Organic Contaminants in Sewage Sludge for Agricultural use

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FOREWORD OF THE EDITORS

European dimension of organic contaminants

Sewage sludge has been used in agriculture over a long time. Since 1986 the utilization of sewage sludge has been subject to provisions stipulated in the EU Directive (86/278/EEC). The Directive sets out requirements with respect to the quality of sludge, the soil on which it is to be used, the loading rate, and the crops that may be grown on treated land. The European Commission considers that 86/278/EEC has been a success because there have been no reports of adverse effects wherever it has been applied. Consideration has been given to revising the directive in order to further improve the situation

In the majority of cases the most direct risk would currently be considered adverse effects to consumers of crops (humans and animals) by virtue of uptake by crops or contamination of crops. An important risk at heavily amended sites is that of groundwater pollution. Many countries in Europe rely heavily on groundwater for drinking water and irrigation water. Persistent contaminants in groundwater can eventually reach and potentially pollute surface waters.

According to the European Commission, the quantity of water available per human being has dropped by 40% since 1970 and two out of five people living on the planet have water supply problems (RTD info 21). One of the reasons for that is the contamination of land and the groundwater resources especially in highly industrialised regions, which are typical for Central and Eastern Europe. Furthermore, 60% of Europe's cultivated land contains fertilisers and pesticide levels, which are a threat to the quality of groundwater. Contaminated soils loose their functions as a buffer for pollutants and eventually the subsoil environment and groundwater will be contaminated.

The European commission aims to control substances which in a general European view (decision) are undesired in it present concentrations. Organic micro pollutants have got greater attention with the increased knowledge about their toxicity. Halogenated organics (PCB and their prohibition by legal regulations, the Seveso accident with PCDD/F, halo forms in drinking water) have received special attention. For sewage sludge Germany in 1992 was the first European country to introduce national regulations. With growing experience and results from scientific sludge and soil examination programmes other countries have gone the same way. This approach has proven to be successful in reducing the load of pollutants to tolerable levels .This study is a review of the present situation with respect to organic contaminants in sewage sludge and existing limits in the EU Member States

JRC Recommendations

Organic contaminants in sludge are not expected to pose major health problems to the human population when sludge is re-used for agricultural purposes. In comparison, metal contamination of sludges is much more important with respect to human health.

The chemical properties of organics of health concern – hydrophobic and not water soluble - results in a low bioavailability to plants. Plant growth is dependent on the water solubility of nutrients and minerals and water is the transporting vector. Organics with a low water solubility will therefore not be taken up by plants. The presence of organic environmental pollutants, like dioxins and PCBs in agricultural crops is more the result of atmospheric deposition than direct absorption from contaminated soil. The analytical procedures for many organics are complicated and expensive – dioxins are a good example – which is an additional factor to be kept in mind when discussing monitoring of organics in sludges. Monitoring must also pay attention to the origin of sludge because the level of organic contamination may be very different when for example comparing municipal sewage sludge (mostly households) with sludges of industrial origin or sludges from storm- and run-off waters.

The conclusion when analysing table 4.2-1 is that it does not make much sense to include dioxins (PCDD/F), PCBs and PAHs in routine monitoring programmes but occasionally it may be motivated with respect to the origin of the sludge. The same applies to TBT, which is indeed very toxic, but at the same time is almost non-existing in sludges because of a use (antifouling) in other contexts.

There are environmental reasons for monitoring sludges for detergents like LAS and nonylphenoles because they are high volume chemicals with an extensive household and industrial use. They are also more water soluble than the organics previously discussed and therefore more mobile and bioavailable in soils. Again the impact on human health is low because of a low transfer from soil to human consumers. The environmental impact, however, could be significant through leaks to surface waters. Many detergents are clearly toxic and harmful to aquatic organisms and detergents have been indicated as responsible for changes in aquatic populations.

Authors' Preliminary Remarks and Acknowledgement

This study gives an overview of the most recent literature on the subject. There seem to be more than a thousand publications. However there are only few field data, especially from studies on soil-water and soil-plant transfer and on the long-term behaviour of contaminants in soils.

Unfortunately there are very little publications in English from some EU-countries. The study gives an overview of the conclusions of various national working groups and makes suggestions on how to direct future research activities.

So far limit values for pollutants in sewage sludge or soils were based on background concentrations and set with the explicit political intention to avoid adverse effects. It will never be possible to derive limit values solely from scientific research. Limiting pollution so far always resulted in improvements of the environmental situation. Accordingly the continuing development of regulations is a very important matter, especially when regarded from an integrative point of view. The study tries to contribute to this attempt.

We thank all the experts who helped us by sending literature, especially Prof. Dr. Leschber and the Joint Research Centre for financing the study.

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TABLE OF ABREVIATIONS

50.P	50. percentile (median)
90.P	90. percentile
AOX	sum of adsorbable organic halogen compounds
BaP	Benzo[a]pyrene
CAS	Chemical Abstracts Service
CB	Chlorobenzene
CMR	Carcinogenicity, Mutagenicity and Reproductive Effects
DBP	Dibutylphthalate
DEHP	Di-2-(ethylhexyl)phthalate
DEP	Diethylphthalate
DNBP	Di-n-butylphthalate
DOC	Disolved organic carbon
EDs	Endocrine disruptors
EDTA	Ethylene diaminetetraacetic acid
EPA	Environmental Protection Agency
GLP	Good Laboratory Practice
HCH	Hexachlorocyclohexane
LD	Lethal Dose
LOES	lowest observed effect concentration
NOEC	no observed effect concentration
NOEL	no observed effect level
NP	Nonylphenole
NPE	Nonylphenole(+ethoxylate)
PAH	Polynuclear aromatic hydrocarbons
PBB	Polybrominated biphenyls
PBDE	Polybrominated diphenyl ether (flame retardants)
PCA	Chlorinated paraffins
PCB	Chlorinated biphenyle
PCDD/F	Polychlorinated dibenzo-p-dioxins and -furans
PCP	Pentachlorphenole
PEC	Predicted environmental concentration
PNEC	Predicted no-effect concentration
POP	Persistent organic pollutants
TBT	Tributyltin
TBTO	Bis-tributyltin oxide
TEF	Toxicity Equivalency Factor
TOC	Total organic carbon
TRGS	Technische Regel für Gefahrstoffe (Technical Rule for Hazardous Substances)
VOC	volatile organic chem.

0 ABSTRACT

The European Union has developed the draft of a "Working document on sludge" (EU 2000), to promote the use of sewage sludge in agriculture while improving the safety and harmonize quality standards. It proposes limit values for concentrations of heavy metals and organic compounds that should restrict the use of sewage sludge in agriculture if the limits are exceeded and provides suggestions for good practice in treatment and agricultural use. The compounds or respectively groups of compounds that are suggested for regulation are LAS, DEHP, NP(E), PAH, PCB and PCDD/F.

This desk study was financed by the EUROPEAN COMMISSION, Joint Research Centre, Ispra. It gives an overview of the occurrence of these organic compounds in sewage sludge, basic toxicological data, a review on persistence of organic contaminants in soils and risk assessments for the various pathways. The attempt was made to identifiy additional substances or substance groups which might cause hazards and should be regulated. Thus it is recommendended that the benzo(a)pyrene concentration in soil is regulated.

To do the review a literature search was run in January 2001 and experts were asked for literature or references, members of ISO TC 190 and CEN TC 308 were contacted and the Internet was searched.

As a result of inquiries and research about 800 references were found. About 150 papers were selected for use in this study. Main criteria for the selection of the papers were, that they were published fairly recently (mostly after 1995) in English or German.

The study gives a priority list of organic contaminants which is meant to be completed with contributions representing the views of the different member states. Chapter 4 gives a summary of conclusions of the pertinent publications and points out where further information is needed.

1 INTRODUCTION

The objective of waste water treatment is to prevent large quantities of substances to reach and impact the environment in high doses and concentrations.

Areas of high population densitiy naturally are areas were production of sewage sludge is high (see Figure 1-1). Presently about 8 million t of sewage sludges (MAGOAROU 2000) are produced each year in the EU member states (Table 1-1). Its high content of organic materials, of nitrogen and phosphorous suggest their use as soil conditioner and fertilizer in agriculture. Consequently it is one of the EU policies to enhance sludge use in agriculture (MARMO 2000).

However a wide variety of undesired chemicals may be found in sludge which could have adverse effects on the environment. They also may affect soils, plant, animals and human health, and have impacts on the environment (LANGENKAMP & MARMO 2000). Because of

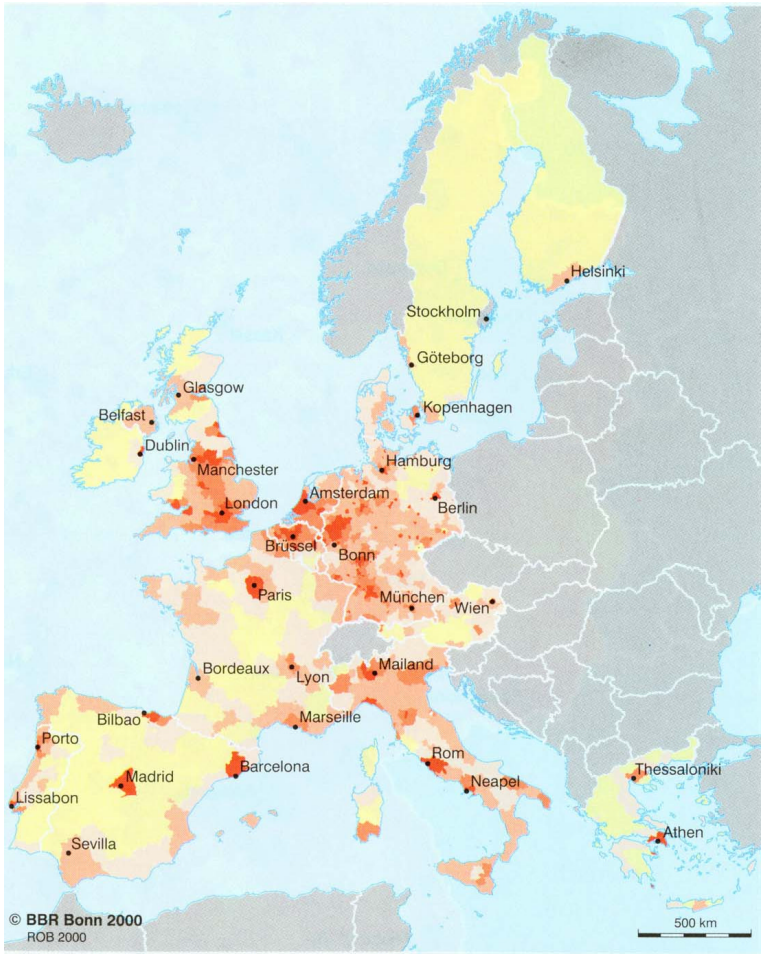

Figure 1-1: *Population densitiy in the EU in 1995 (yellow: <50, red: >500 inhabitants per km^2) (BBR 2000)*

Table 1-1: *Area, population and sewage sludge production of EU member states in the year 2005 (MAGOAROU 2000)*

	Area	Population		Sludge destination [1000 t dm/a] in 2005			Relative sludge production
	[km²]	[Million]	Density	total	reuse	percentage	[kg/person/a]
FIN	338.000	5,1	15	160	115	72%	31
S	450.000	8,9	20	-	-	-	-
IRL	70.000	3,7	53	113	84	74%	31
E	504.782	39,4	78	1088	589	54%	28
GR	131.957	10,5	80	99	7	7%	9
A	88.945	8,1	91	196	68	35%	24
F	550.000	60,4	110	1172	765	65%	19
P	92.072	10,8	117	359	108	30%	33
DK	43.094	5,3	123	200	125	63%	38
L	2.586	0,4	166	14	9	64%	35
I	301.263	57,6	191	-	-	-	-
D	356.854	82,0	230	2786	1.391	50%	34
UK	242.500	58,6	242	1583	1.118	71%	27
B	30.158	10,2	338	160	47	29%	16
NL	41.864	15,8	377	401	110	27%	25

these potential toxicological properties the public expect and demand more legislative control of environmental contamination problems.

Table 1-1 gives an overview of the expected sewage sludge production in the EU member states for the year 2005. Denmark, Luxembourg and Germany are expected to have the highest sewage sludge production per population equivalent. Germany, United Kingdom, France and Spain will probably still be the countries which use the highest amounts of sewage sludges in agriculture (> 500.000 t/a), with Ireland, Finland and United Kingdom reusing the highest percentage of their sludges in agriculture (> 70%).

1.1 Definitions

The terminology used in this review follows the definitions given in the Working Document on Sludge, 3rd draft, (EU 2000):

sludge**:** "mixture of water and solids separated from various types of water as a result of natural or artificial processes"

sewage sludge: sludge from urban waste water treatment plants, whereby 'urban waste water' is understood as: "domestic waste water or the mixture of domestic waste water with industrial waste water and/or run-off rain water" (Directive 91/271/EEC). The definition of 'domestic waste water' in Directive 91/271/EEC reads: "waste water

from residential settlements and services which originates predominantly from the human metabolism and from household activities"

treated sludge: sludge which has undergone one of the treatment processes envisaged in Annex I or a combination of these processes, so as to significantly reduce its biodegradability and its potential to cause nuisance as well as the health and environmental hazards when it is used on land.

1.2 Objective of the study

The European Union has developed the draft of a "Working document on sludge" (EU 2000), to promote the use of sewage sludge in agriculture while improving the safety and harmonize quality standards. It proposes limit values for concentrations of heavy metals and organic compounds that should restrict the use of sewage sludge in agriculture if the limits are exceeded and provides suggestions for good practice in treatment and agricultural use.

The Joint Research Center's objective with this desk study was to give an overview on the occurrence of organic compounds in sewage sludge, basic toxicological data (e.g. teratogenic, mutagenic, cancerogenic effects), a review on persistence of organic contaminants in soils, a review on risk assessment for the various pathways and possibly a priority list of organic contaminants. The study also attempts to summarize conclusions of the pertinent publications and to point out where further information is needed.

The 3rd draft of the "Working document on sludge" proposes limit values for concentrations of the following organic compounds or compound groups if sludge is to be used in agriculture:

- 'AOX', the so-called 'sum of halogenated organic compounds'
- linear alkylbenzene sulphonates (LAS)
- di(2-ethylhexyl)phthalate (DEHP)
- 'NPE' (nonylphenole and nonylphenole ethoxylates with 1 or 2 ethoxy groups)
- polynuclear aromatic hydrocarbons (PAHs)
- polychlorinated biphenyls (PCBs)
- polychlorinated dibenzo-p-dioxins and -furans (PCDD/Fs)

One of the purposes of this study was to review the literature for substances or substance groups which might cause hazards and should be included in the priority list.

2 MATERIAL AND METHODS

The desk study is based on the following steps:

1 A literature search run was done in January 2001 by means of the System STN International The Scientific & Technical Information Network. The following data bases turned up references in the field in question: BIOSIS, ENERGY, MEDLINE, UFORDAT, CABA, ENTEC, NLDB, ULIDAT, CEABA-VTB, GEOREF, POLLUAB, COMPENDEX, HSDB, SCISEARCH, EMBASE, LIFESCI, TOXLINE (background information on the respective databases see <http://www.fiz-karlsruhe.de>). Excluding redundant nominations 280 references were pertinent.

2 More than 30 experts were written to or asked for literature or references in other ways, (e. g. Alice Saabye; Antonio De Angelis; Armin Melsa; Claus Bannick, Claus Bergs; Rufus Chaney, Daniel Villessot; Dieter Fuhrmann; Emanuel Adler; Esch, Franz Mochty; Hans Leser; Hartmut Witte; Helmut Kroiss; Ian Evans; Jeremy Hall; Leschber; Joaquim Pocas Martins; Juan Azcarta; Mach Rudolf; Michal Dohanyos; Nico Hoffmann; Paul Woodcock; Peter Balmer; Roland Wolf; Roman Llagostera; Siguard van Riesen; Steinar Nybruket, R. S. Smith,

3 with the support of DIN members of ISO TC 190 and CEN TC 308 were contacted (AFNOR; BSI; CSNI; DIN; DS; ELOT; IBN; ICONTEC; IPQ; JISC; NEN; NSAI; NSF; ÖNORM; PKN; SEE)

4 the Internet was searched, especially the following websites:
www.ademe.fr
www.ains.at/etc&egc/gov/denmark.html
www.iacr.bbsrc.ac.uk/iacr/tiacrhome.html
www.internat.environ.se/index.php3
www.dino.wiz.uni-kassel.de/dain/
www.vdlufa.de/vdl_idx.htm

5 Further references were taken directly from the literature .

As a result of inquiries and research about 800 references were found. About 150 papers were selected for use in this study. Main criteria for the selection were that the papers were published recently (mostly after 1995) and that they provided an overview of the aspects in question.

