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Risk evaluation of five groups of persistent organic contaminants in sewage sludge.

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Risk evaluation of five groups of persistent organic contaminants in sewage sludge.

Authors & contributors:

John Jensen
Aarhus Universitet
Institut for Bioscience

Simon Toft Ingvertsen, Jakob Magid
Københavns Universitet
Det Biovidenskabelige Fakultet

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Preface

This report is part of a larger effort from the Danish Environmental Protection Agency (Miljøstyrelsen) to create the fundamental knowledge needed to enable future optimal and sustainable use of organic waste on arable land in Denmark. The current regulation of sewage sludge in Denmark includes a set of cut-off values for a number of heavy metals and four groups of organic contaminants, i.e. Linear alkylsulfonates (LAS), Polycyclic aromatic hydrocarbons (PAH), Nonylphenols and Di(2-ethylhexyl)phthalate (DEHP). New information, improved analytic possibilities and/or change in use of consumer products may require regulatory changes. Hence, there is a need to evaluate whether new knowledge may indicate a need for further regulation of novel substances.

The present report is an attempt to give a provisional assessment as to whether selected organic contaminants in sewage sludge could potentially pose a risk to soil ecosystems after soil amendment. It should by no means be considered an exhaustive review of all the relevant literature available. The selection of substances is based on a set of criteria, including, for example, presence in Danish sludge, availability of ecotoxicity data and the fate of substances in the environment. It is important to note that this report exclusively focuses on the potential risk to soil dwelling species. Therefore, the potential risk to aquatic species and the potential risk to humans via leaching to groundwater or uptake in crops have not been assessed.

Sammenfatning og konklusioner

Der eksisterer i dag en del ny national og international viden om, hvilke stofgrupper man kan finde eller forvente at finde i organiske affaldsprodukter, ligesom der i det seneste årti er fremkommet megen ny viden om de økotoksikologiske effekter af kendte såvel som nye stoffer. Denne rapport er et forsøg på at sammenholde denne viden i en analyse af, hvilke stoffer eller stofgrupper udgør et realistisk problem for jordmiljøet. En opsummerende og dog fyldestgørende dansk udgave af denne engelske baggrundsrapport er udgivet af Miljøstyrelsen (Jensen m.fl. 2012). Heri gives en overordnet kortlægning af den relevante viden for fem stofgrupper: Bromerede flammehæmmere, Polyklorede biphenyler (PCB), polyflourede stoffer, lægemidler og muskstoffer.

Fem stoffer/stofgrupper er som nævnt undersøgt i detaljer. Alle stofgrupper er fundet i dansk slam, men typisk i koncentrationer, som ligger under de fleste europæiske og amerikanske målinger. Fire af disse: PCB, lægemidler, muskstoffer og bromerede flammehæmmere udgør med stor sandsynlig ikke et miljøproblem for jordbundsorganismer, afgrøder og andre planter i relation til spildevandsslam. Den fundne sikkerhedsmargin for de polyflourede stoffer ligger derimod på grænsen af, hvad EU anbefaler i deres retningslinjer under REACH-programmet.

Det har ikke været muligt i indeværende projekt at belyse den potentielle risiko af andre relevante stofgrupper i spildevandslam. De mest oplagte kandidater for en yderligere undersøgelse vil være de klorerede parrafiner, parabener samt biociderne triclosan og trichlocarban.

Summary and conclusions

Application of sewage sludge to farmland is favoured internationally as a sustainable management tool of waste from waste water treatment plants, as it contributes positively to the recycling of nutrients, improvement of soil properties and fertility. It is, therefore, the policy in many countries, and e.g. in the European Commission, that sewage sludge should be recycled to farmland to the extent it does not pose a risk to the environment and health. Sewage sludge, however, contains a large cocktail of many substances making it impossible to assess whether all of them creates a risk or not. This report is an attempt to prioritise and select five groups of chemicals commonly found in Danish sludge and to assess the potential risk to soil organisms. The following groups of chemicals have been evaluated: Brominated Flame Retardants, Musk substances, Pharmaceuticals, Polychlorinated Biphenyls and Perfluorinated compounds. Furthermore, a subset of potential candidates has been identified as relevant for future evaluation. These are polychlorinated alkanes and napthalenes, trichloban, trichlosan and parabens.

In order to evaluate the potential risk of the various chemicals, the distance between the predicted soil concentration and the lowest no observed effect level is defined as the margin of safety. Based on the estimated margin of safety, it has been concluded whether it is likely that the studied contaminants will pose any risk to soil dwelling species, taking into consideration the recommended use of uncertainty factors within the REACH programme in the European Union and described in the Technical Guidance Document for risk assessment of new and existing chemicals.

For the brominated flame retardants, the musk substances, the pharmaceuticals and the polychlorinated biphenyls, it was concluded that it was very unlikely that the levels found in Danish sludge should pose a significant risk to the soil dwelling organisms and the soil quality in general, if the current application guidelines of sewage sludge are followed. For the perfluorinated substances, it could not be excluded that the PFOS levels observed in Danish sludge may pose a long term risk to soil ecosystems. Thus, more information on the fate and effects of PFC is needed. In 2009, PFOS and related derivatives were listed under the Stockholm Convention due to their demonstrated toxicity, bioaccumulation, persistence in the environment and ability to travel long distances from the point of release or application. This has already led to restrictions in the use of PFOS in for example Denmark and the EU, which is likely to result in lower environmental load, including the concentration in sewage sludge, in the future.

1 Introduction

Application of sewage sludge to farmland is favoured internationally as a sustainable management tool of waste from waste water treatment plants, as it contributes positively to the recycling of nutrients, improvement of soil properties and fertility. It is, therefore, the policy in many countries, and e.g. in the European Commission, that sewage sludge should be recycled to farmland to the extent it does not pose a risk to the environment and health. Others may, nevertheless, have the opinion that since sewage sludge contains a large cocktail of many substances, it is impossible to assess whether it creates a risk or not. Therefore, following the precautionary principle, sludge should not be used on farmland at all, and alternatives like incineration or dumping would be more sustainable. It is, however, recognized that a decision not to utilise a resource such as sewage sludge may also have unintended global effects in terms of increased greenhouse gas emissions, environmental degradation, e.g. due to phosphorus mining and sludge incineration, and the long-term use of a finite resource like phosphorus. A better assessment of the potential risk of contaminants in sludge would, hence, improve the foundation for a cost-benefit evaluation of recycling organic waste like sewage sludge. This report, therefore, aims to present and organize relevant knowledge regarding a small set of organic substances known to be found in sewage sludge across the world, in order to elucidate whether these may pose a long term risk to the soil environment.

Modern society depends on a large range of organic chemicals. Of the 50 million chemicals entered in the Chemical Abstracts Registry, approximately 143,000 chemicals are registered with the European Chemicals Agency for industrial use. The ones that are commonly used should properly be counted in 10s of thousands. Some of these may ultimately enter our waste water treatment plants, and depending on the intrinsic properties of the substances and the technical specification of the waste water treatment plants, these may end in the sewage sludge. Historically, the first group of chemicals that were paid attention to in this context were the heavy metals and a group of traditional persistent organic pollutants (POPs) like PCB, dioxin and PAHs. A number of countries, therefore, imposed a set of quality standards for these substances during the 80's and 90's. As a result of novel applications for new chemicals and an improved analytical standard, more and more attention has recently been drawn towards the presence of a novel and large group of POPs, often commonly denoted as emerging contaminants. Emerging contaminants may be described as a chemical or a group of chemicals that is characterized by a perceived potential for a threat to the environment or human health and the lack of published international standards or other risk evaluations.

Economic and time constraints within the current project has made it impossible to cover a wide set of emerging substances. In order to aid in the identification of the most relevant groups of substances from a Danish perspective, a number of recently published international reviews on this subject have been studied. These are summarised in Section 1.1.

1.1 International reviews on emerging substances

1.1.1 Risk assessment of contaminants in sewage sludge applied on Norwegian soils

A comprehensive Norwegian study assessed the risk of using sewage sludge or derived products as fertilizer and soil conditioner in agriculture, public parks and private gardens (Eriksen et al. 2009). An assessment was made of the potential risk of dispersal of sewage sludge to soil living organisms, the aquatic environment, grazing animals, animals eating feed based on plants from sludge-treated soil, children eating soil, and humans consuming drinking water, crop plants and/or meat affected by the use of sludge as soil conditioner. A risk assessment of all these exposure routes was made for the following contaminants:

Heavy metals:

Cadmium (Cd), lead (Pb), mercury (Hg), nickel (Ni), zink (Zn), copper (Cu) and chromium (Cr)

Xenobiotic Organic Contaminants:

Phthalates (DEHP and DBP), octylphenols and octylphenol ethoxylates, nonylphenols and nonylphenol ethoxylates, linear alkylbenzenesulfonates (LAS), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs). Furthermore, the study evaluated the risk associated with a range of pharmaceuticals.

The predicted environmental concentrations (PECs) in soil, as well as human and animal exposure to the contaminants following the use of sewage sludge as soil conditioner, were estimated by use of mathematical modelling based on the guidelines given in the European Union's (EU) Technical Guidance Document on Risk Assessment (TGD) within the REACH framework (EU 1996). The risk assessment covered evaluation after one application and the potential accumulation of contaminants following repeated use of sewage sludge in a 100 year perspective. The estimated predicted environmental concentration for each contaminant was compared with the available predicted no-effect concentration (PNEC) for soil. For heavy metals, the model showed that no metal would reach the PNEC values within the timeframe of 100 years. Consequently, it was considered that the present levels of metals in Norwegian sludge constituted a low risk to soil living organisms. However, the model estimates indicated that soil concentrations of Cd, Hg, Cu and Zn, and to some extent also Pb, would increase following repeated use of sewage sludge. Cadmium, Hg and Pb are of particular concern due to their inherent toxic properties. An increase may, therefore, be undesirable even, if the soil remains below the estimated PNEC values.

Octylphenols, nonylphenols and LAS were the only contaminants where the PEC exceeded the PNEC. However, these are rapidly degradable substances (half-lives in soil = 8-10 days). Hence, the highest concentrations are found immediately after application of sewage sludge followed by a rapid decrease. Taking into account the uncertainties related to the environmental concentrations and the rapid degradation in soil, it was considered that octylphenols, nonylphenols and LAS are of low concern. Only a few PAHs and PCBs were expected to accumulate with repeated use of sewage sludge over a 100 year period, and the model indicated that the concentrations of these substances would be well below the PNEC value, even at the end of the 100 year period. The risk assessment of the large group of pharmaceuticals was complicated by the lack of suitable information for a wide set of these. Hence, a tiered criteria-based approach was applied, including a cut-off value in soils. Of the more than 1400 drug substances sold in Norway, only 14 were estimated to exceed a cut-off value of 100, or 10 µg/kg after sludge application. For these substances, no PNEC values in soil were apparently available. Instead, PNEC values for pharmaceuticals were estimated from the aquatic PNEC values when available. The estimated soil concentrations of drug substances were all well below the estimated PNEC values, and it was concluded that pharmaceuticals in Norwegian sewage sludge constitute a low risk for soil-living organisms.

The potential transfer to the aquatic environment, the risk of adverse effects in farm animals grazing on or receiving feed from sewage sludge treated areas and the human dietary intakes via the different exposure routes, i.e. drinking water, plant and animal derived food products, were all considered to be very low for all groups of organic contaminants investigated.

1.2 Organic contaminants in sewage sludge and their significance for agricultural recycling

Smith (2009) reviewed the data for the concentration of organic contaminants (OCs) in sewage sludge and assessed the consequences and significance for the environment, human health and the food chain when sewage sludge is recycled to farmland as a fertilizer. The review is comprehensive and includes available data on bulk-volume and industrial compounds, as well as endocrine disrupters, pharmaceuticals, antibiotics and personal-care products.

It was found that organic contaminants generally pose minimal risk to the human food chain from land application of sewage sludge. Based on the analytical evidence, the most toxic compounds (e.g. the dioxin TCDD) are only detected in very low quantities in sludge. The risk of OC in sludge to humans are influenced by a variety of mechanisms that prevent transfer to crop tissues and the human food chain, including: (i) rapid volatilization and loss to the atmosphere; (ii) rapid biodegradation and minimal or no persistence, or (iii) strong adsorption of lipophillic and persistent compounds with concurrent absence of significant uptake in crops.

In recent years, the potential impacts of classical contaminants, like PAHs, PCDD/Fs or PCBs, have been a key concern for agricultural utilization. However, international emission controls on the main point sources of these priority-persistent compounds have significantly reduced their entry into the environment and, consequently, also into WWTPs, with a decline in sludge concentrations observed over the last decade or two. Thus, atmospheric deposition and environmental cycling are currently the main sources of e.g. PCBs and dioxins in sludge and, consequently, the concentrations of these historically used chemicals in sludge generally represent background environmental levels.

Smith (2009) found no evidence that the vast majority of sludge-borne OCs have a detrimental impact on crop yield or soil microbial processes. Earlier concerns about the potential impact of LAS, a detergent surfactant present in large concentrations in sludge, on soil ecological processes have been further elucidated (Jensen et al. 2001, 2007) and shown to be unfounded. While the presence of large concentrations of certain high-volume bulk chemicals, such as LAS, warrants careful investigation and assessment of the risks to the environment when sludge is used as an agricultural soil amendment, this does not necessarily represent a hazard to the soil ecological environment. Phthalates were not found to cause any significant adverse effects on soil microbial processes or on soil fertility. In general, high-volume usage compounds have low toxicity and/or degrade rapidly in soil. However, a number of emerging compounds were identified in this review as having a potential impact on soil microbes, and these belong to the group of chemicals described as personal care products, e.g. triclosan, and the significance of these warrants further investigation.

Despite the extensive range of organic chemicals that can be present in sewage sludge, the expanding experimental evidence base (147 papers in this review) indicates that these are not a significant limitation as such to the agricultural use of sewage sludge. The view by Smith (2009) is based on an acknowledgement of the current sludge application practises in most countries and the presence of effective source control measures combined with the findings of small concentrations of persistent contaminants in sludge, information about biodegradation and behaviour of bulk contaminants in soil, and the absence of crop uptake for most hazardous substances. In the view of the author, there appears to be no scientific rationale for including numerical limits for organic contaminants within quality assurance systems for the agricultural use of sewage sludge. However, a number of issues, while unlikely to be significant for agricultural utilization, require further investigation according to the author. These include:

1. The impacts of chlorinated paraffins on the food chain and human health,
2. The risk assessment of the plasticizer di(2-ethylhexyl)phthalate, a bulk chemical present in large amounts in sludge,
3. The risk assessment of antibiotic resistant micro-organisms in sewage sludge and sludge-amended agricultural soil,
4. The potential significance of personal-care products (e.g. triclosan), pharmaceuticals and endocrine-disrupting compounds in sludge on soil quality and human health.

1.3 Review of emerging organic contaminants in sewage sludge and research priorities for the agricultural use of sewage sludge.

Clarke and Smith (2011) reviewed the literature for sludge-relevant information on emerging substances and identified research and monitoring priorities based on the following 5 criteria: 1) Environmental persistence in soil environment (>6 months); 2) Potential for human health impacts resulting from the land application of sewage sludge; 3) Evidence or likelihood of bioaccumulation in humans or the environment; 4) Evidence of ecotoxicity, and finally 5) The quality of empirical data and trends on the contaminant in sewage sludge internationally.

The authors concluded that particularly two chemical classes warrant particular note. These were the perflourinated chemicals (PFCs) and polychlorinated alkanes (PCAs).

PFCs are an emerging environmental concern, as they have been detected in human blood and environmental samples throughout the world. They have a unique chemistry for a chemical defined as a POP that facilitates a degree of water solubility, and, therefore, there is an increased likelihood of exposure through all pathways (water contamination, plant accumulation and grazing animal accumulation) compared to other POPs.

PCAs were found at relatively high concentrations in sludge. Comparison of the concentrations of these compounds to PCBs and PCDD/Fs shows that the PCA content in sludge is three orders of magnitude higher than for example PCB. This signals the importance of further investigations of PCAs in sewage sludge land application.

The full list of chemicals of concern is presented in ranked order of priority below:

1. Perfluorinated chemicals (PFOS, PFOA)
2. Polychlorinated alkanes (PCAs)
3. Polychlorinated naphthalenes (PCNs)
4. Organotins (OTs),
5. Polybrominated diphenyl ethers (PBDE)
6. Triclosan (TCS)
7. Triclocarban (TCC)
8. Benzothiazoles
9. Antibiotics and pharmaceuticals
10. Synthetic musks
11. Bisphenol A
12. Quaternary ammonium compounds (QACs)
13. Steroids
14. Phthalate acid esters (PAEs)
15. Polydimethylsiloxanes (PDMSs)

1.4 Selection of substances for risk evaluation

Based on the information presented above, the qualitative knowledge regarding the availability of data relevant for an evaluation of the soil environment and criteria specifically relevant in a Danish context, the following groups of substances have been evaluated for potential risk to the soil environment:

1. Perfluorinated chemicals (PFC)
Members of this group of chemicals have been demonstrated to be very persistent in the environment and found in sewage sludge in relatively high concentrations. Furthermore, sufficient amounts of data have been considered to be available for a reliable risk assessment of some of the PFC.

2. Brominated flame retardants (BFR)
Members of this group of chemicals have been demonstrated to be very persistent in the environment and found in sewage sludge in relatively high concentrations. Furthermore, sufficient amounts of data have been considered to be available for a reliable risk assessment of some of the BFR.

3. Synthetic musks
Members of this group of chemicals have been demonstrated to be very persistent in the environment and found in sewage sludge in relatively high concentrations. Furthermore, sufficient amounts of data have been considered to be available for a reliable risk assessment of some of the musks.

4. Pharmaceuticals
This group of substances are very diverse and represent a wide span of chemical-physical- as well as toxic properties. The Norwegian risk evaluation failed to identify any risk of pharmaceuticals in sewage sludge. However, this was not based on the use of soil ecotoxicity data. Newly published and yet un-published data can help to support the risk assessment. Furthermore, the finding of pharmaceuticals in sewage sludge has regularly been addressed in the Danish and international media as a concern. Hence, there is a need for a solid evaluation focusing on the soil environment.

5. Polychlorinated Biphenyls (PCB)
PCB is generally not found on the list of organic contaminants causing potential concern (see above) in the twentieth century, as the use of the group of persistent substances has been banned for decades and the level in sludge consequently has declined accordingly. However, the finding of PCB in sewage sludge has recently been addressed in the Danish media as a concern, and a temporary cut-off value in sludge has been launched. Hence, there is a need for a solid evaluation focusing on the soil environment.

Besides the five groups of chemicals included in the present report, it would have been appropriate to include an evaluation of other chemicals like the polychlorinated alkanes/naphthalenes and chemicals originating from personal care products like trichlosan, trichloban and parabens. However, within the current project it has not been possible to cover these emerging substances.

1.5 Methodology and limitations

The identification of the papers and information included in this report has been made via a literature search on the Web of Science database using relevant search words and using the possibility of cross-references and citations to identify the most relevant studies. Furthermore, a number of non-peered background information has been identified through a normal search on the internet. This report has aimed at being comprehensive and inclusive within its target area, i.e. risk to soil dwelling organisms and soil quality in general, but should by no means be considered as an exhaustive review of all the relevant literature available. The report is, rather, an effort to give a provisional assessment of whether the selected groups of substances in sewage sludge could potentially pose a risk to terrestrial ecosystems after soil amendment.

The potential risk to above-ground terrestrial species, i.e. terrestrial food webs, and aquatic species has not been evaluated. The same is true for the potential risk to humans via leaching to groundwater, uptake in crops or feed for husbandry. Numerous other reviews and reports have been published internationally covering these aspects for a wide set of the substances covered in this report.

1.5.1 Environmental exposure estimation and predicted soil concentration

Fate and distribution of the releases in the soil compartments are estimated in order to calculate the exposure concentrations in soil, termed Predicted Environmental Concentrations (PEC). Information on substance properties consists of a minimum set of data, including vapour pressure, water solubility, molecular weight, octanol-water partition coefficient, melting point and information on ready biodegradability, which is then used in standard scenarios. For sludge application, accumulation of the substance may occur over consecutive years. As a realistic worst-case assumption, it is assumed that sludge application takes place for 10 consecutive years, and after this an average concentration (over time T) is calculated. The concentration due to 10 years of continuous deposition is given by using an initial concentration of zero and 10 years of input. The concentration just after the first year of sludge application is given by the amount of sludge applied and soil exposed (density and mixing-depth). As only a fraction of the substance remains in the top soil layer at the end of each year, this remaining fraction is calculated by assuming a 1st order removal constant. This removal constant includes biodegradation, volatilisation and leaching. As many of the substances reviewed in this report have very long half-lives, the steady-state concentration in soils after multiple sludge amendments are used for the risk assessment procedure. The initial soil concentration, i.e. 30 days after the last sludge application, in the steady state year (PEC_{ss}) is given as:

$$PEC_{ss} = C_{bg} + (D_{air} / k) + C_{y1} \frac{1}{1 - F_{ac}}$$

Where

PEC_{ss} = The predicted soil concentration at steady state (mg/kg dry weight)
F_{ac} = Fraction of the contaminant remaining in soil after one year. It is calculated as $e^{-(365 * k)}$, where k is the first order rate constant for removal from top soil (see below).
k = First order rate constant for removal from top soil. It is defined as the sum of the rate constant removal by volatilisation, leaching and degradation. As the PEC_{ss} is only calculated for the very persistent substances, it is for pragmatic reasons anticipated that the removal by volatilisation is zero. The removal constant for degradation is defined as ln(2)/DT50.
C_{bg} = The background concentration in the year prior to sludge amendment (year 0). For arbitrary reasons often set at 0.001 mg/kg.
D_{air} = The soil concentration based on the annual aerial deposition (mg/kg). For pragmatic reasons set to zero, as this input is anticipated to be insignificant compared to the deposition by sewage sludge.
C_{y1} = The predicted soil concentration after the first year of sludge application (mg/kg)

For specific description of the equations used for the calculation of the various parameters, like the removal rate constants, a reference is made to the Technical Guidance Document supporting the risk assessment of new and existing chemicals within the REACH programme in the EU (EU 1996).

1.6 Environmental effect assessment and predicted margin of safety

In many risk assessment procedures, the risk is quantified by a comparison of the predicted environmental concentration (PEC) and the predicted no effect concentration (PNEC) as the ratio of PEC/PNEC. The PNEC is established on the basis of the quality and quantity of the available ecotoxicological information and the use of corresponding assessment or safety factors (see Table 1 below). In cases where the risk quotient (RQ) exceeds one, a potential risk is identified. This report has decided to present the risk evaluation slightly differently, as the various assessments *per se* should not be considered as part of a formal risk assessment procedure. Instead of defining the RQ, the distance between the predicted soil concentration and the lowest no observed effect level is defined as the margin of safety (MoS). Based on the estimated margin of safety, it can be concluded whether it is likely that the studied contaminants will pose any risk to soil dwelling species. Within the REACH programme in the European Union, and described in the Technical Guidance Document for risk assessment of new and existing chemicals, a factor of 10-1000 is normally considered sufficient to calculate the PNEC from the lowest effect or no-effect measure (See Table 1.1). Depending on the amount and quality of the available data, a margin of safety between 10 and 1000 would, hence, be considered sufficient for protection of the soil environment, if employing the same level of safety as imposed in the REACH programme.

Table 1.1. The Assessment factors for derivation of $PNEC_{soil}$ given in the European Union's (EU) Technical Guidance Document on Risk Assessment (TGD) within the REACH framework (EU 1996).

Information Avaliable	**Assessment factor**
L(E)C50 short-term toxicity test(s) (e.g. plants, earthworms, or microorganisms)	1000
NOEC for one long-term toxicity test (e.g. plants)	100
NOEC for additional long-term toxicity tests of two trophic levels	50
NOEC for additional long-term toxicity tests for three species of three trophic levels	10
Species sensitivity distribution (SSD method)	5-1, to be fully justified on a case-by-case basis (cf. main text)
Field data/data of model ecosystems	case-by-case

2 Brominated Flame Retardants (BFR)

2.1 Introduction

Flame retardants are chemical compounds used in products such as electronic equipment, furniture textiles, paints, plastics and a wide range of other applications to prevent ignition and retard fire growth. There are three major groups of flame retardants. These are inorganic compounds (e.g. aluminium hydroxide), organophosphate compounds and organohalogenated compounds. The latter, organohalogenated flame retardants, is of particular concern, since these compounds are known to be persistent and harmful to the environment as well as human health. Approximately 25% of all flame retardants contain bromine as the *active ingredient* (Guerra et al. 2010). The bromine atoms play an important role for the functionality of flame retardants, since at sufficiently high temperatures they are released from the products as bromine radicals. These radicals catalytically bind hydrogen and hydroxyl radicals to form water and prevent hydroxyl radicals from participating in further combustive processes.

