Antibiotic resistance with particular reference to soil microorganisms. *Res. Microbiol.* **152**, 421–430. (doi:10.1016/S0923-2508(01)01215-3)

O'Connor, G. A. 1996 Organic compounds in sludge-amended soils and their potential for uptake by crop plants. *Sci. Total Environ.* **185**, 71–81. (doi:10.1016/0048-9697(95)05043-4)

O'Connor, G. A., Chaney, R. L. & Ryan, J. A. 1991 Bioavailability to plants of sludge-borne toxic organics. *Rev. Environ. Contam. Toxicol.* **121**, 129–155.

OECD (Organisation for Economic Co-operation and Development). 2005 OECD SIDS linear alkylbenzene sulphonate (LAS) SIDS initial assessment form for 20th SIAM. Paris, France, April. See http://www.lasinfo.org.

Offenbacher, G. 1992 The PCB transfer from soil into plants depending on supply and degree of chlorination. In *Effects of organic contaminants in sewage sludge on soil fertility, plants and animals* (eds J. E. Hall, D. R. Sauerbeck & P. L'Hermite), pp. 90–102. Luxembourg: Commission of the European Communities.

Onan, L. J. & LaPara, T. M. 2003 Tylosin-resistant bacteria cultivated from agricultural soil. *FEMS Microbiol. Lett.* **220**, 15–20. (doi:10.1016/S0378-1097(03)00045-4)

Overcash, M. R. 1983 Land treatment of municipal effluent and sludge: specific organic compounds. In *Proc. 1983 Workshop on Utilization of Municipal Wastewater and Sludge on Land* (eds A. L. Page, T. L. Gleason III, J. E. Smith Jr, I. K. Iskander & L. E. Sommers), pp. 199–231. Riverside, CA: University of California.

Paul, C., Rhind, S. M., Kyle, C. E., Scott, H., McKinnell, C. & Sharpe, R. M. 2005 Cellular and hormonal disruption of fetal testis development in sheep reared on pasture treated with sewage sludge. *Environ. Health Perspect.* **113**, 1580–1587.

Paxéus, N. 1996 Organic pollutants in the effluents of large waste water treatment plants in Sweden. *Water Res.* **30**, 1115–1122. (doi:10.1016/0043-1354(95)00278-2)

Petersen, S. O., Henriksen, K., Mortensen, G. K., Krogh, P. H., Brandt, K. K., Sørensen, J., Madsen, T., Petersen, J. & Grøn, C. 2003 Recycling of sewage sludge and household compost to arable land: fate and effects of organic contaminants and impact on soil fertility. *Soil Tillage Res.* **72**, 139–152. (doi:10.1016/S0167-1987(03)00084-9)

Philips, B. & Harrison, P. 1999 Overview of the endocrine disrupters issue. In *Endocrine disrupting chemicals* (eds R. E. Hester & R. M. Harrison). Issues in environmental science and technology, vol. 12, pp. 1–26. Cambridge, UK: Royal Society of Chemistry.

Pipe, S. 2007 Ecotoxicological implications of bodycare products as diffuse pollutants in the environment—sources, pathways and significance. MSc thesis, Department of Civil and Environmental Engineering, Imperial College London.

Downloaded from rsta.royalsocietypublishing.org on August 26, 2013

Prats, D., Rodriguez M., Varo, P., Moreno, A., Ferrer, J., & Berna, J. L. 1999 Biodegradation of soap in anaerobic digesters and on sludge amended soils. *Water Res.* **33**, 1331. (doi:10.1016/S0043-1354(98)00199-7)

Prats, D., Lopez, C., Vallejo, D., Varo, P., & Leon, V. M. 2006 Effect of temperature on the biodegradation of linear alkylbenzene sulfonate and alcohol ethoxylate. *J. Surfact. Deterg.* **9**, 69–75. (doi:10.1016/S0043-1354(98)00199-7)

Rhind, S. M. 2004 Concentrations of endocrine disrupting compounds (EDC) in Scottish soils and herbage, and bioaccumulation in sheep. Final Report MLU/766/01, Macaulay Institute, Aberdeen.