3 RESULTS AND DISCUSSION

3.1 General aspects

Sewage sludge as an uncalled for product of wastewater treatment poses the challenge to society of disposing of it, but at the same time gives us the opportunity of beneficial use by closing the cycle of nutrients: sludge derived from agricultural activity must return to soil if a sustainable and ecologically sound management of these materials is desirable (SEQUI et al. 2000). At present the major ways of disposing of sewage sludges are deposition, landfill and incineration, only part of the sludges are used in agriculture.

Application of sewage sludge to agricultural land may be beneficial because it can improve the physical, chemical and biological properties of soils which may enhance crop growth (BECK et al. 1996). To achieve this, sludge application cannot just be a way of disposing of the sludges but a deliberate application in order to recycle nutrients and to restitute organic matter to soils in order to prevent over-exploitation of agricultural soils in the Community (MARMO 2000). In addition the use of sludge as a fertilizer would decrease the amounts of chemical fertilizers needed in agriculture (TIDESTRÖM 1997) and supply micro-nutrients which are not commonly restored in routine agricultural practice. Thus sludge use in agriculture could help save non-renewable materials or energy, a prerequiste to achieve sustainable production (OCDE 1992 cit in SEQUI et al. 2000).

The major organic loading originates from human excreta, and is a complex mixture of fats, proteins, carbohydrates, lignin amino acids, sugars, celluloses, humic material and fatty acids. A large proportion of this organic material is in the form of both live and dead microorganisms which provide a large surface area (0.8-1.7 $m^2 g^{-1}$) for sorption of hydrophobic organic residues and it is within this fraction that most synthetic organic compounds are located (ROGERS 1996).

Waste waters and hence sewage sludges contain a wide variety of pathogens, which can be infectious for different species of animals and plants as well as for humans (BÖHM 2000). Therefore hygienic principles must be followed in collection, transport, processing, storage and distribution of such materials. Pathogens may survive for a remarkable period of time in sludges and the environment (BÖHM 2000).

3.1.1 Legislative measures

While it encourages the use of sewage sludge, the EU Directive 86/278/**EEC** regulates its use to prevent harm to the environment, in particular to soil. In order to improve the long-term protection of Community soils the Commission is currently working on some aspects of the Directive in the light of new scientific evidence and technological progress (MARMO 2000). Table 3.1-1 shows limit values for concentrations of organic compounds in sludge of different countries and as suggested in the 3rd draft of the "Working paper on sludge".

Tabel 3.1-1: *Standards for concentrations of organic contaminants in sewage sludge in different countries of the EU*

	AOX mg/kg dm	**DEHP** mg/kg dm	**LAS** mg/kg dm	**NP/NPE** mg/kg dm	**PAH** mg/kg dm	**PCB** mg/kg dm	**PCDD/F** ng TEq/kg dm
EU 2000 (3rd draft)	500	100	2600	50	6[1]	0,8[2]	100
Denmark (Danish Ministerial Order No. 823, 16 Sept. 1996, cit in MADSEN et al. 1997)	-	50	1.300	10	3[1]	-	-
Sweden (LRF & SEPA & VAV; 1996)	-	-	-	50	3[3]	0.4[4]	-
Lower Austria (NÖ, 1994 cit. FÜRHACKER &LENCE 1997)	500	-	-	-	-	0,2[5]	100
Germany (Sauerbeck & Leschber 1992)	500	-	-	-	-	0,2[5]	100

[1] Sum of acenapthene, phenanthrene, fluorene, fluoranthene, pyrene, benzo(b+j+k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, indeno(1, 2, 3-c,d)pyrene.

[2] sum of 6 congeners PCB 28, 52, 101, 138,153, 180.

[3] sum of 6 compounds

[4] sum of 7 congeners

[5] each of the six congeners PCB 28, 52, 101, 138, 153, 180.

Tabel 3.1-2: *French guide values for PAH concentrations in sewage sludges and maximum amounts in soils of pastures (CSHPF, 1998)*

compound	**concentrations in sludge to be used in agriculture at a rate of no more than 30 tons/ha/10a (mg/kg dw)**	**maximum permissible cumulated input on pasture soils per hectare in 10 years (g/ha dw)**
fluoranthene	4	60
benzo(b)fluoranthene	4	60
benzo(k)fluoranthene	4	60
benzo(ghi)perylene	4	60
benzo(a)pyrene	1,5	20
indeno(1, 2, 3-c,d)pyrene	4	60

Table 3.1-2 gives the French guide values for concentrations of PAH and for the maximum cumulated input over a period of 10 years.

In 1995, a working group of the **Danish** Ministry of Environment and Energy identified organic chemical residues, for which limit values should be elaborated (DK-EPA 1996a, DK-EPA 1996b cit in MADSEN et al. 1997). Until 1997, the use of sludge in Denmark was regulated with respect to the maximum content of selected heavy metals, maximum of phosphorus, nitrogen and dry matter of waste to be applied per hectare and year and regulations regarding the use of waste-treated farmland (no root crops, cattle grazing or

other direct non-processed use for consumption until one year after application) (MADSEN et al. 1997). The primary targets are consumers of products grown on sludge-amended fields, consumers of ground water from areas where sludge is applied as fertilizers and the biological structure and function of the soil ecosystem exposed to contaminants from sludge. The quality criteria elaborated by the above procedure is used as "Predicted no-effect concentration" (PNEC) for protection of farmland quality (PNECsoil , PNECplant , PNECgroundwater) (MADSEN et al. 1997).

In **Germany** the fertilizer effects of sludges have to be taken into account according to the rules of the German Fertilizer Act and its respective ordinances when sewage sludge is to be used in agriculture (LESCHBER 1997). It is prohibited to use sludge in fruit and vegetable cultivation, on grassland, in nature conservation areas, in forests and near water catchments/wells respectively in water protection areas. The German regulation comprises limits for AOX, PCB und PCDD/F. SAUERBECK & LESCHBER (1992) report, that the German Ministry of the Environment set these limit values as a purely precautionary measure, they were not based on scientific evidence of immanent toxicological implications. Instead the limit values were based on the current concentrations of the respective compounds in German sewage sludges. Concentrations of AOX in sludges do not really give information about the absence or presence of hazardous substances, this could mean a measure of careful soil protection to prevent the input of high amounts of anthropogenic compounds into soil, some of which may be persistent pollutants (LESCHBER 1992).

Surface application of undigested or digested sludges on grazing land were banned in the **UK** in January 1999, although the injection of digested sludge into grazed pasture soils is currently allowed (SMITH 2000).

There are, actually, no formal **Swedish** regulations for organic contaminants in sludge. There is an informal agreement between the Swedish EPA, the Farmers Union and the Water and Wastewater Association which includes the recommendations in table 3.1-1. These agreements are based more on practical experience than on scientific data. Sweden also used to have a recommended limit value for toluene, but this has been omitted (WALLGREN 2001).

The **US** regulation on the use of sewage sludge in agriculture does not establish numerical pollutant limits of any organic pollutants, because at least one of the following criteria applied for the organics considered (USEPA 1995): the pollutant is banned for use, has restricted use or is not manufactured for use in the US; the pollutant is detected infrequently in sludge and is present in 5% of sludge samples; the limit for an organic pollutant derived from the 503 exposure assessment is greater than the 99th percentile concentration in sludge (SMITH 2000).

3.1.2 Background information about contaminants

3.1.2.1 AOX

The analytically determined parameter of adsorbable organic halogen compounds (AOX) does not represent a specified chemical substance. Rather, it is defined by the binding of a halogen-containing chemical to activated carbon. In given samples, e.g. different sewage sludges or waste waters, AOX can be composed of quite diverse compounds depending on the origin of the samples. The formation of AOX has been observed in the context of drinking-water desinfection. Both chlorination and ozone treatment may lead to the formation of trihalomethanes (THM) with bromine derivates being formed when small amounts of bromine are present in the water. The German drinking-water directive mentions chloroform, bromodichloromethane, dibromochloromethane and bromoform as analytical parameters for THM. While other organic halogens are formed in these processes as well, which are all detected as AOX, THM serve as an indicator class of compounds. As a rough estimate, the relation of AOX to THM in drinking-water is estimated to be 10 : 1 (GROHMANN 1991). One of the main sources of AOX has been the bleaching of paper pulp leading to the formation of organic halogens. In Finland, this industry was responsible for about 50 % of the total organic halogen emissions into the environment. Several other industries, such as the manufacture of polyvinyl chloride (PVC), and waste incineration are important sources of AOX formation as well. PVC itself, which is otherwise regarded as inert, may enhance the AOX measured significantly. In the context of soil contamination it is noteworthy that some organic halogens may be transformed in the soil to more toxic compounds such as vinyl chloride, which is a known human carcinogen (SALKINOJA-SALONEN et al., 1995; AURAS 2001).

3.1.2.2 NPE

4-Nonylphenole is a widespread degradation product of non-ionic alkylphenole polyethoxylate surfactants (HARMS 1997). Due to the problems caused by foaming on surface waters, there has been an increase in the adoption of more readily biodegradable detergents such as non-ionic 4-alkylphenole polyethoxylates, which are used in large quantities in detergents. 4-nonylphenole has been identified as a toxic degradation product of alkylphenole polyethoxylate (JONES & NORTHCOTT 2000). NPEs are used as surface active agents in cleaning products, cosmetics and hygienic products, and in emulsifications of paints and pesticides. Due to the hazardous properties, the NPEs are slowly being phased-out of the market.

3.1.2.3 LAS

Linear alkylbenzene sulphonates (LAS) are the most widely used anionic surfactants in cleaners and detergents. LAS was introduced as a substitute for the slowly biodegradable ABS in the mid-1960s (JONES & NORTHCOTT 2000). Production is 1.5 to 2 million t/yr worldwide and 300 000 t/yr within the EU. LAS is readily degraded under aerobic conditions, but not at all in anaerobic environments (MADSEN et al. 1997). Since a large part

of the LAS is absorped onto sewage solids during primary settlement of sewage, it will bypass the aeration tank and hence not degrade in the regular treatment process. Degradation can only occur when aerobic conditions are restored during storage of sludge, and after application to land thus preventing LAS accumulation in the soil environment (DE WOLFE & FEIJTEL 1997).

3.1.2.4 DEHP

Phthalates are incorporated into plastics as plasticisers. Di-2-(ethyl-hexyl)-phthalate (DEHP) is the most common of the phthalate esters. Phthalates are used as softeners in plastic (PVCs). Other uses include additive functions in paints, laquers, glues, inks, etc. Many phthalates are degradable under both aerobic and anaerobic conditions but the sorption to particles reduces the actual degradation rate considerably. The substances have a potential for uptake in plants. They are toxic to soil organisms and some phthalates are suspected to have hormone mimic properties (MADSEN et al. 1997).

3.1.2.5 PAH

PAHs are a by-product of incomplete combustion, their main source is the burning of fossil fuels. PAHs are ubiquitous in the environment and may be formed naturally, e.g. by forest fires. Many PAHs are known or suspected carcinogens/mutagens.

3.1.2.6 PCB

Commercial production of polychlorinated biphenyls (PCBs) began in 1929. PCBs are produced by chlorination of biphenyl, which has 10 positions available for chlorine atoms, producing a theoretical mixture of up to 209 possible compounds distributed among 10 levels of chlorination. The chemical and physical stability of PCBs, their electrical resistance, low volatility and resistance to degradation at high temperatures added to the commercial utility of PCBs.

3.1.2.7 PCDD/F

Polychlorinated dibenzo-p-dioxins and -furans (PCDD/Fs) are two groups of tricyclic, planar aromatic compounds. They are not intentionally produced, but may form during the production of chlorinated compounds such as e.g. pentachlorophenole, or during combustion processes where chlorinated substances are present. There are potentially 75 PCDD and 135 PCDF congeners, which belong to 8 homologue groups according to the numbers of chlorine atoms present. PCDD/Fs are ubiquitous in the environment at extremely low levels.

3.1.2.8 Other Pollutants

Organotins

To date, organotins are the most widely used organometallic compounds. Recent estimates assumed that the annual world production of organotins may be 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 tricyclohexxyltin 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).

Musk ketone and musk xyxlenes

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 there useage. TAS et al. (1997) give a review of environmental data and a risk assessment procedure for these compounds.

3.2 Occurrence of contaminants in sewage sludges

3.2.1 General aspects

In a literature review of DRESCHER-KADEN et al. (1992) including 900 papers published since 1977, residue data about the level of organic pollutants in German sewage sludges were collected. 332 organic compounds with known or suspected toxic effects have been detected in sewage sludges, 42 of them regularly, most of them within the range of g/kg to mg/kg dry matter. Except volatile and easily degradable chemicals, the residue level increases from raw to digested sludge. Samples from rural treatment works have a more balanced residue pattern than from urban origin where the highest and also the lowest values have been found. But generally, the residues in rural areas tend to be slightly lower, particularly for typical industrial chemicals (DRESCHER-KADEN et al. 1992).

3.2.2 Pollutant specific data

3.2.2.1 AOX

In a survey of contamination levels of Danish sewage sludges, MADSEN et al. 1997 found concentrations for AOX in the range from 75-890 mg Cl/kg dm in sludge samples of 19 municipal waste water treatment plants in the year 1995. UMK-AG 2000 report concentrations and percentiles for the years 1994 to 1996 (Table 3.2-1).

Tabelle 3.2-1: *AOX content in sewage sludges from Germany (UMK-AG 2000)*

year	**Mean** mg/kg dm	**highest 90-perzentile among German Bundeslaender** mg/kg dm
1994	206	370
1995	201	400
1996	196	363

3.2.2.2 NPE

In their survey of Norwegian sewage sludges PAULSRUD et al. (2000) found Nonylphenole (+ ethoxylates) in high concentrations in sludge samples from all the sewage treatments plants they investigated. All of these sludges would have exceeded the Swedish and Danish standards. There has been a minor decrease in nonylphenole concentration in Norwegian sludges since 1989s, which is mainly attributed to the industries phasing out these compounds from their products (i.e. detergents, paints). Similar experiences have been reported from Switzerland (GIGER 1997 cit. in PAULSRUD et al. 2000). In 1997, at the "Specialty Conference on Mangement and Fate of Toxic Organics in Sludge Applied to Land", the Swedish Environmental Protection Agency reported a mean value for

Nonylphenole of 46 mg/kg dm (TIDESTRÖM 1997). PAULSRUD et al. give an overview of concentrations found in various surveys in Scandinavia (Table 3.2-2)

Table 3.2-2: *Overview of concentrations of Nonylphenole (+ ethoxylates) in Scandinavian sewage sludges*

Investigations	Number of samples	Range	Median	References
	36	22-650 (mg/kg dw)	136	PAULSRUD et al., 2000
Norwegian (1989)	19	25-2298 (mg/kg dw)	189	VIGERUST, 1989
Swedish (1993)	23	23-171 (mg/kg dw)	82	National Swedish Environmental Protection Board, 1995 cit in PAULSRUD et al., 2000
Swedish (1989-91)	27	44-7214 (mg/kg dw)	825	National Swedish Environmental Protection Board, 1992 cit in PAULSRUD et al., 2000
Danish (1995)	20	0,3-67 (mg/kg dw)	8	TÖRSLÖV et. al., 1997
Danish (1993-94)	9	55-537 (mg/kg dw)	–	TÖRSLÖV et. al., 1997

3.2.2.3 LAS

JONES & NORTHCOTT 2000 compiled data on LAS concentrations in sewage sludges for a number of countries (table 3.2-3a). Ranges of concentrations in Danish and Norwegian sludges are found in table 3.2-3b. MADSEN et al. (1997) report LAS concentrations for Norway in the range of < 1 to 424 mg/kg dm which are far lower than in sludges from other countries. The relatively low concentrations in Norway may be accounted for by the predominant use of detergents that do not contain LAS (PAULSRUD et al. 2000). Since LAS biodegrade under aerobic conditions, the low concentrations in part of the German sludges may be due to aerobic digestion, whereas missing treatment (digestion of organic matter leads to relative concentration of contaminants), may have kept the concentrations down in the non-treated Spanish sludges.

