

Background values in European soils and sewage sludges

Results of a JRC-coordinated study
on background values

*Edited by
B. M. GAWLIK and G. BIDOGLIO*



PART I
**Evaluation of the relevance
of organic micro-pollutants in sewage sludge**

R. Leschber

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The mission of the Institute for Environment and Sustainability is to provide scientific and technical support to the European Union's policies for protecting the environment and the EU Strategy for Sustainable Development.

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Abstract

Part 1 of this report gives an overview on relevant organic micro-pollutants in sewage sludges. Publications, results of eco-toxicological studies and national particularities for substance classes such as PCBs, PAHs, PCDD/Fs, PBDE, LAS, NP, etc. have been reviewed and critically analysed.

The report is intended as an input for discussion concerning the necessity to regulate organic micro-pollutants in the revision of the European Sludge Directive 86/278/EEC.

List of abbreviations

Throughout this report the following abbreviations and symbols are used.

ADI	actual daily intake	LAS	linear alkyl sulfonates
AOX	adsorbable organic halogenated compounds	LD	lethal dose
BCF	bioconcentration factor	LOAEL	lowest observed adverse effect level
bw	body weight	LOEC	lowest observed effect concentration
CAS	Chemical Abstracts Service	LOEL	lowest observed effect level
CEN	European Committee for Standardization	NOAEL	non observed adverse effect level
COST	European Co-operation in the field of Scientific and Technical Research	NOAL	non observed adverse level
DBP	dibutyl phthalate	NOEC	no observed effect concentration
DeBDE	decabromo diphenyl ether	NP	nonyl phenol
DEHP	di-(2-ethylhexyl) phthalate	NPEO	nonylphenol ethoxylates
DG	Directorate-General	NPiso	nonylphenol isomer mixture
DIDP	diisooctyl phthalate	OcBDE	octabromo diphenyl ether
DINP	diisononyl phthalate	PAH	polyaromatic hydrocarbons
dm	dry mass (dry matter)	PBDE	polybrominated diphenylethers
DT	degradation time	PCB	polychlorinated biphenyls
EC	effect concentration	PCDD/F	polychlorinated dibenzodioxins/furans
EINECS	European Inventory of Existing Commercial Chemical substances	PCP	pentachlorophenol
EN	European norm	PeBDE	pentabromo diphenyl ether
EU	European Union	PEC	predicted environmental concentration
IES	Institute for Environment and Sustainability	PNEC	predicted non effect environmental concentration
ISO	International Standardization Organization	PVC	polyvinyl chloride
JRC	Joint Research Centre	STP	sewage treatment plant
K_d	adsorption constant	TE	toxicity equivalent
K_{OC}	organic carbon sorption coefficient	TeBDE	tetrabromo diphenyl ether
K_{OW}	octanol water partition coefficient	TGD	Technical Guidance Document

Foreword by the author

The following report may contribute to the discussion about the revision of the EU Directive 86/278/EEC for the use of sewage sludge in agriculture or its extension towards a more general directive covering other biowastes.

Due to the relative short time given for preparation, the report does not cover a lot of data and cannot cite all publications, reports and conference proceedings that have been published during the past decade on the argument. On the contrary, only some valuable examples of these publications have been evaluated, and reported data on occurrence, behaviour, and fate of organic micropollutants are discussed in the light of own experience, which had started with EU research programs COST 68/681 and were continued by advisory activities for the German government when preparing the sewage sludge ordinances.

In the last years the good scientific contacts with national and international experts have been pursued. Together with the experience from present CEN and ISO work in various fields this may help to make proposals of this report valuable.

R. Leschber

1 Common introduction to the reports Part I, II and III

The European Commission has realized that since the “*Sewage Sludge Directive*” 1986 (EEC) was set into force, a rapid development in the field of the agricultural use of sewage sludge has taken place. On the one hand, the Directive confirmed that those European countries, which had set up legal regulations earlier, were on the right way and, on the other hand, it gave the frame for recycling secondary raw materials with a remarkable content of nutrients and soil improving properties for all EU countries.

Although the Directive set up only guide/limit values for heavy metals, the question whether there might be also harmful effects caused by organic micropollutants has been discussed from this time until now, being initiated and promoted by the COST 681 Action of the European Commission (Quaghebeur, D. et al (Eds.) 1989, Hall, J.E. *et al.* (Eds.), 1992) and follow-up activities. The results are revisions of existing national regulations in some countries thus setting up more stringent limit values for heavy metals and introducing new limitations for some organic micropollutants. However, there was no uniform way in handling these problems. Subsequently, in autumn 1999 the European Commission started discussions with governmental representatives of the EU countries as well as with experts/delegates from European economic, technical and scientific organizations. This led to the so-called “*3rd Draft-Working Document on Sludge*” of April 2000, in which general aspects of a long-time improvement of the agricultural use of sludges were laid down.

The document covering proposals for future action contains several Annexes, of which Annex IV includes a table referring to limit values for concentrations of organic compounds and dioxins in sludge for use on land. Since the publication of the 3rd Draft these data have been subject of intensive discussions in the EU and at national conferences (e.g. DG Environment and UKWIR, 2001 and KTBL, Darmstadt, 2002).

The following series of reports give some basic information about selected organic micropollutants in sludges as well as about the establishment of background values for some trace elements in soils, susceptible to receive sewage sludge.

2 General considerations concerning organic pollutants in sewage sludge

As pointed out in the introductory remarks a number of European countries set up sewage sludge ordinances or similar national agreements containing restrictions for organic micropollutants in sewage sludges following the German example where a respective ordinance had been set into force in 1992 (BMU). These rules differ in type of pollutants and limits for dry mass concentrations in some cases. The reasons for that may be found in differences in:

- soil conditions,
- groundwater protection targets,
- industrial and trade structures,
- agricultural production,

- results from sludge and soil examinations programmes,
- national demands for environmental protection and hygiene, and
- political and economical pressure

Looking at these differences, which are in some cases difficult to understand, it seems that the limits set up are not based necessarily on toxicological and ecotoxicological studies, and may be a result of careful precautionary considerations. This would have been reasonable if the agricultural use of sludges had led to environmental problems like soil damages, phytotoxic effects, forage deterioration. However, in fact there are numerous results of studies indicating that sludge application has improved agricultural yields and soil conditions.

On the other hand, it cannot be denied, that the fixation of limits has resulted in remarkable improvements of sludge quality as can be seen in the development of heavy metal concentrations during the last decades and the reduction of contents of organohalogen compounds in German sludges during the last ten years. This was a result of restriction measures and control programs for polluted waste waters. Point sources had been detected and obstructed. In some cases agreements between the government and industry led to a ban of undesired chemicals or at least to considerable reductions of the pollution load (e.g. nonylphenol and -ethoxylates, PCB, dioxins).

Before discussing organic micropollutants in detail and making evaluations, some aspects should be outlined. Firstly, with view of the enlargement of the EU, it will be necessary to set up flexible regulations which take into account the economical differences between the EU-15 and their new members. This could mean that for some basic parameters limits may be fixed, which could be regularly controlled with extensive costs.

Moreover, it may be necessary to set up a catalogue of parameters of interest which must be applied for basic examination programs, for setting up a register for a catchment area or in cases of a sudden increase of pollutant concentrations. This might lead to an extended control program, supervised by local authorities, which may be reduced when remedial measures have taken place.

The following document gives some basic information about selected organic micropollutants, which according to the opinion of the author are relevant for further considerations. In the light of suggestions made earlier and together with benefit-risk consultations it leads to proposals for future handling the problem of these substances in sludges and other secondary raw materials for agricultural use, possibly by setting up limits in certain cases.

Due to the fact that the knowledge (risk assessment, administrative handling) about the well known compounds like dioxine/furane, PCB and AOX in the scientific community is well understood, it was felt that it is not necessary to discuss these compounds in detail. Therefore, only an overview is given. For the more or less interesting compounds like PAH, LAS, nonylphenol/nonyl phenoethoxylates, phthalates and flame retardants the relevant reports and scientific statements were evaluated and respected in the report.

It has to be stressed that for some of compound classes discussed, a risk assessment is still not possible due to lack of information and data. However, risk assessment is only one aspect when assessing the relevance of a given compound class. The report is intended as first starting point for further discussion. Proposed mechanisms of regulations, e.g. guide/limit values are to be seen as a pragmatic approach.

Gathered information is presented without final conclusions. Conclusions and recommendations will be treated in Part III of this report.

3 Persistent halogenated contaminants

A number of waste substances discharged through the sewers tend to accumulate in sewage sludges. From these, the vast group of halogenated contaminants is usually the most considered one. Although in the past, heavy metals were the main objects of control and restriction measures when using sludge in agriculture, there was also a great interest in data about occurrence, behaviour and fate of organics, especially organohalogen compounds in the environment.

Besides the necessity to have information about substance groups, which had been characterized as highly toxic like PCDD/Fs or PCBs, there was a demand for having information about the general input of organohalogenes into soil via the agricultural utilization of sewage sludges. Thus, in the early Nineties, the German government for instance set limits for AOX as a cumulative parameter for halogenated substances. This was done in occasion of a revision of the first ordinance for the agricultural use of sludge, as a consequence of a comprehensive study about the presence of organohalogenes in sludges (Leschber *et al.*, 1990).

3.1 AOX

3.1.1 Occurrence and substantial characteristics

With AOX (adsorbable organic halogenated compounds), a cumulative parameter, the overwhelming part of organohalogenes compounds can be estimated. The principal sources of these substances are solvents, solvent mixtures, oil and grease, resins, rubber, hydraulic oils, lubricants, plasticizers, disinfectants, wood protectives and some pesticides.