Rimkus, G. G. 1999 Polycyclic musk fragrances in the aquatic environment. *Toxicol. Lett.* **111**, 37–56. (doi:10.1016/S0378-4274(99)00191-5)

Roberts, P., Roberts, J. P. & Jones, D. L. 2006 Behaviour of the endocrine disrupting chemical nonylphenol in soil: assessing the risk associated with spreading contaminated waste to land. *Soil Biol. Biochem.* **38**, 1812–1822. (doi:10.1016/j.soilbio.2005.12.006)

Ryan, J. A. 1993 Utilization of risk assessment in the development of limits for land application of municipal sewage sludge. In *Sewage sludge: land utilization and the environment* (eds C. E. Clapp, W. E. Larson & R. H. Dowdy), pp. 55–65. Madison, WI: Soil Science Society of America.

Rysz, M. & Alvarez, P. J. J. 2004 Amplification and attenuation of tetracycline resistance in soil bacteria: aquifer column experiments. *Water Res.* **38**, 3705–3712. (doi:10.1016/j.watres.2004.06.015)

Samsøe-Petersen, L., Winther-Nielsen, M. & Madsen, T. 2003 Fate and effects of triclosan. Environment Project No. 861, Danish Environmental Protection Agency.

Sauerbeck, D. R. & Leschber, R. 1992 German proposals for acceptable contents of inorganic and organic pollutants in sewage sludges and sludge-amended soils. In *Effects of organic contaminants in sewage sludge on soil fertility, plants and animals* (eds J. E. Hall, D. R. Sauerbeck & P. L'Hermite), pp. 3–13. Luxembourg: Commission of the European Communities.

Schmitzer J. L., Scheunert I. & Korte F. 1988 Fate of bis(2-ethylhexyl)[^{14}C] phthalate in laboratory and outdoor soil–plant systems. *J. Agric. Food Chem.* **36**, 210–215. (doi:10.1021/jf00079a053)

Schowanek, D., Carr, R., David, H., Douben, P., Hall, J., Kirchmann, H., Patria, L., Sequi, P., Smith S. & Webb, S. 2004 A risk-based methodology for deriving quality standards for organic contaminants in sewage sludge for use in agriculture—conceptual framework. *Regul. Toxicol. Pharmacol.* **40**, 227–251.

Schowanek, D., David, H., Francaviglia, R., Hall, J., Kirchmann, H., Krogh, P. H., Schraepen, N., Smith, S. & Wildemann, T. 2007 Probabilistic risk assessment for linear alkylbenzene sulfonate (LAS) in sewage sludge used on agricultural soil. *Regul. Toxicol. Pharmacol.* **49**, 245–259. (doi:10.1016/j.yrtph.2007.09.001)

Sengeløv, G., Agersø, Y., Halling-Sørensen, B., Baloda, S. B., Andersen, J. S. & Jensen, L. B. 2003 Bacterial antibiotic resistance levels in Danish farmland as a result of treatment with pig manure slurry. *Environ. Int.* **28**, 587–595. (doi:10.1016/S0160-4120(02)00084-3)

Shanker, R., Ramakrishna, C. & Seth, P. K. 1985 Degradation of some phthalic acid esters in soil. *Environ. Pollut. A* **39**, 1–7.

Shea, P. J., Weber, J. B. & Overcash, M. R. 1982 Uptake and phytotoxicity of di-*n*-butyl phthalate in corn (*Zea mays*). *Bull. Environ. Contam. Toxicol.* **29**, 153–158. (doi:10.1007/BF01606143)

Singer, H., Muller, S., Tixier, C. & Pillonel, L. 2002 Triclosan: occurrence and fate of a widely used biocide in the aquatic environment: field measurements in wastewater treatment plants, surface waters, and lake sediments. *Environ. Sci. Technol.* **36**, 4998–5004. (doi:10.1021/es025750i)

Sjöström, Å. E, Collins, C. D., Smith, S. R. & Shaw, G. 2008 Degradation and plant uptake of nonylphenol (NP) and nonylphenol-12-ethoxylate (NP12EO) in four contrasting agricultural soils. *Environ. Pollut.* **156**, 1284–1289. (doi:10.1016/j.envpol.2008.03.005)

Smith, S. R. 2000 Are controls on organic contaminants necessary to protect the environment when sewage sludge is used in agriculture? *Prog. Environ. Sci.* **2**, 129–146.