Table 3.2-3a: *Concentrations (mg/kg) of LAS in sewage sludge from selected countries (JONES & NORTHCOTT 2000)*

Country	No of WWTP	Sludge description	Range
Denmark	19	Various	11-16100
Germany	8	Anaerobically digested	1600-11800
Germany	10	Aerobic	182-432
Italy	1	Anaerobically digested	11500-14000
Spain	3	Anaerobically digested	12100-17800
Spain	2	Non-treated	400-700
Switzerland	10	Anaerobically digested	2900-11900
UK	5	Anaerobically digested	9300-18800

Table 3.2-3b: *Concentrations (mg/kg) of LAS in sewage sludge from Norway and Denmark*

Country	Number of samples	Range of concentrations	Median	References
Norway (1996-97)	36	< 1-424	54	PAULSRUD et al. 2000
Danish (1995)	20	11-16100	530	TÖRSLÖV et. al., 1997
Danish (1993-94)	6	200-4640	455	TÖRSLÖV et. al., 1997

3.2.2.4 DEHP

DEHP was detected in almost all sewage sludge samples, and three of the plants revealed concentrations above the Danish 1997-standard (MADSEN et al. 1997). DBP was detected less frequently and also at lower concentrations than DEHP. There has been a significant reduction in DEHP content of Norwegian sludges since 1989, but the values are still higher than in the Danish investigations. Both DEHP and DBP were also found in compost and manure, but at lower levels than in sewage sludge (PAULSRUD et al. 2000)

Also DEHP appeared in relatively high concentrations in water extracts of sludge (mean concentration: 55 µg/l, highest measured value: 310 µg/l). Although DEHP is expected to sorb firmly to sludge particles, the concentration in sludge is sufficiently high to result in measurable concentrations in water extracts (MADSEN et al. 1997). MADSEN et al. 1997 found, that the most common phthalates in the sludges were DEHP with concentrations between 4 and 170 mg/kg (d.m.). Table 3.2-4 gives data on concentrations found in various investigations.

Table 3.2-4: *Concentrations of DEHP in Sewage Sludges of various countries (mg/kg dw)*

Investigations	Number of samples	Range	Median	References
Norway	36	<1-140	58	PAULSRUD et al. 2000
Norwegian (1989)	19	27-1115	83	VIGERUST, 1989
Swedish (1989-91)	27	25-661	170	National Swedish Environmental Protection Board, 1992 cit in PAULSRUD et al., 2000
Danish (1995)	20	3,9-170	24,5	TÖRSLÖV et. al., 1997
Danish (1993-94)	9	17-120	38	TÖRSLÖV et. al., 1997

3.2.2.5 PAH

In Danish sludges the concentrations of PAHs (sum of 9 PAHs) were typically below 3 mg/kg (d.m.) (MADSEN et al. 1997). WILD et al. (1992) reported concentrations of polynuclear aromatic hydrocarbons in UK sewage sludges in the range of 1-10mg PAH/kg, which is significantly higher than the normal range of concentrations found in agricultural soils. In their study of Norwegian sludges PAULSRUD et al. (2000) found PAH concentrations below the Swedish and Danish standards of 1997 in most samples. There were large monthly variations in most treatment plants and hence the authors suggest that one single sample is not sufficient to evaluate the level of toxic organics in sewage sludge. The PAH concentrations of this study were almost at the same level as in the previous Norwegian investigation, but above the more recent values reported in Sweden and Denmark (PAULSRUD et al. 2000). Data of different countries are shown in Table 3.2-5.

Table 3.2-5*:Concentrations of PAH in Sewage Sludges of various countries (mg/kg dw).*

Investigations	Number of samples	Range	Median	References
Danish (1995) (sum of 18 compounds)	20	<0,01-8,5	–	TÖRSLÖV et. al., 1997 (cit. in Paulsrud 2000)
Danish (1993-94) (sum of 18 compounds)	9	0,42-2,4	–	TÖRSLÖV et. al., 1997 (cit. in Paulsrud 2000)
Norway	36	0,7-30	3.9	PAULSRUD et al. 2000
Sweden (sum of 6 compounds)	-	-	1.6	TIDESTRÖM 1997
parts of Germany (sum of 6 compounds)	124	0,4-12,83	-	UMK-AG 2000
parts of Germany (sum of 16 compounds)	88	0,25-16,28	-	UMK-AG 2000

3.2.2.6 PCB

SCHAAF (1992) found PCBs in nearly every sample of a selection of sewage sludges from different parts of Germany, with the congeners 138 and 153 being the most important among 28, 52, 101, 138, 153 and 180. MCGRATH et al. (2000) found PCBs in almost all the sample that were examined, with a maximum concentration of 0.105 mg/kg. Results from the first US National Sewage Sludge Survey, confirmed that concentrations of PCBs in most US biosolids were much lower than found in previous US surveys (CHANEY et al. 1998). According to an estimation of the US-EPA the 98th percentile of biosolid PCB concentration was 0.21 mg/kg dw. PAULSRUD et al. (2000) found that PCB contents in Norwegian sludge samples were far below the German and Swedish standards for PCB and, in general, were lower than in previous studies in Scandinavia. They found variations between monthly samples from each plant to be larger than differences between plants. HEMBROCK-HEGER (1992) compared untreated soils and soils treated with sewage sludge. Most PCB concentrations were near the detection limit (1 µg/kg for each congener).

Table 3.2-6a gives an overview of concentrations of PCB sums found in various countries while table 3.2-6b shows mean concentrations of PCB congeners in Germany.

Table 3.2-6a: *Concentrations of PCB in Sewage Sludges of various countries (mg/kg dw)*

Investigations	Number of samples	Number of congeners	Range	Median (Mean)	References
Norway	36	7	0,017-0,10	0,0422	PAULSRUD et al. 2000
Swedish (1993)	23	7	0,0006-0,232	0,113	National Swedish Environmental Protection Board, 1995 cit in PAULSRUD et al., 2000
Swedish (1989-91)	27	7	0,080-7	-	National Swedish Environmental Protection Board, 1992 cit in PAULSRUD et al., 2000
Sweden (sum of 7 congeners)	-	7	-	(0.1)	TIDESTRÖM 1997
Germany	-	each of 6 congeners	< 0,2	-	UMK-AG 2000

Table 3.2-6b: *Mean PCB-concentrations in sewage sludge in Germany (mg/kg dm)(UMK-AG 2000)*

	PCB 28	PCB 52	PCB 101	PCB 138	PCB 153	PCB 180	Sum
1989	0,041	0,028	0,052	0,082	0,084	0,053	0,340
1994	0,015	0,015	0,024	0,039	0,039	0,026	0,158
1996	0,016	0,017	0,020	0,037	0,038	0,026	0,154

3.2.2.7 PCDD/F

Some PCDD/Fs have been shown to form during wastewater treatment processes, however, this is considered minimal and insignificant compared with inputs via the sludge itself (ALCOCK & JONES 1996).

In the **UK** PCDD/F is reported to be ubiquitous in sewage sludge. Estimates of the inputs of PCCD/Fs from sewage sludge applied to agricultural land in the U.K. (JONES & SEWART 1995 cit in DUARTE-DAVIDSON et al. 1997) are currently about 25 g TEQ/year respectively 21 kg/PCDD/F per year. Interestingly, the input of TEQ via sludge use is only about 1.8% of the estimated input from atmospheric deposition, while the PCDD/F input is a more significant portion, because sludge contains very high concentrations of non-2,3,7,8-substituted and/or low TEF-rated congeners (DUARTE-DAVIDSON et al. 1997). For Denmark too, the use of sewage sludge in agriculture is considered a minor source of dioxin emissions to soils than deposition from the atmosphere (HANSEN 2000).

PAULSRUD et al. (2000) found in a survey of **Norwegian** sludges, that concentrations of PCDD/PCDF were in general very low and showed only small monthly variations (PAULSRUD et al. 2000).

I-TEQ values in **Catalonian** sludges of 1987 and of 1993-1994, were higher than those measured in contemporary sludges (ELJARRAT et al. 1999). The lower levels detected in the contemporary samples seem to reflect a general decline in PCDD/F inputs to the environment, owing to tighter controls on PCP use and disposal (ELJARRAT et al. 1999).

Table 3.2-7: *Comparison of Investigations of PCDD/F in Sewage Sludge (ng/kg dm)*

Investigations	Number of samples	Range	50.P	mean	90.P	References
	36	3,0-68,8	6,26	-	-	PAULSRUD et al. 2000
Swedish (89/91)	14	5,7-115	20,5	-	-	National Swedish Environmental Protection Board, 1992 cit in PAULSRUD et al., 2000
Danish (93/94)	9	10,3-34,2	-	-	-	TÖRSLÖV et. al., 1997
Germany 1994			-	22	46	UMK-AG 2000
Germany 1995			-	19	51	UMK-AG 2000
Germany 1996			-	17	56	UMK-AG 2000

In their compilation of environmental levels of dioxins AEA TECHNOLOGY (1999) reported the data given in table 3.2-8 to the European Commissions respectivey to the UK Department of the Environement, Transport and the Regions.

Table 3.2-8: *Comparison of Investigations of PCDD/F in Sewage Sludge (ngTEQ/kg dm)*

Country	***Austria***	***Denmark***	***Germany***	***Spain***	***Sweden***	***UK***
Range	*8,-38*	*0,7-55*	*0,7-1207*	*64*	*0,02-115*	*9-192*
Average	*14,5*	*21*	*20-40*		*20*	

3.2.2.8 Others

3.2.2.8.1 Organotins

From the production figures and use pattern, it becomes evident that a significant portion of organotins may enter wastewaters. A study of FENT et al. (1995) on the occurrence of organotin compounds in municipal wastewater and sewage sludge identified several compounds in these media. These compounds have been found to become enriched in sewage sludge, where they are not substantially degraded during treatment (FENT et al. 1995). 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 (FENT & MULLER 1991 cit in FENT et al. 1995). Other sewage sludge samples from Switzerland were found to be similarily contaminated, whereas sludges of three out of five Canadian cities had butyltin residues which were somewhat lower than those in Switzerland (FENT et al. 1995).

3.3 Basic toxicological data

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3.3.1 Notes on the basic toxicological data sets

Non-carcinogenic as well as carcinogenic effects are described briefly in chapter 3.3.2. Exact dose and effect levels are not mentioned but the most relevant endpoints, i.e. those for which effects at lower dose levels are known, are emphasized. The risk phrases (and their meaning) according to the classification and labelling legislation within the EU are given. The basis for these risk phrases is Annex I of Council Directive 67/548/EEC of June 27 1967 and the respective amendments. Table 3.3-1 lists classifications in relation to carcinogenicity, mutagenicity and reproductive (CMR) effects. The basis for these classifications are the Council Directive mentioned above, the assessment of the German „Technical Rule for Hazardous Substances" (TRGS 905) and classifications by the International Agency for Research on Cancer (IARC) of the World Health Organization (WHO) in its Monograph series. In the section guidance and limit values some health-related guidance and limit values are given. In cases, where reliable risk estimates of carcinogenic potency exists, these are given after the table of guidance / limit values. In general, unit risk estimates are reported in this section which are based on animal experiments or epidemiological data. They describe the excess risk of cancer resulting from lifetime exposure to the respective chemical at a given dose or concentration. These values do not represent a threshold.

Table 3.3-1: *Definitions of terminology used in chapter 3.3.*

Ref.	***Category***	**Erläuterung**
EU, 1993	*Carcinogenicity*	(The assessment of the German TRGS 905 relies on similar criteria)
	Category 1:	Substances known to be carcinogenic to man.
	Category 2:	Substances which should be regarded as if they are carcinogenic to man.
	Category 3:	Substances which cause concern for man owing to possible carcinogenic effects but in respect of which the available information is not adequate for making a satisfactory assessment.
IARC, 1999	*Carcinogenicity*	
	Group 1:	The agent (mixture) is carcinogenic to humans.
	Group 2A:	The agent (mixture) is probably carcinogenic to humans.
	Group 2B:	The agent (mixture) is possibly carcinogenic to humans.
	Group 3:	The agent (mixture or exposure circumstance) is not classifiable as to its carcinogenicity to humans.
	Group 4:	The agent (mixture) is probably not carcinogenic to humans.
EU, 1993	*Genotoxicity*	(The assessment of the German TRGS 905 relies on similar criteria)

Ref.	*Category*	**Erläuterung**
	Category 1:	Substances known to be mutagenic to man.
	Category 2:	Substances which should be regarded as if they are mutagenic to man.
	Category 3:	Substances which cause concern for man owing to possible mutagenic effects.
EU, 1993	*Reproductive effects and fetotoxicity*	(The assessment of the German TRGS 905 relies on similar criteria)
	Category 1:	Substances known to impair fertility in humans.
	Category 2:	Substances which should be regarded as if they impair fertility in humans.
	Category 3:	Substances which cause concern for human fertility.
Guidance and limit values		
WHO - Acceptable daily intake		ADI values (or similar values such as Tolerable daily intake (TDI)) are usually derived for non-carcinogenic endpoints.
EPA - Reference dose		Derived with a similar concept and usually listed in the „Integrated Risk Information Systems“ (IRIS) of the United States Environmental Protection Agency (EPA, 2000a).
EU - Drinking water directive		Drinking water parameters as set out in Commission Directive 98/83/EC (EU, 1998).
WHO - Air quality guidelines		Guideline values for a contaminant in the air derived for non-carcinogenic endpoints (risks for exposure to carcinogens are described below).
EPA - Reference concentration		Same as above („reference dose“) but for inhalation exposure.
D - „water hazard class“		The „water hazard class“ reflects acute toxicity in mammals, acute ecotoxicity, degradation and distribution in environmental media as well as hazardous reactions with water and is detailed in UBA (1996).

3.3.2 Pollutant specific data

3.3.2.1 AOX Adsorbable organic halogen compounds

The analytically determined parameter of adsorbable organic halogen compounds (AOX) does not represent a specified chemical substance. Rather, it is defined by the binding of a halogen-containing chemical to activated carbon. The formation of AOX has been observed in the context of drinking-water desinfection. Both chlorination and ozone treatment may lead to the formation of trihalomethanes (THM) with bromine derivates being formed when small amounts of bromine are present in the water. The German drinking-water directive mentions chloroform, bromodichloromethane, dibromochloromethane and bromoform as analytical parameters for THM. While other organic halogens are formed in these processes as well, which are all detected as AOX, THM serve as an indicator class of compounds. As a rough estimate, the relation of AOX to THM in drinking-water is estimated to be 10 : 1 (GROHMANN 1991).

Because AOX is an analytically determined parameter and represents a wide range of substances, differing not only in their chemical structure but also in their toxicological profile, a description of relevant **toxicological endpoints cannot be given**. There are no toxicologically relevant guidance or limit values for AOX as a parameter.

3.3.2.2 NP nonylphenoles and NPE nonylphenole ethoxylates

This chapter summarizes toxicological data for 4-nonylphenole (NP, CAS No.: 25154-52-3). Because this is the breakdown product of the respective ethoxylates, a discussion of its health effects covers the main effects of the ethoxylates as well. Branched NP (CAS No.: 84852-15-3) is not considered explicitely in this document but seems to exert in part similar toxic effects as the non-branched isomer.

NP is harmful after acute **oral exposure** in rats (LD50 approx. 1900 mg/kg, OECD guideline 401) and should be classified as corrosive (BUA, 1988; ECB, 2000). Reproductive effects represent the most important toxicological endpoint and NP has been recently tested for this endpoint in a number of studies. In vitro, NP showed affinity for binding to the estrogen and progesterone receptors (LAWS et al., 2000). In vivo, data on reproductive effects in the male rate are somewhat conflicting. Postive results obtained by LEE (1988) in neonatal male rats could not be confirmed in a repetition of the central experiment (ODUM & ASHBY 2000). CHAPIN et al. (1999) observed mild reproductive as well as nephrotoxic effects in a recent rat multi-generation study. Reproductive effects in these studies consisted e.g. of accelerated vaginal opening and increased uterine weights in females and effects on testes size and sperm parameters in males. In summary, NP seems to be a reproductive toxicant. Its estrogenic activity, which is believed to be mediating at least some of the reproductive effects, is weak compared to both estradiol and octylphenole (UBA, 1997).

Studies on the **carcinogenicity** of NP could not be located. In vitro and in vivo genotoxicity studies do not point to a mutagenic potential (ECB, 2000; BUA, 1988).

There is no EU risk phrase-or CMR classification. Guidance and limit values are reported in Table 3.3-2.

Table 3.3-2: *Toxicological classification of NP and NPE*

Guidance / limit value for NP and NPE	**Value**	**Remarks**	**Reference**
German "water hazard class"	3 (highly hazardous) 2 (hazardous)	NP NPE	UBA, 1996

3.3.2.3 LAS Linear alkyl benzene sulfonic acids and their sulfonates

There are several linear alkyl benzene sulfonic acids and respective sulfonates with varying chain lengths (C11, C12, C13 and - in the USA - also C14). Commercial mixtures consist of compounds of varying chain lengths and the carbon number given is only an average value, e.g. C11,8. The substances with a chain length of 12 carbon atoms (C12), i.e. dodecylbenzene sulfonic acid and its sodium sulfonate, are referred to as LAS and Na-LAS,

respectively, in RIPPEN (2000). Their CAS No. are 27176-87-0 for the acid and 25155-30-0 for the sodium salt. According to SÖDERLUND (1993), the latter seems to be the most predominant analog in commercial mixtures. Therefore, dodecylbenzene sulfonic acid and its sodium salt are primarily considered in this document and are referred to as LAS and Na-LAS. Some information is given for the group as well.