Besides professional and industrial origin, these substances also find their way into sewage and sludge from household applications as cleaning agents, toilet flush additives and the like. In general, only a small number of AOX-bearing substances can be characterized in detail by other more sophisticated analytical procedures. The heterogeneous mixture does not allow to set-up relations between AOX-content and ecotoxicological effects.

3.1.2 Occurrence in sewage sludge

Leschber *et al.* (1990) reported the analyses of 170 samples of sewage sludges. The programme covered a wide variation in the size of sewage treatment plants (STP) and reflected all kinds of public municipal and industrial influences on the sewage sludge composition. There was a basic level of 60 – 70 mg AOX/kg dm and the main percentage of values amounted to below 400 mg/kg dm with a Gaussian shape of value distribution. It was concluded that municipal sludges without a remarkable industrial influence represented an average AOX level of 200 – 400 mg/kg dm.

In the last years, findings from investigation studies of similar size in Austria and Germany showed that there had been a decline of AOX concentration down to a range of 150 – 350 mg/kg dm (Jäger, 1995; Mertens, 1999; Bursch *et al.*, 2001). This

demonstrated that there had been the same development in reducing the pollution load as for heavy metals one decade earlier after the first sewage regulation came into force. Hence, AOX-monitoring may be used as one part of future European pollution control measures to prevent unwanted chemicals from entering into environmental cycles via waste water and sewage sludges.

A tool for the detection of AOX sources in communities or catchment areas is an analytical procedure already standardized in some countries. In a close cooperation of experts organized in CEN a European AOX standard for sludge and the like might be finalized during 2005-2006. It will be a method which is inexpensive and easy to handle while allowing an adequate frequency of examinations.

3.2 Polychlorinated biphenyls (PCB)

3.2.1 Occurrence and substantial characteristics

PCB cover a group of 209 single congeners, which had been produced commercially since 1929 as mixtures with different combinations of the single low to high chlorinated substances (Aroclor, Clophen, Phenoclor). PCB show a high thermal and chemical stability, low inflammability and good insulating properties, so that they were used as cooling agents, hydraulic liquids, for impregnation and as flame retardants. Moreover, they were found as plasticizers and additives in varnishes, lacquers and papers.

Due to the persistency against biodegradation and the toxicity many countries set up legal restrictions for PCB use (e.g. Germany 1978), stopped their production (e.g. Germany 1983) and inhibited application (e.g. Germany 1989, Austria 1993). This led to a drastic reduction of environmental contamination in various fields, so that PCB today are generally found in wastewater, sewage sludge as well as in atmospheric fallout of industrial regions in very low concentrations. Point sources today may be improper handling of old electrical equipment or production works disposal.

3.2.2 Environmental behaviour

PCB may be transported as air pollutants over wide distances and thus act as non-point pollutants. They are hardly biodegradable but there are differences due to the degree of chlorination. In soil where PCB are mainly bound to humic substances they are quite immobile with half-life times between 8 days and > 1 year (Bursch *et al.*, 2001). Data about PCB transfer into plants are less interesting due to the actual concentrations in soil, ranging from 0,02 to 0,09 mg/kg dm with a median from 0,023 to 0,09 (LfU, 2003). Earlier indications that root vegetables adsorb PCB at their surfaces have not been reported during the past decade.

The following table gives an exemplary overview about PCB concentrations in sewage sludges of some European countries during the last 15 years. The data confirms the decrease of concentrations although the levels in general are very low.

Table 1 – PCB concentrations in sewage sludges from European countries (mg/kg dm)

Country	Year of examination	Number of samples	Concentration range	Median	Reference
Germany	1988/89	—	< 0,1	—	Leschber (1997)
	1991-96		0,01 – 0,04		
Sweden	1993	23	< 0,001 – 0,232	— 0,113	Nat. Swedish Envir. Prot. Board (1995)
Norway	1996/97	36	0,017-0,1	0,04	Pausrud <i>et al.</i> (1998)
Austria	1994 – 2001	70	0,027 – 0,055	—	Bursch <i>et al.</i> (2001)
Great Britain	2002	14	0,044 – 0,18	0,071	Stevens <i>et al.</i> (2003)

3.2.3 Toxicological considerations

The main path on which PCB may enter the human body is the oral intake of fatty food. In laboratory experiments with rats and mice an acute wasting syndrome and liver damage had been observed at high dosages, chronic effects were chlorine acne and liver cancer. LD50 values are assumed to be at < 1000 mg/kg bw. The PCB intake by food is estimated in industrialized countries at 0,1 mg/kg bw and day, but there are no indications for a relation between PCB ingestion and cancer mortality by man (Kimbrough, 1995; Safe, 1994).

3.3 Polychlorinated dibenzodioxins and –furans (PCDD/F)

3.3.1 Occurrence and substantial characteristics

The group dibenzo-p-dioxins (PCDD) comprises 75, the group of furans (PCDF) 135 congeners and is therefore as extended as the PCB group. In contrast to the latter, PCDD/F have never been produced commercially. Their environmental occurrence to a large extent is related to the application of pentachlorophenol (PCP), which was contaminated by PCDD, and atmospheric fallout which was contaminated by exhaust gases containing PCDD being formed during various processes. Respective studies have shown that a certain chlorine concentration in the fuel, the presence of copper as catalyst and a defined temperature range are responsible for PCDD formation in this way, besides incineration of chlorinated solvents. A great number of research projects done after the Seveso accident in 1986 have contributed to a good knowledge about these pollutants.

3.3.2 Environmental behaviour

Similar to PCB the toxicity of PCDD/F congeners varies quite important with the degree of chlorination and the position of the chlorine atoms in the molecule. This is the reason for an agreement not to sum up the very low concentrations of these pollutants but to count the congeners in toxicity equivalence. During sewage sludge treatment there is no remarkable biodegradation because of short residence times but PCDD/F will be nearly completely adsorbed at sewage sludge particles. Due to restrictive measures in the whole field of chlorinated compounds a remarkable decrease in dioxins/furans content in sewage sludge in the past decade has taken place. It is estimated that these substances have half-

life times of some years. There are no indications that they migrate from soil into plants. Measured concentrations in plants merely resulted from atmospheric pollution.

The following table gives information about the dioxins/furans concentrations in sewage sludge of some European countries in the past years.

Table 2 – PCDD/F concentrations in sewage sludges from European countries (ng TE/kg dm)

Country	Year of examination	Number of samples	Concentration range	Median	Reference
London UK	1960	div.	—	166	Evans (1999)
Germany	1988/89	div.	< 50	—	Leschber (1997)
Sweden	1989-91	14	5,7 – 115	20,5	Nat. Swedish Envir. Prot. Board (1992)
Germany	1991-96	div.	15 – 45	—	Leschber (1997)
Norway	1996/97	36	3 –69	6,26	Paulsrud (1998)
London UK	1998	div.	—	4,2	Evans (1999)

A Germany-wide monitoring programme of the Laender with more than 180 results of analyses of sewage sludge resulted in a range of 0,2 – 128 ng TE/kg dm where all median values lay between 7 and 19 and the 90-percentile was < 88.

3.3.3 Toxicological considerations

Like for PCB the oral intake of food is the main path how PCDD/F may enter the human body. The overall value of the daily load was estimated with 0,7 – 1,5 ng TE/kg · d (UBA-Berlin, 2000). The toxic effects of all 210 congeners are highly different. Related to the most toxic 2,3,7,8 tetrachloro-dibenzodioxin (toxic equivalent =1) the other congeners have TE factors of 0,001 – 0,5. Toxic effects on man are similar to those of PCB on humans: chlorine acne, liver, spleen, kidney damage as well as effects upon respiratory and nervous systems. Effects which have been observed in experiments with animals could not be confirmed in all cases and in the extent for humans. A possible carcinogenic effect is discussed but due to the present exposition of the normal population it is hardly difficult to state an elevated risk from PCDD/F (Bursch *et al.*, 2001).

3.4 Polybrominated diphenylethers (PBDE)

3.4.1 Occurrence and substantial characteristics

Flame-retardants are a wide group of compounds containing halogens for protecting fire. When discussing flame-retardants the polybrominated diphenylethers (PBDE) are mainly meant. In general PBDE comprise 209 different brominated diphenylether congeners. The commercial flame-retardants are actually a mixture of only three mayor products called octa-, deca- and penta-BDE. They are used in electrical and electronically devices, furniture, textiles, colours, cars, airplanes, in polymers (polyurethane foam), resins, coatings etc. The following congeners are of interest:

- Tetrabromo diphenyl ether (TeBDE, CAS No 5435-43-1), C₁₂H₅Br₄O
- Pentabromo diphenyl ether (PeBDE, CAS No 32534-81-9) C₁₂H₅Br₅O
- Octabromo diphenyl ether (OcBDE, CAS No. 32536-52-0) C₁₂H₂Br₈O
- Decabromo diphenyl ether (DeBDE, CAS No. 1163-19-5) C₁₂H₅Br₁₀O
- Hexabromodiphenyl ether (HxBDE, CAS No. 68631-40-2) C₁₂H₅Br₄O

The world wide use of PBDE had a volume of about 70000 t in 1999 (Renner, 2000), of which 50 % was used in the USA (Hale *et al.*, 2001). Thereof the decabrominated compounds cover nearly 80 % of the total and the penta- and octa-Derivates nearly 12 and 6 % (Darnerud, 2003). In Europe 7 600 t/a Deca-BDE, 610 t/a Octa-BDE and 150 t/a Penta-BDE (BSEF 2002) were used in 2001. PBDE are resistant against acids, bases, heat, light, oxidation and reduction reactions. In case of burning PeBDE were precursors of polybrominated dioxins and furans. The trade of PeBDE and OcBDE was banned by the EU.