Smith, S. R. & Riddell-Black, D. 2007 Sources and impacts of past, current and future contamination of soil. Appendix 2: Organic contaminants. Final Report to DEFRA. See http://randd.defra.gov.uk/Document.aspx?Document=SP0547_7266_FRA.pdf.

Downloaded from rsta.royalsocietypublishing.org on August 26, 2013

SPT 1999 LAS risk assessment for sludge-amended soils. *Proc. SPT Workshop in Co-ordination with the Danish EPA, Copenhagen, Denmark, April 1999.*

Staples, C. A., Adams, W. J., Parkerton, T. F., & Adams, W. J. 1997 The environmental fate of phthalate esters: a literature review. *Chemosphere* **35**, 667–749. (doi:10.1016/S0045-6535(97)00195-1)

Stark, B. A. & Hall, J. E. 1992 Implications of sewage sludge application to pasture on the intake of contaminants by grazing animals. In *Effects of organic contaminants in sewage sludge on soil fertility, plants and animals* (eds J. E. Hall, D. R. Sauerbeck & P. L'Hermite), pp. 134–157. Luxembourg: Commission of the European Communities.

Stevens, J. L., Northcott, G. L., Stern, G. A., Tomy, G. T. & Jones, K. C. 2003 PAHs, PCBs, PCNs, organochlorine pesticides, synthetic musks, and polychlorinated *n*-alkanes in UK sewage sludge: survey results and implications. *Environ. Sci. Technol.* **37**, 462–467. (doi:10.1021/es020161y)

Sweetman, A. J., Rogers, H. R. & Crathorne, B. 1992 Monitoring of organic contaminants in sewage sludge with differing catchments and assessment of their potential for phytotoxic effects using a barley seedling bioassay. In *Effects of organic contaminants in sewage sludge on soil fertility, plants and animals* (eds J. E. Hall, D. R. Sauerbeck & P. L'Hermite), pp. 112–124. Luxembourg: Commission of the European Communities.

Tas, J. W., Balk, F., Ford, R. A. & van de Plassche, E. J. 1997 Environmental risk assessment of musk ketone and musk xylene in the Netherlands in accordance with the EU-TGD. *Chemosphere* **35**, 2973–3002. (doi:10.1016/S0045-6535(97)00261-0)

Ternes, T. 1998 Occurrence of drugs in German sewage treatment plants and rivers. *Water Res.* **32**, 3245–3260. (doi:10.1016/S0043-1354(98)00099-2)

Thiele-Bruhn, S. 2003 Pharmaceutical antibiotic compounds in soil—a review. *J. Plant Nutr. Soil Sci.* **166**, 145–167. (doi:10.1002/jpln.200390023)

UK SI (UK Statutory Instrument). 1989 The sludge (use in agriculture) regulations 1989. Statutory Instrument No. 1263. HMSO, London, UK.

US EPA (US Environmental Protection Agency). 1992*a* Technical support document for land application of sewage sludge, Volume I. Eastern Research Group, Lexington.

US EPA (US Environmental Protection Agency). 1992*b* Technical support document for land application of sewage sludge, Volume II, Appendices. Eastern Research Group, Lexington.

US EPA (US Environmental Protection Agency). 1992*c* Statistical support documentation for the 40 CFR, Part 503. Final standards for the use or disposal of sewage sludge. Volume I. Final Report, 11 November 1992. US EPA, Washington DC.

US EPA (US Environmental Protection Agency). 1993 Part 503—Standards for the use or disposal of sewage sludge. *Fed. Regist.* **58**, 9387–9404.

US EPA (US Environmental Protection Agency). 1999 Standards for the use or disposal of sewage sludge (Proposed Rules). *Fed. Regist.* **64**, 72 045–72 062. See http://www.epa.gov/fedrgstr/EPA-WATER/1999/December/Day-23/w33033.htm.

US EPA (US Environmental Protection Agency). 2003 Final action not to regulate dioxins in land-applied sewage sludge. EPA-822-F-03-007, October 2003. US EPA, Office of Water, Washington DC. See http://www.epa.gov/ost/biosolids/dioxinfs.html.