LAS is harmful in the rat **after acute oral administration** (LD50 = 500-2000 mg/kg, test according to OECD guidelines, GLP) with similar values for Na-LAS and a couple of mixtures as well. LAS is irritating to the skin and the eyes of experimental animals in tests according to OECD guidelines. Similar results were observed for Na-LAS and other alkylbenzene sulfonic acids/sulfonates. Skin and mucous membrane irritation was also observed in humans. In general, alkylbenzene sulfonic acids/sulfonates may lead to increased skin penetration of other substances due to damage of the lipid layer. They do not, however, seem to be sensitizing to the skin (ECB, 2000; SÖDERLUND, 1993; WHO, 1996). After both oral and dermal repeated exposures to linear alkylbenzene sulfonic acids/sulfonates, hepato- and nephrotoxicity seem to be most relevant apart from local effects (e.g. irritation of the skin or the gastro-intestinal mucosa). One study reported lung damage (e.g. alveolar inflammation and hyperplasia) in monkeys after subchronic inhalation of a commercial detergent containing 13 % Na-LAS. In addition, there is limited evidence for reproductive and fetotoxic effects in some studies but probably only at doses causing maternal toxicity. A larger number of other studies showed no such effects (SÖDERLUND, 1993; WHO, 1996).

There is no evidence of **genotoxicity** (in vitro and in vivo) or **carcinogenicity** (oral and dermal application) of alkylbenzene sulfonic acids or their sulfonates (WHO, 1996; SÖDERLUND,1993). There is no EU risk phrases or CMR classification.

Table 3.3-3: *Toxicological classification of LAS*

Guidance / limit value for LAS	Value	Remarks	Reference
German "water hazard class"	2 (hazardous)	LAS	UBA, 1996

3.3.2.4 DEHP Di(2-ethylhexyl) phthalate

This chapter summarizes toxicological data for di(2-ethylhexyl) phthalate (DEHP; CAS No.: 117-81-7). The acute **oral toxicity** of DEHP is relatively low with LD50 values in rats generally above 25000 mg/kg. Long-term administration of DEHP to laboratory animals resulted in hepato- and nephrotoxic effects. Furthermore, DEHP reduces the fertility of both male and female rats and seems to have effects on the developing fetus. At higher dose levels (several thousand mg/kg diet) DEHP leads to testicular atrophy in a number of species (WHO, 1992; ATSDR, 1993; IARC, 2000). In a recent chronic toxicity study in mice DEHP caused, among other things, changes in kidney, liver and testis weights in male animals (DAVID et al., 2000). Because of pronounced species differences, e.g. in human

metabolism compared to rodents, it is difficult to extrapolate these findings to humans (WHO, 1992; ATSDR, 1993).

While DEHP generally showed no genotoxic effects in vitro and in vivo, the substance proved to be carcinogenic in several studies in mice and rats (ATSDR, 1993; IARC, 2000; WHO, 1992). In a recent re-assessment, the IARC has withdrawn its former classification of DEHP as "possibly carcinogenic" because of the finding that the carcinogenic effects in rats and mice are probably mediated by peroxisome proliferation which has not been seen in human hepatocyte cultures after DEHP application. The current classification is group 3 (not classifiable) (IARC, 2000). A similar approach has been proposed for reconsidering the EPA (U.S. Environmental Protection Agency) carcinogenicity classification of DEHP (DOULL et al., 1999). There is no EU risk phrase. Due to marked species differences a reliable risk estimate for carcinogenicity in humans cannot be given. The CMR classification is: Carcinogenicity, WHO (IARC): 3 and for Reproductive effects and fetotoxicity, Assessment of German TRGS 905: RE2, RF2.

Table 3.3-4: *Guidance and limit values for, respectively* ***t*** *oxicological classification of DEHP*

Guidance / limit value for DEHP	**Value**	**Reference**
Oral exposure, Tolerable daily intake (WHO)	25 µg/kg • d	WHO, 1996
Oral exposure, Reference dose (EPA)	20 µg/kg • d	EPA, 2000a
German "water hazard class"	1 (generally not hazardous)	UBA, 1996

3.3.2.5 PAH Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAH) are formed by various combustion processes and are found in the environment in complex mixtures of differing composition. Benzo[a]pyrene (BaP; CAS No.: 50-32-8) has been chosen as an indicator substance for this group of compounds by numerous national and international bodies (SCHNEIDER et al., 2000). It is therefore treated in this document as representing PAH in general.

The acute **oral toxicity** of PAH appears to be low to moderate. Adverse haematological effects are observed after long-term administration in experimental animals. Other effects include dermal (irritation, sensitizing activity), immunosuppressive as well as reproductive and fetal effects but carcinogenicity (see below) is the most important endpoint as it is already triggered at dose levels necessary for non-carcinogenic effects (WHO, 1998; FRIJUS-PLESSEN & KALBERLAH, 1999).

PAH mixtures lead to tumors of the respiratory tract after inhalation and to **skin tumors** after dermal application. These effects were seen in both experimental animals and epidemiological studies. Carcinogenic activity varies between individual PAH. WHO (1998) found that 26 out of the 33 PAH covered in their monograph are, or are suspected of

being, carcinogenic. The following classifications exist for benzo[a]pyrene (EU risk phrases): 45 (May cause cancer), 46 (May cause heritable genetic damage), 50/53 (Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment), 60 (May impair fertility) 61 (May cause harm to the unborn child).

The following risk estimates for BaP were judged to be reliable (SCHNEIDER et al., 2000): 2,15 • 10-6 per 1 ng/kg • d (SCHNEIDER et al., 2000) (oral exposure). For the evaluation of the carcinogenicity of PAH mixtures see SCHNEIDER et al. (2000).

The following CMR classifications exist for benzo[a]pyrene: Carcinogenicity, EU: 2; Carcinogenicity, Assessment of German TRGS 905: 2; Carcinogenicity, WHO (IARC): 2A; Genotoxicity, EU: 2; Genotoxicity, Assessment of German TRGS 905: 2; Reproductive effects and fetotoxicity, EU: RE 2, RF 2; Reproductive effects and fetotoxicity, Assessment of German TRGS 905: RE 2, RF 2. Various PAH containing mixtures as well as some occupations with contact to PAH are classified as carcinogenic to humans

Table 3.3-5: *Guidance and limit values for, respectively* ***t*** *oxicological classification of benzo[a]pyrene*

Guidance/limit value [1,2]	**Value**	**Remarks**	**Reference**
Acceptable daily intake (WHO)	only risk-based values for carcinogenicity (see below [1])		
Drinking water directive (EU)	0,010 •g/l [2]		EU, 1998
Air quality guidelines (WHO)	only risk-based values for carcinogenicity (see below)		
German "water hazard class"	3 (highly hazardous)	carcinogens not otherwise listed	UBA, 1996

1 WHO (1996) derived a drinking-water guideline of 0,7 •g/l for BaP. This is based on carcinogenic effects and corresponds to an excess risk of 1 • 10-5 (for carcinogenic potency evaluation see below).

2 EU (1998) also lists a value of 0,10 •g/l for the sum of benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene and Indeno[1,2,3,-cd]pyrene.

3.3.2.6 PCB Polychlorinated biphenyls

This chapter summarizes toxicological data for polychlorinated biphenyls (PCB, CAS No.: 1336-36-3), a mixture of individual congeners with a chlorine content of 20 - 68 %. The most well-known of these are "Aroclor" mixtures with a defined chlorine content (e.g. Aroclor 1254, chlorine conten 54 %).

In both animals and humans PCB exposure irritates the skin and the eyes and leads to chloracne, neurotoxicity, hepatotoxicity as well as elevated blood pressure and reproductive effects. Some of the human studies have to be judged carefully due to the presence of contaminants (PCDF, DDE). Immunological changes represent one of the most sensitive endpoint of PCB toxicity in laboratory animals, specifically rhesus monkeys, and have also been observed in humans (HASSAUER & KALBERLAH, 1999).

There is some evidence of carcinogenic activity of PCB in humans although possible concurrent exposure to contaminants makes it difficult to to finally assess carcinogenicity in

humans. In rats and mice, oral exposure to PCB lead to an increased incidence of tumors of the liver (HASSAUER & KALBERLAH, 1999). IARC (1987) judged the human data as "limited evidence" and the data from animal experiments as "sufficient evidence". Older unit risk estimates (see table 3.3-6) by the U. S. Environmental Protection Agency were judged to be not reliable (HASSAUER & KALBERLAH, 1999).

The EU risk phrases are: 33 (Danger of cumulative effects) and 50/53 (Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment). The CMR classification is as follows Carcinogenicity, Assessment of German TRGS 905: 3; Carcinogenicity, WHO (IARC): 2A; Reproductive effects, Assessment of German TRGS 905: RF2, RE2.

Table 3.3-6: *Guidance and limit values for, respectively* ***t*** *oxicological classification of polychlorinated biphenyls*

Guidance / limit value	**Value**	**Remarks**	**Reference**
Acceptable daily intake (WHO)	TCDD-equivalents for dioxin-like compounds including dioxin-like PCB		WHO, 1999
Reference dose (EPA)	70 ng/kg • d 20 ng/kg • d	Aroclor 1016 Aroclor 1254	EPA, 2000a
Air quality guidelines (WHO)	see above		WHO, 1999
German "water hazard class"	3 (highly hazardous)		UBA, 1996

3.3.2.7 PCDD/F Polychlorinated dibenzodioxins und dibenzofurans

There are 75 congeners of PCDD and 135 congeners of PCDF which differ in their degree of chlorination and the position of the chlorine atoms. With regard to PCDD and PCDF, the approach of Toxicity Equivalency Factors (TEFs) is widely accepted although there are different concepts proposed by a number of both national and international organisations (see Safe, 1990). TEFs rank an individual dibenzodioxin or dibenzofuran according to its potency relative to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD; CAS No.: 1746-01-6). As the most toxic and as the best studied compound TCDD is considered in this document as representing PCDD/PCDF.

TCDD exposure may result in a number of different effects only some of which are mentioned below. High doses of TCDD lead to chloracne, porphyria, hepatotoxic effects and neurological symptoms. In addition, diabetes, immunotoxicity, reproductive effects as well as effects on the developing fetus are described in the literature. Reproductive and fetotoxicity were observed at low dose levels and formed the basis for the derivation of a TDI (SCHNEIDER AND KALBERLAH, 1999; SCHRENK & FÜRST, 1999; EPA, 2000b).

TCDD was mostly negative when tested for genotoxicity and DNA-adducts but showed cell transforming activity. TCDD was carcinogenic in rats and mice after oral (e.g. hepatocarcinoma) and dermal application (fibrosarcoma). An increase in tumor incidence

or mortality was found in several studies of occupationally exposed subjects with the respiratory tract as the most consistent localisation (Schneider and Kalberlah, 1999). There exists no EU risk phrase-classicifation. IARC (1997) classified TCDD as carcinogenic to humans (group 1). Other polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans were judged to be not classifiable as to their carcinogenicity to humans (group 3). Based on epidemiological mortality studies in workers, BECHER et al. (1998) in a recent assessment estimated the following risks for TCDD: 0,5 - 5 • 10-3 per 1 pg TCDD/kg • d (oral, Becher et al., 1998). The U. S. Environmental Protection Agency (EPA), in a recent draft document, derived a similiar unit risk for TCDD intake with a slope factor of: 1 • 10-3 per 1 pg TCDD/kg • d (EPA, 2000b (draft)). The CMR-Classification is Carcinogenicity, Assessment of German TRGS 905: 2 (TCDD) and Carcinogenicity, WHO (IARC): 1 / 3.

Table 3.3-7: *Guidance and limit values for, respectively toxicological classification of polychlorinated dibenzodioxins and dibenzofurans*

Guidance / limit value[1]	Value	Remarks	Reference
Tolerable daily intake (WHO) 1	1-4 pg/kg • d	TCDD equivalents for dioxin-like compounds	WHO, 1999; SCHRENK & FÜRST, 1999
Air quality guidelines (WHO)	The publication lists the oral value above	-	WHO, 1999
German "water hazard class"	3 (highly hazardous)	TCDD, because of carcinogenicity	UBA, 1996

1 derived by an expert panel of the WHO but not an official WHO value.

3.4 Occurrence and persistence of organic contaminants in soils

3.4.1 General aspects

The total input rate of organic pollutants to soils should not exceed the rate of degradation. Once added to the soil, sludge-borne persistent organic pollutants are subject to a variety of processes, e.g. adsorption/desorption, degradation (biotic and abiotic), volatilization, erosion/runoff and leaching, that can act to reduce the concentration of persistent organic pollutants potentially available for plant uptake (O'CONNOR 1996). There is accumulation in soils, but the persistence varies between different groups and specific compounds within each group. Soil sorption is now widely recognized to affect microbial degradation of many compounds. Strongly adsorbed chemicals are apparently unavailable to microbes because only low concentrations are desorbed in solution and available for microbial uptake and intercellular metabolism (O'CONNOR 1996).

Surfactants can affect the fate and behaviour of hydrophobic organic compounds in soil, the potential for detergent ingredients to cause significant effects is limited due to the relatively low concentrations found compared with CMCs (critical micelle concentration). Typical soil concentrations of LAS, the most heavily used surfactant in domestic detergents, are significantly lower than those required to produce micelles in pore water. Therefore, it is unlikely that surfactants present in domestic detergents will contribute significantly to the mobilization of hydrophobic organic compounds in sludge-amended soil (HAIGH 1996).

Table 3.4-1: *Chemical properties of organic contaminants in soils (LITZ 1998)*

	soluability in water at 20°C [mg/l]	**vapor pressure bei 20o C [hPa]**	**Henry-Constant [9,8*10^{4} hPa*m3 /mol]**	**n-Okt./ H_2O coeff. log K_{ow}**	**adsorption to humus**	**adsorption to clay**	**aerobic degradation[1]**	**anaerobic degradation[1]**
LAS	62,5	0,0001	-	1,96	3 to 4	1	4	3
DEHP	40	6 x 10^{-4}	1,1 x 10^{-5}	4,88	4 to 5	3 to 4	3 to 4	2
NP	3.000	0,1	-	3,28	2 to 3	2	4	2 to 3
PAH								
Fluorene	1,8	9,6 x 10^{-4}	0,00021	4,31	4to5	3	3	1
Pyrene	150	0,8 x 10^{-5}	0,00002	4,88	5	3	2	1
Benzo[a]pyrene	0,004	0,7 x 10^{-8}	2,4 x 10^{-6}	6,15	5	3	2	1
PCBs								
4toChlorobiphenyl	1,65	2,0 x 10^{-2}		4,5	4 to 5	1 to 2	3	2
2,4,4 TriCB	0,085	1,1 x 10^{-3}	2.4 x10^{-2}	5,8	5	3	2 to 3	2
2,2,4,4,5,5toHexa CB	0,001	1,1 x 10^{-5}	0.8	6,9	5	3 to 4	1	1
PCDD/Fs								
2,3,7,8 TCDD	4,7 x 10^{-5}	6,2 x 10^{-9}	5,4 x 10^{-23}	7,1	5	3	1	1
1,2,3,7,8toPCDF	0,118 x 10^{-3}	5,8 x 10^{-10}		6,79	5	3	1	1
OCDD	0,004 x10^{-3}	4,1 x10^{-10}	0.14	7,59	5	3	1	1

[1]: time to 90% degradation: 1: > 3 years, 2: >1 years, 3: >18 weeks, 4: > 6 weeks

Table 3.4-1 provides an overview of the chemical properties of the respective organic substances from LITZ (1998). Adsorption to humus and clay particles as well as biological degradation (anaerobic or aerobic) are decisive factors for the persistency of organic contaminants in soils. LAS, DEHP and NP are less likely to absorb to humus and more easily degraded than are PAH, PCB or PCDD/F.

3.4.2 Pollutant specific field data

3.4.2.1 AOX

Instead of AOX concentrations as in sewage sludges, in soils the EOX values are used as sum parameters to describe the burden. According to studies in Northrhine-Westfalia EOX values in rural areas range from 0,3 (median) to 0,6 mg/kg (90.P) and from 0,4 (median) to 0,9 mg/kg (90.P) in urban agglomerations (LITZ 1998). Both AOX and EOX values are influenced by the amount of PVC present (MERTENS 1996, MERTENS 1999).

3.4.2.2 NPE

Nonylphenole does not show significant movement towards groundwater, as least in a sandy loam soil (MCGRATH 2000). 4-nonylphenole is more persistent as LAS, but there has been no evidence of an accumulation after repeated applications of sewage sludge at the same site (GÜNTHER & PESTEMER 1994). Under aerobic and anaerobic conditions the nonylphenole poly-ethoxylates will be decomposed to short chain nonylphenole poly-ethoxylates and nonylphenole, which has a tendency to absorb to the sludge, but under anaerobic conditions nonylphenole will degrade very slowly, and hence this substance will increase in concentration during anaerobic digestion of the sludge (GRÜTTNER et al. 1997).