The main source of PBDE in the environment comes from the wide range of commercial products treated with these fire-retardants. Although specific data are missing, incineration of municipal waste is thought to be an important route of release of PBDE into the environment. No study on leaching of PBDE from landfills is available, but the leaching of PBDE from the commercial products may be an obvious, important long-term pathway of contamination. It appears that the primary source of PBDE environmental contamination is discarded furniture. When discarded PBDE-treated furniture is exposed to environmental stressors (sunlight, wind, soil, rain, and extreme temperature), the furniture material starts breaking into small pieces and then into small particles, which then become part of the soil and of air. Subsequently, these pieces and particles may be washed out, or leached out, as a component of surface water.

In general the higher brominated PBDE have a low vapor pressure and are not volatile. More volatile are the lower brominated like TeBDE (de Wit, 2002). Air concentrations of PBDE vary between 1 – 10 pg/m³, near polyurethane factories concentrations above >100 pg/m³ were found.

3.4.2 Environmental behaviour

3.4.2.1 Water path

Information about PBDE in water is very rare. Due to the low water solubility of the PBDE they are mostly found in the sediments of the respective aquatic environments. The levels of TeBDE measured in surface water near STP in Baden-Württemberg (Germany) vary from 0,11 to 0,71 ng/l (Kuch *et al.*, 2001). In surface water of Lake Ontario 4 to 13 pg/l were detected. Kuch *et al.* (2001) found in sewage effluents TeBDE and PeBDE in the range of 1 ng/l. In sediments nearby 0,3 to 27,7 µg/kg dm TeBDE and 0,3 to 4,5 µg/kg dm PeBDE were found. In a leachate of a car part removal centre 0,3 ng/l TeBDE (BDE 47) and two PeBDE (BDE-99 and -100) were analysed. Industrial and urban effluents are significant sources of PBDE for surface water and sediments (ATSDR, 2002). The sediment contamination was increased near a polyurethane foam facility (Hale *et al.*, 2002). In freshwater sediments from Denmark the sum of four PBDE congeners

(BDE-47, -99, -100 and -209) ranged from 0,07 to 10,6 $\mu\text{g}/\text{kg dm}$ (Christensen & Platz, 2001).

Alchin *et al.* (1999) analysed the concentration of PBDE in sediment from rivers and estuaries in the UK. The highest concentration of PeBDE in Tees's estuary was 898 $\text{mg}/\text{kg dm}$, in river Skerne 1405 $\mu\text{g}/\text{kg dm}$ OcbBDE and 3190 $\mu\text{g}/\text{kg dm}$ OcbBDE. In heavily polluted sediments 10 $\text{mg}/\text{kg dm}$ were found. A normal contamination level lies between between 5 –30 $\mu\text{g}/\text{kg dm}$. Because of its stability in environment PBDE and the fact that PBDE had been found in remote areas indicating possible long-range transport (de Boer, 2000) they were classified as potential organic pollutants. This fact is covered by a lot of measurements of PBDEs in arctic flounders, dolphins and sperm whales and shows the global distribution of these compounds.

3.4.2.2 Sewage sludge

The contamination of sewage sludge seems to depend on the size of the treatment plants. In bigger STP higher contamination levels could be found (Wenzel *et al.*, 2003). DeBDE is only found in STP of large cities. The levels of the PBDE from tribrominated BDE to HxBDE in sewage sludge from 13 wastewater treatment plants in Germany were reported. The measured levels per kg dm were 0.1-1 mg triBDE, 0,2-7,5 mg tetra-BDE, 0,2-7,5 PeBDE, and 0-1,2 mg HxBDE (Hagemaijer *et al.*, 1992). In total the concentration of the four PBDE was <17,2 $\text{mg}/\text{kg dm}$. In 20 different sewage sludges samples from the year 2000 PeBDE contents vary between 6 – 20 $\mu\text{g}/\text{kg dm}$ (Litz, 2002). DeBDE were found in maximum of 200 $\mu\text{g}/\text{kg dm}$, but usually in a range of 5 –20 $\mu\text{g}/\text{kg dm}$ (Prösch *et al.*, 2000).

3.4.2.3 Soils

In soils untreated with sewage sludge background concentrations of 0,03 and 0,19 $\mu\text{g}/\text{kg dm}$ PBDE were measured (Matschenko *et al.*, 2002). Dreher *et al.* (2003) investigated some agricultural areas some of them treated with sewage sludge and found no traces above the detection limit of 10 $\mu\text{g}/\text{kg dm}$. After application of sewage sludge of 20 and 60 tons/ha an increase of PBDE to 0,430 and 0,930 $\mu\text{g}/\text{kg dm}$ could be observed (Matschenko *et al.*, 2002). Especially the TeBDE and PeBDE were dominant. Hale *et al.* (2000) found in soil near a foam production building BDE-47, -99 and -100 a sum of 76 $\mu\text{g}/\text{kg dm}$.

3.4.2.4 Adsorption and mobility

Adsorption of PBDE on soils is very strong (Hardy *et al.*, 2000). PeBDE is adsorbed with a K_d -value of 86 (sandy soil, low organic matter) to 685 in a clay rich soil and to 45 000 in a humic rich soil (Litz, 2002). The K_{OC} -value lies near 125 000 in humic rich soil. Sediment-water partition coefficients (k_p) for tetra-, penta-, and hexa-BDE are 28 300; 49 200 and 62 700. On the basis of the K_{OW} values $\log K_{OC}$ values were estimated (Lyman *et al.*, 1990) for tetra- (4,57 – 4,73), penta- (4,89 – 5,17) octa- (5,92 – 6,22) and deca-BDE (6,80).

Investigation of de Boer *et al.* (2000b) implies that adsorption on suspended particles compared to sediment is higher (double or threefold) assuming a better availability of surfaces for adsorption.

The mobility of PBDE in soil is low to the high adsorption. In a small laboratory lysimeter PeBDE moved only in coarse pores at the beginning of a leaching test in very small quantities through the column (Litz, 2002). After an adsorption phase no PeBDE were transported by the leachate. Addition of LAS enhances the mobility of PeBDE slightly. In the presence of solvents a faster movement in leachate of landfills could be assumed.

Table 3 – PBDE concentration in sewage sludge in different countries ($\mu\text{g}/\text{kg dm}$)

Country	Compound	Number of Samples	Range of concentration	Median	Reference
Germany	PeBDE	20	6 - 20	9,7 (mean)	Litz (2002)
	PeBDE	8	77 - 338		Kuch <i>et al.</i> (2001)
Sweden	PBDE	50	76 - 195	130 (mean)	Nylund <i>et al.</i> (1992)
	PeBDE	10	4 - 129	62	Hellström (2000)
	TeBDE		39 - 91		Sellström <i>et al.</i> (1999)
	PeBDE		48 - 129		De Wit (2000)
	HxBDE		11 - 28		
	DeBDE				
	PeBDE	116	<0,9 - 334		Ödberg <i>et al.</i> (2002)
	HxBDE	116	<0,3 - 5		
	DeBDE	116	<0,6 - 390		
Denmark	PeBDE	2	48 - 120		Andersson (2002)
	DeBDE	2	140 - 350		
USA	PeBDE	11	1100 - 2290		Pardini <i>et al.</i> (2001)
	DeBDE	11	85 - 4890		

3.4.2.5 Degradation

Degradation of PBDE is very slow. Photolysis appears to be the dominant process. The photolysis half-lives for DeBDE in sediment were 53 and 81 hours for UV and sunlight exposure. Despite DeBDE showing the widest application, the majority of the PBDE found in the environment are the lower brominated compounds. This can be explained by debromination reactions where the higher compounds degrade to tetra, penta and hexa congeners (Rahman *et al.*, 2001). Degradation studies under aerobic and anaerobic conditions in the laboratory show a faster degradation (Litz, 2002). After 3 weeks 50 % of the applied substance was eliminated, after 8 weeks 25 % of de PEBDE could be

detected. No differences were found between aerobic and anaerobic conditions. The fast degradation kinetics could be a result of developing of bound residues. In contrast, de Wit (2000) reported during 5 month no degradation of DeBDE under anaerobic conditions.

3.4.2.6 PEC and PNEC values

According to the Technical Guidance Document (TGD) a PNEC soil of $\geq 0,38$ mg/kg dm respectively $\geq 23,8$ mg/kg dm for PeBDE respectively OcbDE using the *Zea mays* data as the basis is given in RAR (2000b, RAR 2000a). In Wenzel *et al.* (2003) this procedure was criticised due to the weak data basis of PeBDE and therefore a PNEC of $\geq 1,25$ mg/kg dm proposed. It is recommended that no negative effect to plants and earthworms should be possible by usual soil concentrations given by normal sewage sludge treatment. For HxBDE in RAR (2000 a) a PNEC soil of $\geq 1,3$ mg/kg dm was calculated. Using this data a PNEC soil for DeBDE of ≥ 98 mg/kg dm were proposed in RAR (2000 b). No accumulation of DeBDE in earthworms could be detected. This is in agreement with the evaluation of Hellström (2000).