Some BFRs can be classified as *reactive* substances, which means that they are incorporated (chemically bound) into the material in question, e.g. plastic. Others are so-called *additives* in a wide range of fluids, polymers and resins. These are monomer molecules that are not chemically bound, but adsorbed or mixed into the material. Thus, additive flame retardants are, generally, believed to be more easily released from the products to the environment compared to reactive flame retardants.

Examples of additive BFRs are polybrominated diphenyl ethers (PBDE), which historically have been used in very high volumes. PBDE are ethers, which means that they consist of an oxygen atom bonded to two alkyl groups, in this case two benzene rings (diphenyl) (Table 1). Any of the five available hydrogen atoms on each benzene ring can be substituted by a bromine atom, which gives rise to 209 different combinations or congeners (same number and terminology as for polychlorinated biphenyl, PCB). During the past decades, there has been a large focus on the occurrence, persistence, and harmful effects of PBDE in the environment. Accordingly, they are the most extensively studied group of BFRs in environmental science. According to a review of the latest knowledge on BFRs in Norwegian environmental samples, Møskeland (2010) found that concentrations of decaBDE and Hexabromocyclododecane (HBCD) are increasing in biota and environmental samples, whereas levels of pentaBDE and octaBDE are decreasing. The environmental levels of another group of flame retardants, i.e. tetrabromobisphenol A (TBBPA), were found to be lower, as the compound is not commonly present in environmental samples (Møskeland 2010).

Commercial products of PBDE comprise pentaBDE, octaBDE, and decaBDE (BDE_{209}), however, penta- and octaBDE have been banned from use in some parts of the world, i.e. in the EU. DecaBDE continues to be used, but many countries are currently considering banning or phasing out this product too. Although the use of PBDE is decreasing, the fact that they are still present in many products and materials results in a continuing release to the environment for many years to come.

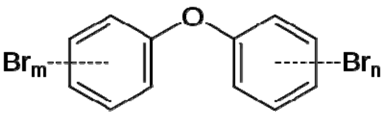
Besides the polybrominated diphenyl ethers, several other types of brominated flame retardants have been and are still being produced in high volumes. The most common ones are tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD). TBBPA is, typically, used as a reactive intermediate (chemically bound) in the production of certain flame-reducing materials, whereas HBCD is used as an additive-like PBDE.

There are several other “new” BFRs that have recently been investigated in the Nordic environment (Harju et al. 2009), but according to Harju et al. (2009) they have often not been found, or have not been analysed for in environmental media. This is backed up by de Wit et al. (2011), who recently reviewed the international literature on emerging BFRs in the environment. More data on these new BFRs is needed in order to determine whether they pose a risk to the environment. Of the reasons listed below, this document will, however, focus on the PBDE among the group of brominated flame retardants:

- Available data indicate that PBDE (still) occur in higher concentrations than most other BFRs in environmental samples, including sewage sludge.
- They are additives and, thus, more prone to leaching from the materials they are a part of.
- Although not many are available, the majority of fate and toxicity data exist for this group of BFR.

As PBDE have approximately the same physical and chemical properties as PCB, they largely end up in the solid sludge fraction within the waste water treatment plant (WWTP). E.g. Ricklund et al.. (2009) found that more than 99% of BDE_{209} was retained in the sludge after waste water treatment in a large WWTP in Stockholm. The apparent similarities in chemical structure between the polychlorinated and polybrominated biphenyl (PCB, PBB) molecules have led to the presumption that these substances also share similar toxicological and environmental properties. However, the physical/chemical properties, applications, environmental release, and toxicology of brominated congeners differ substantially from the former chlorinated products, as they contain heavier and larger molecules than components of the predominant PCB products used in the past, and the commercial products have a lower water solubility and vapour pressure than the former PCB products (Hardy 2002).

Table 2.1. Physical-chemical properties and structure of PBDE (ATSDR 2004)

Parameter	**Value**	**Structure**
Melting point		**PBDE** 
BDE-3 – 209	-	
BDE-209	~300°C	
Boiling point		
BDE-3 – 209	-	
BDE-209	Decomposes at >320°C	
Vapor pressure		
BDE-3 – 209	9.0×10^{-10} - 1.9×10^{-3}	
BDE-209	~3.3×10^{-8} (mm Hg)	
Water solubility		
BDE-3 – 209	< 0.1 – 130 µg/l	
BDE-209	< 0.1 µg/l	
Log K_{OW}		
BDE-3 – 209	5.7 – 8.3	
BDE-209	6.3	
Log K_{OC}		
BDE-3 – 209	-	
BDE-209	6.8	
K_D	n.a.	

2.2 Use and consumption

The main use of bromine world-wide is in the manufacturing of BFR (Guerra et al. 2010). According to Fink et al. (2008, cited from Covaci et al. (2011)), the BFR consumption was 410,000 metric tonnes in 2008, which was an increase of approximately 100,000 tonnes since 2005. On a single compound basis, the consumption of decaBDE, TBBPA, and HBCD amounts to 73,000, 230,000, and 21,000, respectively. Data from 1999 clearly shows that the dominating market at that time was in Asia and the US, while Europe took up less than 15% of the market (De Wit 2002).

2.3 BFR levels sewage sludge

The majority of data on BFR in sewage sludge mainly focuses on PBDE, particularly decaBDE, although some studies also include other common BFRs such as TBBPA and HBCD. Table 2.3 summarises some of the most relevant studies from across the world that have reported sewage sludge concentrations of BFR, primarily PBDE.

BFR has been identified from a wide set of European countries as well as from the USA, Australia and China.

2.4 PBDE in Danish and Scandinavian sewage sludge

Danish analyses of BFR in sewage sludge are very scarce, whereas more information is available from other Nordic countries.

Twelve PBDE congeners were analysed in sewage sludge and wastewater samples from a WWTP near Roskilde in Denmark (Christensen et al. 2003). The mean of the summed concentration of twelve PBDE congeners (17, 28, 47, 49, 66, 85, 99, 100, 153, 154, 183, and 209) was found to be 486 µg/kg dry matter. The BDE_{209} congener alone accounted for 53% of the total PBDE. This concentration is in the same range as in the other Scandinavian and European studies.

In the year 2000, the Danish county Aarhus conducted an investigation regarding the fate of anthropogenic substances in sludge after application to agricultural soils (Aarhus Amt 2005). In this context, the PBDE level in three sludge samples from two WWTPs was identified and the soil concentrations monitored before and up to five months after sludge application (see also section 2.8.3). The concentrations of BDE47, -99, -100, and -153 are shown in Table 2.2. Unfortunately, no data for the most common PBDE, i.e. BDE_{209}, is available in this dataset. A comparison of the concentrations of the four PBDE in Table 2.2 with the data from Christensen et al. (2003) shows that the former were in the range of 51-71 and 82-92 for the two WWTPs, and the latter was 210 µg/kg, i.e. twice as high. Assuming BDE_{209} also would constitute 50% of the total PBDE in the sludge samples from Aarhus County, this would result in an estimated $PBDE_8$ concentration of approximately 200-250 µg/kg.

Table 2.2. The average and range [ ] of concentrations of BDE 47, -99, -100, and -153 in three sludge samples from two Danish WWTPs (Aarhus Amt 2005). All concentrations are in µg/kg dry weight.

WWTP	**BDE_{47}**	**BDE_{99}**	**BDE_{100}**	**BDE_{153}**
Egå	22.2 [20-27]	28.2 [24.5-35]	5.5 [4.9-6.2]	3.3 [2.0-5.4]
Søholt	29 [27-33]	45.2 [41.6-49]	6.6 [5.7-7.2]	4.4 [2.6-7.6]

In a Norwegian screening study by Møskeland (2010), fourteen “new” BFR were investigated in the environmental samples, including sewage sludge. It was found that only three of the investigated BFRs could be detected in the sludge samples, and even then the concentrations were very low, i.e. less than 10 µg/kg.

In a comprehensive Swedish study, 116 sewage sludge samples from 22 different municipal WWTPs were analysed for eight brominated flame retardants (Oberg et al. 2002). The dominating BDE congeners were 209, 99, and 47, with median concentrations of 11 (range from <0.6-390), 10 (<0.3-320), and 7.0 (<0.3-48) µg/kg wet weight, respectively. The median concentration of the sum of PBDE ($PBDE_8$) was 32 µg/kg wet weight. The median concentration of TBBPA was 2.0 µg/kg wet weight, whereas the highest concentration measured was 220 µg/kg wet weight, which was in the same order of magnitude as the various PBDE congeners. The TBBPA concentration of 220 µg/kg is used as a worst-case sludge concentration in the further risk assessment procedure (Section 2.11.1).

Two other smaller Swedish surveys measured the concentrations of the eight common congeners, but on a dry weight (dw) basis. Thus, the concentrations are significantly higher than in the aforementioned case of Oberg et al. (2002). Petterson and Wahlberg (2010) found a mean $PBDE_8$ concentration of 441µg/kg in four samples of sewage sludge with BDE_{209} as the far most dominating congener. Petterson and Wahlberg (2010) furthermore included HBCD in the analyses and reported concentrations between 100 and 200 µg/kg. Haglund and Olufson (2008, 2009) reported the results from a national monitoring programme of hazardous substances in sewage sludge from eight WWTPs. Comparable concentrations of $PBDE_8$ were observed in the eight sludge samples collected in 2007 and 2008, i.e. mean concentrations of $PBDE_8$ of 372 and 345µg/kg, respectively. De Wit (2002) reviewed a number of older Swedish data regarding BFR in sewage sludge. These are, however, considered less relevant in a 2011 perspective than the studies reviewed above.

2.5 PBDE in sewage sludge across the world

In Germany, Knoth et al. (2007) collected 39 samples of sewage sludge from eleven WWTPs during the period 2002-2003. The samples were a mixture of sludge types, such as primary sludge, secondary excess sludge and digested sludge. They analysed for eight congeners ($PBDE_8$) and found a mean total concentration of 555 µg/kg and a span in concentration from 142 to 2,491 µg/kg. On average, BDE_{209} constituted 77% of the total BDE_8 concentration.

Kupper et al. (2008) analysed 19 samples of aerobically or anaerobically stabilized sewage sludge collected from 16 WWTPs in Switzerland in the period from 2003-2005. They analysed for 13 PBDE congeners. By far the most dominating congeners were BDE_{209}, BDE_{99}, and BDE_{47} with mean (and range) concentrations of 310 (138-617), 40 (23-91), and 44 (20-128) µg/kg, respectively. The mean concentration of the sum of eight congeners was 409 µg/kg, with BDE_{209} constituting approximately 75% of the $PBDE_8$ concentration. The mean concentration of HBCD was reported to be 149 (39 – 597) µg/kg.

In another Swiss study, Brändli et al. (2007) collected compost and digestate samples from commercial WWTPs in Switzerland. The median concentration of BDE_8 in the 18 samples was reported to be 10 (0.74-35) µg/kg. It is not clear how many of the 18 samples were compost or digested sludge. The dominating congener was again $BDE_{209,}$ accounting for 72% of total PBDE. The median HBCD and TBBPA concentrations were 100 (21 – 230) µg/kg and 0.51 (0.065 – 2.3) µg/kg, respectively.

Metzger and Kuch (2003, cited from EU 2007) reported the levels of TBBPA in sludge samples collected from 32 municipal WWTPs in Baden-Württemberg, Germany. TBBPA was found to be present at a concentration of 0.6-62 µg/kg dry weight, with a mean level of 16 µg/kg dry weight.

de Boer et al. (2002, cited from EU 2007) reported levels of TBBPA in sludge samples from eight Dutch WWTPs in the range of 2.1-600 µg/kg dry weight (mean 79 µg/kg dry weight).

Morris et al. (2004) reported the level of TBBPA in six sewage sludge samples from three treatment plants in Ireland to be in the range of 7.33-192 µg/kg dry weight (mean 95 µg/kg dry weight). Similarly, they found TBBPA to be present in sludge samples from five WWTPs in the United Kingdom at a concentration of 15.9-112 µg/kg dry weight (mean 59 µg/kg dry weight).

2.6 Non-European data

The United States Environmental Protection Agency (US-EPA) initiated a survey called the Targeted National Sewage Sludge Survey (TNSSS) in which they collected samples of sludge (biosolids) from a representative subset of municipal WWTPs USEPA (2009). Thus, a single sample was collected from 74 individual plants and analysed for a wide range of contaminants, including four PBDE congeners (47, 99, 153, and 209). The mean concentration of the sum of congeners was 3,674 µg/kg of which 2,181 µg/kg was $BDE_{209,}$ corresponding to almost 60% of the total. However, BDE_{209} was measured in concentrations as high as 17,000 µg/kg with a 95th percentile of 7,360 µg/kg.

Andrade et al. (2010) collected 15 samples of dewatered and limed sewage sludge from a mid-Atlantic WWTP from 2005-2008. The samples were analysed for 8 PBDE congeners. The concentrations seemed to be stable during the three years of sampling. The total concentration of $PBDE_8$ ranged between 1320 – 1820 µg/kg, with a mean value of 1500 ±158 µg/kg. BDE_{209} was by far the most abundant congener with a mean concentration of 920 ± 112 µg/kg.

In an Australian survey of sewage sludge samples from 8 urban and 8 rural WWTPs, Clarke et al. (2008) analysed for PBDE. The mean concentration of seven PBDE was 1,064 µg/kg with a maximum concentration of 3,847 µg/kg. BDE_{209} was by far the most dominant congener with concentrations measured as high as 3,780 µg/kg.

In a Chinese study, 31 samples of sewage sludge were collected from WWTPs in 26 different cities around China. The total concentration of 13 PBDE ranged from 5.1 – 1115 µg/kg with a mean value of 94 µg/kg (Wang et al. 2007).

2.7 Conclusions on sewage sludge levels of BFRs

Generally, concentrations of PBDE in sewage sludge are higher in samples from America and Australia compared to data from Europe. The American survey revealed concentrations approximately one order of magnitude higher than most European concentrations. BDE_{209} makes up a significant fraction (typically >70%) of the total PBDE concentration reported in practically every study (Table 2.3). A Danish study found a concentration of $PBDE_8$ of 467 µg/kg, and a concentration of BDE_{209} of 248 µg/kg. The number of samples was rather limited in this study and only from one WWTP. The largest single survey covered 116 Swedish sludge samples from 22 WWTPs. Here, a mean of the $PBDE_8$ was reported at a markedly lower level than the Danish study, i.e. 32 µg/kg wet weight, whereas the maximum level was 450µg/kg wet weight. Other non-European studies have reported $PBDE_8$ concentrations exceeding 3,000 µg/kg. As a conservative, but yet realistic, sludge scenario, a concentration of 1,000 µg $PBDE_8$ /kg or 750 µg BDE_{209}/ kg is chosen for further use in the risk assessment (Section 2.11.1).

Some of the studies also included TBBPA and HBCD in their analyses. HBCD seems to occur in the highest concentrations of the two, with reported concentrations ranging between 100 – 200 µg/kg. TBBPA was only reported in a few studies, and the concentrations were very low, which is in accordance the fact that TBBPA is mainly used as a reactive BFR, i.e. is chemically bound in the material and does not easily leach. For precautionary reasons, the highest reported sludge concentration of 220µg TBBPA/kg is chosen for further use in the risk assessment (Section 2.11.1).

Table 2.3. International data on occurrence of PBDE in sludge from WWTPs. n.s. = not specified.

Country	**Region**	**Year**	**No. of samples**	**Sludge type**	**Included congeners**	**Total PBDE µµg/kg**		**BDE-209 µg/kg**		**Reference**
						Mean	Range	Mean	Range	
Germany	11 WWTPs	2002 – 2003	39	Mixed types: primary, secondary excess, digested	28, 47, 99, 100, 153, 154, 183, 209	555	142 – 2491	429	97 – 2217	(Knoth et al. 2007)
Sweden	22 WWTPs	n.s.	116	n.s.	47, 86, 99, 100, 153, 154, 183, 209	32[1]		11[1]	<0.6 – 390[1]	(Oberg et al. 2002)
	Stockholm 2 WWTPs	2007 – 2008	4	Digested and dewatered	28, 47, 99, 100, 153, 154, 183, 209	441	267 – 641	383	220 – 580	Petterson & Wahlberg 2010
	n.s. 8 WWTPs	2007 2008	8 8	n.s.	28, 47, 99, 100, 153, 154, 183, 209	372 345	102 – 624 173 – 642	291 292	72 – 525 122 – 557	Haglund and Olofson (2008; 2009)
Switzerland	16 WWTPs	2003 – 2005	19	Mixed: aerobically and anaerobically stabilized	28, 47, 99, 100, 153, 154, 183, 209	409		310	138 – 617	(Kupper et al. 2008)
		n.s.	5	Digestate and compost	28, 47, 99, 100, 153, 154, 183, 209	10	0.74 – 35	7.3	2.6 – 31	(Brandli et al. 2007)
Australia	16 WWTPs	n.s.	16	Mixed	47, 99, 100, 153, 154, 183, 209	1064	<LOD – 3847		Max. 3780	(Clarke et al. 2008)

Table 2.3. (cont.)

USA	74 WWTPs	n.s.	74	Mixed	47, 99, 153, 209	3674		2181	Max. 17000	USEPA 2009
	Mid-Adlantic	2005 – 2008	15	Dewatered and limed	28, 47, 99, 100, 153, 154, 183, 209	1500	1320 – 1820	920 ± 112		(Andrade et al. 2010)
China	26 WWTPs	n.s.	31		13 PBDE	94.0	5.1 – 1115			(Wang et al. 2007)
Denmark	1 WWTP Bjergmarken	n.s.	n.s.	n.s.	28, 47, 99, 100, 153, 154, 183, 209	467		248		Christensen et al (2003)

[1] *concentrations in µg/kg wet weight*

2.8 Fate and behaviour of BFRs in soil

Vonderheide et al. (2008) conducted a comprehensive survey of studies on PBDE in the environment. The review clearly showed that soil is by far the least studied environmental component, although fate models may predict it to be the dominant environmental sink (Gouin et al. 2003). Below is a short review of some of the few studies regarding fate and behaviour of BFR in soil systems.

2.8.1 Soil degradation

Nyholm et al. (2010) investigated the biodegradation kinetics of a range of BFRs in aerobic and anaerobic soil mixed with different types of sewage sludge, i.e. activated- , digested- and hygienized sludge. BDE_{28}, BDE_{209} as well as TBBPA were all present in the sludge. In aerobic soils, the estimated half life of BDE_{28} varied between 130 and 600 days, whereas no significant degradation was observed for BDE_{209} over the 120 days period of the study. The same was true for BDE_{28} and BDE_{209} over the 160 day study in anaerobic soils. TBBPA, on the other hand, was relatively rapidly degraded with DT50 values in the range of 58-110 days in aerobic soils. The degradation of TBBPA was, however, significantly lower in an anaerobic soil, with extrapolated DT50 values ranging from 340 to 600 days. It should be noted that the authors extrapolated DT_{50} reaching beyond the experiment period. Such extrapolation should always be used with caution, but as a conservative estimate to be used in the generic risk assessment procedure degradation, a half-life of 110 days could be used for TBBPA, as most agricultural soil receiving sewage sludge would be considered aerobic. No reliable DT50 could be obtained for BDE209. The high observed persistency of BDE_{209} is consistent with findings by Gerecke et al. (2006), who reported a half-life of 700 days in digested anaerobic sewage sludge. A conservative DT_{50} of 10 years for BDE_{209} is used in the further risk assessment procedure.

2.8.2 Leaching and vertical transport

Very few studies exist which have investigated the leaching of BFRs from sludge-amended soils. However, recently, Gorgy et al. (2011) performed leaching column tests to determine the mobility of PBDE in soils amended with sewage sludge corresponding to an application rate of approximately 80 tonnes/ha. After four weeks, approximately 34 pore volumes of water had passed through the column and the PBDE distribution along the flow path of the infiltrating water was determined. The initial concentration of total PBDE decreased by 38% in the amended soil layer. PBDE concentrations in the first 14-mm soil layer increased up to 234 µg/kg dw, whereas in the second and third soil layers, the concentration increased up to 20 and 25 ng/kg dw. PBDE in the leachate increased from below detection to 31 ng/l. In general, lower brominated PBDE were more easily mobilised than higher brominated congeners such as BDE_{209}.

Gottschall et al. (2010) applied liquid municipal sludge from a local WWTP to plots on an agricultural field. The purpose was to study the levels of contaminants in tile drainage following application. Additionally, different surface application methods were tested. The concentration of $PBDE_7$ (47, 99, 100, 153, 154, 183, 209) in the applied sludge was 1.5 µg/kg. They found that the mass loss of $PBDE_7$ to tile drains two hours after application ranged between 0.04 and 1.7% of the total amount applied.

Xia et al. (2010) observed a sharp decrease with increasing soil depth of PBDE in sludge amended soils, indicating limited soil leaching of these compounds (see more details of study below).

2.8.3 Soil concentrations

The background concentration in European soils of BFR has been reported in the higher ng/kg or lower µg/kg dw range by e.g. Hassanin et al. (2004) and Harrad and Hunter (2006).

In 2000, the Danish county Aarhus conducted an investigation regarding the fate of anthropogenic substances in sludge after application to agricultural soils (Aarhus Amt 2005).The soil concentrations were monitored before and up to five months after sludge application. Sludge was applied at a dose of 17 t/ha and soil was sampled from two different sites, i.e. a sandy soil and a clay soil, after 1 day, 2 weeks, 1 and 5 months. PBDE was detected at very low concentrations in both soils up to five months after sludge application. The concentration was, somehow, higher in the sandy soil, most likely due to the fact that the concentration of PBDE in the sludge was twice as high as the sludge applied to the clay soil. The detection limit for the individual PBDE ranged from 0.4 to 6 ng/kg wet weight. The highest reported soil concentration was 0.053 µg/kg wet weight. As the dry matter of the soil was reported as 83.7%, this corresponds to a soil concentration of 0.063 µg/kg dry weight.

Vinkelsoe et al. (2002) investigated the occurrence and vertical distribution of PBDE in Danish soils, which had been differently cultured and sludge-amended. Three different sites were investigated: 1) a preserved natural reference area which had not been cultivated, dressed or fertilised for more than 50 years, but only used for grazing cattle. Deposition was expected to be the main source of pollution in this area; 2) a cultured area annually amended with about 0.7 t dw/ha/y of sludge for more than 25 years and 3) a site that received approximately 17 t sludge/ ha from more than 25 years, but changed to mineral fertilisers eight years prior to soil sampling. No information regarding the PBDE concentration in the applied sludge was available. Four different PBDE were monitored in the soils, i.e. BDE47, - 99, -100 and -153. The mean $PBDE_4$ concentration in five soil samples from the three sites was 0.01, 0.15 and 4.8-31.2 µg/kg dry matter.

Andrade et al. (2010) studied the concentration and fate of PBDE in agricultural soils after fertilisation with sewage sludge. They found that the most dominant congeners were BDE_{47}, BDE_{99}, and, especially, BDE $_{209}$, both in the investigated sludge samples and in the surface soil samples that had been fertilised with the sludge. The total $PBDE_8$ concentration in sludge ranged from 1,320 to 1,820 µg/kg dw. The average PBDE concentration in soils amended once with sewage sludge was 15.2 ± 10.2 µg/kg d.w., which was three times higher than in un-amended soils, where the concentration was 5.01 ± 3.01 µg/kg d.w. Fields with multiple sludge applications had an average concentration of 53.0 ± 41.7 µg/kg d.w.