3.4.2.3 LAS

LAS is rapidly degraded in soils under aerobic conditions (half-life < 10 days) (LITZ et al. 1987, MADSEN et al. 1997). Aerobic biodegradation in soil is considered the most important removal mechanism of LAS loading to the terrestrial environment through sludge-amendment (DE WOLFE & FEIJTEL 1997). The rates of degradation are described by GIGER et al. (1997) in terms of three periods: The initial one (0 to 10 days) shows a very fast rate of disappearance, followed by a time of transition (approximately 90 days), and then finally a long term (>150 days) persistence in the soil. Immediately following the application of the sludge to the soil, LAS disappear quickly (initial period) because they are readily available to the soil microorganisms, e.g. LAS is in the aqueous phase or sorbed to the surface of the particles. The residues are slowly incorporated into the soil particles and/or more strongly bound to the soil organic fraction making them less available (transition period) or unavailable (final period) to biodegradation. Similar types of transformation kinetics are very common in pesticides in soil which also can lead to persistent residual levels.

MIEURE et al. (1990) found four groups of researchers that had studied the concentrations and fate of LAS in sludge amended soil in field situations. LAS half-lives were calculated to be between **7 and 22 days**. Investigations by MARCOMINI et al. (1989 cit in Amundsen et al.

1997) demonstrated a decrease in concentrations of alkylbenzene sulphonate (LAS) of as much as 80% within the first month after sludge application. All of them exhibited, however, a residual concentration in the soil after 320 days, indicating that the residual fraction may be incorporated into organic material in the soil and be **less available for biodegradation** (AMUNDSEN et al. 1997). According to LITZ (2000) the degradation of 90 % of LAS takes place within 22 to 122 days depending on the type of soil (Table 3.4-2).

Table 3.4-2: *Degradation (dt 90%), leaching of LAS in different soils (summarized by LITZ 2000 from different sources)*

Soil type	Rainfall (mm)***	Mean temperature (°C)	dt 90**	Leaching Max. (cm)
Luvisol	195	17,8	28	30
Cambisol	563*	13,9	>56	30
Gleysol	187	13,8	24	30
Eutric Gleysol	175	16,4	100	40
Humic Gleysol	228	17,0	93	30
Dystric Gleysol	214	13,0	122	40
Rendzina	125	17,5	78	35
Calcic Gleysol	100	16,0	68	30
Vertisol	furrow irrigation	>25 (arid)	60	≥50

* inclusive waste water irrigation, ** 5 g LAS/m2 *** first 2 months of the field investigations

3.4.2.4 DEHP

DEHP shows rapid degradation in soils (DUARTE-DAVIDSON et al. 1995, GRÜTTNER et al. 1997). According to RIPPEN (2001) 50% of the DEHP are degradated within a time span from one week to three months after application of sludges on agricultural soils. Frequently 90% of DEHP will have disappeared within half a year, but there is little field data on how long complete degradation will take.

Examples of typical phthalate concentrations in soils of the area around Stuttgart are given in table 3.4.2.4-1. It is interesting that grassland concentrations are higher than concentrations in tillage land, inspite of the fact that sludge application to grassland has been forbidden for many years. This suggests that deposition from air is an important source for DEHP in soils. DEHP concentrations in agricultural soils range from 0,3 to 0,7 mg/kg (median and 90.P, Table 3.4-3).

Table 3.4-3: *Phtalate concentrations in soils of the area of Stuttgart, Germany (UMEG 1999)*

	n	50.P [µg/kg]	90.P [µg/kg]
sum of phtalates according to EPA 606			
arable land	61	786	1262
grassland	99	893	1825
individual compounds			
Dimethylphtalate (DMP)	152	78	252
Diethylphtalate (DEP)	159	73	250
Di-n-butylphtalate (DNBP)	162	307	421
Butylbenzylphtalate (BBP)	160	18	59
Bis(2-ethylhexyl)phtalate (DEHP)	162	249	667
Di-n-octylphtalate (DNOP)	108	82	199

3.4.2.5 PAH

In 1968, the UK AGRICULTURAL DEVELOPMENT ADVISORY SERVICE and the MACAULAY INSTITUTE FOR SOIL RESEARCH set up identical experiments at the Luddington and Lee valley experimental field stations. Results from these sites show a clear decrease in PAH concentrations through time and chemical breakdown and biotic degradation seem to be responsible for it. At both sites the higher molecular weight PAHs, such as benzo[ghi]perylene and coronene appear to be more persistent (WILD et al. 1992). Volatilization was only significant for naphthalene. However strong retention to soil organic matter will reduce losses by volatilization (WILD et al. 1992).

Literature data on benzo[a]pyrene degradation in soils vary strongly (see RIPPEN 2001), but for highly contaminated soils (> 10 mg/kg BaP) degradation rates of up to 90% within one year are reported. There seem to behardly any reliable field data on BaP degradation for soils BaP concentrations of 0,1 to 1 mg/kg.

Table 3.4-4 gives examples of PAH concentrations in soils of the area of Mannheim/Heidelberg; Germany. Apart from medians and 90.Ps it shows the average PAH profile (percentages of compounds). The PAH profiles are basically the same in rural and urban soils and seem to be independent of sewage sludge application. This suggests that the persistence of compounds is more decisive for their presence in soils than the original characteristic of the contamination.

Table 3.4-4: *Medians and 90.Ps of PAH concentrations in soils of the area of Mannheim/Heidelberg, Germany (UMEG 1998)*

	Rural soils				Urban soils			
	n	**median [µg/kg]**	**%**	**90.P [µg/kg]**	**n**	**median [µg/kg]**	**%**	**90.P [µg/kg]**
Naphthalin	52	-	-	<0,10	80	-	-	<0,10
Acenaphtylen	52	-	-	<0,10	80	-	-	<0,10
Acenaphten	52	-	-	<0,10	80	-	-	<0,10
Fluoren	52	-	-	<0,10	80	<0,10	0,70%	0,08
Phenanthren	52	0,06	7,10%	0,28	80	0,14	6,00%	0,66
Anthracen	52	<0,10	2,20%	0,09	80	<0,10	1,90%	0,2
Fluoranthene	52	0,16	17,80%	0,71	80	0,45	18,20%	1,99
Pyren	52	0,15	15,00%	0,6	80	0,42	18,70%	2,04
Benzo[a]anthracen	52	0,08	8,70%	0,35	80	0,29	9,70%	1,06
Chrysen	52	0,08	8,70%	0,35	80	0,24	7,20%	0,79
Benzo[b]fluoranthene	52	<0,10	7,90%	0,32	80	0,14	6,10%	0,66
Benzo[k]fluoranthene	52	0,05	6,30%	0,25	80	0,17	5,70%	0,63
Benzo[a]pyren	52	0,09	9,60%	0,38	80	0,3	9,30%	1,01
Indeno[c,d]pyren	52	0,06	4,60%	0,18	80	0,19	6,40%	0,7
Dibenz[a,h]anthracen	52	<0,10	2,70%	0,11	80	0,06	2,30%	0,25
Benzo[ghi]perylen	52	0,08	8,00%	0,32	80	0,24	7,60%	0,83
PAH - Sum (16)	52	0,82	100%	3,99	80	2,67	100,00%	10,92

3.4.2.6 PCB

Fifteen years after sewage sludge was used as filler material, as much as 20 percent of the added PCB are still present in the surface soil (AMUNDSEN et al. 1997). The result of AMUNDSEN et al. (1997) further indicates a high stability of heavily chlorinated PCBs in the sludge, which suggests a more precautious use of sewage on surface soils in public areas.

The experimental data of COUSINS et al. (1997) suggest that for the surface and plough layer applications volatilisation is an important loss process for PCBs. Volatilisation losses of PCBs from the subsurface layer of sludge were very low during the 32-day experiment, although fluxes were steadily increasing with time (COUSINS et al. 1997).

In a study of GAN & BERTHOUEX (1994) seventy-nine PCB congeners were identified in the sludge and soil. Each of these was quantified and studied. About 85% of the total PCBs in the sludge were 2-, 3-, 4-, and 5-chlorinated PCB congeners, and most of these showed a significant decrease in their soil concentrations over time. More highly chlorinated PCBs were more persistent in the sludge-amended farmland, but some of them did disappear. Most of the 2-, 3-, and 4-chlorinated PCB congeners showed significant decreases in their soil concentrations with half-lives in the range of **4 to 58 months**. The PCBs were associated with the runoff sediments and there was no measurable PCB in the liquid portion of the runoff.

There are no persuasive reasons to believe that dislocation by leaching or volatilisation are significant mechanisms for PCB disappearance from the surface soil layer. Biodegradation

is thought to be the predominant mechanism. The environment in the surface soil is predominantly aerobic and most of the disappearing PCB species are aerobically biodegradable. Anaerobic micro-environments also exist in soil and this could explain the degradation of the more highly chlorinated forms, which degrade anaerobically but not aerobically (GAN & BERTHOUEX 1994).

Table 3.4-5 contains PCB concentrations in soils of the Stuttgart area as examples. Contrary to PAH, PCB concentrations in soils are largely influenced through local sources. That grassland soils show higher PCB concentrations than field soils suggests that athmospheric depositions is very important. The PCB profiles of urban soils are not significantly different from the ones in rural areas. As was shown with PAH compounds, the physico-chemical properties of the individual PCB congeners seem to be more important for the occurrence in soils than the composition of the original contamination. In more than 1000 soil samples of Southwest Germany, only one profile could be attributed to a single source (UMEG 1995).

Table 3.4-5: *Medians and 90.Ps of PCB concentrations in soils of the area around Stuttgart (UMEG 1999)*

		[µg/kg]		
	n	**50.P**	**90.P**	**%**
Sum PCB 6				
rural vs. urban				
rural soils	290	14	98	-
urban soils	74	34	243	-
according to land use				-
arable land	85	10	40	-
grassland	171	16	101	-
special cultures	14	13	39	-
private gardens	40	30	284	-
forest and ecosyst.	20	18	85	-
parks	16	80	193	-
industrial and traffic	11	48	484	-
single congeners				
rural vs. urban				
rural soils				
PCB 28	283	1	3	3%
PCB 52	288	1	4	5%
PCB 101	290	2	12	13%
PCB 138	290	4	28	29%
PCB 153	290	4	23	24%
PCB 180	290	2	19	20%
urban soils				
PCB 28	74	<1	2	1%
PCB 52	74	<1	7	3%
PCB 101	74	4	35	14%
PCB 138	74	10	85	35%
PCB 153	74	10	73	30%
PCB 180	74	9	50	21%

3.4.2.7 PCDD/F

The literature shows that PCDD/Fs are ubiquitous contaminants in municipal sewage sludge and that they are virtually completely persistent in soil following application of sewage sludge to agricultural land (HEMBROCK-HEGER 1992). The concentrations of PCDD/F in soils generally increase with the applied rate of sewage sludges (MCLACHLAN & REISSINGER 1990; ELJARRAT et al. 1997). Assuming that all sources of PCDD/F can be capped, there will still be residual contamination of sewage sludge due to atmospheric deposition through surface runoff. Land application of sewage sludge will therefore continue to contribute to the contamination of soils (MCLACHLAN et al. 1996).

Table 3.4-6 shows average PCDD/F profiles in top soils of the area around Stuttgart. As with PAH and PCB, the profiles of PCDD/F homologues get to be similar over time, in only one case of the above mentioned series of samples the profile found could be connected to a particular source (UMEG 1995b).

Table 3.4-6: *Concentrations of the 17 PCDD/F-cogeneres and average profile of homologues in soils of tillage land, grass land and forest of the area around Stuttgart (UMEG 1999)*

			[ng/kg]		
	I-TEF	**n**	**50.P**	**90.P**	**%**
Rural soils					
2,3,7,8-TCDD	1,0	107	<0,5	<0,5	-
1,2,3,7,8-PCDD	0,5	107	<0,5	2,0	-
1,2,3,4,7,8-HCDD	0,1	107	<0,5	2,0	-
1,2,3,6,7,8-HCDD	0,1	107	2,0	10,0	-
1,2,3,7,8,9-HCDD	0,1	107	<0,5	6,0	-
1,2,3,4,6,7,8-HeptaCDD	0,01	107	18,0	185,6	-
Octa-CDD	0,001	107	105,0	928,8	-
2,3,7,8-TCDF	0,1	107	3,0	7,1	-
1,2,3,7,8-PCDF	0,05	107	2,0	6,7	-
2,3,4,7,8-PCDF	0,5	107	2,0	7,0	-
1,2,3,4,7,8-HCDF	0,1	107	3,0	13,8	-
1,2,3,6,7,8-HCDF	0,1	107	2,0	7,0	-
1,2,3,7,8,9-HCDF	0,1	106	-	<0,5	-
2,3,4,6,7,8-HCDF	0,1	107	1,4	6,8	-
1,2,3,4,6,7,8-HeptaCDF	0,01	107	13,0	101,2	-
1,2,3,4,7,8,9-HeptaCDF	0,01	107	1,0	9,0	-
Octa-CDF	0,001	107	20,8	367,8	-
I-TEq nach NATO	**-**	**132**	**2,4**	**13,3**	-
Summe TCDD	-	86	4,1	13,1	1%
Summe PCDD	-	86	7,0	32,8	2%
Summe HexaCDD	-	87	14,8	63,0	3%
Summe Hepta CDD	-	87	31,0	126,8	7%
Summe Octa-CDD	0,001	107	105,0	928,8	50%
Summe TCDF	-	87	23,0	92,6	5%
Summe PCDF	-	87	23,0	84,9	5%
Summe HexaCDF	-	87	18,0	72,9	4%
Summe Hepta CDF	-	87	18,7	81,6	4%
Summe Octa-CDF	0,001	107	20,8	367,8	20%

3.4.2.8 Others

Organotins

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 (FENT et al. 1995).

CB and pesticides

There is little information about the biodegradation of CBs in soils. A few studies have shown that the level of the biodegradation was generally very low (Baize 1994). Compounds (like 1,2-DCB) with a higher tendency to volatilise (higher vapor pressure and Henry's constant) had smaller residues than those (like HCB) with lower volatility. This implies that the CBs may have continually spread over other habitats since they were introduced into the soil (WANG et al. 1995).

Tabelle 3.4-7: *Concentrations of chlorinated pesticides in soils of the area of Stuttgart (UMEG 1999)*

		[µg/kg]	
	n	**50.P**	**90.P**
Hexachlorobenzene (HCB)	291	<1,0	5,0
Alpha-HCH	212	-	<1,0
Beta-HCH	147	-	<1,0
Gamma-HCH (Lindan)	269	<1,0	3,4
Delta-HCH	128	-	<1,0
HCH-Summe	269	<1,0	4,3
Aldrine	47	-	<1,0
Heptachlor	71	-	<1,0
Dieldrin	106	-	<1,0
Endrinee	99	-	<1,0
Alpha-Chlordan	42	-	<1,0
Gamma-Chlordan	65	-	<1,0
Chlordan-Summe	42	-	<1,0
DDE p,p'	246	1,3	20,9
DDE o,p'	96	<1,0	3,2
DDD o,p'	106	-	<1,0
DDD p,p'	200	<1,0	2,0
DDT o,p'	216	<1,0	2,6
DDT p,p'	229	1,2	15,2
DDT-Summe	260	3,6	45,5

Concentrations of CBs in sludge usually decrease with increase of chlorination level. Most CBs applied to field soils in sewage sludge are likely to evaporate into the atmosphere over relatively short periods, but a certain proportion of the chemicals would stay in the soil for much longer periods, especially HCB and PCB. About 10% of the CBs introduced into field soil by multiple application of sewage sludge became recalcitrant and remained in the soil for more than thirty years after the application (WANG et al. 1997).

Table 3.4-7 gives background values of chloro-organic pesticides. Besides DDT, HCB and Gamma-HCH are the most frequently found pesticides in soils.

3.5 Risk assessment

CHANEY et al. (1998) conclude, that beside direct ingestion of biosolids by children, the greatest risk from persistent lipophilic organic compounds arises when fluid biosolids are applied so that they adhere to to forage/pasture crops and are subsequently ingested by livestock used as human food.

SMITH (2000) too considers uptake of organic contaminants via direct ingestion of sludge adhering to grass and/or sludge-treated soil by grazing livestock and subsequent accumulation in animal as the main route of human exposure from agricultural use of sludge. However he summarizes, that the total human intake of identified organic pollutants from sludge application to land is minor and is unlikely to cause adverse health effects.