3.4.3 Toxicological considerations

PBDE is only taken up by plants in low concentrations. For BDE-47, BDE-99 and -100 a transfer factor of 0,13, 0,06 and 0,07 was reported for sugar beets using the EUSES-model.

An accumulation depending on the amount of halogens in the molecule passing the food chain had to be considered (Kruse *et al.*, 2001). Especially in fish a higher contamination could be observed (Rahman *et al.*, 2001). Accumulation takes place in fat tissue and breast milk. The log K_{OW} of the penta- and decabrominated congener is 7,42 and 11.15.

PBDE may be ingested by insects, as well. In this way, PBDE become a part of the food chain, and then bioaccumulation in humans will be possible.

In an experiment with frogs, which had been housed with PeBDE-treated foam as dry substrate and fed with crickets, accumulation of 10,1 mg/kg dm was found. The crickets contained 14,4 mg/kg dm of the flame retardant (Hale *et al.*, 2002).

Bioconcentration factors from Baltic blue mussels were found to be 1 300 00 for BDE-47, 1 400 000 for BDE-99 and 220 000 for BDE-153 (Gustafsson *et al.*, 1999). High bioaccumulation could also be found for fish, marine mammals and human breast milk.

In a EU risk assessment report (RAR, 2000 b) PeBDE, OCBDE and DeBDE shows the following NOEC concentrations (table 4).

An extent review about the effects of PBDE to mammals and humans was given by De Wit (2002). Guinea pigs, chicken and monkeys were sensitive, rats mice cattle sheep and swine had intermediate sensitivity (Rahman *et al.*, 2001)).

Some congener may induce cancer on mammalians. Some effects to the hormone systems and to the neuronal development to mice and rats at higher concentrations were described by Darnerud (2003). PeBDE seemed to be the toxiest PBDE. OcbDE showed embryo toxicity and teratogenic effects for rabbits and rats ≥ 2 mg/kg dm. For OcbDE no data on carcinogenicity were available. Also no mutagenicity of OcbDE was observed. DeBDE caused negative effects on liver, kidney and thyroid ≥ 80 mg/kg dm. In very high

concentrations DeBDE cancer was caused. For humans such a classification was not possible (Darnerud, 2003).

In a risk assessment for the oral consumption for humans US-EPA reported LOEL and ADI values (Hellström, 2000) and Hellström (2000) proposed in his evaluation for small children limit values for soil considering oral path (vegetables, meat, soil uptake etc. see table 5).

Table 4 – No observed effect concentrations (NOEC) (mg/kg dm) of different species for different PBDE

<i>Organisms</i>	<i>Test</i>	<i>Concentration range</i>	<i>NOEC</i>
PeBDE			
Soil micro organisms	Nitrification	0,01 – 1	> 1
Plants:			
Zea mays			16
Allium cepa			> 1000
Lolium perenne	Plant growth test after OECD 208	62,5 – 1000	> 1000
Cucumis sativa			> 1000
Glycine max.			> 1000
Lycopersicum escu.			125
Earth worm Eisenia fedita	OECD 207 mortality	3,1 – 500	> 500
OcBDE			
Plants:			
Zea mays			> 1190
Allium cepa			> 1190
Lolium perenne	Plant growth test after OECD 208	94 – 1500	> 1190
Cucumis sativa			> 1190
Glycine max.			> 1190
Lycopersicum escu.			> 1190
Earth worm Eisenia fedita	OECD 207 mortality	94 – 1500	> 1470
DeBDE			
Plants:			
Zea mays			> 5349
Allium cepa			> 5349
Lolium perenne	Plant growth test after OECD 208	292 – 5349	> 5349
Cucumis sativa			> 5349
Glycine max.			> 5349
Lycopersicum escu.			> 5349
Earth worm	OECD 207	320 - 4910	> 4910

<i>Organisms</i>	<i>Test</i>	<i>Concentration range</i>	<i>NOEC</i>
Eisenia fetida	mortality		

Table 5 - Lowest observed effect level (LOEL), actual daily intake (ADI) and soil limit values of different PBDE

<i>Compound</i>	<i>LOEL mg/kg dm/day</i>	<i>ADI mg/kg dm/day</i>	<i>Soil limit values mg/kg dm</i>
PeBDE	1	0,002	108
OcBDE	2	0,003	
DeBDE	100	0,1	1000

Due to their structures, effects on the endocrine system have been of particular concern (Legler and Brouwer, 2003). The effects seem to be 10 to 6 fold lower comparing to 17 β -estradiol.

4 Other organic contaminants

4.1 LAS

4.1.1 Occurrence and substantial characteristics

Linear alkyl benzene sulphonates (LAS) are anionic surfactants. LAS is a mixture of closely related isomers and homologues containing an aromatic ring sulphonated at the para-position and attached to a linear alkyl chain. The chemical formula of LAS is C₁₀₋₁₃H₂₁₋₂₇C₆H₄SO₃Na. The CAS No. of the linear alkyl benzene sulphonates (C₁₀–C₁₃ alkyl derivates) is basically 68411-30-3 and the EINEC No. 270-115-0. The commercial LAS mixture contains more than 20 individual components. In 2000 2 million tons of LAS were produced worldwide, the European part being 400.000 tons. 80 % was used for household purposes, 20 % in industry.

4.1.2 Environmental behaviour

4.1.2.1 Water path

Because of its broad application in households and industry LAS can be classified as a relevant compound in sewage sludge (UMK-AG, 2000). Several monitoring studies in Europe were carried out (Cavalli *et al.*, 1993; Schöberl *et al.*, 1994; Matthijs *et al.*, 1999; Hold *et al.*, 2000). LAS levels in raw sewage ranged from 1 – 15 mg/l, in effluents of sewage treatment plants (STP) 9 – 140 μ g/l (Feijtel *et al.*, 1995b; Matthijs *et al.*, 1999). In river waters receiving effluents from the STP LAS concentrations were 31 μ g/l at 4,8 km from the STP outfall. In sediments below sewage outfall Cavalli *et al.* (2000) found 0,5 – 5,3 mg/kg dm with a mean of 2,9 mg/kg dm.

4.1.2.2 Sewage sludge

In sewage sludges in Europe the LAS concentration lies between <1 g/kg dm and 30 g/kg dm. In a comprehensive study in North Rhine Westphalia in Germany more than 150 different STP sludges were analysed for LAS (Stock & Friedrich 2002). They found a correlation between the size of the STP and the level of LAS. In bigger STPs the LAS level increased up to 6 g/kg dm. An explanation of these results could be that the extended aerobic treatment of sludge is common in smaller treatment plants.

Table 6 – Recent LAS levels in European sewage sludge (mg/kg dm)

Country	Sewage sludge treatment	Number of samples	Mean or range of concentration	Reference
Denmark	Sewage sludge (stored)			Carlsen <i>et al.</i> (2002)
	sample depth		16,5	
	cm	0-10	865	
	cm	40-50		
Germany	Aerobic Treatment	5	3,16	Schaecke and Kape (2003)
Germany	Aerobic Treatment	156	1723 4000 (90Perzt.)	Fragemann (2003)
Norway	Aerobic Treatment	36	< 1 – 424	Paulsrud <i>et al.</i> (2000)
Great Britain	Aerobic Treatment	10	182 - 432	Jones and Northcott (2000)
Denmark	Aerobic Treatment	600	670	Brink (1999)
Italy	Aerobic Treatment	1	11500-14000	Jones and Northcott (2000)
Spain	Aerobic Treatment	3	12100-17800	Jones and Northcott (2000)
Switzerland	Aerobic Treatment	10	2900-11900	Jones and Northcott (2000)

LAS concentration of anaerobically treated sludges is generally higher than of aerobically treated sludges. The LAS concentration is influenced by the content in the raw sewage, the treatment process (aerobic, anaerobic), the water hardness, the age of the sludge after storage etc. Composting sludge leads to a decrease of LAS concentration (Hera, 2002; Prats, 2000b).

4.1.2.3 Soils

In untreated soils the LAS content is normally less than 0,2 mg/kg dm . Although sewage sludge is the main source for LAS in soils, minor LAS concentrations in soils not treated with sludge may originate from cow manure and fertilizer application (Carlsen *et al.*, 2002). In fields not recently treated with sludge, LAS levels were general less than 1 mg/kg dm.(Waters *et al.*, 1989). But also in soils having a known history of sludge amendment after prevailing agricultural rules LAS contamination of the soils was found to be less than 1 mg/kg dm (Carlsen *et al.*, 2002).

Holt *et al.* (1989) reported that higher application rates (>5 ton/ha·y) had increased the LAS concentration in soil only at the beginning of the field test (16 – 66 mg/kg dm), during the test period the values had decreased < 1 to 20 mg/kg dm. Comparable results were reviewed by Mortensen *et al.* (2001).

Carlsen *et al.* (2002) found a slight increase of LAS concentration in untreated meadows of 0,45 mg/kg dm from 0-10 cm depth to 0,98 mg/kg dm in 40 – 50 cm depth. Also surface soils from eco farming land were contaminated in the same range.

In sewage sludge treated soils in 0-10 cm depth 1,12 mg/kg dm LAS could be found, in highly amended soils LAS contamination raise up to 11,23 mg/kg dm in 0-10 cm depth. In the depth of 10 to 50 cm only a slow decrease could be observed. In contrast to this result an investigation in Germany showed another picture (Dreher *et al.*, 2003). At 14 sites, LAS contents above the recovery limit of 0,1 mg/kg dm be could only found at one site (after sewage sludge application of 85 tons during 17 years) with 1,1 mg/kg dm LAS.