A study by Xia et al. (2010) evaluated the levels of PBDE in soils from field plots that had received annual applications of sewage sludge for 33 years. Sludge had been applied annually at rates of 0 (control), 16.8, 33.6, and 67.2 t/ha (dry wt). The total concentrations of five PBDE (47, 99, 100, 153, and 154) in the nine samples of aerobic sewage sludge collected in the same period ranged from 71 to 1,020 µg/ kg (dry wt) with a median concentration of 630 µg/kg. The level of PBDE in the surface soil increased with increasing application rate. The levels of PBDE in the top 15 cm of the soil that had received the highest loading were 658 µg/kg compared to 28 µg/kg in the control plot.

Sellström et al. (2005) collected soil and earthworm samples from three research stations, i.e. a reference plot and two controlled sewage-sludge-amended plots. The sludge-amended fields at two of the research farms had received a total of 20 or 60 tonnes/ha in the period 1981 – 1997. More specifically, the sludge application was 4 or 12 tonnes every fourth year, corresponding to an annual application rate of 1 or 3 t/ha. The last research station had only applied a single load of 2.3 tonnes/ha. Sewage-sludge amendment at the research stations increased concentrations of all BDE congeners with a factor of 2-13 compared to the reference plots, with the highest increase observed for BDE_{209}. The soil concentration of $PBDE_{sum}$ at the two different sites amended with sludge in multiple years was 0.84 and 2.1 µg/kg after the highest sludge load. In the soils receiving one sludge application, the concentration was measured as 0.063 µg/kg, which was twice as high as the reference site.

Sellström et al. (2005) also measured the soil concentration at two farm sites in Sweden potentially contaminated by either flooded sediment material or sewage sludge from an area known for its textile industry using BFR. Sewage sludge had been applied at an average dose of 5 t/ha/y over the period 1978 to 1982. At both farm-sites, markedly elevated soil concentrations were observed when compared to nearby reference areas. The soil concentration of $PBDE_{sum}$ at the farm site was 3,900 µg/kg with BDE_{209} as the predominant congener having a measured concentration of 2,200 µg/kg. In the flooded farm soils, the soil concentration of $PBDE_{sum}$ was reported to be 750µg/kg. These elevated concentrations should be compared to background concentrations of 0.84 and 1.9 µg/kg in the two respective reference areas. The high levels found at one farm 20 years after the last application of PBDE-contaminated sludge indicate high persistence of PBDE in soils, especially for the highly brominated congeners like BDE_{209}.

Eljarrat et al. (2008) studied the fate of PBDE in sewage sludge amended soils from a number of agricultural sites in Spain. The sludge application rates ranged from 15 to 25 t/ha and had taken place at least once a year from 1997-2005. PBDE levels in soils ranged between 21 and 690 µg/kg dw, also with BDE_{209} as the predominant congener in all soil samples. Compared to a control soil that had never received sewage sludge, sewage sludge amendment was shown to increase soil concentrations of all BDE congeners by a factor of 1.2- to 45, with the highest increase observed for BDE_{209}. Results evidenced the cumulative effect of the sludge application rates. Moreover, high levels found in soils four years after the last sludge application indicate persistence of PBDE in soils.

Matscheko et al. (2002) analysed soils from five agricultural sites, i.e. three research sites and two privately owned farms, for PBDE. The impact of adding 1 to 3 tonnes of sludge (DM) per hectare per year over a twenty-year period on the concentrations was studied at the three research sites. For each plot, a useful reference site was chosen. No information about the level of PBDE in the used sludge was available. In soils that had not received sludge (reference soils), the sum of PBDE ranged from 0.034 to 0.19µg/g dry matter (DM), whereas the concentration ranged from 0.029 to 840 µg/kg DM in the sludge treated soils. The very high concentration of 840 µg/kg was an exception, as the second highest soil concentration was measured to be 4 µg/kg.

2.8.4 Summary of fate and concentration of BFR in soils

A number of the BFRs are highly persistent in soils with no observed degradation even under aerobic conditions over long study periods. Hence, no interpolated DT_{50} are available for e.g. BDE_{209}, but it is apparent that the DT_{50} should be counted in years. For other less brominated substances like TBBPA, more valid DT50 values are obtained, i.e. DT50 of 110 days. Soil concentrations exceeding 1000µg PBDE/kg have regularly been observed in soils treated with large amounts of sludge for multiple years, whereas background concentrations are, typically, reported to be below 1 µg PBDE/kg.

2.9 Bioaccumulation of BFR

Generally, only a few bioaccumulations with BFR are available in the open literature. Short presentations of the most relevant studies are presented in the sections below.

2.9.1 Bioaccumulation in soil fauna

Sellström et al. (2005) studied the uptake of PBDE in earthworms collected from various sewage sludge amended soils (see details of the study in the section 2.8.3 above). PBDE concentrations in worms ranged from 3.1 to 38,000 µg/kg lipid weight (lw) and were correlated to soil concentrations. Biota-soil accumulation factors (BSAF) increased with the degree of bromination. Thus, higher brominated PBDE, including BDE_{209}, seem to have the potential to accumulate in earthworms. The concentration of $PBDE_9$ in worms from reference soils were low, ranging from 3.4 to 9.3 µg/kg lw. Compared to worms from the reference soils, concentrations were higher in worms collected from sewage sludge- amended soils. The highest PBDE concentrations were found in earthworms collected from a farm site that had received industrial sewage sludge 20 years ago. The concentration in earthworms was 38,000 µg/kg lw for the sum of PBDE and 5,200 µg/kg lw for BDE_{209}. Biota-soil accumulation factors (BSAF) declined in the following order: TeBDE > PeBDE > HxBDE > OcBDE > NoBDE > DeBDE. More specifically, the mean BSAF from the various sites was calculated to be 5.0 (BDE_{47}), 4.2 (BDE_{99}), 4.6 (BDE_{100}), 2.5 (BDE_{153}), 2.3 (BDE_{154}), 0.6 (BDE_{196}), 0.3 (BDE_{206}), 1 (BDE_{207}), and 0.3 (BDE_{209}), respectively.

Liang et al. (2010) exposed earthworms to artificially PBDE spiked soils to investigate the bioaccumulation of PBDE in earthworms. All major PBDE were taken up by the earthworms, however, both the uptake and the elimination rates decreased with increasing lipophilicity. The bioavailable fraction, as measured by Tenax extraction, correlated well with the concentration in earthworms, suggesting that the bioavailable fraction of PBDE in soils is related to the faction of easily desorbed PBDE from soils. This was supported by the fact that the uptake decreased with increasing ageing time. Almost all of the PBDE congeners were detected in earthworm tissue after short term exposure (48 h), and body burdens had a positive correlation with the concentrations in soil. The concentration of eight $PBDE_{sum}$ was after 28 days 89 µg/kg in the soil and 3,279 µg/kg in the earthworms. The half-life of the eight PBDE congeners ranged from 10 to 15.2 days in the earthworm. When based on the initial spiked soil concentration, BSAFs ranged from 0.88 (BDE_{183}) to 55.77 (BDE_{47}).

Matscheko et al. (2002) analysed for PBDE in soils and earthworm samples from five agricultural sites, three research sites and two privately owned farms. For each plot, a useful reference site was chosen. The sum of PBDE ranged from 0.029 to 840 µg/kg dry matter in the soils treated with sewage sludge. The BSAFs for the four PBDE congeners were highest at the sludge treated sites. The highest BSAF for the reference sites was identified to be 8, whereas it was 34 at one of the sludge amended sites, and 17 and 18 at two other sites.

In the EU Risk Assessment report for TBBPA (EU 2007), a reference is made to a toxicity study by Wildlife International (2003c), where the uptake of TBBPA by earthworms (*Eisenia fetida*) from the soil was elucidated. The BSAF declined with increasing exposure concentration (0.63-40.0 mg/kg) and ranged from 0.019 to 5.1.

2.9.2 Bioaccumulation by plants

The Danish county Aarhus measured a single sample of barley collected from sludge amended soils (see details in section 2.8.3). Among the four PBDE congeners that were monitored in barley (47, 99, 100 and 153), only BDE_{99} was detected in reliable concentrations according to the detection limits. The concentration was 0.036 µg/kg dry weight. When compared to the initial soil concentration measured in the arable soil, i.e. 0.011 µg/kg ww or 0.013 µg/kg dw, this corresponds to an approximate BSAF of 2.75.

Xia et al. (2010) could not detect any uptake of PBDE in corn tissue collected from experimental plots that had received substantial amounts of sewage sludge over a 33 year period (see a more detailed description of study in section 2.8.3).

In a study of potential plant uptake of PBDE from contaminated sewage sludge, Vrkoslavová et al. (2010) measured the content of several BDE-congeners in two plant species grown not in soil, but directly in sewage sludge containing relatively high concentrations of PBDE. The highest concentration of a single congener was for 400 µg /kg for BDE_{209}, whereas the total concentration of all (12) congeners was 1,110 µg/kg. The control plants were grown in peat substrate for garden plants. The experiment showed that Nightshade (*solanum nigrum*) accumulated about 4.8 µg/kg dw, which was about 10 times less than Tobacco (*Nicotiana tabacum*). In Tobacco, most of the PBDE was detected in the stem and leaves, whereas Nightshade mostly had PBDE in the roots and stem. The BSAF differed among plant species and among BDE congener, but ranged from 0-0.02 for Nightshade and 0.05-0.30 for Tobacco, with the highest BSAF for BDE_{47} in both cases.

Li et al. (2011) studied the uptake of TBBPA and HBCD by two plant species (cabbage and radish). A soil was spiked with TBBPA and HBCD to reach a final concentration of 1000 µg/kg alone and in mixture. Radish and cabbage were grown in the spiked soil for approximately 8 weeks, after which they were harvested and analysed. The concentrations of both compounds decreased markedly in the soil during the experiment. TBBPA decreased to about 10% of the initial concentration in all pots. The same trend was observed for HBCD in all but one case. Both plant species did take up TBBPA and HBCDs, but cabbage showed greater accumulating abilities. The TBBPA concentrations in cabbage plants were up to 18 µg/kg tissue, whereas TBBPA concentrations in the tissue of radish plants were less than 5 µg/kg. Cabbage plants accumulated as much as 70 µg HBCD/ kg, whereas the concentrations of HBCD in radish plants were less than 30 µg/kg. The calculation of BSAF is not reported in the paper and is hampered by the significant degradation of both substances in soil, but if using the final soil concentration, i.e. approximately 100 µg/kg, as a conservative estimate of the exposure concentration, then an approximation of the BSAF for TBBPA would be 0.2 for cabbage and 0.05 for radish. Similarly, the approximate BSAF for HBCD can be estimated to be 0.8 and 0.3 for cabbage and radish, respectively. These BSAFs are considered sufficiently conservative, as the time-weighted average of the exposure concentration over the eight weeks would be expected to exceed the final concentration of 100 µg/kg.

Mueller et al. (2006) spiked a top-soil with an environmentally relevant level (75 µg/kg) of a commercial penta-BDE mixture and monitored the extractability of the BDE congeners 47, -99, and -100 over a 10-week period in planted and unplanted pots. The extractability of each congener decreased rapidly, i.e. down to 10% after 10 weeks, largely due to abiotic sorption to soil particles, which was demonstrated by low PBDE recovery from sterilized and dry soils. When radish and zucchini plants were grown together in PBDE spiked soils, PBDE recovery increased nearly eight times compared to unplanted soil and soil planted with either plant species alone. Thus, bioavailability of adsorbing substances like PBDE may be influenced by plant growth. Both plant species accumulated PBDE in root and shoot tissue in relatively limited amounts, i.e. the total concentration of the three congeners was less than 5 µg/kg plant tissue. PBDE uptake was higher in zucchini than in radish, and the translocation to zucchini shoots was congener-specific in the order $BDE_{100}> BDE_{99} > BDE_{47}$. If basing the BSAF on initial or extractable concentration after 10 weeks, it would be less than 0.07 or 0.7, respectively.

In a study by Huang et al. (2010), the behaviour of BDE_{209} in a soil-plant system was investigated. A loamy soil without detectable PBDE was spiked with a solution of BDE_{209} and incubated for four weeks to reach an initial concentration of 4960 ± 310 µg/kg. Seeds of Italian ryegrass (*Lolium multiflorum* L.), alfalfa (*Medicago sativa* L. cv. Chaoren), pumpkin (*Cucurbita pepo* ssp. *Pepo* cv. Lvjinli), summer squash (*Cucurbita pepo* ssp. *Pepo* cv. Cuiyu-2), maize (*Zea mays* L. cv. Nongda 108), and radish (*Raphanus sativus* L. cv. Dahongpao) were grown in pots with the spiked soil for 60 days in a growth chamber. Accumulation of BDE_{209} was observed in the roots and shoots of all the six plant species examined. Root concentrations ranged between 513 ± 26 and 2088 ± 104 µg/kg dw with the highest concentrations observed in pumpkin (2088 ± 104), squash (1946 ± 97), and ryegrass (1878 ± 94). Root uptake was positively correlated with root lipid content. Concentrations of BDE_{209} in shoots ranged between 177 ± 11 and 490 ± 29 mg/kg dw. Evidence of a relatively higher proportion of penta- through di-BDE congeners in plant tissues than in the soil indicates either that debromination of PBDE may occur within the plants, or that lower brominated PBDE are more readily taken up by plants. The data above shows soil-to-biota accumulation factors for PBDE all were below 1, and for above ground parts at least one order of magnitude below 1.

In the laboratory, Huang et al. (2011) exposed three plant species to three soils containing PBDE taken from a Chinese waste site. The total PBDE concentrations in the three soils were 236, 674, and 1177 µg/kg. BDE_{209} was present in the largest quantities in all three soils, accounting for 36-53% of the total PBDE. They found a significant concentration gradient for the total PBDE in the plants with the highest concentrations in the roots, followed by the stems and the lowest in the leaves. The uptake was, generally, significantly higher in pumpkin compared to maize and ryegrass at all three sites. The highest reported tissue concentration was approximately 310 µg/kg in the roots of pumpkins exposed to a soil concentration of 1177 µg/kg. An approximate BSAF can, hence, be estimated to 0.26. The highest BSAF of approximately 0.5 was, however, observed in the lowest contaminated soil (236.4 µg/kg).

2.9.3 Terrestrial food webs

Voorspoels et al. (2007) studied the biomagnification of eight PBDE in three small terrestrial food chains. The PBDE were measured in passerines (great tits - *Parus major*), wood mice (*Apodemus sylvaticus*), and bank voles (*Clethrionomys glareolus*). Also, data on PBDE in common buzzards (*Buteo buteo*), sparrowhawks (*Accipiter nisus*), and red fox (*Vulpes vulpes*) were reported. This enabled estimation of the biomagnification potential of PBDE in the following three terrestrial food chains: 1) great tit to sparrow hawk, 2) small rodents to buzzard, and 3) small rodents to fox. The biomagnification of BDE $_{209}$ could not be assessed because levels of this congener were below the limit of detection in the prey species. Other congeners were biomagnified in both predatory bird species, except for BDE_{28} where no biomagnification could be observed from rodents to buzzard. Biomagnification factors were calculated as the ratio between the lipid-normalized concentrations in the predator and in the prey, and ranged from 2 to 34 for the sum of PBDE in predatory birds. Although the fox is a top-predator, this was not reflected in its PBDE-levels, as no biomagnification could be observed. As speculated by the authors, this could be related to the high metabolic capacity of the fox with regard to organohalogens. This study cannot be linked to PBDE in sludge, but may indicate that PBDE taken up by for example earthworms may, to some extent, be biomagnified in top-predators of terrestrial food chains.

Vermeulen et al. (2010) investigated the bioaccumulation of PBDE in the soil-earthworm-hedgehog food chain in a number of Belgian residential parks. Concentrations of selected PBDE were measured in soil and earthworms collected in grassland and open woodland, and in hair and blood of hedgehogs foraging in the two parks containing these habitats. The background concentrations in soil ranged from 0.08 to 0.20 µg/kg for PBDE, and the BSAFs for earthworms ranged from 1.99 to 5.67. The BSAF decreased with increasing soil concentrations, suggesting that steady-state equilibrium was not reached in soil or earthworms. Hair from hedgehogs was used as a potential biomonitoring tissue for animals higher up in the food chain. No significant relationship between PBDE concentrations in earthworms and hair of hedgehogs was, however, established, possibly due to variation in individual foraging behaviour and uptake rates.

2.9.4 Summary on the bioaccumulation of BFR.

BFR may bioaccumulate in plants and soil fauna. In plants, the observed bio-to-soil accumulation factors (BSAF) were generally below 1, whereas BSAFs higher than 1 have been observed for earthworms, i.e. up to approximately 50. There are a few studies available, which may indicate a potential for accumulation of BFR in terrestrial food chains like earthworms-rodents-raptors, although the magnitude of biomagnification is, generally, lower than from the scenarios reported in marine food chains, e.g. deWit et al. (2010).

2.10 Ecotoxicity of BFR to soil dwelling organisms

Generally, only a few bioaccumulation and ecotoxicity studies with BFRs are available in the open literature. However, as part of the Risk Assessment Procedure for new and existing chemicals in EU, The European Chemicals Bureau has published risk assessment reports for decabromodiphenyl ether (BDE_{209}) (EU 2002) and Tetrabromobisphenol A (TBBPA) (EU 2007). In this context, un-published data conducted by Commercial contract laboratories have been evaluated and summarised. These data are included in this chapter as well.

2.10.1 BDE_{209}

In the EU Risk Assessment report for BDE_{209} (EU 2002), a reference is made to a toxicity study with six species of plants, using OECD Guideline 208 (Porch and Krueger, 2001). The soil used in the test was an artificial sandy loam soil. The following six plant species were tested over 21 days: Corn (*Zea mays*), onion (*Allium cepa*), ryegrass (*Lolium perenne*), cucumber (*Cucumis sativa*), soybean (*Glycine max*), and tomato (*Lycopersicon esculentum*). The nominal concentrations of BDE_{209} were 391, 781, 1,563, 3,125 and 6,250 mg/kg dry soil. The visual observations carried out during the test revealed no signs of treatment-related phytoxicity in any species at any treatment level. Overall, the NOEC from these studies was given as ≥6,250 mg/kg dry soil, based on nominal values or ≥5,349 mg/kg dry soil, based on the mean measured concentration in soil at the start of the test.

In the EU Risk Assessment report for BDE_{209} (EU 2002), a reference is made to an earthworm study conducted by ABC (2001). The test was carried out according to the OECD 207 test guideline “Earthworm Reproduction Test (*Eisenia fetida/andrei*)” using the artificial OECD soil. The organisms used in the test were *Eisenia fetida*. The nominal concentrations of BDE_{209} used in the test were 313, 650, 1,250, 2,500, and 5,000 mg/kg dry weight. Overall, no significant adverse effects on survival or reproduction were seen in this study, and so the NOEC was ≥ 4,910 mg/kg dry weight when based on measured concentrations. In this study, the concentration of BDE_{209} was also determined in adult earthworms after 28 days of exposure. BDE_{209} was found to be present below the limit of quantification (<0.75 mg/kg) at all exposure levels.

Sverdrup et al. (2006) tested the toxicity of two BFRs to soil nitrifying bacteria, a terrestrial plant (red clover, *Trifolium pratense*), and a soil invertebrate (*Enchytraeus crypticus*). BDE_{209} was not toxic to any of the test organisms up to the highest nominal test concentration of 1000 mg/kg. Exposure concentrations were verified by chemical analysis and showed slightly higher concentrations for BDE_{209}, especially at the higher exposure concentrations. For example, the highest exposure concentration of BDE_{209} was measured to 2,274 mg/kg, i.e. twice as high as the nominal concentration.

In a study of plant uptake of PBDE from contaminated sewage sludge, Vrkoslavová et al. (2010) observed the growth of two plant species grown directly in sewage sludge containing relatively high concentrations of PBDE. The highest concentration of a single congener was for 400 µg /kg for BDE_{209}, whereas the total concentration of all (12) congeners was approximately 1,110 µg/kg. The control plants were grown in peat substrate for garden plants. The experiment showed that Nightshade (*solanum nigrum*) as well as Tobacco (*Nicotiana tabacum*) were positively affected by the sewage sludge compared to the controls. The growth of Tobacco and Nightshade was 350% and 59% higher in the sludge media compared to the peat substrate, indicating a non-toxic effect of PBDE up to an exposure concentration of 1,110 µg/kg. The 400 µg/kg of BDE_{209} can be used as a soil concentration where no effects on plant species were observed, supporting the low phytoxicity of BFR reported by Sverdrup et al. (2006).

In the EU Risk Assessment report for BDE_{209} (EU 2002), a reference is made to two sediment studies with *Lumbriculus* variegatus by Wildlife International Ltd (Krueger et al. 2001ab), which confirm the low toxicity of BDE_{209} to oligochaetes species. Based on the analytical results, the NOECs from these studies are 4,536 mg/kg dry weight for the 2.4% organic carbon sediment and 3,841 mg/kg dry weight for the 5.9% organic carbon sediment. No further explanation regarding the unexpected higher toxicity observed at the high organic sediment compared to the low organic sediment is given, but it could be an indication of a relative importance of exposure by ingestion of organic material by these sediment dwelling oligochaetes.

2.10.2 TBBPA

Sverdrup et al. (2006) tested the toxicity of two BFRs to soil nitrifying bacteria, a terrestrial plant (red clover, *Trifolium pratense*), and a soil invertebrate (*Enchytraeus crypticus*). TBBPA was toxic to enchytraeids, with significant effects on reproduction detected at a nominal concentration of 10 mg/kg (NOEC=3 and EC10 = 2.7 mg/kg). The EC10 and NOEC for nitrifying bacteria were estimated to 295 and 300 mg/kg (nominal) for TBBPA. No effects were observed when exposing red clover to TBBPA up to the highest nominal test concentration of 1000 mg/kg. Exposure concentrations were verified by chemical analysis and showed slightly lower concentrations than the nominal for TBBPA.

In the EU Risk Assessment report for TBBPA (EU 2007), a reference is made to a phytotoxicity study (Wildlife International 2002).The effect of TBBPA on emergence and growth of six species of plants was determined using the OECD Guideline 208. The following six plant species were tested: Corn (*Zea mays*), onion (*Allium cepa*), ryegrass (*Lolium perenne*), Dicots - cucumber (*Cucumis sativa*), soybean (*Glycine max*), and tomato (*Lycopersicon esculentum*). The nominal test concentrations were 20, 78, 313, 1,250 and 5,000 mg/kg dry soil. The NOECs obtained for the various plant species were in dry weight: Corn (253 mg/kg), Cucumber (16 mg/kg), Onion (253 mg/kg), Ryegrass (64 mg/kg), Soybean (>4,595 mg/kg) and Tomato (253 mg/kg).

In the EU Risk Assessment report for TBBPA (EU 2007), a reference is made to a reproduction test using the earthworms (*Eisenia fetida*) (Wildlife International, 2003). The nominal concentrations tested were 313, 625, 1,250, 2,500, and 5,000 mg/kg dry weight. Due to high variability in the controls, the NOEC value was less reliable. The EC10 and EC50 values based on analytical measurements were estimated to 0.12 and 1.7 mg/kg dw, respectively. The study was later repeated (ABC Laboratories 2005) with nominal concentrations of 0.31, 0.63, 1.3, 2.5, 5.0, 10, and 20 mg/kg dry weight. The NOEC for reproduction was determined as 0.29 mg/kg dry weight and the EC50 for reproduction to 0.91 mg/kg dry weight.

In the EU Risk Assessment report for TBBPA (EU 2007), a reference is made to a toxicity study of TBBPA to soil microorganisms using the OECD 216 nitrogen transformation test (Wildlife International, 2005). The nominal concentrations were 10, 32, 100, 316, and 1,000 mg/kg dry weight. The inhibition percentage was below 10% in all treatment groups, and it was concluded that the EC10 was >1,000 mg/kg dry weight.

Li et al. (2008) investigated the biochemical responses of wheat (*Triticum aestivum*) to exposure of TBBPA. The chlorophyll content in wheat leaves was significantly ($p < 0.05$) lower than that in the control after both 7 and 12 days of exposure to TBBPA at all exposure concentrations, from the lowest of 0.5 to the highest of 5000 mg/kg. However, no clear dose-response relationship could be established, as no further significant reduction of TBBPA was observed from 50 to 5000 mg/kg. Similarly, no dose-response relationship between changes in activity of antioxidant enzymes (SOD, POD and CAT) and the concentration of TBBPA could be established. Hence, these data are not very useful in a risk assessment context, also because the use of biomarkers in risk assessment procedures is uncertain.