FRIES (1996) reports, that of the many organic contaminants in sludges, only lipophilic halogenated hydrocarbons accumulate in animal tissues and products. Compounds like phthalatee esters, PAHs, acid phenoleics, nitrosamines, volatile aromatics, and aromatic surfactants are metabolized and do not accumulate. Among halogenated hydrocarbons, compounds with low degrees of halogenation are metabolized and do not accumulate, but higher degrees of halogenation block metabolism, and concentrations in milk and tissue fat may be several-fold greater than in the diets. Polyhalogenated organics, including halogenated biphenyls, chlorinated pesticides and hydrocarbons, and chlorinated dibenzo-p-dioxins and dibenzofurans, are of greatest importance to animal farming because these compounds are persistent and tend to bioconcentrate in the lipids of tissues and products (FRIES 1996).

3.5.1 Transfer sludge-man by handling

All available epidemiological data indicate that probably the level of sanitary risks is low: workers on wastewater treatment plants or on composting units do not show more specific disease than others (LEGAS 2000). Workers and farmers may also be exposed during treatment, handling or application of sludge to land. This exposure is assumed to be small, but would need further documentation (ANDERSEN 2001).

3.5.2 Transfer soil-man (soil ingestion by humans)

The EU draft is the first regulation to allow the use of sewage sludge in parks, providing it is sufficiently treated to be hygienically benign. If sludge is to be used in parks, however, its burden with contaminants gains importance because of the contamination pathway sludge-soil-man. The German Soil Protection Directive (Bundesbodenschutzverordnung, BBodSchV 1999) gives an example of threshold values for organic pollutants in soil (table 3.5-1), which are meant to limit the uptake of contaminants via direct ingestion through young children to tolerable levels (cf. EIKMANN et al., 2000)

Table 3.5-1: *Threshold values for organic contaminants in soils of playgrounds, parks and residental areas in Germany*

compound	unit	playgrounds	parks	residential areas	industrial areas	Quelle
Aldrine	mg/kg soil	2	**10**	4	-	BMU (1999)
BaP	mg/kg soil	2	**10**	4	12	BMU (1999)
DDT	mg/kg soil	40	**200**	80	-	BMU (1999)
HCB	mg/kg soil	4	**20**	8	200	BMU (1999)
HCH-mix.	mg/kg soil	5	**25**	10	400	BMU (1999)
PCP	mg/kg soil	50	**250**	100	250	BMU (1999)
PCB_6	mg/kg soil	0,4	**2**	0,8	40	BMU (1999)
PCDD/F	ng I-Teq/kg	100	**1.000**	1.000	10.000	UM (1996)

3.5.3 Transfer soil-plant-animal

3.5.3.1 Transfer soil-plant

Four main pathways by which a chemical in the soil can enter a plant have been described by (TOPP et al. 1986 cit in DUARTE-DAVIDSON & JONES 1996) as follows:

- Root uptake from soil solution and subsequent translocation from roots to shoots (i.e. liquid phase transfer) in the transpiration stream;
- absorption by roots or shoots of volatilized organics from the surrounding air (i.e. vapour phase transfer);
- uptake by external contamination of shoots by soil and dust, followed by retention in the cuticle or penetration through it; and
- uptake and transport in oil channels which are found in some oil-containing plants such as carrots.

SMITH (2000) reports, that soluable organic compounds have the potential to enter the soil-root-plant system and to accumulate in crop tissues, but these chemicals are also usually subject to volatilization and/or degradation. The strongly bound compounds (e.g. PCBs, PAHs) are insoluble; they are not biologically active or available for crop uptake and soil-plant transfers are very low. Accordingly they are not considered to constitute a risk to the human foodchain from this environmental pathway (USEPA 1992a cit in MCLACHLAN et al. 1996). Except when vegetables have been sprinkled with raw wastewater, there is no proof of any epidemic induced by consumption of vegetables. Furthermore, analysis of food products coming from soils receiving sludge or coming from soils receiving others fertilizers do not indicate important differences (LEGAS 2000). Plant uptake is concentration dependent, hence a compound's persistence in soil has an obvious impact on potential uptake (O'CONNOR 1996).

Chemicals may come into contact with foliage following direct application (e.g. by spraying of pesticides or the surface application of sludge), deposition in association with dust, aerosols or atmospheric particulate matter and contacting the surrounding compound vapour volatilized from soil. Organic compounds may reach plant foliage directly from the air through the cuticle or the stomata. Retention by root surfaces and root crops has been shown for several compounds, mainly chlorobenezenes, PAHs, PCBs, PCDD/Fs and some organochlorine pesticides (pentachloronitrobenzenes, DDT, heptachlor epoxide and delta HCH) (DUARTE-DAVIDSON et al. 1996).

Plant uptake will be influenced by the soil type so that availability to plants will generally be highest in sandy soils and soils with low organic matter content. According to HEMBROCK-HEGER 1992 transfer factors of PAH, PCB and PCDD/PCDF from soil to plants seems to be lower than 0.1, probably lower than 0.01. Hence deposition from ambient air to plants predominates for these compounds.

Plant uptake of non-ionic organic chemicals from sludge-amended soils is usually dominated by vegetative uptake of contaminated vapour from the surrounding air. Heavily contaminated soils can influence the concentrations of organics in above-ground vegetation by the soil-air-plant route (BECK et al. 1996). Even if a compound can penetrate the plant, the polar nature of sap will avoid its transfer to the upper parts (DUARTE-DAVIDSON & JONES 1996). Carrots can concentrate lipophilic chemicals in their roots because of their lipid content (WILD & JONES 1992).

In pot experiments with carrots in sandy soil with a low sorption capacity several pesticides were more easily available to plants when LAS was added. In a high sorptive humic soil surfactants in average caused a decrease of availability (GÜNTHER & PESTEMER 1992).

ROMMEL et al. (1998) summarise the results of an extensive literature review about the transfer of organic contaminants as follows: Compared to other parts of plants, the surfaces of root and tubers are especially prone to absorb contaminants from soil, with the transfer from surface into the interior depending on the contents of lipophillic substances (cf carrots). For leaves, the volatiliziation of organic contaminants from soils (2-3 ring PAHs, lowchlorinated PCBs) and their condensation on the leave surfaces, is a more important pathway than systemic transport. This is especially true for plants grown under foil. Fruit and fruity vegetables as well as cereals hardly take up any organic contaminants.

The concentrations of **PAHs** in different crops/crop parts were measured in some archived crop materials from Luddington, Lee Valley and Woburn Market Garden experiments (WILD et al. 1992). Of the crops, carrots showed the highest concentrations, and adsorption of the PAHs to the root surface was considered to be responsible for this. In above ground parts, the plant materials were relatively enriched with low molecular weight PAHs.

MCGRATH 2000 concluded from a comparison between the PAH congeners in soil, sludge, air and plants that to the atmosphere was the main source of PAHs in the above-ground plant parts.

HEMBROCK-HEGER (1992) found an enrichment of **PCBs** from vegetable products over the food chain up to mother's milk. The author considers this enrichment to be predominantly caused by other paths of input than the transfer soil - plant. The results of an investigation into the uptake of polychlorinated biphenyls (PCBs) from soil by barley and tomato plants by QIUPING et al. (1991) suggest that there is no active transport of these compounds. However they concluded, that plants readily trap airborne PCBs escaping from soil and observed a close correlation between vapor pressure of PCBs and their concentration in plant tissue.

MCLACHLAN et al. (1994) found similar PCB concentrations in hay from different farms despite large differences in their soil levels of PCBs and concluded that under normal circumstances atmospheric deposition is responsible for most of the PCBs and **PCDD/Fs** in plant leaves. However they consider the presence of contaminated soil particles in the feed as an important pathway for PCDD/F or PCB uptake in farm animals (MCLACHLAN et al. 1994).

3.5.3.2 Transfer soil-(plant)-animal

The influence of the agricultural use of sewage sludge on the concentrations of PCBs and PCDD/Fs in soil, feed and milk was investigated on four **dairy farms** by MCLACHLAN et al. (1994). Evidence of contaminant accumulation in the soil was found on both farms that fertilized with sewage sludge. The concentrations in feed and milk from one of these farms were elevated. MCLACHLAN found out, that the agricultural use of sewage sludge does under some conditions lead to higher levels of PCBs and PCDD/Fs in food products.

Application of sludge to established forage crops provides the greatest potential for transport of persistent chemicals to human foods. The importance of this pathway relative to other pathways depends on the time between the application of sludge and harvest, including grazing (FRIES 1996)

A large number of studies have shown that livestock regularly ingest soils, and that soil ingestion is able to cause significant transfer of contaminants from soil to edible tissues of grazing livestock (CHANEY et al. 1996; JONES & ALCOCK 1997). CHANEY & LLOYD (1979; cit in CHANEY et al. 1996) evaluated adherence of spray applied fluid biosolids to forage crops and observed that biosolids adhered to forages for a prolonged period after application. Compared to the intake of roughage (stems and leaves of plants) as a source of contamination, the intake of feeds derived from seeds is not important (FRIES 1996).

Cattle can ingest soil either directly while grazing or indirectly through contamination of feed with soil. There are indications that the latter process may on average be more important. The amount of soil ingested and hence the risk of food chain contamination is largely dependent on farming practices employed. (MCLACHLAN et al. 1996).

Thus when sewage sludge containing organic compounds is spread on grassland, the effects are dependent upon the concentrations of contaminants in the sludge and upon the level of soil intake. Measures taken to minimize soil intake by livestock will have significant effects on the intake of organic contaminants (STARK & HALL 1992)

Soil ingestion will vary inevitably according to the individual situation and it may be prudent to recommend that sludge should only be applied to **grazing land where soil conditions and grazing management are such that soil intakes are likely to be low**. It is also important to ensure that sludge disposal techniques do not increase the risk of soil ingestion. Soil injection of sludges should avoid any increase of contaminants in the soil surface of pastures (STARK & HALL 1992).

3.5.3.3 Threshold values for the path soil-plant-animal

In 1996 for the first time in Germany threshold values were set for DDT, PCB, PAH and PCDD/F in respect to the pathway soil-plant (UM 1996, table 3.5.3-1). Extensive evaluation of literature had shown that benzo(a)pyrene concentrations in carrots and other root, tuberous or leavy vegetables in many cases surpassed the critical value of 1 µg/kg BaP fm when soil concentrations were above 1 mg/kg BaP (see DELSCHEN et al. 1996, ROMMEL et al. 1998). The threshold value for BaP concentrations in soil was therefore set for 1 mg/kg (BMU 1999), the thresholds for the other substances were set on a precautionary basis.

Table 3.5-2: *Threshold values for organic pollutants in respect to the contamination pathways soil-plant and soil-animal*

Substance	unit	threshold value	pathway	reference
HCB, HCH, heptachlor, Endrine	mg/kg soil	0,05	Soil-plant/-animal	UM 1996
DDT-Sum	mg/kg soil	0,10	Soil-plant/-animal	UM 1996
PCB (congere)	mg/kg soil	0,05	Soil-plant/-animal	UM 1996
PAH 16	mg/kg soil	10	Soil-plant/-animal	UM 1996
BaP	mg/kg soil	1	Soil-plant	BMU 1999
PCDD/F	ng I-TEq/kg soil	40	Soil-plant/-animal	UM 1996

3.5.4 Transfer soil-water

The transfer soil-water of organic contaminants has only been studied intensively for a few years. This is partly due to the high cost of such studies but also to the uncertainty of methods. Building lysimeters is very expensive and methodically questionable. The extraction of seepage water by use of vacuum lysimeters (suction cups) is less expensive, but necessitates assessing the water balance of the respective soil. Sampling soil water by centrifugation or extraction of soil samples is debatable and the results can only be evaluated by means of lysimeter or suction cup results. Most of the time the occurrence of substances in deeper layers of the soils is used as an indirect means for assessing soil-water transfer.

The transfer of organic substances from applied sewage sludges depends on the following factors:

- soil erosion (wash off of soil particles with precipitation)

- DOC-content (the proportion of soluable organic substance is the most important parameter for the transfer of hydrophobic contaminants. A prognosis of the mobility of contaminants therefore has to take the DOC into account)
- the soluability of contaminants in water

The following measures are important for avoiding the transfer of substances when sewage sludges are applied on land:

- sewage sludge is not applied close to surface water
- sewage sludge is not applied in areas where the ground water table is just below the surface
- sewage sludge is not applied when the soil is saturated with water.

MADSEN et al. (1997) describe that if LAS content in sludge samples was high, water extracts of the sludges were also high. Consequently, even though LAS is expected to degrade in the soil system, there may be a risk of groundwater contamination. The long-chained NPEs have a potential for leaching to ground water.

Table 3.5-3 contains the current German threshold values based on the soil-water pathway for seepage water in soil (BMU 1999) and for the soil matrix (UM 1996).

Table 3.5-3: *German threshold values for the soil water and soil matrix .*

compounds/compound groups	unit	threshold value	reference
Aldrine	µg/l soilwater	0,1	BMU 1999
DDT	µg/l soilwater	0,1	BMU 1999
Phenole	µg/l soilwater	20	BMU 1999
PCB 6	µg/l soilwater	0,01	BMU 1999
PAK 15 (without naphthalene)	µg/l soilwater	0,20	BMU 1999
HCB, HCH, heptachlor, Endrine, total-DDT, PCB (per congener)	µg/kg soil	20	UM 1996
PCB6	µg/kg soil	100	UM 1996
PAK16	µg/kg soil	5.000	UM 1996
BaP	µg/kg soil	200	UM 1996

3.5.5 Effects on microbial activity, soil living animals and plant growth

For effects on microbial activity, soil living animals and plant growth only POPs in dissolved state or gasous phase are of importance, because they have to actually enter cells in order to affect organisms. Effects of organic contaminants in sewage sludges on microbial activity, soil living animals and plant growth are difficult to study, because they are influenced by a multitude of interdependent factors (e.g. fertilization, water capacity, etc.).

SCHNAAK et al. (1997) found out, that all the sludges examined demonstrated a fungitoxic effect in the plate-inhibition test which was not explicable by the heavy-metal content.

FLIEßBACH et al. (1994; cit in KROGH et al. 1997) reported that sludge deposited over a period of ten years at rates of 5 or 15 t ha^{-1} yr^{-1} d.m. increased microbial biomass and decreased the bacterial activity relative to the fungal activity. BRENDECKE et al. (1993; cit in KROGH et al. 1997) found that applications of 2 or 6 t $ha^{-1}yr^{-1}$ over a period of years did not result in detectable long-term changes in microbial populations and activity.

Eartworms are known to accumulate many non-ionic, hydrophobic compounds such as chlorobenezenes, chlorophenoles and polychlorodibenzo-p-dioxins (BECK et al. 1996).

Xenobiotic organic compounds may inhibit nitrifiers. KROGH et al. (1997) reported, that field measurements of ammonium oxidation potential resulted in either no response or a positive response of sludge compared to manure. Accumulated effects after repeated sludge applications cannot be excluded on a long-term basis, although no toxic effects on ammonia oxidizing bacteria were found six months after sludge application in his study.

KROGH et al. (1997) used two types of sludge in a study, both having a relatively high content of heavy metals, nonylphenole, LAS and phthalates. At doses of up to 21 t ha^{-1}, which are 5 to 10 times higher than the average sludge application rate in Denmark, no negative effects on soil fauna or microbial ammonium oxidation rate were apparent.

3.5.5.1.1 NPE

The nonylphenoles may bioaccumulate and are highly toxic to living organisms, the long-chained NPEs having a potential for uptake in plants (MADSEN ET AL. 1997). Microbial activity is significantly reduced if concentrations of NP are higher than 50 mg/kg soil (BMU 1999a). In laboratory-tests by KROGH et al. (1997) acute and chronic effects on microorganisms and other soil fauna were observed, but only when LAS and NP were present in concentrations at least 50 times above the concentrations likely to be found in soils treated with sewage sludge. In fields where sewage sludge had been applied no adverse effects were found one year after application. HARMS & KOTTUTZ (1992) investigated phytotoxic effects of **4-nonylphenole**. Carrot growth did not seem to be influenced by 4-nonylphenole at any concentration, whereas in tomato, concentrations higher than 0.05 mM inhibited growth completely.

3.5.5.1.2 LAS

KLOEPPER-SAMS et al. (1996) list a number of studies with different plant species, study designs and test durations concerning phytotoxicity of LAS. The growth of plants appeared to be a more sensitive endpoint than their emergence.

FIGGE & SCHÖBERL (1989; cit in KLOEPPER-SAMS et al. 1996) applied LAS concentrations of 16 and 27 mg/kg dry soil to plants in metabolism boxes and found that no changes in growth or yield of bush beans, grass, radish and potatoes were to be observed in a complete growing season (76 and 106 days).