4.1.2.4 Adsorption

LAS will be readily adsorbed in soils, sediments and sewage sludge. Normally LAS is present in soils as anionic organic compound and can be adsorbed by protonation of the mineral surface, hydrogen bonds and hydrophobic binding. Because of its negative charge a special attraction to organic substances and a less strong binding to clay minerals may occur. A special relation does exist to sesquioxides and hydroxides in the soil. Adsorption constants after FREUNDLICH vary between 1,6 and 11,2, depending on the organic matter content (Litz *et al.*, 1987). In sediments a higher adsorption could be observed (Hand and Williams, 1987). K_{OC} -values vary between 100 and nearly 3000. For soils a typical K_{OC} -value should be assumed of 300 – 500.

Desorption of LAS is possible. In desorption studies 12 respectively 37 % of the adsorbed LAS could be determined (Fox *et al.*, 1997).

Leaching studies (Litz *et al.*, 1987) showed that only a very small proportion of the applied LAS had migrated into deeper soil layers.

4.1.2.5 Degradation

Under aerobic conditions LAS will be degraded by ω -oxidation followed by a β -oxidation with subsequent degradation of the alkyl chain. Degradation will be influenced by oxygen availability, temperature, adsorption and bioavailability. A conclusion of degradation studies from field tests was reviewed in Langenkamp *et al.* (2001). Half life values vary between nearly one week to 4 weeks. During winter time an increase to 80 – 120 days could be observed (Litz *et al.*, 1987; Soap and Deterg. Assoc. 1991). DT 90 experiments yield values between 28 to 122 days under summer conditions (Litz, 2000).

Degradation in deeper soil layer will proceed quite slowly because of oxygen deficiency.

4.1.2.6 PEC and PNEC values

A risk assessment for LAS is possible on a broad basis of information (NOEC, LOEC, EC 10, EC 50) needed for calculation of PEC and PNEC values for the different medias.

Local PEC calculation for soil, water and sediments according TGD (1996). Hera (2002) compared modelling PEC data with data of a monitoring.

Table 7 – Predicted environment concentration values for different matrices (Hera, 2002)

	Calculated	Estimated by monitoring
Local PEC in soil mg/kg dm	6,3	1,4
Local PEC in sediment mg/kg dm	5,9	5,3
Local PEC in water mg/l	0,027	0,047
Regional PEC in water mg/l	0,003	-

In a recent publication (Wenzel *et al.* (2003) a discussion about the PNEC values for soil organisms is reviewed on the basis of results of Carlsen *et al.* (2001) and Jensen *et al.* (2001). A PNEC for soil organisms is proposed for < 1mg/kg dm LAS in soils. For invertebrates a PNEC of 4,6 mg/kg dm. For plants a PNEC of 5,3 mg/kg dm and for a terrestrial ecosystem a PNEC value of 4,6 mg/kg dm is proposed (Hera, 2002).

Table 8 – PNEC values for terrestrial ecosystems (Hera, 2002)

LAS	PNEC (mg/kg dm)	Lowest EC 10 (mg/kg dm)
Plants	5,3	9
Soil fauna	4,6	6
Microorganisms	-	< 8
Terrestrial ecosystem	4,6	-

In soils LAS show a low toxicity (Lokke *et al.*, 2000; Solbe *et al.*, 2000). The acute toxicity for plants (EC 50) is in the range of between 16 – 316 mg/kg dm, for the soil fauna EC 50 values differ between 41 and >1000 mg/kg dm and for micro organisms in the soil from 17 > 1000 mg/kg dm (Hera, 2002).

The data of chronic toxicity studies (EC 10, NOEC) from Holmstrup *et al.* (2001), Jensen *et al.* (2001) and Elsgaard *et al.* (2001) could be summarized for plants to be 9 – 200 mg/kg dm, for soil fauna 6 – 670 mg/kg dm for micro organisms 8 – 793 mg/kg dm. NOEC values for 12 different plants were between 10 and 30 mg/kg dm.

The lowest EC 10 for invertebrates was found for *Enchytraeus albidus* to be 6,2 mg/kg dm, the NOEC for *Lumbricus terrestris* was 667 mg/kg dm respectively. 320 mg/kg dm for *Platynothrus peltifer* (Hera, 2002). Microbial functions and processes were influenced in many cases above values of 8 mg/kg dm.

Bioaccumulation in plants or organisms seems to be less important because of a BCF of between 100 and < 1000.

Investigations of Jensen *et al.* (2001) conclude that LAS concentrations of 5 to 15 mg/kg dm are not causing any harm to the soil ecosystem. It has been found that application of sewage sludge containing LAS had not produced any short- or long-term adverse effects on microbial processes and function, also for soil invertebrates.

For benthic organisms effects of chronic toxicity could be observed above the NOEC of 81 mg/kg dm for *Lumbricus variegates*, and for *Caenorhabditis elegans* of 100 mg/kg dm, other organisms show NOEC values > 200 mg/kg dm.

Investigations on estrogenic effects with LAS and its intermediates had shown that no endocrine effect could be observed (Navas *et al.*, 1999).

For human toxicity the uptake of drinking water and the ingestion of plants are possible routes to be discussed here. In general the acute and chronic toxicity of LAS is medium to low. The acute oral toxicity (LD 50) is for rats 1980 mg/kg bw, for mice 2205 mg/kg bw, (Hera 2002). For chronic effects by oral uptake the NOAEL in different studies was set between 20 to 260 mg/kg bw·d. According to the CESIO (2000) recommendation LAS is classified as “*harmful if swallowed at concentrations equal or greater than 65 %*”. LAS shows no carcinogenic, teratogenic or mutagenic effects.

In drinking water LAS was not found. For drinking water a LOAEL of 500 mg/kg bw·d (in diet) and a NOAEL of 250 mg/kg·bw d (in water) were assumed (Hera 2002).

Transfer in plants does not play an important role as investigations of Figge and Schöberl (1989) and Litz *et al.* (1987) show. Only traces of LAS would be transferred into the leaves of plants.

4.2 Nonylphenol and nonylphenol-ethoxylates (NP, NPEO)

4.2.1 Properties and substantial characteristics

Commercial nonylphenol consists of a large number of isomers of the general formula $C_6H_4(OH)C_9H_{19}$. It can vary in the substitution position of the nonyl group on the phenol group and in the degree of branching of the nonyl groups. Therefore individual branched isomers have own CAS. Following nonylphenol compounds can be differentiated: 4-nonylphenol (NP) (branched) with CAS no. 84852-15-3 (EINECS no. 284-325-5), nonylphenol isomer mixture (NPiso) with CAS no. 25154-52-3 (EINECS no.246-672-0), 4-n-nonylphenol (4-n-NP) with CAS no. 104-40-5 and two nonylphenol ethoxylates (NP1EO and NP2EO) CAS no 27986-36-3 and 9016-45-9. In the environment nonylphenol is found as a degradation product of nonylphenol ethoxylates. The European nonylphenol production in 1997 comprised nearly 74 000 tons. For the nonylphenol ethoxylates a production of 118 000 ton was reported in 1997 (CEFIC, 1996).

NP is used in production of NPEO (60 %), stabilisers, resins and plastics (37 %). NPEO is used in industrial cleaning (30 %), emulsion polymerisation (12 %), textile auxiliaries (10%), synthesis of chemicals (9 %), leather auxiliaries (8 %) and others (24 %). Since 1986 a dispense of the use of nonylphenol in household detergents in Germany has been reported. In 2001 a general dispense also for industrial use was accepted. In Europe, a similar agreement was made for household detergents in 1995 and respectively for the industrial sector in 2000.

4.2.2 Environmental behaviour

4.2.2.1 Water path

In the river Glatt in Switzerland NP and NPEO concentrations vary in the range of between 0,1 – 0,3 µg/l with a mean of 0,18 µg/l (Giger, 1998). Monitoring data from

Bavarian river water, Zellner and Kalbfus (1997) had shown nonylphenol concentrations, downstream of waste water treatment plants levels of 0,1 – 0,4 µg/l. In groundwater near the river Glatt, Ahel *et al.*, (1996) found nonylphenol concentrations of 0,95 µg/l. In German surface waters mean values of 0,13 µg/l of NP were measured while a maximum of 3,27 µg/l was observed (Fromme *et al.*, 1998). Effluents of STPs showed a maximum concentration of 2,24 µg/l, and median and mean concentrations of 0,47 and 0,55 µg/l. In Austrian raw wastewater concentrations of nonylphenol ethoxylates (Hohnblum *et al.*, 2000) were found to be 3,63 for NP1EO and 639,00 for NP2EO and after treatment in a STP concentrations of 2,09 and 13,09 µg/l were observed. In sediments nonylphenol was found in the range of between 0,056 – 14,82 mg/kg dm (BLAU, 1995). Sediment contaminations by NP were in maximum 1,9 mg/kg dm, in mean 0,75 and in median 0,77 mg/kg dm. In general the contamination of sediments depends on the received input by industrial cleaning agents or STP effluents.