2.10.3 Summary on the ecotoxicity of BFR

Relatively little information is available regarding potential ecotoxicity of BFR to soil dwelling species. The few studies available indicate a very low toxicity of the higher brominated BFRs like BDE_{209}, most likely due to their size and strong adsorption to the soil matrix. Effects by TBBPA, on the other hand, have been observed below 1 mg/kg.

2.11 Provisional risk evaluation of BFR in sludge

Based on the data presented in sections above, a provisional risk evaluation for the soil environment can be conducted.

The risk is assessed by comparing the predicted soil exposure (predicted environmental concentration – PEC) to the predicted level in soil where no effects are observed or anticipated (No Observed Effect Level – NOEL). The ratio between PEC and NOEL indicates the so-called margin of safety, so to speak, which essentially is the reverse of the more common "risk quotient" utilised in many risk assessments. As all exposure scenarios cannot be foreseen and all soil dwelling species cannot be tested, a certain margin of safety is needed in order to conclude that significant effects of BFR in sewage sludge would be unlikely. Based on the amount of data available, the margin of safety should fall within a range of at least 10 to 1000 in order to be in line with the use of assessment factors in the REACH programme in the European Union and described in the Technical Guidance Document for risk assessment of new and existing chemicals.

2.11.1 Predicted soil concentration (PEC)

As some brominated flame retardants, like the group of PCDEs, are persistent compounds in the environment with half-lives exceeding one year, it is necessary to calculate the long-term plateau or steady state level in soil after repeated sludge applications. The PEC_{soil} at steady state is calculated according to the guideline outlined in the REACH programme (see Chapter 1 for details).

The risk assessment of brominated flame retardants for the soil environment is clearly limited by the scarce amount of available ecotoxicity data. Only data for PBDE and TBBPA are available. However, these are apparently also currently the most dominant BFRs in sewage sludge and are both relatively persistent in the soil environment. As a model substance for the group of PBDE, BDE_{209} is chosen, as numerous studies have shown that this congener commonly occupies >50% of the total amount of PBDE in sludge. The input parameters for the model two substances are listed in Table 2.4.

Table 2.4. Input parameters for calculation the PEC steady state for BDE_{209} (2,2',3,3',4,4',5,5',6,6'-Decabromodiphenyl ether) and TBBPA (Tetrabromobisphenol-A) according to the guideline outlined

in the REACH programme (see Chapter 1 for details). The numbers in italic are include for information and are not used in the PEC estimations.

Parameter	**BDE_{209}**	**TBBPA**
Molecular weight	959.2	543.92
Log Koc	6.80[1] *4.3-8.2*[2] *6.2*[3]	4.4[2] *4.7*[3]
Vapour pressure[4]	< 0.00013 Pa	<133 Pa
Water solubility[4]	0.02-0.03 mg/L[5]	0.7 mg/L
Half-live (DT50) in soil[6]	3650 days	110 days
Bg. concentration[7]	0.001 mg/kg	0.001 mg/kg
Load of sludge	3 t dm/ha/y	3 t dm/ha/y
Sludge concentration[8]	0.75 mg/kg	0.22 mg/kg

Based on the input parameters listed above in Table 2.4 and the formula described in Chapter 1, the following steady-state soil concentration can be predicted after multiple sludge applications:

PECss (BDE_{209}) = 0.011 mg/kg
PECss (TBBPA)= 0.001 mg/kg

These predicted concentrations are at the lower end of the observed concentrations reported for agricultural fields amended with very large amounts of sewage sludge for multiple years. Such scenarios are, however, no longer valid for a typical situation in Denmark, where sludge amendment of agricultural land is strongly regulated. An additional margin of safety may, however, be needed in order to encompass the possibility of higher soil concentrations in areas that are not in compliance with e.g. the Danish sludge regulations, or areas receiving sludge from WWTP treating waste water specifically from industries producing or making use of BFR.

2.11.2 No Observed Effect Level (NOEL)

Based on the relatively limited data reviewed above, the lowest concentrations where no effects on the tested species were observed are listed below:

BDE_{209}:	> 1000 mg/kg	(3 species; NOEC; Sverdrup et al. 2006)
TBBPA:	0.26 mg/kg	(Earthworms; NOEC; EU2007)

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[1] ATSDR 2004. Estimated value calculated using the EPIWIN v3.10 programme. This logKoc is used for PECss calculations

[2] Calculated value based on the correlation between log Kow and log Koc outlined in Sabljié et al (1995). The log Kow is taken from WHO (1994) or WWHO (1995)

[3] The log Koc values used in the EU Risk Assessment reports for PBDE (EU 2002) or TBBPA (EU 2007)

[4] BDE_{209}: WHO (1994) and TBBPA: WHO (1995)

[5] 0.025 mg/L is used in the PECss calculations

[6] See Section 4.1 for detailed information

[7] Arbitrary values based on information presented in Section 4.4.

[8] See Section 2.4 for detailed information

It should be mentioned that suitable ecotoxicity data for three trophic levels were available for both substances, i.e. soil microorganisms, plants and soil invertebrates.

2.11.3 Margin of safety and potential risk

Based on a comparison between the lowest test concentration, where no significant effects where observed, and the predicted concentrations in soils after multiple sewage sludge amendment, a margin of safety (MoS) can be estimated as the ratio between the NOEL and the PEC (NOEL/PEC).

MoS (BDE_{209}) = 1000/0.011 = **9091**
MoS (TBBPA) = 0.26/0.001 = **260**

Suitable and valid toxicity studies have been found for three trophic levels (microorganism, earthworms and plants). A margin of safety of 260-9091 is, hence, considered sufficient according to the outline of the REACH programme in the European Union, as an assessment factor of 10 is normally considered adequate when chronic sub-lethal studies for three trophic levels are available.

2.12 Summary and conclusions

The widespread global use of brominated flame retardants, their high log *K*ow values, and persistency has resulted in their widespread occurrence in the environment, including in sewage sludge from WWTPs across the world. The majority of information has been found for the group of polybrominated diphenyl ethers (PBDE), which has structural similarities with PCBs. Among the PBDE, the decabrominated congener BDE_{209} is shown to be more or less consistently dominant in sewage sludge. A few Danish studies have shown sludge concentrations approaching 500 µg/kg. The majority of international studies report sludge concentrations below 1000 µg/kg, although there are exceptions to this from countries outside Europe. PBDE have the potential of bioaccumulating in organisms, especially the higher brominated substances like BDE_{209}, which bear resemblances to some of the persistent PCB congeners. Whereas plants do not tend to up-concentrate PBDE, biota-to-soil accumulation factors exceeding one have been observed for earthworms. From the data available, the most critical route of biomagnification in the terrestrial environment seems to be the food webs starting with earthworms and ending with raptors, as mammals like foxes seems to be better at eliminating and/or metabolising BFRs.

Relatively little information is available regarding potential ecotoxicity of BFRs to soil dwelling species. The few studies available indicate a very low toxicity to soil dwelling organisms by the higher brominated BFRs like BDE_{209}. This is most likely due to their size and strong adsorption to the soil matrix. Effects by TBBPA, on the other hand, have been observed in the lower mg/kg range, but the concentrations of TBBPA in sludge are generally lower than for PBDE, and the compound is far less persistent in the soils than e.g. BDE_{209}. It is, therefore, considered very unlikely that the levels of TBBPA, BDE_{209} or other brominated flame retardants found in Danish sludge should pose a significant risk to the soil dwelling organisms and the soil quality in general if the current application guidelines are followed.

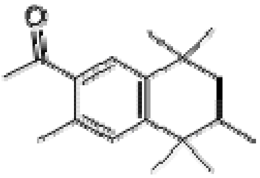
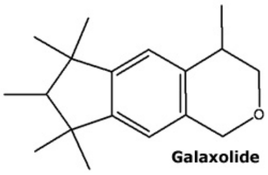
3 Musk substances

3.1 Introduction

The polycyclic musks and other musk substuances are used as fragrance ingredients in consumer products like cosmetics, detergents, and cleaning agents. They are important ingredients because of their typical musky scent and their fixative properties.

Polycyclic musks are, generally, not readily degradable and have a high affinity for lipids. It is logical, therefore, that these substances have been found throughout the environment, including fish. Furthermore, their wide usage, high log *K*ow values (see Table 3.1) and persistency make them likely to occur in sewage sludge from waste water treatment plants (WWTP) across the world (Balk and Ford, 1999).

Table 3.1. Physical-chemical properties and structure of AHTN and HHCB. (Reference: Balk and Ford 1999a)

Parameter	**Value**	**Structure**
Melting point		
AHTN	54.5°C	**AHTN**
HHCB	*n.a.*	
Vapor pressure		
AHTN	6.82×10^{-2}	
HHCB	7.27×10^{-2} (Pa, 20°C)	
Water solubility		**HHCB**
AHTN	1.25	
HHCB	1.75 (mg/l)	
Log K_{OW}		
AHTN	5.7	
HHCB	5.9	
Log K_{OC}		
AHTN	4.80	
HHCB	4.86	
K_D	n.a.	

3.2 Use and consumption

The polycyclic musks AHTN (7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene) and HHCB (1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta- g-2-benzopyran) are widely used fragrance ingredients in detergents and other household products. Together they represent about 95% of the total market volume for the class of fragrance ingredients known as the polycyclic musks. Thus, the majority of data available in the open literature concerns these two substances and, accordingly, they will receive primary focus in this review.

Musk ketone and musk xylene are used in fragrances for cosmetics (extrait perfumes, personal care products such as leave-on and wash-off cosmetics), detergents, fabric softeners, household cleaning products, air fresheners, etc. Musk xylene is mainly used for fabric washing and household cleaning products, whereas Musk ketone is used in many well-known fragrances and other cosmetic products.

Today, the polycyclic musks dominate the global musk fragrance market. From 1987 to 2000, the global use of the polycyclic musks has more than doubled, from 4300 metric tons to 10 000 metric tons. In the year 2000, the global use of nitro musks was 800 metric tons, which was less than one-third of their use in 1987 (Peck and Hornbuckle 2006). The use and consumption of the four dominating musk substances in Denmark, HHCB, musk xylene, AHTN and musk ketone were in 2004 reported to be 333, 134, 33, and 20 kg, respectively (Mogensen et al. 2004).

3.3 Musk levels in sewage sludge

As synthetic musks have a relatively high affinity for solids, these substances will, typically, move from water to solids in WWTPs. Thus, the removal of musks like HHCB and AHTN from wastewater occurs primarily via sludge separation. There is limited evidence that synthetic musk fragrances are actually degraded, neither by chemical nor biological processes, during wastewater treatment (Peck and Hornbuckle 2006).

3.3.1 Musk in sewage sludge in Denmark and Scandinavia

A screening project of synthetic musk compounds in the environment of the Nordic countries was carried out in the second half of 2002 (Mogensen et al. 2004). 27 samples of sludge from WWTPs were analysed for content of nine synthetic musk compounds, representing the major part of synthetic musk compounds used in cosmetics, washing, and cleaning agents. The results show high concentrations of especially polycyclic musk compounds, ranging from 250-26,500 µg/kg dry matter for HHCB and 70-3,600 µg/kg dry matter for AHTN. The data from Denmark are listed in Table 3.2.

Table 3.2. Concentration of AHTN and HHCB in sludge samples collected from five different WWTPs in Denmark. All data is in mg/kg dry matter (Mogensen et al. 2004).

WWTP / City	**AHTN**	**HHCB**
Bjergmarken /Roskilde	3.61	26.5
Stige / Odense	2,02	13.7
Skævinge	2.18	14.6
Hasselø	1.84	14.1
Avedøre / Copenhagen	1.13	11.4
Mean value	2.16	16.06

Within the Danish national monitoring programme, NOVANA, Bossi et al. (2009) reported the level of musks in sludge samples from five different WWTPs. Unfortunately, two of the five data sets were not useful due to analytical problems. The concentration of HHCB and AHTN in sludge from the three remaining WWTPs ranged from <LOD-1.2 mg/kg and 0.1-5.7 mg/kg, respectively. Thus, contrary to the data in Table 3, AHTN was the dominant musk

in these observations. The concentrations of the four other musks that were measured in the sludge samples were all below 0.02 mg/kg.

Within the screening programme of 2007, the Swedish Environmental Protection Agency initiated measurement of the musk substances in a wide set of matrixes including sewage sludge in Sweden (SWECO 2008). The HHCB and AHTN concentrations ranged from 1.43 – 29.4 and 0.88 – 2.6 mg/kg dw, respectively, in sludge samples analysed from 14 different WWTPs. These concentrations were in line with previous reported sludge concentration in Sweden (Mogensen et al. 2004).

3.3.2 Musk in sewage sludge across the world

Difrancersco et al. (2004) found background concentrations of fragrances in anaerobically digested sludge from two US municipal WWTPs. Analysis in July 2000 (N =7) showed significant concentrations of HHCB and AHTN in sludge from both WWTP. Analysis in 2002 (N=3) resulted in the detection of six and four additional fragrances, respectively. The maximum concentrations of selected fragrances in the sludge were:

AHTN	17.7 mg/kg
HHCB	86.0 mg/kg
Musk ketone	3.8 mg/kg
Musk xylene	1.3 mg/kg
OTNE[9]	30.7 mg/kg

Müller et al. (2006) reported the result of a German screening study, where samples of activated sewage sludge were taken both in summer and in winter at 21 WWTPs and analysed for polycyclic musks. The level of HHCB and AHTN accounted for about 95% of all the polycyclic musk identified in the samples. The concentrations of HHCB and AHTN in the activated sludge samples varied between 2.9 and 10.4 mg/kg dry mass (dm) and 1.1 to 4.2 mg/kg dm, respectively. Although different types of WWTPs were investigated, similar levels were found, showing the widespread input of musk compounds into domestic waste water treatment plants.

In a survey of musk concentrations in sludge from 39 municipal sewage treatment plants from The Netherlands and Germany, Rimkus (1999) reported a maximum concentration of HHCB and AHTN in sludge of 63 mg HHCB/kg dry matter and 34 mg AHTN/kg dry matter.

Yang and Metcalf (2006) reported the result of a survey of 11 synthetic musks in samples of effluent and sludge collected from the Peterborough WWTP, Ontario, Canada. The results showed that HHCB and AHTN were the dominant fragrances in sewage sludge, but other polycyclic musks and nitro musks were also present at lower concentrations. The annual average concentrations of HHCB and AHTN in sludge were reported in the range of 3.3-6.8 and 0.7-1.3 mg/kg d.m., respectively, depending on where the sludge samples were collected in the WWTP.

Balk and Ford (1999a) reviewed the results from surveys of sewage sludge concentrations of AHTN and HHCB from three different unpublished studies (Table 3.3).

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[9] 1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetramethylnaphthalen-2yl] ethan-1-one

Table 3.3. The concentrations of AHTN and HHCB (mg/kg dm.) in sludge from three different studies as reported in Balk and Ford (1999a)

Country	**Sludge type Samples (N)**	**AHTN Mean or Median* [range]**	**HHCB Mean or Median* [range]**
The Netherlands	Primary (11) Activated (12) Digested (13)	8.3 [3.3-14.0] 16.0 [2.3-34.0] 16.0* [0.9-22.0]	13.9 [5.4-27.0] 27.9 [4.4-63.0] 23.0* [9.0-31.0]
The Netherlands	Primary (8) Activated (7) Digested (2)	8.2* [3.7-11.7] 5.3* [0-13.5] 12.0 [11.0-13.0]	13.5* [6.0-17.0] 9.7* [0-21.0] 20.0 [19.0-21.0]
Germany	Primary (2) Activated (17)	8.3 [4.0-12.6] 2.1 [0.1-8.9]	8.9 [4.3-13.4] 1.4 [0.1-5.2]

Kinney et al. (2006) investigated nine different sewage sludge types produced by municipal WWTPs in seven different states of the USA. The analyses covered 87 different organic substances, including the fragrances AHTN and HHCB. They found concentration ranges of 0.28-1,340 (mean 11.6) and 0.05-553 mg/kg carbon (mean 3.9), respectively. Recalculated to sewage sludge concentrations, this corresponds to approximately maximum and median concentrations of 4,201 and 44.8 mg/kg for AHTN and 1,737 and 10,6 mg/kg for HHCB in sludge from the nine US WWTPs.

3.4 Fate and behaviour of musk in soil

3.4.1 Soil degradation

Litz et al. (2007) reported the behaviour of polycyclic musks in three soils and two plant species. They found a very strong adsorption of both substances to soil with K_{oc} values between 4,200 and 7,900 for HHCB and between 4,800 and 13,600 for AHTN. Due to this strong sorption, the dissipation of the musks occurred very slowly with elimination rates after 37 weeks of approx. 50% and 25% for HHCB and AHTN, respectively. On average, the dissipation rate of AHTN was almost 27% lower compared to HHCB. Extrapolating these results lead to a DT50 value for HHCB of 10–17 months and a DT90 of 7–120 years and for AHTN of 2 to 24 years and of 160–2,000 years, respectively. As stated by the authors, these values should, however, be viewed with caution, as the duration of the dissipation test (32 weeks), in fact, was too short to allow for such an extrapolation. Nevertheless, the data show that HHCB and AHTN can be regarded as very persistent pollutants.

Yang and Metcalfe (2006) observed the fate of HHCB and AHTN on an agricultural field amended with sewage sludge. The results showed that these compounds persisted in low concentrations, i.e. up to approximately 0.003 mg/kg in soils for the first two weeks post sludge application, but also that the concentrations declined thereafter. HHCB was, however, detectable in the field six months after application. But since the sludge was applied just before the winter months when soils are frozen in Canada, the degradation rates most likely reflect worst case situations.

Difrancesco et al. (2004) followed the fate of 22 fragrances in four different sludge-amended soil types. After 3 months, only seven fragrances were present in all spiked soils at concentrations significantly above the quantification limits. These were musk ketone, musk xylene, AHTN, HHCB, acetyl cedrene, OTNE, and DPMI (Cashmeran, 6,7-dihydro- 1,1,2,3,3-pentamethyl-4(5*H*)-indanone). At the end of the 12 month dissipation period, the only fragrances that remained were the nitro and polycyclic musks. The dissipation of AHTN and musk ketone was particularly slow with removal rates between approximately 15 and 50% in one year, depending on the soil type.

The fate of radio-labelled HHCB in soil was studied in microcosms according to protocols by the US Food and Drug Administration and reported by Balk et al. (1999a). The three test soils included a forest soil, an agricultural soil, and a sludge amended soil, all sampled in the US. The disappearance of HHCB and formation of metabolites was monitored over time. After one year, significant amounts of polar metabolites were found in all samples. Of the initial HHCB concentration, 7, 9, and 35 % remained in the forest soil, the sludge-amended soil and the agricultural soil, respectively. The total recovery of radiolabel from the solvent extraction was 104% for the forest soil, 73% for the sludge-amended soil and 52% for the agricultural soil. For the sludge amended soil, it was shown that an additional 20% of the radiolabelled material was recovered in an aqueous extract after an alkaline hydrolysis. The authors hypothesised that the majority of unrecovered HHCB could be covalently bound and immobilised by soil organic matter. For the different soil types, an average of 14% HHCB remained after one year, which according to the authors demonstrates a half-life value for the parent substance of about four months.

3.4.2 Leaching and vertical transport

Due to the strong adsorption properties onto sludge and soils, the mobility of polycyclic musks like HHCN and AHTN would be assumed to be very low. However, only limited information is available on the leaching potential of musks to support this hypothesis. Difrancesco et al. (2004) studied vertical movement of musks in an out-door microcosm study where leachate samples were collected for the first 3-5 months. Up to 12 musks were detected in leachate collected from the spiked soil/sludge samples, whereas no musks were found in leachate from any of the un-spiked sludge/soil mixtures. The total mass fraction leached was less than 1% for all the detected musks, except for DPMI. The mass fraction of DPMI leached ranged from 1.4% to 26.5% and, generally, increased with decreasing organic matter content of the soil.

Litz et al. (2007) studied the leaching behaviour of HHCB and AHNT in soil-column experiments under saturated conditions. Sewage sludge spiked with HHCB and AHTN was applied on top of the soil columns, but not mixed into the soil. In all but one of the soil types, the effluent concentrations were below the detection limit. The leaching experiments showed leaching rates of < 0.001% for HHCB and AHTN during the test period of 48 hours. The observed leaching was speculated to primarily be a result of preferential flow.

3.4.3 Soil concentrations

Very limited field-related data on soil concentrations of musk was identified in the open literature. Yang and Metcalfe (2006) studied the fate of HHCB, AHTN, and the musk ketone and xylene on an agricultural field amended with sewage sludge and showed that these compounds persisted in low concentrations, i.e. up to approximately 0.003 mg/kg, in soils for the first two weeks post sludge application, but also that the concentrations declined thereafter, although HHCB was detectable at low quantities in the field six months after application. But since the sludge was applied just before the winter months, when soils are frozen in Canada, the degradation rates most likely reflect worst case situations.

3.4.4 Summary on the fate and behaviour of musks in soils

Polycyclic musks adsorb strongly to sludge material and soils, which may lead to very high persistence with dissipation half-lives measured in the range of years for some of the substances. These properties result in low leaching potentials, while they on the other hand may lead to potential accumulation in the soil environment. However, very little field-related information is available to assess the long term soil concentration of polycyclic musks in sludge amended soils.

3.5 Bioaccumulation of musks in soil biota

Litz et al. (2007) reported the uptake of musks into lettuce and carrots in uptake experiments. The plants were grown in a soil/sludge mixture containing 30 mg/kg of HHCB or AHTN. The biota-to-soil accumulation factor (BSAF) in three different soil types ranged for HHCB from 0.003 and 0.03 in lettuce and carrot leaves, whereas for carrot roots it was 0.095 in a humic soil and 0.48 in a loamy soil. The BSAF for AHTN were similar, as they ranged from 0.007-0.026 for salad and carrot leaves to a maximum of 0.37 in carrot roots. The higher uptake in carrot roots was speculated to be due to partitioning into the essential oil cells of the roots.

Chen et al. (2010b) showed that the concentration of AHTN in wheat seedlings increased with increasing concentrations of AHTN in the soil. The concentration was highest in the roots followed by stems and leaves. The BSAFs were below one for stems and leaves at all exposure concentrations, whereas it reached approximately 3.5 in the roots at the highest exposure concentration (20 mg/kg) (estimated from graph). The slopes of the linear regressions for uptake were reported as 3.12, 0.755 and 0.173 for roots, stems, and leaves, respectively.

3.6 Ecotoxicity of musks to soil dwelling organisms

Very limited information regarding the terrestrial ecotoxicity of fragrances exists. No ecotoxicity studies focusing on microorganisms have been identified, whereas few studies with soil invertebrates and plants are available.

3.6.1 Soil invertebrates

In 1997, Tas et al. (1997) conducted an environmental risk assessment of musk ketone and musk xylene. They cited three unpublished studies from the musk industry with musk ketone and musk xylene for effects on earthworms and springtails. In the test with musk ketone, no mortality of adult earthworms was observed after four weeks at any of the test concentrations. The NOEC for growth was established at 100 mg/kg. Growth inhibition was 88% when exposed to 316 mg/kg (LOEC). The inhibition of reproduction after eight weeks was 15% at 100 mg/kg (LOEC), whereas no significant effects were observed at 32 mg/kg (NOEC). The mortality of musk ketone to springtails varied between 4 and 20 % when exposed up to 1000 mg/kg, but a dose-response relation could not be established. Reproduction was inhibited by 65% at 316 mg/kg (LOEC) and by 87% at 1000 mg/kg. The NOEC value of the reproduction was 100 mg/kg. The toxicity of musk xylene to earthworms was studied in a 14 day test. No effects were observed on survival, general health or behaviour of the worms at any of the test concentrations up to 50 mg/kg.

Balk and Ford (1999b) reported the results from a wide set of (unpublished) ecotoxicological studies with the polycyclic musks AHTN and HHCB in order to conduct an ecological risk assessment according to the approach developed under the European Union and described in the Technical Guidance Document for risk assessment of new and existing chemicals. For the soil compartment, an 8-week study with earthworms (*Eisenia fetida*) resulted in a NOEC of 105 mg/kg for AHTN. Reproduction was significantly (39%) inhibited (LOEC) at 250 mg/kg. When exposed 14 days to 1000 mg/kg, all earthworms died. For HHCB, a NOEC of 45 mg/kg was established. Reproduction was significantly (57%) inhibited at 105 mg/kg (LOEC). When exposed 14 days to 1000 mg/kg, all earthworms died. A 4-week study with springtails (*Folsomia candida*) resulted in a NOEC of 45 mg/kg for both substances. At 105 mg/kg (LOEC), the reproduction of springtails was reduced by 51 and 84% by AHTN and HHCB, respectively.