US FDA (US Food and Drug Administration). 2001 Safety assessment of di(2-ethylhexyl)phthalate (DEHP) released from PVC medical devices. Center for Devices and Radiological Health, US FDA, Rockville. See http://www.fda.gov/cdrh/ost/dehp-pvc.pdf.

Van Wezel, A. P., van Vlaardingen, P., Posthumus, R., Crommentuijn, G. H. & Sijm, D. T. H. M. 2000 Environmental risk limits for two phthalates, with special emphasis on endocrine disruptive properties. *Ecotoxicol. Environ. Safety* **46**, 305–321. (doi:10.1006/eesa.2000.1930)

Vikelsøe, J., Thomsen, M. & Carlsen, L. 2002 Phthalates and nonylphenols in profiles of differently dressed soils. *Sci. Total Environ.* **296**, 105–116. (doi:10.1016/S0048-9697(02)00063-3)

WEAO (Water Environment Association of Ontario). 2001 Fate and significance of selected contaminants in sewage biosolids applied to land through literature review and consultation with stakeholder groups. Final Report, WEAO, Aurora, Ontario, Canada.

Webber, M. D. & Goodin, J. D. 1992 Studies on the fate of organic contaminants in sludge treated soils. In *Effects of organic contaminants in sewage sludge on soil fertility, plants and animals*

Downloaded from rsta.royalsocietypublishing.org on August 26, 2013

(eds J. E. Hall, D. R. Sauerbeck & P. L'Hermite), pp. 54–69. Luxembourg: Commission of the European Communities.

Webber, M. D., Pietz, R. I., Granato, T. C. & Svoboda, M. L. 1994 Plant uptake of PCBs and other organic contaminants from sludge-treated coal refuse. *J. Environ. Qual.* **23**, 1019–1026.

Wild, S. R., Harrad, S. J. & Jones, K. C. 1994 The influence of sewage sludge applications to agricultural land on human exposure to polychlorinated dibenzo-*p*-dioxins (PCDDs) and -furans (PCDFs). *Environ. Pollut.* **83**, 357–369. (doi:10.1016/0269-7491(94)90158-9)

Wilson, S. C. & Jones, K. C. 1999 Volatile organic compound losses from sewage sludge-amended soils. *J. Environ. Qual.* **28**, 1145–1153.

Wilson, S. C., Burnett, V., Waterhouse, K. S. & Jones, K. C. 1994 Volatile organic compounds in digested United Kingdom sewage sludges. *Environ. Sci. Technol.* **28**, 259–266. (doi:10.1021/es00051a012)

Wilson, S. C., Duarte-Davidson, R. & Jones, K. C. 1996 Screening the environmental fate of organic contaminants in sewage sludges applied to agricultural soils: I. The potential for downward movement to groundwaters. *Sci. Total Environ.* **185**, 45–57. (doi:10.1016/0048-9697(95)05041-8)

Witte, W. 1998 Medical consequences of antibiotic use in agriculture. *Science* **279**, 996–997. (doi:10.1126/science.279.5353.996)

Yang, J.-J. & Metcalfe, C. D. 2006 Fate of synthetic musks in a domestic wastewater treatment plant and in an agricultural field amended with biosolids. *Sci. Total Environ.* **363**, 149–165. (doi:10.1016/j.scitotenv.2005.06.022)

Yin, R., Lin, X. G., Wang, S. G. & Zhang, H. Y. 2003 Effect of DBP/DEHP in vegetable planted soil on the quality of capsicum fruit. *Chemosphere* **50**, 801–805. (doi:10.1016/S0045-6535(02)00222-9)

Ying, G.-G. & Kookana, R. A. 2007 Triclosan in wastewaters and biosolids from Australian wastewater treatment plant. *Environ. Int.* **33**, 199–205. (doi:10.1016/j.envint.2006.09.008)

Young, W. F., Fawell, J. K. & Davis, R. D. 1998 Oestrogenic chemicals and their behaviour during sewage treatment. Report Ref. No. 98/TX/01/4, UKWIR, London.