Table 9 - Recent nonylphenol and NPEO concentrations in sewage sludge from European countries (mg/kg dm)

Country	No. of samples	Concentration range	Median	Reference
Austria	17	NP 0,46 - 65	13	Gangl <i>et al.</i> , (2001)
		NP1EO 0,15 - 23		
Denmark	11	NP 0,02 – 0,13	0,02	Torslov <i>et al.</i> , (1997)
	20	NP+NPEO 0,3 - 67	7,95	
Germany	147	0,04 - 650	5,1	Fragemann <i>et al.</i> , (2003)
Germany		25,5	—	Petrovic and Barcelo (2000)
Germany	5	3,6 - 21,3	11,7 (mean)	Schaecke and Kape (2003)
Germany	13	1,2 - 493	18,4	Gehring <i>et al.</i> , (2003)
Great Britain		256 - 824		Sweetmann (1994)
Switzerland	11	NP 44 - NP1EO 9 602 - 275		Bätscher <i>et al.</i> , (1999)
Sweden	19	—	3,9 (mean)	Samsøe-Petersen (2003)
Sweden	182	—	10,1 (<20000)* 18,3 (<100000)* 25,8 (>100000)*	Levin <i>et al.</i> , (2001)

* STP Number of inhabitants/equivalence

4.2.2.2 Sewage sludge

Sewage sludge concentrations of NP and the respective ethoxylates vary over a wide range. In some investigations maximum values were found at 60 to 70 mg/kg dm with a median value below 25 mg/kg dm, Hohenblum *et al.*, (2000) reported sewage sludge contamination of NP in the range from 5,26 to 30,54 mg/kg dm. Lower median values can

be found in aerobically stabilized sludges and in sludges from smaller STP (Levin *et al.*, 2001). Fragemann (2003) observed in his investigation a higher contamination of sludges coming from big cities. As for instance in Germany such treatment plants preferably work with anaerobic digestion, higher NP levels have to be assumed. A summary of the latest available data is presented in Table 9. Comparing with results from earlier investigations this shows a remarkable decline in NP contamination.

4.2.2.3 Soils

Krogh *et al.*, (1997) found in untreated sandy soil and loamy soil NP and NPEO of 0,003 and 0,007 mg/kg dm. In soils amended with sewage sludge values of 0,3 – 1 mg/kg dm should be usual (Torslöv *et al.*, 1997). In soils which were treated with high amounts of sewage sludge NP concentrations between 0,1 – 4900 mg/kg dm were observed (Vikelsee *et al.*, 1999). Dreher *et al.*, (2003) found some years after sewage sludge treatment NP in a concentration of less than 0,1 mg/kg dm in 14 soils after 8,8 and 31,5 ton/ha sewage sludge application.

In agricultural used soils an input of nearly 100 g nonylphenol per ha may be caused by applying pesticides (Kubiak, 1997).

4.2.2.4 Adsorption and mobility

Under normal soil conditions NP is present in the soil as non-dissociated compound. Nonylphenol is adsorbed at the organic matrix of soil and it can be assumed that a hydrophobic interaction between the ethoxy chain and the organic substance takes place. Freundlich constants vary between 230 to 560 for sediments (John *et al.*, 2000) and 107 for soils. K_{OC} -values of 5360 to 9100 were measured (EU, 1999; Höllrigl-Rosta, 2001). It could be shown that nonylphenol and the different NPEO were adsorbed differently. A shorter alkyl chain enhances the adsorption.

Due to the moderate adsorption of NP onto soils a movement into surface water could be possible. Ejlersson *et al.*, (1998) found NP in pore water of a sewage sludge landfill in concentrations of <0,17 – 100 µg/l. Therefore DEPA (1997) classified NP as potential mobile into groundwater. In general, it could not be assumed that higher amounts of NP are transferred into the underground.

4.2.2.5 Degradation

The first step of degradation of alkylphenol ethoxylates is the hydrolysis of the ethoxylate group to nonylphenol. But also mono- and dioxylated intermediary products (NP1EO and NP2EO) together with more than 20 other nonanol and octanol alcohols are developed (Marcomini *et al.*, 2000). The carboxylated intermediates have a higher persistence comparing with nonylphenol. Degradation is influenced by temperature.

4.2.2.6 PEC and PNEC values

PEC and PNEC values were calculated after TGD uses EUSES for natural soils, agricultural soils and grassland (CSF, 2001). For nonylphenol only limited data of

terrestrial effects are available. Using data from Krogh *et al.*, (1996) a PNEC of 0,3 mg/kg dm was calculated.

PNEC values for sediment and agricultural soil are generally supported by the available monitoring data. For surface water the PEC values calculated are higher than measured values due to less valid databases. From laboratory mammal data a PNEC for oral ingestion is set to 10 mg/kg food (EU Risk Assessment, 2001).

Table 10 – Regional PEC and PNEC values for different matrices for nonylphenol (mg/kg dm)

Matrix	PEC	PNEC
Natural soil	0,000014	
Grassland	0,0079	
Agricultural soils	0,265	0,3
Sediment	0,103	0,039
Surface water (mg/l)	0,0006	0,00033
Earthworm food chain	1,69	10 based on mammals data

4.2.3 Toxicological considerations

Only some information about effects on aquatic and terrestrial organisms is available. A very sensitive reaction was observed by some fishes, *Daphnia magna* and *Scenedesmus sub.* as shown in Table 11. Less sensitive were tested plants, some microorganisms and *E. albidus*. Because nonylphenol affects mainly the aquatic path, measures are necessary to reduce the concentrations of the effluents of the STP. It is well known that nonylphenol causes endocrine effects on fish and daphnids. For nonylphenol ethoxylates it was found that the effects increased with decreasing chain length, with nonylphenol showing the greatest activity (an overview in EU Risk Assessment 2001). The estrogenic effects start to occur at concentrations of 10 – 20 µg/l. This is two orders of magnitude higher than the PNEC derived from standard test. For example, Baldwin *et al.*, (1997) could show a reduction of the elimination of testosterone by approximately 50 % at nonylphenol concentration of 100 µg/l. Effects on gonad weight of rainbow trout were found after a prolonged exposure to nonylphenol by Ashfield *et al.* (1998). In a field study in 2-hectare ponds it was shown that nonylphenol decreases after a prolonged application rapidly at about 50 % in <0,74 days by increasing the sediment concentrations (Heinis *et al.*, 1999).

NP showed to bioconcentrate in aquatic organisms. A log K_{OW} of 4,48 was estimated. BCF for fish varied between 10-1300, for mussels and algae 2000 and 10 000 (CSF 2001).

NP is distributed in the body of mammals with highest concentration in fat. Nearly 10 to 20 % of the applied dose is biologically available. Nonylphenol is moderately toxic by the oral route with LD 50 values for rats in the range of about 1200 to 2400 mg/kg. NP has spermicidal effects.

NP is classified as not carcinogenic. Mutagenicity and teratogenicity were tested negative. Regarding the effects on the reproductive system, in a multigenerational study a NOAEL of 15 mg/kg/day was fixed (EU Risk Assessm., 2001).

Table 11 – Ecotoxicological risk characterisation of nonylphenol

Species	Parameter	EC 10	E(L)C 50	NOEC	LOEC	Reference
Zooplankton	Reproduction			76	243	O'Halloran <i>et al.</i> , (1999)
Molluscs	Reproduction			23	76	Schmude <i>et al.</i> , (1999)
<i>Daphnia magna</i>	Reproduction			0,001		Kopf (1997)
<i>Scenedesmus sub.</i>	Biomass	0,003	0,056	0,003		Kopf (1997)
Fish	Embryo study		0,128	0,0074		CSF (2001)
micro organisms	Nitrification	57	343	150	300	Gejlsbjerg <i>et al.</i> , (2001)b
<i>Folsomia fimataria</i>	Reproduction	27	39			EU Risk Assessm. (2001)
<i>Folsomia candida</i>	Reproduction	51	71			Gejlsbjerg <i>et al.</i> , (2001)b
<i>Enchytraeus albidus</i>	Reproduction	98	473	500	800	Gejlsbjerg <i>et al.</i> , (2001)b
<i>Eisenia fetida</i>	Reproduction	3,44	13,7			Krogh <i>et al.</i> , (1997)
<i>Sorghum bicolour</i>	Growth reduction			100	1000	EU Risk Assessm. (2001)
<i>Helianthus rodeo</i>	Growth reduction			100	1000	EU Risk Assessm. (2001)

4.3 Polycyclic aromatic hydrocarbons (PAH)

4.3.1 Occurrence and substantial characteristics

The substances of this group or organic micropollutants, although consisting only of carbon and hydrogen bound in simple to complex ring systems, have with respect to their benzene ring arrangements a wide diversity of physical, chemical and toxicological characteristics. This is in contrast to the other cumulative parameters like PCB and PCDD/F discussed before, which belong to one basic chemical structure. This must be taken into consideration when discussing restriction measures or limitations for the application of secondary raw materials as fertilizers or soil improvers. The number of substances discussed in this context varies from 6 to 16 in dependence on existing or proposed regulations. In table 12 an overview is given upon the PAH proposed by the American EPA priority pollutant list concerning their structure and arrangement of benzene rings.

The chemical structure of PAH is of importance for a number of properties: The stability of linear substances is low, of angular PAH high. The solubility in water decreases with the number of benzene rings, so the half life times show a wide variation up to a number of years e.g. for phenanthrene and benz[a]anthracene (Wild and Jones, 1992).

PAH are a by-product of incomplete combustion, their main source is the burning of fossil fuels like heating processes, waste incineration, automobile exhaust, but to a lesser extent they may be formed naturally. In hot summer periods forest fires may contribute to the PAH pollution of the environment. Direct effects on man result from tobacco smoke, fumigation and barbecue activities.