Liu et al. (2011) studied sub-lethal effects after exposing the potworm *Eisenia fetida* to soil contaminated with HHCB. No mortality rate was observed throughout the experiment period, whereas a significant increase in for example lipid peroxidation level was observed at the two highest test concentrations of 50 and 100 mg/kg, but not at 10 mg/kg.

Mori et al. (2006) tested the effects of various musks on the soil dwelling nematode *Caenorhabditis elegans* in aqueous solutions. They found limited effects on survival of the nematodes, but significant effects on the development of the nematodes were reported at 12.8 and 9.8 mg/L for AHTN and HHCB, respectively.

3.6.2 Plants

Chen et al. (2010a) studied the ecotoxicological effects of the polycyclic musks AHTN and HHCB on seed germination and seedling growth of wheat (*Triticum aestivum*). Using a natural agricultural soil, they exposed the plants in the laboratory to concentration series of musk and musk-cadmium mixtures. The change in biomass of the plants was not monitored. They found NOEC/LOEC values for seed germination of 77/194 and 100/500 mg/kg dw, respectively. A 50% reduction in the germination success of the seeds was estimated at 847 mg/kg for HHCB and 763 mg/kg for AHTN. Changes in root elongation and shoot elongation were evaluated as measures of growth impairment. Shoot elongation proved to be the more sensitive of the two parameters, with EC10/EC50 values of 25/929 mg/kg for HHCB and 9.9/945 mg/kg for AHTN. Finally, the study showed that the toxicity of the musk in combination with cadmium was higher than for the individual substances alone, indicating a synergistic effect of the two substances.

Chen et al. (2010b) also tested the single and joint molecular effects of AHTN and cadmium (Cd) on early developmental stages of wheat. The presence of Cd inhibited the uptake of AHTN in wheat seedlings, while low concentrations of AHTN could induce the uptake of Cd. AHTN had, in the absence of Cd, a significantly negative impact on the chlorophyll content in wheat leaves at the lowest test concentration of 1 mg/kg. Furthermore, it was shown that AHTN decreased the content of various biomarkers for oxidative stress (malondialhyde, superoxide dismutase and peroxidise) in the plants when exposed at 1 or 10 mg/kg. It is uncertain to what extent effects on such biomarkers can be linked to population effects. They are, therefore, not used in the risk evaluation.

Fan et al. (2008) investigated the toxic effect of musk ketone through the determination of wheat (*Triticum aestivum*) seed germination and seedling growth. The results showed that 10 mg/ kg of musk ketone could significantly inhibit the seed germination rate. As only the abstract and not the primary source of this study has been available in English, it is not possible to report the NOEC of the study or to evaluate the general quality of data.

Biochemical responses of wheat (*Triticum aestivum L.*) seedlings stressed by HHCB in aquatic solutions were experimentally investigated by An et al. (2009). The results showed that wheat shoot, but not root, elongation was significantly (33%) inhibited at 50 mg/L. The root elongation was significantly (4.3%) inhibited at 100 mg/L. The median effect concentration (EC50) of HHCB on shoot and root elongation was 143 and 422 mg/ L, respectively. Moreover, the statistical analysis showed that there was no significant difference in the germination frequency of wheat seeds exposed to HHCB up to 250 mg/L. Toxicity data deriving from aquatic studies are not directly useful for establishing NOEL for soils, although they may be transformed to soil concentrations by transfer functions based on equilibrium partitioning. Compared with toxicity data for algae, daphnia, and fish, the data above do, however, indicate that terrestrial plants are not particularly sensitive to HHCB. Balk and Ford (1999b), for example, reported EC50 values up to two orders of magnitude lower for algae, daphnia and fish, i.e. 0.723, 0.293 and 0.452 mg/L, respectively.

3.6.3 Summary and conclusion on the ecotoxicity of musks

Molecular effects in plants exposed to polycyclic musks were observed at 1 mg/kg. However, since molecular biomarkers are not normally used in risk assessment procedures, these data are omitted in the final risk evaluation. The lowest sub-lethal growth related NOEC/EC10 values for plants were observed at 25 mg/kg for HHCB and 9.9 mg/kg for AHTN. The lowest NOEC for soil dwelling fauna for AHTN and HHCB was 45 mg/kg, as reported for earthworms and springtails in Balk and Ford (1999b).

3.7 Provisional risk evaluation of HHCB and AHTN in sludge

Based on the data presented in the Sections above, a provisional risk evaluation in the soil environment can be conducted.

The risk is assessed by comparing the predicted environmental exposure (predicted environmental concentration – PEC) to the predicted level in soil where no effects are observed or anticipated (No Observed Effect Level – NOEL). The ratio between PEC and NOEL indicate a so-called margin of safety (MoS), which essentially is the reverse of the more common “risk quotient” utilised in many risk assessments. As all exposure scenarios cannot be foreseen and all soil dwelling species cannot be tested, a certain margin of safety is needed in order to conclude that significant effects of PFCs in sewage sludge would be unlikely. Based on the amount of available data, the MoS should fall within a range of at least 10 to 1000 in order to be in line with the use of assessment factors in the REACH programme in the European Union and described in the Technical Guidance Document for risk assessment of new and existing chemicals.

3.7.1 Predicted soil concentration (PEC)

As polycyclic musks like HHCB and AHTN are persistent compounds in the environment with half-lives exceeding one year, it is necessary to calculate the long-term plateau or steady state level in soil after repeated sludge applications. The PEC_{soil} at steady state is calculated according to the guideline outlined in the REACH programme (see Chapter 1 for details). The input parameters for the two substances are listed in Table 3.4.

Table 3.4. Input parameters for calculation the PEC steady state for HHCB and AHTN according to the guideline outlined in the REACH programme (see Chapter 1 for details).

Parameter	**HHCB**	**AHTN**
Molecular weight	258.4	258.4
Log Koc	4.8	4.86
Vapour pressure	0.0727 Pa	0,0682 Pa
Water solubility	1.75 mg/L	1.25 mg/L
Half-live (DT50)[10]	12 months	18 months

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[10] These are qualified conservative estimates based on the information in Litz et al. (2007) and Difranco et al. (2004)

Background concentration[11]	0.001 mg/kg	0.001 mg/kg
Load of sludge:	3 t dm/ha/y	3 t dm/ha/y
Sludge concentration[12]	26.5 mg/kg	3.6 mg/kg

The calculations results in a predicted soil concentration at steady state (PECss) of:

PECss (AHTN) = 0.009 mg/kg
PECss (HHCB) = 0.047 mg/kg

3.7.2 No Observed Effect Level (NOEL)

Based on the relatively limited data reviewed above, the lowest concentrations where no effects on the tested species were observed are listed below:

NOEL (AHTN) = 9.9 mg/kg(Wheat; EC10; Chen et al. (2010a)
NOEL (HHCB): = 25 mg/kg (Wheat; EC10; Chen et al. (2010a)

It should be mentioned that only suitable ecotoxicity data for soil invertebrates and plants were available. Suitable ecotoxicity test with microorganisms were not available.

3.7.3 Margin of safety and potential risk

Based on a comparison between the lowest test concentration, where no significant effects where observed, and the predicted concentrations in soils after sewage sludge amendment, a margin of safety (MoS) can be estimated as the ratio between the NOEL and the PEC (NOEL/PEC).

MoS (AHTN) = 25/0.009 = 2778
MoS (HHCB) = 9.9/0.047 = 211

Suitable and valid toxicity studies have been found for two trophic levels (invertebrates and plants) for both AHTN and HHCB. A margin of safety ranging between 211 and 2778 is therefore considered sufficient according to the outline of the REACH programme in the European Union (see Chapter 1), where an assessment factor of 50 is normally considered sufficient when two long-term toxicity tests from two trophic levels are identified. It should, however, be stressed that it is unclear to which extent the exposure in the plant studies by Chen et al. (2010ab) can be considered as long-term. More information regarding the toxicity of musks to plant species and microorganisms would be required in order to be able to strengthen conclusions on the potential long-term risk to the soil environment induced by the levels of HHCB and AHTN found in sewage sludge.

3.8 Summary and conclusions

The widespread global use of polycyclic musk, their high log *K*ow values and persistence has resulted in widespread occurrence in sewage sludge from WWTPs across the world and in the environment. The majority of information shows that the two dominating musks in sewage sludge are HHCB and AHTN. A few studies have shown sludge concentrations approaching 100 mg/kg, although the majority of studies report markedly lower concentrations. In Denmark, the highest reported concentration of HHCB and AHTN is 26.5 and 3.6 mg/kg, respectively. HHCB and AHTN are both persistent in soils with half-lives that may exceed one year.

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[11] Arbitrary value for a soil not previously receiving sewage sludge

[12] The highest reported sludge concentration in Danish sludge according to Mogensen et al. (2004)

Based on the limited available information, the two substances do not tend to bioconcentrate in large quantities in plants and crop species.

The toxic effects of HHCB and AHTN are relatively well documented on soil invertebrates and plants, whereas no information is available on their toxicity to soil microorganisms. The musk ketone and musk xylene are not considered highly toxic to soil dwelling species, with the lowest observed effect at approximately 100 mg/kg. No information regarding the toxicity of musk ketone and xylene to plants and microorganisms is, however, available.

A provisional assessment of the risk of HHCB and AHTN shows that long term risk to the soil environment as a result of normal sludge application in Denmark is unlikely. The information for other musks and fragrances is less than for HHCB and AHTN, but as the toxicity of other musks, e.g. musk ketone and musk xylene, seems to be comparable to the toxicity of HHCB and AHTN and the concentration in sludge are markedly lower, it is also unlikely that the levels of these musks in Danish sludge would pose an environmental problem.

4 Pharmaceuticals

4.1 Introduction

Some pharmaceuticals are easily broken down and processed by the human body, whereas others may be excreted as parent compounds or as metabolites and thereby enter domestic waste water systems. Excretion of biologically unused and unprocessed drugs depends on the individual drug composition and the ability of persons to break down drugs. This ability depends on age, sex, health, and individual idiosyncrasies. In general terms, most pharmaceuticals will dissolve easily and do not evaporate at normal temperatures or pressure and, hence, they make their way into terrestrial and aquatic environments via waste water discharges, sewage sludge and/or irrigation with reclaimed water.

As a vast amount of pharmaceuticals are produced and used regularly in Denmark and globally, it would be impossible to assess the potential risk to the soil environment for all of these. In this report, the choice of substances selected for evaluation of their potential risk is based on a number of criteria, including their occurrence in sewage sludge, their potential to persist in the soil environment, and the availability of ecotoxicological effect data.

4.1.1 Use and consumption

Pharmaceuticals often refer to a chemical prepared or dispensed in pharmacies used to prevent or ease the symptoms of disease or physiological dysfunction. In principle, the extent to which pharmaceuticals may be found in sewage sludge, therefore, depends only on the prescription of drugs. The number of drugs catalogued from e.g. Germany and the EU in 2005 included roughly 9,000 preparations in over 11,000 different dosage forms and 35,000 products (Daughton 2007). It is, therefore, obvious that this report cannot relate to all of these.

The most used pharmaceuticals in Denmark in 2005 are listed in Table 4.1 (Pedersen et al. 2007). From this, it is clear that especially the painkillers paracetamol, acetylsalicylic acid, and ibuprofen are used in large quantities.

Table 4.1. The consumption of the most used pharmaceuticals in Denmark in 2005. Table taken from Pedersen et al. (2007).

	Pharmaceutical (kg)		
Active	**Total**	**Primary Sector**	**Hospitals**
Acetylsalicylsyre	366.186	362.316	3.870
Paracetamol	339.870	329.148	10.722
Ibuprofen	46.844	45.738	1.108
Metformin	31.018	30.812	206
Phenoxymethylpenicillin	21.600	20.754	846
Etodolac	13.067	12.971	96
Cimetidin	5.177	5.168	9
Metoprolol	5.021	4.965	57
Valproinsyre	4.662	4.479	183

Table 4.1 (Cont.)

	Pharmaceutical (kg)		
Active	**Total**	**Primary Sector**	**Hospitals**
Tramadol	4.460	4.313	147
Gabapentin	4.273	4.099	175
Furosemid	4.050	3.890	160
Oxcarbamazepin	3.552	3.484	69
Dipyridamol	3.293	3.223	70
Allopurinol	2.571	2.476	95
Amoxicillin	2.496	2.372	124
Simvastatin	2.145	2.122	23
Verapamil	2.080	2.053	26
Erythromycin	1.819	1.782	37
Naproxen	1.666	1.599	68
Losartan	1.469	1.461	10
Ranitidin	1.453	1.447	6
Theofyllin	1.446	1.426	19
Irbesartan	1.372	1.366	6
Lamotrigin	1.368	1.338	30
Diclofenac	1.357	1.297	65
Kodein	1.306	1.256	50
Venlafaxin	1.264	1.233	31
Carbamazepin	1.193	1.171	22
Diltiazem	1.146	1.135	12
Enalapril	1.090	1.080	10
Disulfiram	1.011	899	112
Atenolol	936	932	4
Citalopram	916	899	17
Noretisterone	37	37	0
Østradiol	31	31	0
Østriol	7	7	0
Etinyløstradiol	0,041	0,041	0,000

Data on Swedish consumption from Carlson et al. (2006) shows a relatively high consumption of beta-blockers (atenelol and metoprolol) and the anti-inflammatory drug Diclofenac. In Norway a total of 1414 active substances were used in 2500 different medicinal products in 2006 (Eriksen et al. 2009).

The amount of pharmaceuticals that reach the WWTP depends not only on the total consumption, but also on the proportion of the parent compound that is excreted by users. Jjemba (2006) divided a wide set of pharmaceuticals according to the relative proportion excreted in clinical settings. He found that for substances like acetylsalicylic acid, ibuprofen, paracetamol, fluoxentine, and carbamazepine, less than 5% are excreted as parent compound. Dichlofenac has a somewhat higher excretion percentage, whereas more than 70% of ciprofloxacin and tetracycline are excreted as parent compound. Jjemba (2006) did not find any correlation between the log K_{ow} or the pKa and (1) the bioavailability of the pharmaceuticals in the target organisms, (2) the proportion excreted, or (3) their concentration in the environment.

4.2 Levels of pharmaceuticals in sludge

4.2.1 Sorption and persistence in sludge

The proportion of pharmaceuticals that are transferred into the solid phase, i.e. the sewage sludge within the WWTP, to a large extent depends on the respective substance properties. For example, sorption experiments with sewage sludge found negligible sorption coefficients for carbamazepine, diazepam, ethinyloestradiol, the cytostatics, cyclophosphamide and ifosphamide, phenazone, ibuprofen, and clofibric acid. Only diclofenac exhibited a relevant degree of sorption (Ternes et al. 2004).

Chenxi et al. (2008) determined the persistence of pharmaceuticals in sludge samples in three different treatment scenarios. Treatment one simulated a dark and anaerobic condition, treatment two simulated dark and aerobic conditions, whereas treatment three simulated light and aerobic conditions. No elimination of carbamazepine and ciprofloxacin was observed throughout the 77 days of the experiment. The concentration of the antibiotics tetracycline and doxycycline decreased slowly (DT50 generally higher than 40 days), while clindamycin, clarithromycin, and erythromycin displayed a relatively fast elimination rate (DT50 generally lower than 10 days) with the slowest degradation observed under anaerobic conditions.

4.2.2 Pharmaceutical levels in Danish and Scandinavian sludge

A recent Danish screening programme of pharmaceuticals in WWTP (sludge, effluent, and adjacent fresh waters) analysed for the presence of a wide set of active substances (Mogensen et al. 2007). The set of pharmaceuticals included human as well as veterinary pharmaceuticals. Regarding sludge, samples were collected from eight different WWTPs covering in total more than 1.7 million person equivalents. Besides 11 antibiotics, the monitoring programme for sludge included the following substances: Acetylsalicylic acid, Amlodipine, Bendroflumethiazide, Cimetidine, Clofibrinacid, Enalapril, Furosemide, Ibuprofene, Omeprazole, Paracetamol, and Salicylic acid. No selection criteria were presented in the report. The findings are presented in Table 4.2 which shows that the concentrations of 15 of the 25 pharmaceuticals were below the limit of quantification. Among the pharmaceuticals detected in the Danish sludge samples, paracetamol, salicylic acid, and cimetidine were detected at the highest concentrations, i.e. in the mg/ kg dry weight range.

Table 4.2. The minimum-maximum range of pharmaceuticals in sewage sludge samples from eight Danish WWTPs. Data taken from Mogensen et al. (2007).

Substance	**Influx (µg/l)**	**Number of finds/samples**	**Outflow (µg/l)**	**Number of finds/samples**	**Sludge (µg/kgdw)**	**Number of finds/samples**
Aspirin	0.5-2	5/10	-	0/11	-	0/10
Amlodipine	-	0/10	-	0/11	43-310	8/10
Bendroflumethiazide	0.1-0.1	3/10	0.05-0.070	3/11	-	10/10
Cimetidine	1.8-46	10/10	0.59-22	10/10	110-1,200	10/10
Enalapril	0.2-0.7	4/10	0.06-0.23	2/11	-	0/10
Erythromycin	-	0/10	-	0/11	15-69	6/20
Furosemide	2.1-11	10/10	0.2-4.6	11/11	32-180	10/10
2-hydroxy-ibuprofen	4.3-24	10/10	0.3-20	7/11	-	0/10
Ibuprofen	4.4-26	10/10	0.1-6.5	6/11	-	0/10

Table 4.2 (Cont.)

Substance	**Influx (µg/l)**	**Number of finds/samples**	**Outflow (µg/l)**	**Number of finds/samples**	**Sludge (µg/kgdw)**	**Number of finds/samples**
Paracetamol	140-	10/10	0.5-280	7/11	690-2,000	2/10

	1200					
Salicylic acid	12-170	10/10	0.05-18	9/11	59-2800	7/10
Sulfadiazine	0.29	1/10	0.03-0.16	3/11	-	0/10
Sulfamethizole	0.3-6.4	10/10	0.09-2.4	11/11	31-110	10/10
Sulfamethoxazole	0.1-0.3	4/10	0.03-0.089	7/11	-	0/10
Tetracycline	0.2-0.3	4/10	-	0/11	n.a.	0/0
Trimethoprim	0.2-4.4	4/10	-	0/11	n.a.	0/0
Triclosan	0.2-1.4	7/10	0.1-0.2	2/11	690-11,000	10/10
Methyl-triclosan	-	0/10	-	0/11	330	1/10

As a follow up to the investigation above, a limited set of sludge samples were analysed for a smaller set of 20 pharmaceuticals and personal care products before and after composting (Andersen, unpublished). The observations covered only three samples of sludge from one WWTP. The concentrations of the pharmaceuticals before and after composting are presented below in Table 4.3.

Table 4.3. The concentration of pharmaceuticals in three sludge samples from a Danish WWTP before and after 12 months of composting (all data in µg/kg dry weight)

	Sample 1		**Sample 2**		**Sample 3**	
	Sludge	**Compost**	**Sludge**	**Compost**	**Sludge**	**Compost**
Ibuprofen	5.8	<1	12	1.4	13	2.1
Naproxen	3.9	<1	5.4	<2	6.6	<3
Ketaprofen	5.9	<2	<2	<2	<2	<4
Diclofenac	7.1	<1	11	<1	14	<1
Tetracycline	547	<15	362	<9.3	414	<11
Docycycline	<63	<5	<39	<9.2	<42	<11
Oxycycline	<57	<15	<39	<9.6	<38	<11
Demeocycline	<48	<12	<31	<9.0	<41	<8.6
Chlortetracycline	<58	<15	<37	<10	<40	8.6

Twelve antibiotic substances for human use were subjected to a screening study at five Swedish sewage treatment plants during two subsequent years (Lindberg et al. 2005). The detection frequencies of antibiotics were: Norfloxacin (10/10), ciprofloxacin (10/10), ofloxacin (8/10), doxycycline (3/10), trimethoprim (0/10), and sulfamethoxazole (0/10). The concentration ranges (µg/kg dry weight) were as follows: Norfloxacin (100-4,200), ciprofloxacin (500-4,800), ofloxacin (100-2,000) and doxycycline (1,300-1,500).

Three antibiotics belonging to the group of fluorquinolones are included in the Swedish monitoring programme of hazardous substances in sewage sludge (Haglund and Olufsson 2010). The maximum concentrations in 2009 of norfloxacin, ofloxacin and ciprofloxacin in sludge samples from eight WWTPs were reported to be 490, 390 and 10,400 µg/kg dry weight, respectively. These were comparable to the concentrations reported in 2008.

In dried sludge from a sewage treatment plant in Sweden, Sagrista et al. (2010) measured the average concentrations of ketoprofen, naproxen, diclofenac and ibuprofen to be 0.029, 0.138, 0.039 and 0.122 mg/kg, respectively.

In Norway, only a limited set of monitoring data for pharmaceuticals in sewage sludge is available. Thomas (2007) reported the occurrence of twenty pharmaceutical compounds in effluents from two major Oslo hospitals along with influent, sludge, and final effluent from the city's wastewater treatment plants. Sludge samples contained a different profile of substances compared to effluents reflecting their physico-chemical properties. Hydrophobic antibiotics such as oxytetracycline, tetracycline, and ciprofloxacin were detected in all of the collected sludge samples with maximum concentration reported as 2,057, 7,733 and 97,470 µg/kg wet weight, respectively. The antibiotic sulfamethoxazole (171 ug/kg), the pain killer ibuprofen (33 ug/kg), the beta-blocker metoprolol (21 ug/kg), and the anti-inflamatory and antirheumatic diclofenac (20 ug/kg) were the only other pharmaceuticals reported to have verified concentrations exceeding 10 µg/kg wet weight.

4.2.3 Pharmaceuticals in sewage sludge across the world

A survey of sewage sludge from a wide set of US WWTPs found that only two of the 72 monitored pharmaceuticals, i.e. ciprofloxacin and diphenhydramine, were detected in all the 84 samples (US EPA 2009). The collected sewage sludge samples came from 74 randomly selected municipal WWTPs in 35 states. Samples were collected in 2006 and 2007 and showed that 8 of the 72 pharmaceuticals (11%) were found in at least 95% of the sludge samples analysed. However, 15 pharmaceuticals were not found in any samples, and 29 were present in fewer than three samples. The findings are summarised in Table 4.4 below. The data shows that not only antibiotics and the biocides triclosan and triclocarban were found in the mg/kg range, but also fluoxetine and carbamazepine were found at relatively high levels, although they had mean/median concentrations below 1 mg/kg, i.e. 0.329/0.147 and 0.298/0.055 mg/kg, respectively.