Comparing concentrations that caused harm to terrestrial animals and plants with concentrations found in soils after fertilization with sludge, MIEURE et al. (1990) point out, that the margins of safety appear more than adequate. The assessment was based on

toxicity test results from 22 terrestrial plant species and two strains of terrestrial invertebrate and on more than 100 measurements of LAS concentrations in the environment.

In long-term assays covering the whole growth period LAS and 4-nonylphenole caused inhibition of growth and germination of test plants. The injury of the plants increased during the trial (GÜNTHER & PESTEMER 1992)

In laboratory experiments the EC10 values of LAS and NP in spiked sludge were higher than or equal to the EC50 values for the pure chemicals mixed directly in the soil. The effect levels observed in the laboratory (EC10, EC50) appeared at concentrations approximately 25-50 times higher than the estimated soil concentration of 7,5 mg LAS/kg and 1.0 mg NP/kg in a corresponding field experiment (KROGH & JENSEN cit in KROGH et al. 1997).

3.5.5.1.3 PAH

In a investigation of phytotoxic effects of environmental chemicals HARMS & KOTTUTZ (1992) incubated cell suspension cultures of barley, carrot and tomato plants with different concentrations of **phenanthrene**. Whereas carrot growth was hardly influenced at any of the tested concentrations, tomato cultures showed a drastic decrease in growth at concentrations higher than 0.01 mM. Barley growth was decreased by about 35% at concentrations higher than 0.5 mM.

3.5.5.1.4 Others

Ecotoxicological consequences of sludge derived **organotin** pollution to soils are not well understood. Apart from possible bioaccumulation within the terrestrial food webs, ecological effects of sludge derived organotin soil pollution are assumed not to be serious (FENT et al. 1995). A study with a terrestrial microcosm has shown that 5% of TBTO which was applied to wood blocks as a preservative was released into the upper soil layer and distributed through biota (FENT et al. 1995). Concentrations of up to 50 µg/g TBT were shown to enhance nitrate-nitrogen production in soil, and to inhibit ammonification (FENT et al. 1995). Inhibitory effects on nitrification were found at concentrations of 100-250 µg/g, whereas ammonification was stimulated. It should be noted, however, that photo- and biodegradation may diminish organotin residues transferred to agricultural fields, and that TBT residues found in sludge amended soils are lower. However, possible effects on mould counts, fungi and algae, which are also essential for soil biocoenoses, have to be considered (FENT et al. 1995).

3.6 Priority of organic pollutants

Table 3.6-1 shows a list of organic pollutants relevant in the field of soil protection. The priorities of organic contaminants for the sludge-soil pathway is set according to UMK-AG (2000). However, some pollutants (e.g. PAHs and PCDD/Fs) seem to have relatively high rates of deposition from air, so that there is considerable discussion about the significance of atmospheric deposition of pollutants onto soils versus introduction via sludge. For comparison table 3.6-1 shows priorities for the air-soil pathway of the various pollutants according to JENSEN & ENDRES (1999) and some typical concentrations in rain water. The compounds' names and abbreviations in the table are used as done in literature, the grouping is done mostly according to the compound's chemical properties (e.g. PAH, PCB) in some cases according to its use (e.g. flame retardants, organochlorinated pestizides).

Table 3.6-1: *Typical concentrations of organic pollutants in rain water, their vapor pressure, priorities in respect to the air-soil pathway according to JENSEN AND ENDRES [1999] and priorities in respect to the sludge-soil pathway according to UMK-AG (2000, see also LITZ 2000)*

Compounds/compound groups	typ. conc. in rain [ng/l]	typ. conc. in sludge [mg/kg dm]	vapour pressure at 20-25 °C [Pa]	priority* air-soil pathway	priority** sludge-soil pathway	EU 2000
AOX	-	< 400	-	-	1 (no)	x
Brominated Flame retardants	-	-	-	-	-	-
PBB Polybrominated Biphenyls	-	-	-	-	-	-
PBDE Polybrom. diphenyl ether	-	-	-	-	-	-
Decabromodiphenylether	-	-	-	-	3	-
Pentabromodiphenylether	-	-	-	-	3	-
Octabromodiphenylether	-	-	-	-	3	-
TBBPA Tetrabromoobisphenol	-	-	-	-	-	-
CB Chlorobenzenes	< 15	-	-	No	-	-
1,4-Dichlorobenzene	-	-	-	-	2	-
1,2,4 - Trichlorobenzene	-	-	-	-	2	-
HCB Hexachlorobenzene	0,1 - 2	-	1,40E-03	No	2	-
Chloroorganic Phosphate	-	-				-
Bromophosethyl	-	-	-	-	2	-
Tris-(chloroethyl)-phosphate	-	-	-	-	3	-
Chlorophenols	-	-	-	No	-	-
2,4-Dichlorophenol	-	-	-	-	2	-
2,4,6-Trichlorophenol	-	-	-	-	3	-
PCP Pentachlorophenol (1986)	-	-	5,00E-03	No	2	-
Chloro aceti acids	-	-	-	A	-	-
Monochloro acetic acid	-	-	-	A	-	-
TCA Trichloro acetic acid	50 - 5.000	-	-	A	-	-
Ethylenediaminetetraacetate	-	-	-	-	3	-
Lipid-lowering substances	-	-	-	-	-	-
Clofibrine acid	-	-	-	-	3	-
EDs Endocrine disruptors	-	-	-	-	-	-

Compounds/compound groups	typ. conc. in rain [ng/l]	typ. conc. in sludge [mg/kg dm]	vapour pressure at 20-25 °C [Pa]	priority* air-soil pathway	priority** sludge-soil pathway	EU 2000
Ethynyl estradiol	-	-	-	-	3	-
Ethanolamine	-	-	-	-	-	-
EDTA Ethylenediaminetetraacetic acid		-	-	-	3	-
Musk xylenes and ketones	-	-	-	-	-	-
Musk xylene	-	-	-	-	3	-
Musk ketone	-	-	-	-	-	-
Pestizides	-	-	-	-	-	-
Aldrine (1979)	-	-	3,10E-03	C	-	-
Chlordan (1971)	-	-	-	-	-	-
DDT+metabolites (1977)	-	-	2,50E-05	B	2	-
DDE	0,1 - 20	-	9,90E-04	C	2	-
DDD	0,1 - 2	-	-	-	2	-
Dieldrine	-	-	3,60E-04	B	-	-
Endosulfan (1991)	-	-	1,40E-03	-	-	-
Endrine (1982)	-	-	-	-	-	-
Hexachlorocyclohexane (HCH)	-	-	-	-	-	-
Alpha-HCH	0,1 - 5	-	5,30E-03	A	-	-
Beta-HCH	-	-	4,30E-05	A	-	-
Gamma-HCH (Lindane)	0,1 - 150	-	2,90E-03	A	2	-
Heptachlor (1981)	-	-	-	-	-	-
Nitrofen (1980)	-	-	-	-	-	-
Quintozen (1987)	-	-	-	-	-	-
Precipitation chemicals	-	-	-	-	-	-
Polyacrylamide (cationic)	-	-	-	-	3	-
Phenols	-	-	-	-	2	-
Alkylphenol	-	-	-	-	-	-
Methylphenol	-	-	-	-	-	-
NP Nonylphenol	-	-	1,00E+01	No	1	x
NPE Nonylphenol (+ethoxylate)	-	1 – 1.000	-	-	-	x
Nitrophenol	-	-	-	A	-	-
DNOC 2-Methyl-4,6-dinitrophenol	-	-	8,70E-03	A	3	-
2,4-Dimethylphenol	-	-	-	-	3	-
Phthalates	-	-	-	-	-	-
DEHP Di-2-(ethylhexyl) phthalate	-	200 - 3.000	1,00E-05	A	1	x
DBP Dibutylphthalate	-	50 - 1.000	9,70E-01	(A)	-	-
DEP Diethylphthalate	-	-	2,40E-01	(A)	-	-
DNBP Di-n-butylphthalate	-	-	-	-	3	-
PAHs	-	0,1 - 30	-	-	-	x
Naphthalene (2-Ring)	-	-	1,10E+01	-	-	-
Acenaphtene (3-Ring)	-	-	3,10E-01	B	-	-
Fluorene (3-Ring)	-	-	9,60E-02	B	-	-
Fluoanthene (4-Ring)	1 - 150	-	7,00E-04	B	-	-
Pyrene (4-Ring)	1 - 100	-	8,20E-04	A	-	-
Benz[a]anthracene (4-Ring)	1 - 25	-	2,50E-05	B	-	-

Compounds/compound groups	typ. conc. in rain [ng/l]	typ. conc. in sludge [mg/kg dm]	vapour pressure at 20-25 °C [Pa]	priority* air-soil pathway	priority** sludge-soil pathway	EU 2000
BaP Benzo(a)pyren (5-Ring)	1 - 15	-	7,00E-05	A	1	-
Dibenz[a,h]anthracen (5-Ring)	-	-	1,30E-08	A	-	-
PCA Chlorinated paraffins	-	-	-	B	3	-
C10-13	-	-	-	-	-	-
C14-17	-	-	2,30E-03	-	-	-
C20-30	-	-	2,70E-02	-	-	-
PCB Chlorinated biphenyle	0,1 - 5	0,001 – 0,1	-	-	3	x
Coplanar PCBs	-	-	-	-	no	-
Trichlorobiphenyls (PCB 28)	-	-	1,30E+01	-	-	-
Tetrachlorobiphenyls (PCB52)	-	-	4,40E+00	-	-	-
Pentachlorobiphenyls (PCB101)	-	-	8,80E-01	-	-	-
Hexachlorobiphenyls (PCB 138, 153)	-	-	2,00E-01	-	-	-
Heptachlorobiphenyls (PCB180)	-	-	4,80E-02	-	-	-
PCDD/F	-	-	-	-	1	x
2,3,7,8-TCDD	-	-	6,00E-07	-	-	-
1,2,3,7,8-PeCDD	-	-	5,80E-08	-	-	-
1,2,3,4,7,8-HxCDD	-	-	5,10E-09	-	-	-
1,2,3,4,6,7,8-HpCDD	-	-	7,50E-10	-	-	-
OCDD	-	-	1,10E-10	C	-	-
2,3,7,8-TCDF	-	-	2,00E-06	-	-	-
OCDF	-	-	5,00E-10	B	-	-
Polycarboxylates (anionic)	-	-	-	-	-	-
Polyacrylic acid-Na-salt	-	-	-	-	3	-
Silicones	-	-	-	-	-	-
Silicone oil	-	-	-	-	2	-
Surfactants		-	-	-	-	-
Fluortensides	-	-	-	-	No	-
LAS Linear alkylbenzol sulphonates	-	10 – 10.000	-	-	1	x
TBTO Tinorganic compounds	-	-	-	-	-	-
TBT Tributyltinoxide	-	-	-	-	1	-
Ugilec (60% Tetrach.benzyltol.)	-	-	-	-	2	-
VOC volatile organic chem.	-	-	-	-	-	-
BTX-Aromatics	<15 - 250	-	> 100	No	-	-
Toluene	-	-	-	-	2	-
Trichloroethylene	-	-	-	-	2	-
Tetrachloroethylene	-	-	-	-	2	-

* Volatility of substances found in the geosphere: A: very low to low volatility, B: medium volatility and C: compounds with high volatility from soils

** Prioritization of compounds according to their behavior in the environment or the amounts in which they are present in sewage sludges: highly relevant (1), relevant (2) and (3) there seems to be not enough information

4 CONCLUSIONS AND SUGGESTIONS FOR FURTHER ACTIVITIES

4.1 General conclusions

(1) Sewage sludge application in agriculture is only one source for organic contamination of soils, water or plants. Consequently environmentally sound decisions need to be based on an **integrative evaluation** of contaminant sources and transfer pathways.

(2) The centuries' old idea of nutrient recycling gains new importance as development is seen in the light of **sustainabilitiy**. There is general agreement however, that the recycling of nutrients by means of sludge application in agriculture must not lead to adverse effects on the quality of products nor on the environment and hence contamination of the sludges has to be prevented.

(3) Among fertilizers sewage sludge is generally the product **carrying the highest load of organic contaminants** (KJÖLHOLT 1997).

(4) The **monthly variations** in toxic organic content can be substantial for most of the parameters analyzed, and the **variation within each waste water treatment plant** can be greater than the variation between different plants (PAULSRUD et al. 2000, MCGRATH et al. 2000).

(5) In a risk assessment KROGH et al. (1996) expect from laboratory tests with earthworms and Collembola that the detergents LAS and nonylphenole, have no effect at presently allowed doses of sludge

(6) Persistent compounds such as PCBs, PCDD/Fs and PAHs are generally not **transferred** from soil to crops, meat and milk although the possible evaporation of PCBs and foliar uptake needs more attention. Little is known about the uptake of phtalates and nonylphenole which are present in relatively high levels in sludge (RUDLING et al. 1997).

(7) To prevent elevated levels in digested sewage sludge, organic substances must be **aerobically and anaerobically degradable**. Such properties must be postulated in particular for chemicals like the components of laundry- and dish-washing detergents and surface cleaners which are used in high amounts directly in water. If this condition is not fulfilled, problems of residual levels in sludge-treated soils will be encountered (GIGER et al. 1997).

(8) The objective of sewage sludge application to farmland must be for the purpose of fertilization and hence the need for fertilizer should decide on the amount applied. Except for soils with a deficit in phosphorous supply or where sludge is used on tillage land, MCGRATH et al. (2000) consider 1 t/a dm of sludge as a prudent maximum application rate.

(9) Ideally, the total input rate of organic pollutants to soil should not exceed the rate of degradation. Maximum application rates are thus determined by the local factors that control the physical, chemical, and biological properties. (AMUNDSEN ET AL. 1997).

(10) The Norwegian authorities have decided not to include limit values for toxic organics in the existing regulations for sewage sludge and compost (PAULSRUD et al. 2000). However, nonylphenole (+ ethoxylates) will be phased out in domestic and industrial products in Norway by the year 2000 and thus the presently high amounts of these chemicals in sewage sludge will be reduced. The new regulation aims at promoting sludge management practices that allow the beneficial use of sludge in agriculture while maintaining or improving environmental quality and protecting human health. One goal announced by the authorities is to recycle at least 75% of the total sewage sludge production by the year 2000.

(11) JONES and NORTHCOTT (2000) state that the existing limits have no scientific basis and are set rather arbitrarily and are inherently pre-cautionary. According to their findings, there is little uptake of organic chemicals by crop plants from soil and for many chemicals the transfer from the atmosphere onto leaves or grain is a more important route of contamination. The standards proposed in the Draft Document for PAHs, PCDD/Fs, phthalate, nonylphenole and LAS would have very serious implications for the use of sewage sludge in agriculture in the UK, if they were to be adopted. The authors expect that many/most sewage sludges in Europe are likely to exceed the proposed limits for PAHs and LAS, even those originating from rural/domestic waste water treatment plants. Also they point out that analyses of trace organic contaminants require sophisticated analytical instrumentation and specialized analysts and can be very expensive. There are often no 'recommended or certified methods' and no commercially available certified reference materials to ensure analytical compliance (JONES & NORTHCOTT 2000).

(12) According to the German Ministry of the Environment the limit values for AOX, PCB and PCDD/F are intended as precautional and are not justified solely by toxicological implications (SAUERBECK & LESCHBER 1992). In 1999 the Ministery reconsidered the regulation and did not see it necessary to introduce limits for organic contaminants of sewage sludge beyond PCDD/F, PCB and AOX (BMU 1999a). A working group set up by the Conference of the Ministers of Environment is currently reviewing the relevance of organic pollutants in sewage sludge (UMK-AG 2000, LITZ 2000). They found PCDD/F contents in sewage sludges have decreased in recent years and recommend that monitoring sewage sludges for PCDD/Fs should be reduced (UMK-AG 2000) accordingly. Since the use of PCP as a fungicide on textiles was identified as one major source of PCDD/F in waste water (MCLACHLAN et al. 1996), UMK-AG (2000) recommend to intensify monitoring such textiles for their content of PCP and PCCD/F. Also water used for cleaning buildings where PCBs were used in building materials, could be a source of PCBs in sewage sludge and should be monitored. DEHP and TBT should be replaced altogether. In the case of PAHs only general reductions of emissions will improve the situation.