Table 12 – Structural chemical characteristics of PAH from EPA list

Number of rings	Arrangement of benzene rings		
	linear	spherical	angular
2	naphthalene		
3	fluorene anthracene	acenaphthylene acenaphthene	phenanthrene
4		pyrene	chrysene fluoroanthene benz[a]anthracene
5		benzo[a]pyrene	benzo[b]fluoroanthene benzo[k]fluoroanthene dibenz[ah]anthracene
6		benzo[ghi]perylene indeno[1,2,3-cd] pyrene	

4.3.2 Environmental behaviour

PAH have a low solubility in water and are preferably bound to the organic matrix in soil, so that less than 0,2 % are found and a PAH transport into deeper soil layers by percolation takes place only at a minor extent.

Transfer into plants is mainly caused by atmospheric fallout and to a minor part by adhering soil particles bearing PAH. In Germany, benzo[a]pyrene has a guide value for fumigated food and cheese of 1 µ/kg dm. Transferring this to vegetables one may conclude that this may lead to a limited soil concentration of 1 mg/kg dm (Rosenkranz *et al.*, 1986).

Generally it may be stated that there is at present no proof that a contamination of vegetable fruits or cereals with PAH has resulted from soil pollution. There is a long list of publications, especially from the UK (Jones and Northcott, 2001) which give more specific information and describe actual PAH concentrations which is not mentioned here in detail. Together with results of examinations in other countries table 13 gives a picture of the present situation.

4.3.3 Toxicological considerations

The acute toxicity of PAH is quite low, so is the LD50 of benzo[a]pyrene for mice 250 mg/kg bw. Large singular doses of PAH lead to deterioration of organs and tissues with a high mitosis rate (hematopoietic systems, gonads and intestine epithelium). It is assumed that these effects are caused by inhibition of the DNA synthesis by PAH metabolites. The main aspects of health risk caused by PAH are congenital modifications and cancerogenesis. But only some of the PAH are characterized as cancerogenous preferably those with 4 or more benzene rings like benz[a]anthracene and benzo[a]pyrene the latter being the leading substance (Bursch *et al.*, 2001). As there are no harmless threshold concentrations for carcinogenic substances precautionary values are set up generally low. This is a reason why soil concentrations of 1 – 2 mg/kg dm for benzo[a]pyrene as guide/limit values were discussed. According to effects upon soil organisms there is less information. In a CEFIC-LRI project of the European Chemistry Industry Council, Long

Range Initiative standard toxicity tests to determine effects of benzo[a]pyrene on plant growth, earthworm reproduction and functional parameters of microorganisms were tested. Up to the highest test concentration (128 mg/kg dm) no negative effect could be observed.

Table 13 – PAH concentrations in sewage sludge from European countries [mg/kg dm]

Country	Year of examination	Number of samples	Number of PAH	Concentration range	Median	Reference
Germany	1989	89	6	0,07 – 5,6	0,57	Leschber <i>et al.</i> (1992)
Sweden	1993	23	6	0,3 – 49	2,0	Nat. Swed. Envir. Prot. Board (1995)
Denmark	1995	20	18	< 0,01 – 8,5	—	Torslöv <i>et al.</i> (1997)
Norway	1996/97	36	16	0,7 – 30	3,9	Paulsrud <i>et al.</i> (1998)
		36	10	0,7 – 26	3,1	
Germany	1999	124	6	0,4 – 12,8	—	UMK-AG (2000)
Great Britain	1999	14	24	67 – 246	—	Jones <i>et al.</i> (2000)
		14	10	18 - 46	34	Stevens <i>et al.</i> (2003)

4.4 Di-(2-ethylhexyl) phthalate (DEHP) and Dibutyl phthalate (DBP)

4.4.1 Occurrence and substantial characteristics

Di-(2-hexyl) phthalate C₂₄H₃₈O₄ (CAS no 117-81-7) EINECS no 204-211-0 and Dibutyl phthalate C₁₆H₂₂O₄ (CAS no 84-74-2) EINECS no. 201-557-4 are world wide used as additives for giving plastics flexibility and durability. Approximately 95 % of DEHP is used in PVC in an amount of 1 – 40 % (ATSDR 2000, IARC 2000). About 1 Mio. tons of phthalates are produced in Europe. The most commonly used are DINP (Diisononyl phthalate), DEHP and DIDP (Diisooctylphthalate). In Western Europe DEHP comprises 30 % of all plasticisers (European Council of Plasticiser and Intermediates, 2003). The European consumption can be calculated to be 480 000 tons (Risk Reduction Strategy of DEHP, 2003). DBP is also used in cosmetics and dental impression material.

Since phthalates are common laboratory contaminants, laboratory and field blanks sometimes show concentrations similar to those which have to be investigated. Since this was neglected, the accuracy of data of former examinations should be considered carefully. The principal sources of DEHP and DBP for soil contamination are the disposal of industrial and municipal waste to landfills and sewage sludge application (Bauer and Herrmann, 1997).

4.4.2 Environmental behaviour

4.4.2.1 Water path

DEHP and DBP have been frequently detected in rainwater, surface water and ground water (US DHH, 2000). Concentration of DEHP in German surface water varies between

0,33 µg/l and 97,8 µg/l (median: 2,27 µg/l) and for DBP between 0,12 and 88,8 µg/l (median 0,5 µg/l). In 35 sediments samples 0,21 to 8,44 mg/kg dm (median 0,7 mg/kg dm) of DEHP and 0,06 to 2,08 mg/kg mT (median 0,45 mg/kg dm) of DBP were measured (Fromme *et al.*, 2002). Vitali *et al.*, (1997) showed comparable contamination of surface waters in Italian rivers, for sediments lower contaminations were measured. Sewage in a Danish STP was contaminated with 13,1 to 44,3 mg/l DEHP. A 8 day mean inlet concentration of this STP was 35,5 mg/l DEHP and 1,03 mg/l DBP (Fauser *et al.*, 2001). Outlet concentrations measured in 38 STP (for DEHP) and 34 STP (for DBP) were 1,74 to 182 µg/l (median 8,8 µg/l) and 0,2 to 10,4 µg/l (median 0,7 µg/l) Fromme *et al.*, (2002). DEHP levels in two dump runoff samples were 26,4 and 168,9 µg/l thus being drastically lower when compared to older dumping sites in the Netherlands and USA (Fromme *et al.*, 2002).

Sediment concentrations ranging from 0,1 – 10,1 mg/kg dm were reported by Friedmann *et al.* (2000). In USA 39,2 % of the collected sediment samples showed medium contents of 1,8 mg/kg dm (Lopes *et al.*, 1997).

DEHP and DBP released to water adsorb intensively at suspended and sediment particles (Staples *et al.*, 1997). In marine water DEHP was distributed in a ration of 1:99 between water and sediment at concentrations of 280 to 640 µg/kg.

4.4.2.2 Sewage sludge

Due to their world wide use in consumer products DEHP and DBP can be classified as relevant compounds in the environment and also in sewage sludge (UMK-AG, 2000). In sewage sludge DEHP concentrations of 27,9 to 154 mg/kg dm (median 67,3 mg/kg dm) and DBP concentrations of 0,2 to 1,7 mg/kg dm (median 0,5 mg/kg dm) were found. Between industrially dominated and municipal STP differences in phthalate contamination in sludge could not be observed. Comparing to earlier monitoring programs the DEHP contamination of recent sludge has been reduced (Wenzel *et al.*, 2003). Data about the contamination level for DEHP and DBP are presented in table 15.

4.4.2.3 Soils

DEHP content of untreated, natural soils is below 0,015 mg/kg dm (Dreher *et al.*, 2003), in such cases the DBP contamination is below 0,005 mg/kg dm. Soils are contaminated mainly by application of sewage sludge, manure and use of plastic material in agriculture. Atmospheric fallout especially by wet deposition may be between 157 to 1000 µg/m² of DEHP and 100 to 664 µg/m² DBP per year (Vikelseoe *et al.*, 1999). These values are more orders higher compared to German assumptions where for DEHP 0,45 – 1,5 µg/m² (DEHP) and 0,82 to 1,1 µg/m² (DBP) were calculated. This corresponds to results of examinations where concentrations of 0,84 to 2,8 µg/kg dm for DEHP and 1,5 to 2 µg/kg dm for DBP were found (Kaiser *et al.*, 1999). In some investigations a slight increase could be observed, when sewage sludge had been applied over long times or by massive application in a short time. In such cases DEHP and DBP contamination increased to nearly 2 mg/kg dm or nearly 0,5 mg/kg dm not alone in the surface layer, but also in deeper soil layers (50 – 60 cm depth) (Vikelseoe *et al.*, 1999).

Table 14 – DEHP and DBP concentration in sewage sludge in Europe (mg/kg dm)

Country	Compound	Number of samples	Concentration range	Median	References
Germany	DEHP	15	27,9 - 154	67,3	Fromme <i>et al.</i> , (2002)
	DBP	15	0,2 - 1,7	0,5	
	DEHP	156	0,93 - 110	22	Fragemann (2003)
	DEHP	1		8,0 (mean)	Petrovic and Barcelo (2000)
	DBP	1		9,7 (mean)	
	DEHP	5	1,51 - 5,09	3,16 mean	Schaecke and Kape (2003)
Austria	DEHP	17	<0,19 - 47	7,2	Gangl <i>et al</i> (2001)
	DBP	17	<0,2 - 0,69		
Danmark	DEHP	20	3,0 - 170	24,5	Torlov <i>et al</i> (1997)
	DBP	20	0,02 - 260	0,3	
	DEHP	6	9 - 61		Boutrup <i>et al</i> (1998)
	DEHP	2	14 - 23		Krogh <i>et al</i> (1997)
Norway	DEHP	36	<1 - 140	58	Paulsrud <i>et al.</i> , (2000)
Sweden	DEHP	19		6,6 (mean)	Samsøe-Petersen (2003)

4.4.2.4 Adsorption and mobility

Due to the low water solubility (0,4 mg/l) DEHP and DBP (8 – 12 mg/l) are strongly adsorbed to soil material, especially to organic matter. Between organic matter (fulvic acid) and DEHP a complexation reaction has to be assumed (HAZDAT, 2002). K_{OC} -values vary between 100 000 to 480 000. Otte *et al.*, (2001) calculated for DEHP a log K_{OC} of 5,37 and for DBP of 2,98. Other values from literature show log 2,7 to 3,8 (Fransen and Voogt (1997)). K_d values for DEHP were 3700 –5600 according to Fauser *et al.*, (2001). Information about the mobility of DBP is rare.