Table 4.4. The findings of pharmaceuticals in sewage sludge from a wide set of US WWTPs. Source: USA EPA (2009)

Analyte	**Observed Values**		**Estimates**							
	Minimum	**Maximum**	**99th**	**98th**	**95th**	**90th**	**50th**	**Mean**	**Standard Deviation**	**Percent POTWs with Detected Conc**
Pharmaceuticals (µg/kg)										
Ciprofloxacin	75	40,800	79,636	57,975	36,095	23,703	5,367	10,501	17,658	100
Diphenhydramine	37	5,730	5,255	4,021	2,696	1,891	541	871	1,101	100
Doxycycline	34	5,090	7,021	5,046	3,082	1,989	424	877	1,588	92.8
Erythromycin-Total	2	180	264	194	123	82	19	36	58	92.9
Fluoxetine	10	3,130	1,555	1,178	778	539	147	245	329	96.1
Miconazole	7	9,210	16,931	10,083	4,652	2,341	207	1,239	7,311	95.8
Ofloxacin	25	58,100	85,562	57,929	32,363	19,304	3,113	8,573	21,998	98.5
Tetracycline (TC)	38	5,270	10,042	7,250	4,458	2,895	630	1,278	2,255	97.5
Triclocarban	187	441,000	276,708	205,043	131,079	88,120	21,677	39,433	59,924	100
Triclosan	334	133,000	197,288	124,176	62,217	33,693	3,862	16,097	65,135	92.4
4-Epitetracycline (ETC)	41	4,380	8,026	5,937	3,787	2,540	620	1,135	1,741	96.0
Azithromycin	8	5,205	8,717	5,811	3,172	1,853	278	831	2,342	96.0
Carbamazepine	9	6,030	1,234	856	497	306	55	135	298	89.9

Cimetidine	4	8,330	19,128	10,975	4,789	2,294	171	1,332	10,314	

The mean concentration of 72 pharmaceuticals and personal care products (PPCP) were determined in 110 sludge samples collected by the U.S. Environmental Protection Agency (EPA) in its 2001 National Sewage Sludge Survey (McClellan and Halden 2010). Triclocarban and triclosan were the most abundant PPCPs, with mean concentrations of 36 ±8 and 12.6 ±3.8 mg kg^{-1}, respectively, accounting for 65% of the total PPCP mass found. The only pharmaceuticals with mean sludge concentrations in the mg/kg range were ciprofloxacin (6.9 mg/kg), ofloxacin (5.5 mg/kg), 4-epitetracycline, a degradation product of tetracycline (2.4 mg/kg), tetracycline (1.9 mg/kg), minocycline (1.9 mg/kg), and diphenhydramine (1.2 mg/kg). For other selected pharmaceuticals the concentration in US sludge was: cimetidine (0.5 mg/kg), ibuprofen (0.25 mg/kg), and carbamazepine (0.16 mg/kg).

Wu et al. (2010a) reported the levels of 14 PPCPs in sludge samples from two US based WWTPs. The anti-histamine diphenhydramine (173 mg/kg) and the antidepressant fluoxetine (1.5 mg/kg) were the only pharmaceuticals detected in the mg/kg range. Next to these, carbamazepine and norfluoxetine were found at levels of 0.1 and 0.43 mg/kg, respectively. The maximum level of diclofenac was 0.035 mg/kg.

Kinney et al. (2006) investigated nine different sewage sludge samples produced by municipal WWTPs in seven different states in the USA. The analyses covered 87 different organic substances, including the pharmaceuticals carbamazepine and fluoxetine. They found concentration ranges of 0.051-1.2 (mean 0.068) and 0.13-4.7 (mean 0.37) mg per kg of organic carbon, respectively. Recalculated to sewage sludge concentrations, this corresponds to approximately maximum and median concentrations of 3.8 and 0.4 mg/kg dry weight for carbamazepine and 10.5 and 2.1 mg/kg for fluoxetine in sludge from the nine US WWTPs.

Khan and Ongerth (2002) analysed sludge samples from a WWTP in Sydney and found very low concentrations (< 0.01 µg/kg) of paracetamol, naproxen, salicylic acid, ibuprofen, and carbamazepine in digested sludge, whereas the concentrations in the primary sludge were significantly higher (1.1 – 13.7mg/kg).

Miao et al. (2005) determined the distribution of carbamazepine (CBZ) and its major metabolites in both aqueous and solid phases through different treatment processes of a WWTP in Peterborough, Canada. A mass balance calculation showed that the majority of CBZ and its metabolites existed in the aqueous phase (i.e. wastewater), rather than in the sewage sludge. In the sludge samples, only CBZ and three of the metabolites, CBZ-2OH, CBZ-3OH, and CBZDiOH were detected, with CBZ as the predominant analyte with a measured concentration of 0.258 mg/kg dry weight.

Nieto et al. (2010) evaluated the presence of 20 pharmaceuticals such as anti-inflammatories, lipid regulators, and antibiotics in sewage sludge from two sewage treatment plants in the Tarragona area of Spain. Only tylosin (1.516-1.958) and roxithromycin (1.074-1.453) were detected in the mg/kg range, but also the following substances were found with maximum concentrations above 0.1 mg/kg: paracetamol (acetaminophen) (0.419); ibuprofen (0.114), and sulfamethoxazole (0.112). Dichlofenac was detected at maximum concentration of 0.087 mg/kg. Tylosin is an antibiotic only prescribed to husbandry and companion animals. It must be expected that the primary source in WWTPs is from treatment of companion animals like cats and dogs.

Martin et al. (2010) analysed for a wide set of pharmaceutical compounds in sludge samples from Seville, including the nonsteroidal anti-inflammatory drugs acetaminophen, diclofenac, ibuprofen, ketoprofen, naproxen, and salicylic acid; the antibiotics sulfamethoxazole and trimethoprim; the anti-epileptic drug carbamazepine; the beta-blocker propranolol; and the lipid regulator clofibric acid (a metabolite of clofibrate and gemfibrozil). By far, the highest concentrations were observed for ibuprofen, i.e. 5.1 mg/kg. Other pharmaceuticals detected above the limit of quantification in secondary or digested sludge were naproxen (0.029), salicylic acid (0.055), and carbamazepine (0.128).

4.2.4 Summary of sewage sludge concentrations

Compared to many other anthropogenic substances, most pharmaceuticals are relatively water soluble and, hence, will primarily be associated with waste water rather than sewage sludge in WWTPs. Nevertheless, high concentrations of pharmaceuticals in sludge may be observed due to their high usage and adsorption properties, which often are not (solely) linked to their log K_{oc} value, as a number of mechanisms such as cat-ion exchange, cat-ion bridging at clay surfaces, surface complexation, and hydrogen bonding also appear to be involved (Tolls 2001). It is difficult to conclude which pharmaceuticals are the most dominant in sewage sludge across the world, as this largely depends on which substances were included in the studies in the first place. However, the following substances have all been reported to have sludge concentrations exceeding 1.0 mg/kg (See Table A1 in Appendix A): cimetidine, ciprofloxacin, diphenhydramin, doxycycline, fluoxetine, ibuprofen, minocycline, ofloxacin, paracetamol, roxithromycine, salicyclic acid, and tetracycline.

4.3 Fate and behaviour of pharmaceuticals in soil

4.3.1 Sorption in soil

Thiele-Bruhn (2003) reviewed the sorption of antibiotics to soils. The Kd values ranged from less than one, e.g. sulfachloropyridazine, to more than 750,000 for the fluorquinolones, e.g. enrofloxacin. Other antibacterial groups with reported Kd values above 1000 include tetracyclines, macrolides (tylosin), and lipoglycosides (efrotomycin). Beausse (2004) also reviewed the sorption of pharmaceuticals to soil with the same conclusion, i.e. enrofloxacin and tetracyclines had the highest Kd values.

Xu et al. (2009) investigated the adsorption and degradation of a number of pharmaceuticals in agricultural soils. They found the adsorption to be in the following order clofibric acid > naproxen > diclofenac > ibuprofen.

Kwon and Ambrust (2008) investigated the sorption properties of selective serotonin re-uptake inhibitors (SSRI). This class of drugs is prescribed for the treatment of clinical depression in humans and they are some of the most heavily prescribed drugs in the western world. For the substances citalopram, fluoxetine, fluovoxamine, paraxetien, and sertraline they found water solubility to range from 3,220-15,460 mg/L and log K_{ow} values from 1.12 to 1.39. Furthermore, they concluded that different soils or sediments had different sorption capacities for SSRIs, but in general all the SSRIs had high sorption coefficients and were negatively correlated with the pH of the soils and sediment for all SSRIs. The data also indicated that the organic matter contents positively affected sorption, although cation exchange mechanisms are also likely, since the substances are organic bases and will be positively charged at environmentally relevant pH values. The range of Kd values for the three soils are listed below:

Citalopram : 17,540 - 42,579
Fluoxetine : 992 – 12,546
Fluovoxamine : 60 - 649
Paraxetien : 355 – 6,386
Sertraline : 149 - 787

Kreuzig et al. (2003) reported the Kd values for five different pharmaceuticals in four different soil types. The highest Kd values were 10, 64, 6, 20, and 46 for diclofenac, ibuprofen, ketoprofen, diazepam, and paracetamol, respectively. The same authors also studied the biodegradability of diclofenac over an incubation period of 102 days. Only 13 % of the radioactivity applied was released as 14C-carbon dioxide. They observed a two-phase course of the mineralisation, which was also reflected by the formation of extractable and non-extractable residues. The extractable fraction rapidly decreased from 79 to 23 % in 3 days, while the non-extractable fraction increased to 72 % with only little changes in the following days of the study.

The sorption and mobility of the six pharmaceuticals carbamazepine, propranolol, diclofenac sodium, clofibric acid, sulfamethoxazole, and ofloxacin were investigated in two soil types with different organic carbon and clay content (Drillia et al. 2005). The sorption experiments were performed according to the OECD test Guideline 106. Ofloxacin was particularly strongly adsorbed (except in the case of using anaerobic biomass for the solid matrix), while clofibric acid was found to be weakly adsorbed. The values of the Freudlich distribution coefficient, KF, decreased in the following order, in the case of soils and activated sludge: ofloxacin > propranolol > diclofenac > carbamazepine > sulfamethoxazole > clofibric acid, while in the case of anaerobic sludge the order was: propranolol hydrochloride > diclofenac sodium > carbamazepine > ofloxacin > sulfamethoxazole = clofibric acid.

Wu et al. (2010b) studied the fate of five pharmaceutical compounds (carbamazepine, diphenhydramine, fluoxetine, diltiazem, and clindamycin) and two metabolites (carbamazepine-10, 11-epoxide and norfluoxetine) in leaching experiments using three different soil types. They found that the selected pharmaceuticals have low mobility in the tested soils, although small portions of the applied pharmaceuticals were recovered in the leachates, likely attributed to sorption to dissolved organic matter.

Rabølle and Spliid (2000) conducted laboratory studies to characterise four different antibiotic compounds with regard to sorption and mobility in various soil types. Distribution coefficients (Kd values), determined by a batch equilibrium method, ranged between 0.5 and 0.7 for metronidazole, 0.7-1.7 for olaquindox, 8-128 for tylosin, and 417-1026 for oxytetracycline. Only tylosin sorption seemed to correlate positively with the soil characteristics. Soil column leaching experiments indicated large differences in the mobility of the four antibiotic substances, corresponding to their respective sorption capabilities. Whereas for metronidazole and olaquindox the entire added amount was recovered in the leachate, none of the added oxytetracycline and tylosin was detected in the leachate of both sandy loam and sand soils.

4.3.2 Degradation of pharmaceuticals in soils

Thiele-Bruhn (2003) reviewed the degradation of antibiotics in soils. Generally, the most persistent antimicrobials seem to be tetracyclines and fluorquinolones. However, most of the information indicates that the DT50 even of these two groups of antimicrobials would be significantly less than one year. Hamscher et al. (2001, cited from Thiele-Bruhn 2003) observed no degradation of chlortetracycline in soil initially containing 4.7 mg/kg after 180 days, and Marengo et al. (1997) observed that less than 1% of the fluorquinolones sarafloxacin disappeared after 80 days.

Redshaw et al. (2008b) investigated the susceptibility of fluoxetine to microbial degradation in a long-term (270 day) soil study. The agricultural soil had been amended with sewage sludge in known quantities for 2 years. The application rate was on average 16.6 m^3 sludge /ha / year. Soils from a selection of sampling points (days 0, 18, 32, 109, 125, 165, 180, 238, and 270) were chosen for analysis in order to estimate the degradation. Only a very slight decline in fluoxetine concentrations was observed with time. There was, however, considerable variability between the data sets. A large similarity between sterile controls and the non-sterile sewage sludge amended soils suggests that no biodegradation occurred. Statistical analyses confirmed these findings.

Winker et al. (2010) studied the behaviour of carbamazepine and ibuprofen in a greenhouse experiment, growing ryegrass in soil fertilized with pharmaceutical-spiked urine. Approximately 50% of the applied carbamazepine was recovered in soil samples taken after three months.

Boxall et al. (2006) studied the degradation in soil and uptake in plants of a wide set of veterinary antibiotics used in husbandry. Four of these, oxyteracycline, trimethoprim, sulfadiazine, and amoxicillin, are also used as human pharmaceuticals. The DT50 of the first three was estimated to be lower than 103 days, whereas more than 50% of the latter was degraded already within the first day. The nominal start concentration in the test soils was in all cases 1 mg/kg dw.

Boonsaner and Hawker (2010) showed rapid disappearance of two antibiotics in soil. A very saline soil was spiked with 105 mg kg^{-1} dry weight oxytetracycline and 55 mg kg^{-1} dry weight norfloxacin. The antibiotics were shown to degrade rapidly in soil with DT50 below10 hours for both antibiotics.

Xu et al. (2009) investigated the degradation of a number of pharmaceuticals in agricultural soils. The range of DT_{50} values in four different soil types were estimated to 4.52-18.48, 5.68-16.82, 3.07-20.44, and 0.91-6.09 days for clofibric acid, naproxen, diclofenac and ibuprofen.

Topp et al. (2008) studied the persistence characteristics of naproxen in three agricultural soils in laboratory microcosms of moist soil incubated at 30 °C. Radio-labelled naproxen was rapidly and fully mineralized with comparable kinetics in a sandy loam soil, a loam soil, and a silt loam soil.

Wu et al. (2010b) followed the disappearance of a number of pharmaceuticals in soils (carbamazepine, diphenhydramine, fluoxetine, diltiazem, and clindamycin and the metabolites carbamazepine- 10, 11-epoxide and norfluoxetine). In order to simulate sludge amended soils, the sludge was first spiked with pharmaceuticals and then added into each soil at a ratio equivalent to an application rate of approximately 20 tons/ha. The final calculated concentration of each compound in amended soil was 100 µg/kg. Under these conditions, they found no disappearance of carbamazepine or diphenhydramine in soils over a period of 80 days.

Walters et al. (2010) conducted an outdoor mesocosm study in Baltimore, Maryland, to explore the fate of 72 pharmaceuticals and personal care products (PPCPs) over the course of three years. Of the 72 PPCPs tested, only 15 were initially detected in the amended soil at concentrations ranging from low µg/kg to mg/kg. Compounds showing no significant loss over three years of monitoring included diphenhydramine, fluoxetine, thiabendazole, and triclocarban. The following half-life estimates were obtained for compounds showing first-order loss rates: azithromycin (408-990 d) carbamazepine (462-533 d), ciprofloxacin (1155-3466 d), doxycycline (533-578 d), 4-epitetracycline (630 d), gemfibrozil (224-231 d), norfloxacin (990-1386 d), and tetracycline (578 d). These half-lives exceeded those reported from laboratory studies or predicted from fate models, suggesting that pharmaceuticals under realistic out-door conditions can persist in soils for extended periods of time when applied via sludge.

Al-Rajab et al. (2010) studied the degradation of diclofenac in laboratory studies. They found that this pharmaceutical was rapidly degraded in three different soil types. Over a range of temperature and moisture conditions, extractable ^{14}C-diclofenac residues decreased with half lives of less than 5 days. Furthermore, no extractable transformation products were detectable by HPLC. Diclofenac mineralization in the loam soil was abolished by heat sterilization. Addition of sludge to sterile or non-sterile soil did not accelerate the disappearance of diclofenac. These findings indicate that diclofenac is readily biodegradable in agricultural soils.

In a field study, Halling-Sørensen et al. (2005) reported the dissipation of the antibiotics in two agricultural soils in Denmark. The half-lives (95% confidence limits in parentheses) were estimated for both fields with DT50 for chlotetracycline of 25 d (20–34) and 34 d (28–42) and DT50 for tylosin of 67 d (54–86) and 49 d (40–64) in the two fields. Although the antibiotics were applied to the soil via manure and not sewage sludge, the data still gives a good estimate of the potential fate of these substances in agricultural soils.

4.3.3 Soil concentrations after sludge amendment

A recent Norwegian risk assessment (Eriksen et al. 2009) screened pharmaceutical compounds in sludge against consumption, estimated mass entering WWTPs, human metabolism, biodegradation and behaviour in WWTPs. The 1400 pharmaceutical compounds currently prescribed in Norway were screened in the risk assessment. Based on this initial screening, 14 were identified for further detailed investigation. The identification of the 14 compounds was based on a generic and tiered evaluation process that in short included: **Tier 0)** the exclusion of substances not considered toxic (vitamins proteins ect); **Tier 1)** Use of a trigger value in soil, eliminating substances with a predicted soil concentration of less than 0.1 mg/kg when based on the very conservative assumption that all used pharmaceuticals in Norway will end up in the sewage sludge; **Tier 2)** A refinement of Tier 1, eliminating substances based on their physiochemical properties (e.g. log K_{ow}, Pka and molecular size); **Tier 3)** A refinement of Tier 2, eliminating substances based on their drug metabolic properties in humans; **Tier 4)** Refinement of Tier 3, by excluding substances based on experimental data on biodegradation and removal efficiencies in WWTPs. The refined predicted concentrations of all the 14 remaining pharmaceuticals in agricultural soils amended with 60 t sewage sludge/ha were estimated to be below 0.1 mg/kg, with the exception of mesalazin, where a predicted soil concentration of approximately 1.0 mg/kg was estimated.

Wu et al. (2010a) monitored the levels of 14 PPCPs in sludge samples from two US WWTPs (see above) and the subsequent concentrations in soil collected from four different fields receiving two sewage sludge applications. In the field soils, elevated background concentrations of carbamazebine and diphenhydramine were detected, which were likely deposited from previous sludge applications. Earlier application events occurred two to three years before this study was conducted, reflecting that these compounds may be persistent in soils. After two sludge applications, soil concentrations were typically below 1µg/kg with a few exceptions, i.e. fluoxine (up to 6.7 µg/kg), diltiazem (up to 1.6 µg/kg), and diphenhydramine (up to 6.7 µg/kg).

Golet et al. (2002) determined ciprofloxacin (CIP) and norfloxacin (NOR) in sewage sludge from several wastewater treatment plants with concentrations ranging from 1.40 to 2.42 mg/kg of dry matter. The two antibiotics were also identified in topsoil samples from experimental fields where sewage sludge had been applied. The soil concentrations after 8 and 21 months in two soil types after sludge application ranged from 0.35-0.40 and 0.27-0.28 mg/kg for ciprofloxacin and 0.29-0.32 and 0.27-0.30 mg/kg for norfloxacin, indicating a relatively slow degradation of the two antibiotics in sludge amended soils. In a similar study, Golet et al. (2003) observed concentrations of ciprofloxacin and norfloxacin ranging from 2.3 to 3.3 mg/kg of dry matter in digested sludge. Measurement of the ciprofloxacin and norfloxacin concentrations across a soil profile 5 and 21 months after sludge application (50 t/ha) showed that during the initial period both antibiotics seemed to accumulate in the topsoil, after which only a limited mobility to the subsoil was observed. The measured concentrations in the top 2.5 cm were 0.45 and 0.35 mg/kg for ciprofloxacin and norfloxacin, respectively.

4.3.4 Summary of the fate of pharmaceuticals in soils

Most pharmaceuticals do not adsorb very strongly to the soil matrix and show relatively fast degradation compared to many other persistent anthropogenic substances. There are, however, some pharmaceuticals for which K_d values have been reported above 100,000 in certain soils, and half-lives in the range of months or, under rare specific conditions, up to one year. Nevertheless, the collected information does not indicate the need for calculating a steady state concentration in soil that is based on a build-up over years. Most, if not all, of the applied pharmaceuticals are expected to disappear from the soil between two consecutive years of sewage sludge applications. This is supported by monitoring studies in the field showing findings of antibiotics typically below 1 mg/kg or, in some cases, in the lower mg/kg range. It must, however, be stressed that there are individual studies indicating a slow degradation rate of certain pharmaceuticals.

4.4 Bioaccumulation of pharmaceuticals in soil dwelling biota

Boonsaner and Hawker (2010) observed the uptake of two antibiotics in soybeans (*Glycine max*) exposed in a very saline soil spiked with 105 mg kg^{-1} dry weight oxytetracycline and 55 mg kg^{-1} dry weight norfloxacin. Soybean plants accumulated low levels of antibiotics from the saline soil, and no translocation from the roots was observed. In the roots, the biota-to-soil accumulation factor (BSAF) ranged from <1-3.3 and 0.13-1.52 over the 30 day period for oxyteracycline and norfloxacin, respectively, showing a very low potential for bioaccumulation of antibiotics in soybeans.

Herklotz et al. (2010) investigated the potential uptake of various pharmaceuticals in cabbage (*Brassica rapa var. peinensis*) and Wisconsin Fast Plants (*Brassica rapa*). The plants were grown hydroponically under high-pressure sodium lamps, so the results can only be considered as indicative of the accumulation from a soil medium. All of the studied pharmaceuticals, i.e. carbamazepine, salbutamol, sertraline, sulfamethoxazole, or trimethoprim, showed relatively low solution-to-plant accumulation factors, as the highest bioaccumulation factor of 10.9 was observed for sulfamethoxazole in the roots of cabbage. In stem and leaf, all BSAFs were below 0.1. Based on this, it can be concluded that all the studied pharmaceuticals have very low potential for accumulation in plants when grown in soil, as the bioavailability of substances generally must be considered significantly lower in soils compared to hydroponic growth media.

Boxhall et al. (2006) observed very low BSAF, i.e. below 1, in plants exposed to a wide set of veterinary antibiotics used in husbandry, including oxyteracycline, trimethoprim, sulfadiazine, and amoxicillin, also used as human pharmaceuticals. The nominal start concentration in the test soils was 1 mg/kg.

Winker et al. (2010) studied the behaviour of carbamazepine and ibuprofen in a greenhouse experiment growing ryegrass in soil fertilized with pharmaceutical-spiked urine. After three months, 34% of carbamazepine was found in aerial plant parts and 0.3% in roots. They concluded that carbamazepine transport was driven by transpiration. Ibuprofen was not detected in any plant parts after three months.

Dolliver et al. (2007) studied plant uptake of sulfamethazine in corn (*Zea mays* L.), lettuce (*Lactuca sativa* L.), and potato (*Solanum tuberosum* L.) grown in soil amended with this antibiotic. Results from the 45-d greenhouse experiment showed that sulfamethazine was taken up by all three crops, with concentrations in plant tissue ranging from 0.1 to 1.2 mg/kg dry weight. The total accumulation of sulfamethazine in plant tissue after 45 d was, however, less than 0.1% of the amount applied to the soil. The effects of sulfamethazine on the growth of plant species were also monitored. The results did not follow a classical dose-response pattern. Furthermore, differences were not significant. For example, the final biomass of all three crop species in the pots exposed to the high amount of antibiotic were lower than the controls, but higher than the biomass in the pots with half the amount of antibiotic.

Eggen et al. (2011) studied the uptake of the anti-diabetic compound metformin, the antibiotic agent ciprofloxacin, and the anti-coccidial narasin in carrot (*Daucus carota ssp. sativus cvs. Napoli*) and barley (*Hordeum vulgare*). The root concentration factors were higher than the corresponding leaf concentration factors for all of the three test pharmaceuticals with the highest uptake rates observed for metformin. Metformin was, hence, studied more explicitly with regard to uptake and translocation in meadow fescue (*Festuca pratense*), three other carrot cultivars, wheat (*Triticum aestivum*), and turnip rape seed (*Brassica campestris*). BSAFs from 2-10 were observed in roots, whereas the BSAF for seeds generally was well below 1 with the exception of turnip rape seeds, where a BSAF of 1.5 was observed.

4.4.1 Summary

Data shows that bioaccumulation of pharmaceuticals in plants is limited with biota-to-soil accumulation factors well below 1 in most cases. No accumulation studies have been identified for soil invertebrates.

4.5 Ecotoxicity of pharmaceuticals to soil dwelling biota

The number of studies investigating the toxic effects of pharmaceuticals on soil dwelling organisms is rather limited. Even with aquatic species, only relatively few of the commonly used pharmaceuticals have been tested (see Appendix A). Effects of antibiotics on soil organisms have only been included in cases where the effects have been monitored in soil systems in the laboratory or in the field. The potential risk of resistance development and transfer of resistant genes caused by antibiotics in sewage sludge have not been assessed in this report. Instead, a reference to the review by Thiele-Bruhn (2003) is made.

4.5.1 Soil microorganisms

Thiele and Beck (2001, cited from Thiele-Bruhn 2003) reported the levels in soil that reduced the substrate induced respiration (SIR) with 10%, ED_{10}, in two different soil types. For oxytetracycline, the ED_{10} ranged from 0.81 to 31.2 mg/kg and for sulfapyridine, the ED_{10} ranged from 0.05 to 6.2 mg/kg.