(13) The following priorities are recommended for research projects on organic compounds in Germany (UMK-AG 2000):

Group 1:	AOX, NPE, LAS, DEHP, BaP, PCB, PCDD/F, TBT
Group 2:	Toluolene; 1,4-Dichlorobenzene; 1,2,4-Trichchlorobenzene; Hexachlorobenzene; 1,1,1-Trichloroethan; Tetrachloroethan; DDT and Metabolite; Lindan; 2,4-Dichlorophenol; Pentachlorophenol; Ugilec; Bromophosethyl; Siliconoil; Phenols
Group 3:	Clofibrine acid; Chloro paraffines; Ethylenediaminetetraacetate; Musk xylol; Tris-(choroethyl)-phosphate; Decabromodiphenylether; Pentabromodiphenylsäure, Octabromodiphenylether; 2,4,6-Trichlorophenole; 2,4-Dimethlyphenole; Ethinylöstradiol; Polyacrylic acid-Na-salt (anionic); Polyacrylamide (cationic) und Dibuthylphthalate

(14) CHANEY et al. (1998) conclude that biosolids can be beneficially used in sustainable agriculture with so low risk to agriculture or environment, that utilization on farmland should be the preferred method of "Ultimate Disposal". Pretreatment of industrial and non-industrial sources of some contaminants may be required to achieve the NOAEL biosolids quality. Technology is presently available to achieve the needed pretreatment. They conclude, that PCB concentrations will limit utilization of biosolids from only a few of the 14,000 POTWs in the US. (CHANEY et al. 1998).

4.2 Pollutant specific conclusions

Table 4.2-1 provides an overview on the behaviour of organic substances in soils.

Table 4.2-1: *Classification of organic substances (UMK-AG 2000, see also LITZ 2000)*

Substance	Mammalian/ human toxicity (acute)	Ecotoxicity	Water solubility	Persistence	Concentration levels
AOX (summative parameter)	-	-	-	-	high, indicator
LAS	Medium	aquatic: high; terrestrial: medium; bioaccumulation: high	high; enhances mobility of other pollutants	medium	high
DEHP	low; suspected estrogenic effect	aquatic: medium to high; terrestrial: low; bioaccumulation: high	low	medium	high
Nonylphenole	medium; suspected estrogenic effect	aquatic: high; terrestrial: medium; bioaccumulation: high	high	medium	high
B[a]P single substance (**PAH**)	carcinogenic, mutagenic, teratogenic	high; bioaccumulation: high	low	high	high
PCBs, single substances/summative parameter	medium; tumour promoting, immunotoxic	aquatic: high; terrestrial: high; bioaccumulation: high	low	high	low and continuing to decline
PCDD/Fs,single substance/summative parameter	high; carcinogenic	aquatic: high; terrestrial: high; bioaccumulation: high	low	high	low
TBT Tributyltin oxide	high	aquatic: high; bioaccumulation: high; endocrine effect	medium	high	high

AOX

(15) AOX as a sum parameter does not represent a specific chemical substance and is not a direct measure for toxicity. PVC which is otherwise regarded as inert, may enhance the AOX measured significantly. In Finland, paper pulp industry was responsible for about 50 % of the total organic halogen emissions into the environment. Several other industries, such as the manufacture of polyvinyl chloride (PVC), and waste incineration are important sources of AOX formation as well. In the context of soil contamination it is noteworthy that some organic halogens may be transformed in the soil to more toxic compounds such as vinyl chloride, which is a known human carcinogen (SALKINOJA-SALONEN et al., 1995; AURAS 2001). Concentrations in 90% of German sludge samples were below the German limit values and concentrations have been decreasing in recent years (UMK-AG 2000).

DEHP

(16) PAULSRUD et al. 2000 report a significant reduction of phthalates (DEHP) in Norwegian sewage sludges, even though three plants in Norway exceeded Danish standards. In Germany too, the use of DEHP is decreasing slowly, with DEHP being replaced by more highly substituted phthalates (UMK-AG 2000) and other plasticizers.

LAS

(17) In sewage treatment, a proportion of the LAS is absorbed onto sewage solids during primary settlement of sewage and will not undergo normal aerobic treatment since this part of the sewage stream will bypass the aeration tank (BIRCH et al. 1993 cit in DE WOLFE & FEIJTEL 1997). Thus sludges can still contain considerable amounts of LAS when they are applied to soils. However, laboratory and environmental studies show that LAS is biodegradable at high rates under aerobic conditions. Thus, when judging potential risk, the rapid biodegradation of LAS after application of the sludges to soils has to be taken into account. However, when the Danish PEC values were calculated this was not considered which makes the Danish scenario unrealistic as compared to the EU-approach. (DE WOLFE & FEIJTEL 1997).

The LAS content of Norwegian sewage sludges is very variable, but in general far below the Danish standard and the concentrations reported in the Danish investigations (TÖRSLÖV et al. 1997 cit in PAULSRUD et al. 2000). This is mainly due to the fact that most Norwegian households use **eco-labeled detergents** which do not contain LAS (PAULSRUD et al. 2000). In Germany the amounts of LAS used are approximately constant and hence no significant change of concentrations in sewage sludges is to be expected (UMK-AG 2000). The majority of the UK samples exceed the LAS concentrations limits of the 3rd Draft of the EU-Initiative (JONES & NORTHCOTT 2000).

NPE

(18) There has been a significant reduction of nonylphenole (+ ethoxylates) in Norwegian sewage sludges between 1989 and 1997, still Nonylphenole (+ ethoxylates) were found in high concentrations in sludge samples from all the sewage treatments plants in the survey, and all the plants would have been classified as non-compliant with the Swedish and Danish standards (PAULSRUD et al. 2000) and hence the proposed EU standards. Of the UK samples three exceeded the EU proposal (JONES & NORTHCOTT 2000). In Germany NPE is also a relevant contaminant in waste water, but here too amounts have drecreased since the eighties, because industries volontarily reduced the amounts used in household and industrial cleaners (UMK-AG 2000).

PAH

(19) The most relevant sources for PAHs are coal burning for heating of buildings and tractor-trailer traffic. Shifting from coal to oil for heating and improvements in heating technology have reduced PAHs emissions in Germany significantly in recent years. This has resulted in a steady decrease of PAH concentrations in sewage sludges (UMK-AG 2000). The EU proposals include limit values for the sum of 9 PAHs (including benzo(b+j+k)fluoranthene), but it is not clear what criteria have been used to select these compounds (JONES & NORTHCOTT 2000). The PAH concentrations in sewage sludges in relation to the limits of the 3rd Draft of the EU-Initiative are as such:

Norway	The PAH content was low in most sewage sludge samples and well below the Swedish and Danish standards	PAULSRUD et al. 2000
UK	all samples above EU limit, even those WWTPs for which there was 0% trade effluent and purely rural, domestic wastewater	JONES & NORTHCOTT 2000

(20) On the grounds that a soil limit value for benzo[a]pyrene is set in BMU (1999) in respect to the pathway soil - plant, the introduction of a limit value for soil concentrations of BaP into the EU-Initiative is recommended. A regulation seems important, because there will be atmospheric deposition as well as introduction of benzo[a]pyrene to agricultural soils via sludge application for years to come.

PCB

(21) JONES & NORTHCOTT (2000) conclude from the small variation in PCB-values between WWTPs in UK, that there are very few fresh or ongoing primary sources of PCBs to the environment. In Germany concentrations have been nearly constant during the last decade (UMK-AG 2000). AMUNDSEN et al. (1997) warn that the high stability of heavily chlorinated PCBs in the sludge, calls for a more precautious use of sewage on surface soils in public areas. CHANEY et al. (1996) consider the low concentrations of PCBs in sludges and the setback distances and use of erosion control practices required in the US as providing high protection against the risks from sludges getting washed into surface waters. The PCB concentrations in sewage sludges in relation to the limits of the EU-Initiative (3rd draft) are as such:

Norway	all samples far below German and Swedish Standards	PAULSRUD et al. 2000
UK	all below EU-limit	JONES & NORTHCOTT 2000
Germany	all samples below German limit	BMU 1999a
Ireland	all samples below German limit	MCGRATH et al. 2000

PCDD/F

(22) HORSTMANN &MCLACHLAN (1994) estimates that ~20 to 40% of the TEQ entering German WWTPs nationally comes from imported **cotton textiles** that were treated with pentachlorophenole. The banning of PCP use in Germany and restrictions on the allowable concentrations in consumer products brought about a significant **reduction** in PCDD/F levels in sewage sludges (MCLACHLAN et al. 1996, UMK - AG 2000). The concentration of PCDD/PCDF show only **small monthly variations** (PAULSRUD et al. 2000). Addition of sewage sludges to agricultural land will increase the soil PCDD/F concentration. While **atmospheric deposition** provides a direct source of PCDD/Fs to foliage, the transfers of PCDD/Fs from soils into plant roots and their translocation into the aboveground portions of plants are **negligible,** except in Cucurbitacea (HÜLSTER 1994). Root crops may take up PCDD/Fs from soil, but mostly it stays restricted to the peel (JONES & SEWART 1995). PCDD/F transfer into livestock via soil ingestion or uptake of sludge adhering to feed are critical with respect to human dietary intake and are believed to be the major exposure

route (>99%), while intake from water and air are negligible (WILD et al. 1994). The PCDD/F concentrations in sewage sludges in relation to the limits of the EU-Initiative (3rd draft) are as such:

Norway	all samples below German Standard	PAULSRUD et al. 2000
Germany	average sewage sludges are below limit of "Klärschlammverordnung" (some exceed limit!)	BMU 1999a

Others

PBB/PBDE Brominated flame retardants

(23) The ubiquitous presence ofpolybrominated biphenyls (PBB) and polybrominated diphenyl ether (PBDE) flame retardants in the environment has begun to attract international attention. Researchers and environmental groups are concerned about emerging pollution problems and evidence suggesting that low-level exposures may produce detrimental health effects in humans and animals (RENNER 2000). Sweden has requested a freeze on the use of PBB and PBDE with EU authorities, because of an increase of concentrations found in breast milk and fish (HELLSTRÖM 2000)

EDs Endocrine disruptors

(24) More than a hundred chemicals are suspected to have hormone-like effects in organisms, that potentially result in reproductive impairment or disorders. Most are likely to be found in sewage sludge (SMITH 2000). Many persistent organic pollutants like PCBs, dioxins and pesticides (DDT) have endocrine properties, however, since persistent pollutants are already covered by a number of EC Directives and Regulations because of their toxic properties, their potential as EDs does not necessitate additional regulatory activity (PÄRT 2000). SMITH (2000) states that natural **estrogens** are readily biodegraded by the activated sludge process, PÄRT (2000) reports that little is known about the extent to which natural hormones (**estrogens**) and **pharmaceutical residues** are accumulated in sewage sludge and what happens with these compounds when the sludge is used on soils.

CB Chlorobenzenes and COP Chlororganic Pestizides

(25) Sludge application to soil can increase the CB content in crops which may limit the land use of sewage sludge in a certain extent. Sludges from industrial areas may contain significantly higher amounts of CBs than those from urban areas. CB concentrations in sludges from sewage treatment works can be relatively stable, with certain effluent sources. CB content of modern sludges is somewhat higher than those sampled during the 1940's and 1950's (WANG et al. 1997).

(26) Chlorobenzenes (CBs), a major group of substituted monocyclic aromatics, are ubiquitous in sewage sludges. Volatilisation is regarded as the main loss mechanism for CBs from the soils. The 1,4-dichlorobenzene (DCB) content in both the sludge-amended and the control

soils increased remarkably during the 1960s; trace level impurities in pesticides and /or atmospheric deposition are possible sources (WANG et al. 1995).

(27) The CB concentrations in U.K. sewage sludges have been reported to be between 0.795 and 193 mg kg^{-1} (Wang et al. 1995). Dichlorobenzenes (DCBs), 1,2,4-trichlorobenzenes (1,2,4-TCB), and hexachlorobenzene (HCB) have been classified as priority pollutants by the United States Environmental Protection Agency (U.S. EPA) and by the EC. Some CBs (e.g., HCB) are known human carcinogens (U.S. ENVIRONMENTAL PROTECTION AGENCY 1985 cit in WANG et al. 1995), (WORLD HEALTH ORGANIZATION 1991 cit in WANG et al. 1995).

Musk ketone and Musk xylene

TAS et al. (1997) consider the risk that musk ketone and musk xylene pose to organisms in the aquatic environment and to fish-eating birds and mammals as low. No monitoring data are available to evaluate the predicted soil concentrations, whereas presently PEC/PNEC ratios in soil around 1 indicate a need for refinement of the risk assessment for this compartment by obtaining experimental data under realistic environment conditions.

PCA Chlorinated paraffins

(28) Following their widespread and unrestricted use in predominantly open systems, PCAs are now present in a range of environmental compartments (TOMY et al. 1998 cit in JONES & NORTHCOTT 2000). PCAs are not known to occur naturally and are of concern owing to their toxic properties and to their capacity to bioaccumulate (BMU 1999a). They can be classified as persistent organic pollutants (POPs). Total concentrations in UK sewage sludges of the short-chained and medium-chained PCAs ranged between 7-200 mg/kg and 37-9700 mg/kg, respectively. Nonetheless, some of the sludge samples contain very high levels of these substances (JONES & NORTHCOTT 2000). At present a satisfactory evaluation of the environmental effects of chlorinated paraffins seems not possible (BMU 1999a).

TBTO Organotins

(29) Municipal wastewater and sewage sludge are contaminated with organotins, but knowledge in this field is till limited. It is necessary to quantify inputs from wastewater and sludge, and to understand the fate and behavior in aquatic and terrestrial environments in order to predict the impact of the growing use of organotins, in particular related to the use of TBT compounds in wood preservation. It should be borne in mind that tributyltin compounds are among the most hazardous organic pollutants known for aquatic systems. The availability to biota, uptake by plants, biodegradation and possible toxic effects should be investigated in order to evaluate and assess risks arising from sewage sludges as sources of organotins in sludge amended soils (FENT et al. 1995). According to UMK-AG (2000) knowledge about pathways of organotin compounds in the environment and its presence and fate in sewage sludges is not yet satisfying.

VOC Volatile organic chemicals

(30) The sludge application to agricultural land is unlikely to increase the VOC concentration of the soil to levels which may cause concern for human health and the environment (WILSON et al. 1994). Volatilization and loss of VOC occur rapidly from soils. VOC in sludge do not represent a hazard to agriculture except possibly where sludge is spread on soils with high content of organic carbon. It is recommended that sludges containing VOC not be spread on organic soils (WEBBER & GOODIN 1992).

4.3 Suggestions for further work

(31) The Priority list of contaminants should be elaborated and the member states should contribute their priorities so that the list gains pertinence EU-wide and regionally (Harmonized EU Priority List)

(32) The Priority list of contaminants should contain key substances instead of substance classes as long as there are no internationally recognized toxicity equivalence factors.

(33) Concerning organic contaminants in sewage sludge existing information should be reviewed or research be initiated on the relative importance of contamination sources **(air-water-soil integrated research**). This would clarify for which contaminants the contribution of sewage sludge to soil concentrations is important enough to necessitate regulation in the future and have influence on the priorities of contaminants in sewage sludge (see table 3.6-1).

(34) An EU website on "Organic Contaminants in Sewage Sludge for Agricultural Use" could be built up e.g. in connection with http://europa.eu.int. Such a website could offer the following informations
- original literature, e.g. reports initiated by national authorities,
- the priority lists of pollutants with background information,
- state of the art of national standardization,
- information on national research projects,
- knowhow on the prevention or reduction of the contamination of sewage sludges.

(35) Research soil-plant and soil-water transfer of organic contaminants should be initiated on a number of sites across the EU that were given extremely high amounts of sewage sludge in the past. These field studies could provide the scientific basis for limit values for soil concentrations. If soil-plant and soil-water transfer would not exceed the limits mentioned in chapter 3.5, it would not seem necessary to set limits for soil concentrations for regulating sludge use in agriculture.

(36) If quality standards for sewage sludges are to be set, there will be need for standardized methods of analysis. Therefore **prenormative research** in coordination with ISO- and CEN-groups should be supported.

(37) To facilitate the further development of the EU guideline on sewage sludge a „Survey of Organic Pollutants in EU Sewage Sludges" (**EU-databank/cadastre**) should be carried out. To standardize data the median/90-perzentile-method should be established.

(38) The input of organic pollutants to soil via sludge application cannot be considered separately from other inputs. If the **total input rate** is to be kept below the rate of degradation, tolerable total yearly input rates have to be determined that take all possible pathways into account. These tolerable total yearly input rates could later be used for a EU-soil-protection Directive.

(39) So far only incomplete information on the fate of contaminants and their metabolites in soils is available. **Permanent (>30 years) soil observation** with standardized methods should be established EU-wide as a prerequisite for final evaluation of persistence.

(40) **New technologies** such as wet oxidation, pyrolysis or gasification have come up. More information concerning their effectiveness with sludges and their environmental impact is needed (ANDERSEN 2001). Such technologies may have to be applied if sludge production goes up as predicted. According to BÖHM (2000) surveillance of pathogens could be developed further.

(41) The EU-draft contains a number of important measures for the „Safer practice of sewage sludge application". Some of these methods can still be refined, e.g. application of sludge on **hydrogeologically sensitive areas** ("water-saturated soils"). A setback distance for sludge application near surface waters should be considered in order to prevent particles from being washed into water bodies with run-off or floods.

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