Movement of DEHP to groundwater may occur during rapid infiltration. In presence of organic solvents thereby increasing amounts may leached from the waste site into groundwater. In landfill leachate 34 – 7900 µg/l were found (Roy, 1994). But also some investigations of groundwater showed DEHP contaminations (US DHH, 2000). An increase of the emissions from landfills is expected (CSTEE, 2002).

4.4.2.5 Degradation

Both phthalates are degraded in relative short times under aerobic soil conditions. The biodegradation half-lives in soil are for DBP 2 – 23 days, in surface water 1 to 14 days and in groundwater 2 – 23 days (RIWA, 1998). In Torsløv *et al.* (1997) a half life time of >50 days for DEHP is given. In comparison of reported half lives of the parent compound under environmental conditions 14 to 200 days have to be assumed (Roslev *et al.*, 1998). There is no indication for an environmental risk of the mayor intermediate, mono (2-ethylhexyl)phthalate. The expected removal from STP after aerobic treatment is > 90 %.

Hartlieb and Kördel (1999) found degradation of DEHP to CO₂ in compost and municipal biowaste of 70 % in 29 weeks. Only 2 % of the applied DEHP remained as non-extractable residue.

4.4.2.6 PEC and PNEC values

PEC values for DEHP were estimated to be 33,7 mg/kg dm for sediment and for water of 2,2 µg/l on a regional scale. PEC (local) ranges for surface water from 2,2 to 220 µg/l and from 21 to 2058 mg/kg for sediments. For algae a PNEC of 0,00035 mg/l was proposed.

4.4.3 Toxicological considerations

There are some results available about the effects of DEHP and DBP on micro organisms, earthworms and plants (table 15), on aquatic organisms (fish, daphnids) from a higher number of short and long term studies

Table 15 – Effects of DEHP and DBP to micro organisms, earthworm and plants

Species	Compound	Effect upon	Concentration	Effect	Reference
Micro-organisms	DEHP	soil respiration	250 mg/kg	none	Lundberg and Nilson (1994)
	DEHP	nitrification	250 mg/kg	none	
	DEHP	Nitrification	>250 mg/kg	NOEC	Kirchmann <i>et al.</i> , (1991)
	DEHP	Respiration	>250 mg/kg	NOEC	
Eisenia fetida	DEHP		25 mg/cm ²	none	WHO (1992)
	DBP		1,4 mg/cm ²	LC 50, 48 h	Neuhauser <i>et al.</i> , (1985)
Avena sativa	DEHP		1000 mg/kg	low	Pedersen and Larsen (1996)
Pisum sativum	DBP		1000 mg/kg	none	
Spinacia ol.	DBP		1000 mg/kg	none	
Zea mays	DEHP		200 mg/kg	NOEC	Shea <i>et al.</i> (1982)

Uptake of DEHP from soil by plants was also reported by O'Connor *et al.*, (1996). But due to the strong adsorption to soil it takes place only in small extent.

A NOEC of 130 mg/kg dm for plants was derived from a 18 d seed germination test on plants. A foliar deposition of 8,75 µg/cm² via air was indicated.

Because of the missing information about ecotoxicity effects of DEHP to organisms an estimation of PNEC values should be taken carefully. From the NOEC of Zea mays a PNEC for soil of 2 mg DBP/kg dm could be proposed (Wenzel *et al.*, 2003) A value of 1,25 mg/kg dm was calculated by RAR 2001). In case of DEHP a PNEC soil of 10 mg/kg dm was proposed provisionally by Wenzel *et al.* (2003). This is comparable to a proposal of 13 mg/kg dm for a PNEC in soil (CSTEE, 2000). For agricultural soil PEC/PNEC is often above 1.

Due to its lipophilicity, DEHP has a high potential for bioaccumulation. Data indicated higher BCF in aquatic invertebrates than in fish. Staples *et al.*, (1997) reported bio concentration factors (BCF) for different species (table 16).

Table 16 – Bioconcentration factors (BCF) of different species (Staples *et al.*, 1997)

Species	BCF	Number of species	Species	BCF	Number of species
Algae	3,17	2	Polychaetes	422	1
Molluscs	1,147	5	Fish	280	5
Insects	1,01	3	Amphibians	605	1
Crustacea	1,16	4	Invertebrates	43	

About the toxicity of DEHP some information is available, but for DBP a lack of information has to be concluded. DEHP has a very low toxic potential by oral or inhalation route. Oral exposure from drinking water is not expected to be an important route for humans (Duel *et al.*, 1999; NTP, 2000b). Traces of DEHP had been found in several kinds of biota and food (fish, milk, meat, eggs etc.) as Petersen and Breindahl (2000) reported. In general DEHP shows no mutagenic effect. Cancerogenic effects could be observed in several studies only by rodents in case of very high doses. Because of the different reaction to humans DEHP is not classified as human carcinogen. DEHP and DBP are classified as reproductive toxicants. An NOAEL value for rats is 200 mg/kg/d. Weak indication for estrogenic activities of DEHP and DBP (premature breast development by young girls) was reported by Colon *et al.*, (2000). Some indications for endocrine effects (weak anti-androgenic effects) in very high doses of DEHP were reported (CSTEE, 2002). There is no evaluation that clarifies the relation of exposure to DEHP with effects on the human endocrine system and reproductive system. In vitro tests indicated the binding to estrogen receptors and the response mediated by receptor binding were weak or negative in most cases. CERHR (2000) suggests that the influence of DEHP on the reproductive and development systems, especially on male reproductive system, is attributed to anti-androgen activity not mediated by androgen receptors.

4.5 Organometallic compounds and emerging pollutants

A number of compound groups were not considered in this report, which is in part to lack of data, but also to the major analytical difficulties in determining them. These "Emerging Contaminants" correspond in most cases to irregularly regulated contaminants, e.g. surfactants, pharmaceuticals and personal care products (PPCP), or gasoline additives, but also organo-metallic compounds. Two of them are mentioned below and the attention of the reader is drawn to the fact that research on many of these compounds is still ongoing.

4.5.1 Organotin

Organotins are the most widely used organometallic compounds. In 1995 it was estimated that the annual world production of organotins was reaching 50.000 tonnes (Fent *et al.* 1995). They have high fungicidal, bactericidal, algicidal, and acaricidal properties. Of particular importance to the environment is the high toxicity of tributyl-, triphenyl-, and tricyclohexyltin derivatives. Organotins are used as agrochemicals and as general biocides in a broad spectrum of applications. The use of TBT containing antifouling paints is now controlled or banned in many countries, but a change in applications from antifouling paints to wood preservation seems to occur at present (Fent *et al.* 1995).

From the production figures and use pattern, it becomes evident that a significant portion of organotins may enter wastewaters. Indeed, these compounds have been found to become enriched in sewage sludge, where they are not substantially degraded during treatment. A survey conducted in four treatment plants in 1988-1990 showed that MBT, DBT and TBT were generally present in digested sludges. In addition to butyltins, in one sample mono-, di and triphenyltin residues in the range of 0.1-0.4 mg/kg were found. Mono-, di and tributyltin concentrations in nine sludge samples of four different treatment plants were in the range of 0.10-0.97, 0.41-1.24 and 0.28-1.51 mg/kg (d.m.), respectively (see literature cited by H. Langenkamp *et al.* 2001). Other sewage sludge samples from Switzerland were found to be similarly contaminated, whereas sludges of three out of five Canadian cities had butyltin residues which were somewhat lower than those in Switzerland. Photo- and biodegradation may diminish organotin residues transferred to agricultural fields. TBT residues found in sludge amended soils are low. Dumping of sludge and transfer to soil are of ecotoxicological relevance, since these transfer paths give rise to organotin pollution of both aquatic and terrestrial systems.

4.5.2 Musk ketone and musk xylenes

Musk xylene and musk ketone are used as substitutes for natural musk in perfumes and other cosmetics, soaps and washing agents, fabric softeners, air fresheners etc. The production in Europe is estimated to be 124 tonnes/yr for musk ketone and 75 tonnes/year for musk xylene (Alcock *et al.*, 1999), most of which is expected to be released into sewers because of their useage. Tas and co-workers (1997) give a review of environmental data and a risk assessment procedure for these compounds.

5 Literature

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Abstract

The report is intended as an input for discussion concerning the necessity to regulate organic micro-pollutants in the revision of the European Sludge Directive 86/278/EEC.

Part 1 of this report gives an overview on relevant organic micro-pollutants in sewage sludges. Publications, results of eco-toxicological studies and national particularities for substance classes such as PCBs, PAHs, PCDD/Fs, PBDE, LAS, NP, etc. have been reviewed and critically analysed.

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