Streptomycin applied at 0.001 mg kg^{-1} soil did not decrease bacterial populations during the experimental incubation (Ingham and Coleman 1984). At 0.003 mg kg^{-1} soil, streptomycin decreased the number of bacteria that grew on tryptone agar and reduced active hyphae in soils.

Ingham and Coleman (1984) observed, after spiking forest soils with streptomycin at concentrations of 3,000 and 30,000 mg kg^{-1}, that the application of the highest dose reduced both total and viable bacterial populations on nearly every sample date. There was a similar initial decrease of ammonia at the lower dose, also indicating the reduction of nitrifying bacteria.

Liu et al. (2009) studied the potential impact of six antibiotics (chlortetracycline, tetracycline and tylosin; sulfamethoxazole, sulfamethazine, and trimethoprim) on soil respiration and phosphatase activity tests. Only small effects of tetracyclines and tylosin on soil microbial respiration were observed, with statistically significant variations only observed at the higher concentration of 300 mg/kg. In contrast, sulfonamides and trimethoprim were found to cause significant decreases in soil respiration within the first 4 days, even at the lowest test concentration of 1 mg/kg. The EC10 values in the first 2 days were calculated to be 7 mg/kg for sulfamethoxazole, 13 mg/kg for sulfamethazine, and 20 mg/kg for trimethoprim. Regarding the soil phosphatase activity, EC10 values calculated for the six antibiotics ranged from 1 mg/kg for sulfamethazine to 406 mg/kg for tetracycline.

Jjemba (2002) studied the effects of the anti-protozoa agents chloroquine, metronidazole, and quinacrine dihydrochloride. The number of bacteria and protozoa in soil was either unchanged or increased in the presence of 4000 mg/kg of chloroquine or quinacrine. However, in the presence of 500 mg/kg metronidazole, the density of protozoa in the rhizosphere was reduced 10-fold.

4.5.2 Soil invertebrates

Baguer et al. (2000) investigated and reported the effects of two widely used antibiotics, tylosin and oxytetracycline, on three species of soil fauna: Earthworms, springtails, and enchytraeids. The lowest observed effect concentration was 3000 mg kg^{-1} and in many cases no effect was seen even at the highest test concentration of 5000 mg kg^{-1}.

Jensen et al. (2003) showed that the veterinary antibiotics tiamulin, olanquindox, and metronidazole were not toxic to adult soil invertebrate species (springtails and enchytraeids). Effects on reproduction (EC_{10}) were found in the range of 61–111 and 83–722 mg kg^{-1} dry soil for springtails and enchytraeids, respectively.

Jensen et al. (yet unpublished) tested the effects of four commonly used pharmaceuticals on the reproduction of springtails (*Folsomia candida*). They observed EC10 and EC50 values for reproduction and LC50 values on survival of the adults at 169, 293 and 585 mg/kg for ibuprofen and 832, > 1000, and >1000 mg/kg for propranolol. The EC10 values for reproduction for cabamazepine and dichlofenac were estimated to be 12.5 and 65.7 mg/kg, respectively. No adverse effect of fluoxetine on the reproduction of springtails was observed up to the highest test concentration of 200 mg/kg.

4.5.3 Terrestrial Plants

Batchelder (1982) conducted a series of greenhouse experiments to determine the effects of chlortetracycline and oxytetracycline on plant growth and development in a sandy loam. The test concentration was 160 mg/kg. Radish *(Raphanus sativus* L.), wheat *(Triticum aestivum* L.), and corn *(Zea mays* L.) were all either unaffected or positively affected by the antibiotics, whereas Pinto beans *(Phaseolus vulgaris* L.) were adversely affected as the yield, plant heights, top and root dry-weights, and the Ca, Mg, K, and N contents were all decreased by both the antibiotics.

Liu et al. (2009) studied the potential impact of six antibiotics (chlortetracycline, tetracycline and tylosin; sulfamethoxazole, sulfamethazine, and trimethoprim) on plant growth. The effects varied between the antibiotics and between the plant species (rice and cucumber). The lowest NOEC of 1 mg/kg was observed for trimethoprim (cucumber), sulfamethazine (rice), and sulfamethoxazole (rice), whereas the lowest NOEC for tylosin, tetracycline and chlortetracycline was 50, >300 and 70 mg/kg, respectively.

Winker et al. (2010) studied the effects of carbamazepine and ibuprofen in a greenhouse experiment using ryegrass grown in soil fertilized with pharmaceutical-spiked urine. The application of pharmaceuticals resulted in an initial soil concentration of 32 and 490 µg/kg carbamazepine and ibuprofen, respectively. Carbamazepine and ibuprofen, individually and in combination, did not adversely affect the growth of ryegrass over the entire experimental period of three months.

Boonsaner and Hawker (2010) reported that the rate of germination and seedling emergence of soybeans (*Glycine max*) in a very saline soil spiked with 105 mg kg^{-1} dry weight oxytetracycline and 55 mg kg^{-1} dry weight norfloxacin was reduced by 23% compared to that of uncontaminated soil. This reduction was largely due to the high salinity, as a reduction of 20% was observed within the saline soil in absence of antibiotics.

Jjemba (2002) tested the effect of three antimicrobials to soybean (*Glycine max*). Phytotoxic effects on the plant species were observed at 8,000, 500 and 10,600 mg/kg for the substances chloroquine, metronidazole, and quinacrine, respectively.

Dolliver et al. (2007) studied the effects of sulfamethazine in corn (*Zea mays* L.), lettuce (*Lactuca sativa* L.), and potato (*Solanum tuberosum* L.) Results from the 45-d greenhouse experiment showed effects of sulfamethazine on the growth of plant species. The results did not follow a classical dose-response pattern, and differences were not significant. The final biomass of all three crop species exposed to the high amount of antibiotic were, for example, lower than the controls, but higher than the biomass in the pots with the only half the amount of antibiotics.

Eggen et al. (2011) studied the uptake and effects of the anti-diabetic compound metformin, the antibiotic agent ciprofloxacin, and the anti-coccidial narasin in carrot (*Daucus carota ssp. sativus cvs. Napoli*) and barley (*Hordeum vulgare*). All three pharmaceuticals produced negative effects on growth and development of carrots when grown in soil with initial concentration of 11.3 mg/kg dry weight. The most pronounced effect was observed for Narasin, while negative impacts on biomass were also measured for ciprofloxacin and metformin, particularly on carrots.

An et al. (2009) tested the ecotoxicological effects of paracetamol on seed germination and seedling development of wheat (*Triticum aestivum* L.) exposed on filter papers placed in Petri dishes (germination) or in solution hydroponics in growth chambers (seedling development). Wheat roots were the most sensitive sites of the plants to paracetamol, and the median effect concentration (EC50) of paracetamol based on the inhibition of root elongation was 668.8 mg/L, indicating a relatively low acute toxicity of paracetamol to plants.

4.5.4 Summary of soil ecotoxicity

Only a very limited selection of the vast amount of pharmaceuticals used in today’s society has been tested for their ecotoxicity to soil dwelling organisms. With the exception of the anticipated effect of antimicrobials to soil microorganisms, the remaining data all show a relatively low toxicity of pharmaceuticals, i.e. with the lowest observed effect levels starting from approximately 50 mg/kg, with the exception of the antibiotics trimethoprim and ciprofloxacin and the anti-diabetic compound metformin, where significant effects on the seedling height of plant species like cucumber and carrots were observed at approximately 10 mg/kg.

4.6 Provisional risk evaluation of pharmaceuticals in sludge

Based on the data presented in the sections above, a provisional risk assessment of pharmaceuticals in the terrestrial environment can be conducted.

The risk is assessed by comparing the predicted environmental exposure (predicted environmental concentration – PEC) with the predicted level in soil where no effects are observed or anticipated (No Observed Effect Level – NOEL). The ratio between PEC and NOEL indicates a so-called margin of safety (MoS), which essentially is the reverse of the more common "risk quotient" utilised in many risk assessments. As all exposure scenarios cannot be foreseen and all soil dwelling species cannot be tested, a certain margin of safety is needed in order to conclude that significant effects of PFCs in sewage sludge would be unlikely. Based on the amount of available data, the MoS should fall within a range of at least 10 to 1000 in order to be in line with the use of assessment factors in the REACH programme in the European Union and described in the Technical Guidance Document for risk assessment of new and existing chemicals.

4.6.1 Predicted Environmental Concentration (PEC)

The estimated soil concentration immediately after one sludge application, the $PEC_{initial}$, can be calculated assuming no disappearance and using the following universal input parameters:

Sludge application rate: 3 t /ha
Mixing depth: 0.2 m
Soil density: 1.7 kg/L
Background concentration: 0.0 mg/kg

Very little soil-related ecotoxicity data is available for a PNEC-estimation. The $PEC_{initial}$ is, therefore, only calculated for the substances where suitable ecotoxicity data is available and valid reports on sludge concentration can be identified. These are listed in Table 4.5. The basis for the choice of sewage sludge concentration can be found in Section 4.2 and Table A1 in Appendix A.

Table 4.5. The calculated soil concentrations for a selected number of pharmaceuticals after one single sludge application ($PEC_{initial}$).

Pharmaceutical	**Sludge concentration (mg/kg)**	**$PEC_{initial}$ (mg/kg)**
Carbamazepine	6	0.005
Dichlofenac	0.087	0.00008
Fluoxetine	3.1	0.003
Ibuprofen	5.1	0.005
Oxytetracycline	0.11	0.0001
Propranolol	0.025	0.00002
Sulfamethoxazole	0.068	0.00006
Sulfapyridine	0.028	0.00003
Trimethoprim	0.076	0.00007

4.6.2 Long term environmental concentrations of persistent substances

None of the substances above have been identified as very persistent in soil under laboratory settings. Therefore, it has not been deemed necessary to calculate the long term steady state soil concentrations for any of the pharmaceuticals mentioned above.

4.6.3 No Observed Effect Level (NOEL)

Based on the relatively limited data reviewed above, the concentrations (mg/kg dw) where no or insignificant effects (NOEC and EC10) on the tested species were observed are listed in Table 4.6 together with the calculated Margin of Safety, i.e. the ratio between the NOEL and the $PEC_{initial}$.

Table4.6. The lowest no-observed-effect-level (NOEL), the $PEC_{initial}$ from Table 6, and the calculated Margin of Safety (MoS) for a selected number of pharmaceuticals. See details for the selection and calculation in the text above.

Pharmaceutical	**Lowest NOEL (mg/kg)**	**$PEC_{initial}$ (mg/kg)**	**MoS (NOEL:PEC)**
Carbamazepine	12.5	0.005	2,500
Dichlofenac	65.7	0.00008	821,250
Fluoxetine	>200	0.003	>67,000
Ibuprofen	169	0.005	33,800
Oxytetracycline	0.81	0.0001	8,100
Propranolol	832	0.00002	>1,000,000
Sulfamethoxazole	1.0	0.00006	16,667
Sulfapyridine	0.05	0.00003	1,667
Trimethoprim	1.0	0.00007	14,286

Pharmaceuticals are not regulated within the REACH programme in the European Union, as these are regulated according to guidelines laid down by the European Medicine Agency (EMA), which in general are less conservative than the guidelines described in the Technical Guidance Document for risk assessment of new and existing chemicals within the REACH programme for new and existing chemicals.

Within the REACH programme, a factor of 100 is normally used to extrapolate to a safe level (called $PNEC_{soil}$) for soil dwelling species when NOEC/NOEL values for only one group of species (trophic level) is available. Although ecotoxicity for more than one trophic level was available for a number of the listed substances, a factor of 100 can be used as a target for a conservative and cautious margin of safety. None of the pharmaceuticals listed in Table 7 was identified to have a margin of safety between the anticipated exposure concentration and the soil concentration that was below 100. Hence, the present concentration of pharmaceuticals in sewage sludge should be considered to be on the safe side according to the framework outlined in the REACH programme for new and existing chemicals. Furthermore, for the lowest reported NOEL-value of 0.05 mg/kg observed with sulfapyridine, it should be mentioned that the observed EC10 value for the substrate-induced soil respiration (SIR) was obtained in a silty sand, and that in a loamy sand the EC10 value was reported as 6.2 mg/kg, i.e. almost 125 times higher.

A recent Norwegian risk assessment (Eriksen et al. 2009) screened pharmaceutical compounds in sludge against consumption, estimated mass entering WWTPs, human metabolism, biodegradation, and behaviour in WWTPs. The 1400 pharmaceutical compounds currently prescribed in Norway were screened in the risk assessment. See section 4.3 for further description of the assessment. Based on this initial screening, 14 substances were identified for further detailed investigation. For all of these 14 substances, a risk characterisation revealed that the risk quotient (RQ), i.e. the PEC:PNEC ratio, was well below 1. Typically, RQ values of less than 0.001 were obtained, except for ciprofloxacin with a RQ of 0.02. The report did not, however, contain any details about how the PNEC values for soil were derived.

4.7 Summary and conclusions

Generally, far too little information is available for a solid evaluation of the potential risk of many pharmaceuticals. The lack of suitable ecotoxicological data for soil dwelling species is substantial. Furthermore, only a relatively small set of the vast amount of pharmaceuticals in use has been monitored in sewage sludge and only from a limited number of WWTPs. Finally, the (combined) effect of the various pharmaceuticals has hardly ever been studied in the field.

Based on the information of monitored sludge concentrations, predicted soil concentrations were established for a set of pharmaceuticals for which ecotoxicological data for soil dwelling species have been identified. A comparison between the predicted soil concentration and observed no-effect levels in soil tests revealed a large margin of safety for all pharmaceuticals. No unacceptable risk to soil dwelling species is, therefore, expected. This is supported by strong indications that most pharmaceuticals are relatively rapidly degraded in the soil environment and no significant uptake in plants or soil fauna has been reported. It must, however, be recommended to improve the dataset for a number of relative slowly degradable pharmaceuticals such as ciprofloxaxin, nrofloxaxin, tetracyclins and flouorquinolones.

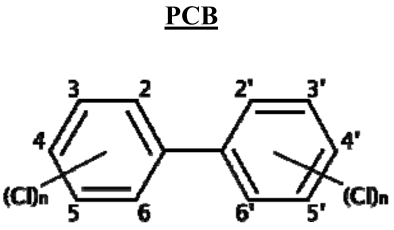
At this point, iIt is important to stress that the present screening has not considered risks by leaching into ground water and adjacent fresh water systems. As a consequence of this, hormones like estrogens have not been included in the evaluation, as the potential risk of these are mainly associated to the aquatic environment. This analysis has, furthermore, not evaluated the consequences of a potential resistance development in microorganisms in sewage sludge or soils caused by the presence of antibiotics.

5 Polychlorinated biphenyls (PCB)

5.1 Introduction

Polychlorinated biphenyls (PCB) cover a group of 209 different PCB congeners, which can be divided into two groups according to their toxicological properties. One group, consisting of 12 congeners with toxicological properties similar to dioxins, is termed “dioxinlike PCB” (DL-PCB). The other group, referred to as “non dioxin-like PCB” (NDL-PCB), covers the remaining 197 congeners. There are no known natural sources of these compounds in the environment. PCBs are colourless to light yellow oily liquids or solids with no distinct smell or taste. They enter the environment as mixtures containing a variety of individual components and mixtures. Seven types of PCB mixtures constitute 35% of all the PCBs commercially produced and 98% of PCBs sold in the United States since 1970. Some commercial PCB mixtures are known in the United States by their industrial trade name, Arochlor. The name Arochlor 1254, for example, means that the molecule contains 12 carbon atoms (the first two digits) and approximately 54% chlorine by weight (second two digits).

Table 5.1. Physical-chemical properties and structure of PCBs (209 congeners).

Parameter	Value	Reference	Structure
Melting point	n.a.		
Boiling point	> 200°C	Henry & Devito 2003	
Vapor pressure	$7.7 \times 10^{-5} - 4.1 \times 10^{-3}$ mm Hg	Gatehouse 2004	
Water solubility	2.7 – 590 µg/l	Gatehouse 2004	
Log K_{OW}	~ 4 – 8	Henry & Devito2003	
Log K_{OC}	4.61 – 6.54	Hansen et al. 1999	
K_D	25 – 23,000 l/kg	Paya-Perez et al. 1991	

5.2 Use and consumption

Because they don't burn easily and possess good insulating properties, PCBs have been widely used as coolants and lubricants in transformers, capacitors, and other electrical equipment as well as in construction materials such as sealants, glue, and paint. It is estimated that more than 1 million tonnes of technical PCB mixtures were produced world-wide since their first commercial use in the late 1920s. Although produced by comparable production processes, technical PCB mixtures contain both DL and NDL-PCB and may vary considerably with respect to congener composition due to differences in the amount of chlorine and the reaction conditions applied. Although the manufacturing, processing and distribution of PCB has been prohibited in almost all industrial countries since the late 1980s, e.g. in Denmark since 1986, entry into the environment may still occur, especially due to improper disposal practices or leaks from electrical equipment, hydraulic systems and housing materials such as paint and joint material around windows and doors. PCBs are highly persistent and are globally circulated by atmospheric transport and, thus, are present in all environmental media, including sewage sludge.

5.3 PCB levels in sewage sludge

Besides atmospheric deposition, sources of PCBs to wastewater treatment plants have been found to be sanitary flows and runoff from urban areas that enter combined sewer systems (Loganathan et al. 1997; Rossi et al. 2004).

Proposed standards for maximum allowable PCB concentrations in sewage sludge for agricultural purposes issued in a range of countries can be seen in Table 5.2. The rationale or scientific background for the limit values has not been investigated further in this report. Table 5.2 also includes the provisional guidance value of 80 µg/kg for the sum of seven common PCB congeners, which was launched by the Danish EPA in October 2010. As can be seen from the table, this proposed guidance value is markedly lower than what is practice in other countries.

Table 5.2. Limit or guidance values for PCB in sewage sludge in other countries. Modified from Smith (2009).

Country	**Limit value (µg/kg dw)**	**Comment**
Sweden	400	PCB_7^*
Lower Austria	200	PCB_6^{**}
Germany	200	PCB_6^{**}
France	800 500	PCB_7^*, Arable land PCB_7^*; Grassland
Australia	500	Not specified
Denmark	80	PCB_7^*

** Sum of 7 congeners: PCB 28, 52, 101, 118, 138, 153, 180*

*** Each of six congeners: PCB 28, 52, 101, 138, 153, 180*

5.3.1 The level of PCB in Danish sludge

The first large survey of organic contaminants in Danish sludge was published in 1996 (Kristensen et al. 1996). The survey included PCB_7 in sludge from 20 municipal WWTPs throughout Denmark. The overall data is presented in Table 5.3. It shows that all but two of the PCB congeners were detected in less than half of the plants. In 7 out of 20 WWTPs (35%), no PCB could be detected at all. The median and average concentration of the PCB_7 was 27 and 42.6 µg/kg d.m., respectively. The highest sum value for the PCB_7 was 140 µ/kg dw.

Tabel 5.3. The concentration of PCB in 20 sludge samples taken from WWTP in Denmark as reported by Kristensen et al. (1996). All data in µg/kg d.w.

PCB	**Mean**	**Median (=LOD)***	**Maximum**	**% of samples > LOD**
28	4.40	4	12	10%
52	9.01	5	39	50%
101	7.68	5	31	50%
118	5.75	3	28	20%
138	7.08	5	29	30%
153	8.64	5	34	35%
180	5.77	5	13	20%
Sum of PCB_7	42.6	27	140	65%

** The median of the individual congener corresponds to the limit of detection, i.e. is at the LOD or lower.*

For a few years, a number of organic contaminants in sewage sludge were included in the national monitoring programme in Denmark called NOVANA. The monitoring data from 2003 and 2004 has been published and covers data from approximately 35 and 7 WWTPs, covering approximately 65 and 7 samples, respectively (Miljøstyrelsen 2005ab). The following 10 PCB congeners were among these contaminants: 28, 31, 52, 101, 105, 118, 138, 153, 156, and 180. The 2003 data showed that some of the PCBs (28, 31, 105 and 156) were detected in less than 10% of the WWTPs, whereas others were detected in up to 46% of the WWTPs. In the smaller 2004 data set, the various congeners were detected in two of the seven WWTPs, but with two exceptions (PCB 138 and 153) which were detected in three of the plants. The 95% percentile of the observed concentrations of the sum of 10 congeners was 0.01 µg/kg. It can, therefore, be concluded that in practical terms, no PCB was detected in any of the 7 WWTPs in 2004. In 2003, the average and the maximum (95% percentile) value of the individual congeners were found in the range of 1.7-5.1 and 8.1-18 µg/kg dw. However, the concentration level was only reported for six of the 10 congeners.

In 2010, a set of unpublished analytical data for PCB in Danish sludge destined for incineration in Germany was reported by Danbørs, a Danish sludge distribution company. The PCB content was measured by a German laboratory in connection with routine control of hazardous substance in sludge incinerated in Germany. PCB was detected in 8 out of 27 samples, with sum values of PCB_6 in the range of 41-518 µg/kg dw. The average and median value of PCB_6 in the eight samples were 183 and 99 µg/kg dw. Two of the eight samples were significantly higher than the others, with concentrations of 520 and 450 µg/kg. In both cases, the individual concentrations of congeners 101, 138 and 153 ranged between 110-150 µg/kg and, thus, constituted the great majority of the summed concentrations.

The Danish Association “Recycling of Organic Residual Products in Agriculture (BGORJ)” has recently collected a wider set of unpublished data on the level of PCB in Danish sludge from their members. It covers nation-wide data from 62 samples from more than 50 different Danish WWTPs collected in the years 2007-2011 with a dominance of data from 2010. A summary of the data is presented below in Table 5.4. The data shows that the PCB concentration in the vast majority of WWTPs, i.e. 5-95 percentiles, is found in the range of approximately 9 to 71 µg/kg dw. Only three of the 62 samples were unable to meet the new provisional Danish limit value of 80 µg/kg, whereas all samples were able to meet the lowest existing permanent international limit value of 400 µg/kg found in Sweden.

Table 5.4. The concentration of PCB in 62 sludge samples from approximately 50 different Danish WWTPs. All data is in µg/kg dw and covers the period from 2007-2011 with the majority of data from 2010 and 2011. (BGORJ, unpublished).

	28	**52**	**101**	**118***	**138**	**153**	**180**	**Total**
Mean	6.0	5.5	6.2	2.8	7.6	7.9	5.5	41.6
Median	5.0	5.0	5.0	2.8	5.0	6.0	5.0	35.0
5% Percentile	1.1	2.0	1.1	0.0	2.0	2.1	1.0	9.3
95% Percentile	10.0	11.0	12.9	10.0	19.7	18.8	10.0	71.0
Maximum	56.0	16.0	32.0	10.0	56.0	56.0	42.0	196.0

** PCB_{118} were not analysed in 25 samples (40%) and are, hence, not included in the PCB_{total} for these samples. The PCB_6 analyses include mainly the older analyses. All statistical values listed above are, however, lower if based only on the 60% of samples where PCB_7 has been monitored.*

In 2002, a small Danish data set from two sludge samples (each being a mixtures of five subsamples collected daily over the work-week) from the WWTP Lynetten in Copenhagen showed that no PCB could be detected in the sewage sludge (detection limit was 10 µg/kg) (Lynettefællesskabet 2003).

Recently, a Danish water company, Faxe Forsyning, analysed a single sample of sewage sludge from three individual WWTPs (Faxe Forsyning 2010, unpublished). None of the samples contained any of the seven common PCB congeners in detectable amounts (LOD = 10 µg/kg).

In 2000, the Danish county Aarhus conducted an investigation regarding the fate of anthropogenic substances in sludge following application on agricultural soils (Aarhus Amt 2005). In this context, the PCB levels in three sludge samples from two WWTPs as well as the soil concentrations before and after sludge application were determined (see also section 5.4.3). The total concentration of PCB_7 in the sludge samples ranged from 5.5-18.2 (Egå WWTP) and 120-145 µg/kg (Søholt WWTP), respectively.

5.3.2 PCB in sludge across the world

A targeted review of national and international literature revealed that analyses of PCB in sludge samples from wastewater treatment plants are relatively sparse. World wide data, focusing on Europe, is reported in Table 5.5. Data older than 10 years have been omitted, as they are probably no longer are representative of the current level of PCB in sludge. As seen in Table 5.5, data has been collected mainly from European countries as well as a comprehensive Australian data set and a minor Chinese study.

As the only Nordic country, Sweden still runs an annual monitoring programme on PCB in sludge (Haglund and Olofsson 2008; 2009). Additional information from Sweden is available from other recent reports (Petterson and Wahlberg 2010; Sternbeck and Österås 2010). Generally, the PCB concentrations appear to be low in Swedish sludge, with sum values of the 12 WHO PCB in the lower µg/kg range (Haglund and Olofsson 2009), but in the samples from the Stockholm WWTPs the concentrations of PCB_7 were often higher than 80µg/kg (Petterson and Wahlberg 2010). Note that the set of congeners analysed in the data from Haglund and Olofson (2008; 2009) is different from that of the other Swedish studies and, thus cannot be directly compared to the limit values in Table 5.2.

Paulsrud et al. (1997) and Nedland et al. (2002) reported the levels of PCB in Norwegian sludge from eight WWTPs. The number of collected samples was 36 and 40 and the average concentration of PCB was 46 and 13 µg/kg in 1997 and 2002, respectively. In 2002, PCB was detected in four of the eight WWTPs, with the highest concentration measured as 96 µg/kg. The highest mean value for a WWTP was 51 µg/kg. Since 2002, PCB has not been included in monitoring programmes of Norwegian sludge, as the levels were expected to decrease further (VKM 2009).

The PCB content in German sewage sludge decreased by approximately 50% (from 340 to 154 µg/kg on average) between 1989 and 1996 (UMK-AG 2000, cited from Umlauf et al. 2011).

In a study from the United Kingdom published in 2003, samples were collected from the digested fraction of sewage sludge from 14 WWTPs (Stevens et al. 2003). The sum of 46 PCB congeners ranged from 110 - 440 µg/kg, with a mean value of 220 µg/kg. The sum of PCB_7 ranged from 44 – 180 µg/kg, with a mean concentration of 81 µg/kg.

Two Spanish publications containing data on PCB concentrations in sludge were found (Abad et al. 2005, Aparicio et al. 2009). The mean concentrations of PCB_7 in both studies where below 35 µg/kg, whereas only very few samples from Seville (Table 5.5) had concentrations above 80 µg/kg. The highest concentration measured was 115 µg/kg.

The highest concentrations of PCB_7 were found in sludge collected in the year 2000 from the WWTP in Seine Aval within the Paris area (Blanchard et al. 2004). 76% of the incoming PCB was retained in the WWTP and, thus, in the sludge. The concentration of PCB_7 in the sludge samples increased following anaerobic digestion and dehydration, probably due to degradation and loss of organic matter in the processes. The average PCB_7 concentration of the final sludge was 623 µg/kg, but concentrations where found as high as 1,930 µg/kg. It should be noted that the concentrations observed here are much higher than what has been observed in any of the other studies listed in Table 5.5. The authors estimate that the PCBs found in the wastewater flow most probably originated from diffuse atmospheric sources in the drained area of 500 km^2 (Paris and close suburbs).

An Australian review of PCB content in sewage sludge from six WWTPs sampled from 1995 to 2006 showed that PCB levels had decreased significantly during this period (Clarke et al. 2010). Only in 5.6% out of 2,266 samples were PCBs found above the detection limit. In the period from 2004 to 2006, only 10 samples out of 829 (from 58 WWTPs) had a content of PCBs above the detection limit, and the highest concentration detected was 410 µg/kg. The mean concentration for both periods was less than 10 µg/kg.

Table 5.5. International data on occurrence of PCBs in sludge from WWTPs. n.s. = not specified.

Country	**Region**	**Year**	**No. of samples**	**Sludge type**	**Included congeners**	**∑PCB µµg/kg**		**Reference**
						Mean	Range	
Sweden	Stockholm 2 WWTPs	2007 – 2008	4	Digested and de-watered	PCB_7^*	85	60 – 130	Petterson & Wahlberg (2010)
	National Monitoring	2000 – 2008	14 – 46	Mixed	PCB_7^*	42.8 (sum of congener means)	17.6 – 68.7 (Standard dev.	Sternbeck & Österås (2010)
	n.s. 8 WWTPs	2007 2008	8 8	n.s.	77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189	5.06 12.7	2.80 – 7.48 7.58 – 18.6	Haglund and Olofson (2008; 2009)
UK	n.s. 14 WWTPs	n.s.	14	Secondary treated / activated sludge	PCB_7^*	81	44 – 180	Stevens et al. (2003)
	Ashford	n.s.	1	Mesophilic anaerobically digested	52, 101, 118, 138, 153, 180	46	-	Gibson et al. (2005)
	-	n.s.	1	n.s.	PCB_7^*	42	-	Rhind et al. (2009)
Spain	Catalonia 22 WWTPs	2001 - 2003	22	Mostly raw sludge, also composted, thermally dried	PCB_7^*	30	3 – 60	Abad et al. (2005)
	Seville 4 WWTPs	2005	~40	Primary, secondary, digested, com-	PCB_7^*	< 35	<LOD - 115	Aparicio et al. (2009)

Country	**Region**	**Year**	**No. of samples**	**Sludge type**	**Included congeners**	**∑PCB μμg/kg**		**Reference**
						Mean	Range	
				post				
France	Paris area	1999 – 2000	45	Anaerobically digested, dehydrated	PCB_7^*	623	120 – 1930	Blanchard et al. (2004)
Switzerland	n.s.	n.s.	5	Digestate	77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189	9.06	2.96 – 16.7	Brandli et al. (2007)
Australia	n.s. 58 WWTPs	2004 – 2006	829	“Freshly generated sewage sludge”	n.s.	< 10	< 10 – 410	Clarke et al. (2008)
China	8 WWTPs in Beijing	2007	8	n.s.	PCB_7^*	13.7	7.46 – 19.4	Guo et al. (2009)
Germany								

5.3.3 Conclusions on sewage sludge levels of PCB

Based on the data gathered on PCB in sewage sludge, it can be concluded that, except for the sludge samples from the Paris area and two samples from a smaller data set in Denmark, practically every sludge sample analysed complies with the limit values set out in most countries. In a screening survey conducted on 62 samples of Danish sludge from more than 50 WWTPs, three samples were unable to meet the temporary Danish criteria of 80µg/kg, whereas all of them were able to meet the lowest existing permanent international limit value of 400 µg/kg found in Sweden. For risk assessment purposes, a PCB_7 sludge concentration of 71 µg/kg is suggested, as this corresponds to the 95% percentile of the 62 Danish samples mentioned above.

5.4 Fate and behaviour of PCB in soil

Following sludge application and incorporation into agricultural soil, loss of contaminants may occur by volatilization, leaching, plant uptake, abiotic degradation and biodegradation. Another known phenomenon is the aging and subsequent irreversible occlusion of compounds into the soil matrix, making them unavailable for the abovementioned processes (Hatzinger and Alexander 1995).

A wide set of laboratory studies exists which attempts to elucidate the potential for leaching and degradation of PCB in soil. These have not been evaluated in this report. Instead, studies on the disappearance of sewage sludge associated PCB under field conditions is included below together with field studies evaluating the vertical transport of PCB in soil.

5.4.1 Soil degradation

Alcock et al. (1996) reported the long term fate of PCB from sludge amended soils. Four different samples of sewage sludge were applied once to two field soils in the UK back in 1968. Samples of the sludge, sludge-amended soils and soils from untreated control plots were stored and analysed retrospectively. The sum of PCB in the sludge samples ranged from 1,000 to 7,000 µg/kg. The sum of PCB concentrations in the two control soils declined over the next 20 years from initially 137 and 299 µg/kg to 32 and 57 µg/kg, indicating a reduction in atmospheric deposition of PCBs to soil. The PCB concentrations also declined on the sludge-amended plots, reaching the control plot concentrations (30-60 µg/kg) in the late-1980s. Half-lives ranged from less than 1 year to 8.5 years for the congeners 18, 28 and the sum of PCB. Biodegradation and/or the formation of reversibly sorbed soil PCB residues could not alone account for the losses observed; hence, volatilisation was implied as one of the most important processes for PCB loss in both the control and sludge-amended plots.

Gan and Berthoex (1994) studied the disappearance of PCBs from sludge-amended farmland in a five year field experiment. Eight different treatments with PCB contaminated sludge were included in the experiment. Four repeated plots received a one-time only application of PCB-contaminated sludge in the spring of 1986. Four other repeated plots received annual applications of contaminated sludge at the specified loading rates in each spring season from 1986 to 1990. Two levels of PCB concentration in spiked sludge (25,000 and 75,000 µg/kg) were used. The low-level PCB sludge was applied at two different rates, i.e. 2.5 and 7.5 t dm/ha/year, whereas the high-level PCB sludge was applied at a rate 0.8 and 2.5 t dm/ha/year. The study indicated a relatively rapid disappearance of most PCBs from the sludge-amended farmland, with half-lives in the range of 7 to 11 months for 2-chlorinated PCBs, 5 to 17 months for 3-chlorinated PCBs, and 11 to 58 months for 4 chlorinated PCBs. Many of the higher chlorinated PCBs are, however, more persistent in soil, whereas others disappeare as fast as the lower chlorinated PCBs. The total sum of PCBs had an average half-life of 19 months in the sludge-amended farmland. The longest half-life of 311 month, i.e. almost 26 years, was estimated for PCB_{18}.

5.4.2 Leaching and vertical transport

Wang et al. (2010) observed the impact of wastewater irrigation on the distribution of PCBs in Chinese agricultural soils. The total concentrations of the 26 analyzed PCBs were in the range 0.256–2.14 µg/kg on dry weight basis. There was a higher accumulation of PCBs in farms irrigated by wastewater, with PCB_{209} as the predominant congener. The vertical distribution was quite uniform in the topsoil (the plough layer) and thereafter decreased exponentially. Furthermore, the soil vertical distribution was found to be congener specific for PCBs, where less chlorinated congeners were able to penetrate deeper into the soil, while heavier congeners were more restricted in their movement.

In a long term field study (see details below), Umlauf et al. (2011) showed that vertical transport of PCB in sludge amended soils was low, as the main load of PCBs was aggregated in the topsoil. Hardly any PCB could be detected below 30 cm.

5.4.3 Soil concentrations

In the vast majority of studies that report PCB levels in soils, it is not possible to distinguish the origin of the PCB and, hence, to determine to what extend potentially elevated PCB concentrations may be due to sewage sludge application. However, the most relevant studies found regarding sewage sludge associated PCB loading to arable soils are presented below.

Meijer et al. (2003) reported the global background level of PCB. The minimum, mean and maximum levels of total PCB from the 191 sites located world wide were in 1998: 0.026, 5.4 and 96.9 µg/kg respectively. The same numbers for PCB_7 were 0.001, 2.9 and 57.91 µg/kg.

Desaules et al. (2008) reported the surface soil concentrations (0–20 cm) of PCB found in the Swiss soil monitoring network (NABO) with 105 observation sites representing all major land use types. The sum of PCB_7 ranged from 0.5 to 12 µg kg^{-1}, with an overall median of 1.6 µg kg^{-1}. The concentration ranges were overlapping between all land use types. For comparison with the overall result, the median value of PCB_7 in arable land, extensive grassland, intensive grassland, coniferous forest and deciduous forest were (with number of samples in brackets) 1.4 (35), 0.9 (17), 1.1 (8), 2.3 (16) and 2.0 (12) µg/kg dw. Tendencies for higher PCB concentrations were observed at urban and viticulture sites. Overall, the general congener rank order was PCB no. 153 > 138 > 101 > 180. Desaules et al. (2008) referrers to a large Swiss monitoring data set covering the period 1990-1996 (Keller and Desaules 2001). Here, the median PCB_7 concentration in the upper 20 cm of soil of 357 samples was reported to 4.0 µg/kg, with a median of 2.0 µg/kg in both the 79 samples from arable land and the 99 samples from grassland. The 23 soil samples from forests contained in comparison a median level 5.1 µg/kg. In other words, both studies indicate that the level in soil from arable land is lower then the average soil concentration in Switzerland.

Holoubek et al. 2009 reported the concentration ranges of persistent organic pollutants, including PCB in the Czech Republic, according to different soil uses and locations. Soil samples analyzed originated from two complementary sources, i.e. from a monitoring programme of agricultural soils performed since 1992 and covering 38 arable and 6 grassland soil samples, and another 59 soils from the RECETOX soil survey project that includes 8 arable soils, 28 grasslands, and 23 forest soils. Each site was represented by ten sub-samples collected from the area. The results are summarised below in Table 5.6. Results clearly differentiated between arable, grassland and forest soils and showed that due to the global atmospheric transport, the mountain ecosystems can reach contamination levels higher than the ones found in urban and industrial regions. It was most significant for a group of the dioxins and furans, where concentrations in mountain forests were 20 times higher than those in arable and grassland soils, but also PCB concentrations were 3-4 times higher in mountainous forests compared to arable land.

Table 5.6. PCB concentration (µg/kg dw) in various soil types in the Czech Republic. Data from Holoubek et al. (2009)

Soil type (N)	**Mean**	**Median**	**Min-Max**	**5-95% P**
Arable land (39)	6.86	3.60	3.5-42.1	3.5-34.6
Grassland (22)	9.34	6.31	2.0-29.2	4.1-24.7
Forest (9)	8.87	8.40	3.42-13.37	7.6-13.13
Mountain forests (9)	22.76	22.64	7.90-36.18	15.32-34.72

Heywood et al. (2006) reported the results from a survey on the PCB content in 200 rural soils across Great Britain as part of the Countryside Survey Project. The soil concentrations ranged from 0.274-80.58 µg/kg, with a mean soil concentration for the sum of 33 congeners of 5.028 ± 8.411 µg/kg dw. The median level was 2.524 µg/kg dw. Spatial statistical techniques showed clusters of high soil PCB concentrations predominantly in the west and south east of Great Britain, either associated with urbanized areas in the south or on the coastline in the west. The authors speculated that the hotspots on the west coast could be the result of long-range transport of the lighter PCBs or the result of cycling from oceans to land.

Webber and Wang (1995) reported the PCB concentrations in soil samples taken from 30 agricultural fields in eight Canadian provinces and eight sludge-treated fields in Ontario. PCBs were observed in all of the agricultural soils in concentrations ranging from 150 to 235 µg/kg, but were detected in only two of the eight sludge-treated soils, where the highest level recorded was 514 µg/kg at a sludge disposal area with repeated sludge applications each year during 1982-1989.

Armitage et al. (2006) collected and analyzed the PCB concentrations in different layers of soil cores collected at one agricultural and five non-agricultural sites in Sweden. No information was given regarding the potential use of sewage sludge at the agricultural site. PCB concentrations at the agricultural site were nearly uniform on a dry weight basis throughout the depth considered (0–12 cm), while a distinct gradient with depth was observed at the five non-agricultural sites. The sum of the 13 measured PCBs (ΣPCB13) in the surface layer of the agricultural site (0–2 cm) was approximately 1.6 µg/kg dw, while for the non-agricultural sites the concentration ranged from approximately 0.55 to 55.0 µg/kg dw, with a median concentration of approximately 4.4 µg/kg dw.

In 2000, the Danish county Aarhus conducted an investigation regarding the fate of anthropogenic substances in sludge following application on agricultural soils (Aarhus Amt 2005). In this context, the PCB levels in three sludge samples from two WWTPs were identified (see section 5.3.1above) and the soil concentrations monitored before and after sludge application. Sludge was applied at a dose of 17 t/ha ,and soil samples were collected after 1 day, 2 weeks, 1 and 5 months from two different sites, a sandy soil and a clay soil. PCB was not detected at any time in the soil samples. The detection limit for the individual PCBs was 0.2 µg/kg wet weight.

Vikelsoe et al. (2002) investigated the occurrence and vertical distribution of PCB in Danish soils that had been sludge-amended. Three different sites were investigated: 1) a preserved natural reference area that had not been cultivated, dressed or fertilised for more than 50 years, but only used for grazing cattle. Deposition was expected to be the main source of pollution in this area; 2) A cultured area annually amended with about 0.7 t dw/ha/y of sludge and 3) A site that received approximately 17 t sludge/ ha from more than 25 years, but changed to mineral fertilisers eight years prior to soil sampling. No information regarding the PCB concentration in the applied sludge was available. The mean PCB_7 concentrations in five soil samples from the three sites were 0.1, 0.37 and 553-558 µg/kg dry matter. The PCB_{138} was the most dominant PCB congener.

In a long-term field experiment established in 1962, Umlauf et al. (2011) investigated the influence of sewage sludge, compost, and farmyard manure application on the PCB levels in soil. Control plots amended only with mineral fertilisers served as a basis to compare the waste-amended soils with soils affected only by atmospheric deposition. Soil samples were collected to a depth of 90 cm and analyzed for dioxin-like PCBs. The soil profiles revealed that the main load of PCBs is aggregated in the topsoil, as hardly any PCB was detected below 30 cm. No specific data was presented, but based on graphical estimation the concentration in the topsoil of the sewage sludge amended plots was approximately 3.0 ng I-TEQ/kg compared to 1.25 ng I-TEQ/kg at the plots receiving mineral fertilisers. Thus, the study showed that thirty-nine years of experimental sewage sludge and compost applications of 15 and 58 t dm/ha/y resulted in a 2.5 fold increase for DL-PCBs as compared to control plots, whereas application of manure had no effect on the PCB content in the soil.

5.4.4 Conclusion on fate and soil concentrations

In summary, the information listed above shows that the PCB content in European soils is highly variable and that, generally, PCBs have half-lives ranging from months to years, depending on their level of chlorination. For conservative purposes, a half-life of 10 years can be assumed, acknowledging that in rare cases longer half-lives may have been observed for a few single persistent congeners. Various soil surveys have shown that with a few exceptions, soil PCB concentrations in the lower µg/kg range, i.e. 1-10 µg/kg, are typical throughout Europe. There is no indication of a consistently higher PCB concentration on arable land that may have received sewage sludge. On the contrary, some data show elevated PCB concentration in (mountainous) forests and urban areas compared to agricultural soils.

The two long-term studies above clearly show that elevated PCB concentrations have been observed in soils that historically received massive doses of highly polluted sludge from the 60´s to the 80´s where the PCB concentration in sludge presumably peaked. However, in the context of assessing the risk of current sludge application practises these studies prove less useful, as both the contamination level of sludge and the maximum allowable sludge load have been reduced markedly in the last couple of decades.

5.5 Bioaccumulation of PCB in soil biota

Bioaccumulation is a critical aspect of the environmental fate and behaviour of PCBs. PCBs accumulate in almost all organisms as a result of their high lipid solubility and slow rates of metabolism and elimination. These characteristics permit PCBs to accumulate to relatively high levels in for example marine food webs. The biomagnification is less dominant in the terrestrial food chain, although studies have reported high and critical levels of PCB in predators such as raptors (Helander et al. 2008). A number of bioaccumulation studies most relevant for the sewage sludge scenario are reviewed below in order to elucidate the potential of PCB to accumulate in plants and soil dwelling invertebrates. Whenever possible, the biota-to-soil accumulation factor (BSAF) is presented, which indicates the potential of an organism to accumulate PCB to internal concentrations that exceed those of their surroundings.

5.5.1 Bioaccumulation by plants

Sewage sludge is mainly used on arable land and grassland. Focus in this review has, therefore, been to elucidate the potential of PCB to be taken up by crop species and vegetables.

The Danish county Aarhus (Aarhus Amt 2005) measured a single sample of barley collected from sludge amended soils (see details in section 5.3.1 and 5.3.4). Among the three PCB congeners that were monitored in barley (77, 126 and 169), only PCB_{126} was detected in reliable concentrations according to the particular limit of quantification. The concentration in the barley was 0.0003 µg/kg dry weight. No PCB could be detected in the sludge amended soils. Hence, it seems plausible that the low level of detected PCB could derive from atmospheric deposition.

Iwata and Gunther (1976) studied the translocation of PCB from soil to carrots under field conditions. Aroclor 1254 was sprayed on the top soil of a sandy loam and subsequently ploughed into the soil to reach an estimated concentration of 100 mg/kg. Hereafter, carrots were grown in the soil under field conditions. Two non-specified congeners of PCB were detected in the carrot root corresponding to 30-50% and 3-4%, respectively, of the content in the soil. However, it is important to note that 97% of the PCB was found in the peel of the carrot. Carrot foliage contained only 1-6 % of the PCB residues in the soil.

Moza et al. (1979) studied the uptake of radio-labelled PCB in carrots and sugar beets under semi-field conditions. PCB_{31} (1.28 kg/ha) and PCB_{100} (1.12 kg/ha) were each applied to soil in a lysimeter-type box under outdoor conditions, and subsequently carrots were grown. In the following year, sugar beets were grown without further re-amendment of the soil. For PCB_{31}, only 32.5 and 28.8 % of the applied radioactivity was recovered after the first (carrots) and second (sugar beet) growth season. More than 88% of the PCB detected in soil was found in the top soil and hardly any vertical movement was observed. The loss of PCB was primarily due to volatilization, as less than 0.1% of the applied radio-labelled PCB was detected in the leeching water. The radioactivity in roots, leaves and weeds of the carrot was 9.4, 1.4 and 0.3% of the radioactivity measured in the soil. Uptake by sugar beets was far less, with only 0.8 % radioactivity measured in the roots compared to the soil. For PCB_{100}, the overall recovery was higher, i.e. 58.5 and 54.3 in year one and two. The radioactivity in roots, leaves, and weeds of the carrot was 2.4, 0.4, and 2.4 % of the radioactivity measured in the soil, i.e. at least three times lower uptake in roots and leaves compared to PCB_{31}. Only very small amounts of PCB_{100} were detected in the roots of sugar beets.

Weber and Mrozek (1979) studied the uptake of radio-labelled PCB residues in soybean and fescue plants grown in the greenhouse in a contaminated sandy soil. They observed that approximately 0.01% and 0.17% of the applied radioactivity was found in soya beans and fescue after 16 and 50 days of exposure.

Strek et al. (1981) continued the work of Weber and Mrozek (1979) by studying the bioaccumulation of PCBs in a wider set of crop plants, i.e. peanut (*Arachis hypogaea*), beet *(Beta uulgaris*), corn *(Zea mays*) and sorghum (*Sorghum bicolor*). Based on fresh weight, they found BSAF of 0.001, 0.003, 0.024 and 0.041 for corn, sorghum, peanut and beet, respectively. The exposure concentration was 20 mg/kg of PCB (Arachlor 1254).

Fries and Marrow (1981) studied the PCB movement from soil to soybean plants. Soybean plants were grown in soil spiked with three different PCBs (18, 52 and 101) spiked either to the surface or subsurface soil at soil concentrations in the range of 2-3 mg/kg. Plants were harvested after 52 days and divided into five parts for analysis: top stem, bottom stem, top leaves, bottom leaves, and seed pods. Detectable residues were found only in plants grown with surface-treated soil, with most of the residues confined to the lower leaves. Concentration of residues in plants increased with increasing chlorination of the PCB. There was little loss of radio-labelled PCB from subsurface applications, whereas 20-30% was lost by volatilization from the surface applications. It was concluded that plants grown on PCB contaminated soil would not be contaminated by root uptake and translocation, whereas some foliar contamination could occur from vaporisation.

Webber et al. (1994) conducted a field study of PCB-uptake in growing crops at sludge treated plots in Illinois, US. The plots received a one-time massive load of sludge at the rates of 785, 1570, 2240, 2800, and 3360 t/ha. Corn *(Zea mays* L.), cabbage (*Brassica oleracea capitata* L.), and carrot *(Daucus carota* L.) were grown on the sludge treated plots and plant samples were analyzed. Mean PCB concentration in the soils ranged from 1,300-2,900 µg/kg at the plot where corn was grown, and 1,500-3,700 µg/kg at plots where the vegetables were grown. There was no apparent consistency between sludge application rate and soil concentration. Mean PCB concentrations in the plant materials were, generally, less than 100 µg/kg dry wt, with the exception of carrot peel and –top, where up to 271 µg/kg dry wt were found. Tissue concentrations decreased in the order: carrot peels > carrot tops > cabbage wrapper and inner leaves > carrot core > corn ear leaf and stover > corn grain. Except for cabbage wrapper leaves, the PCB concentrations in plant materials were not related to those in soil. The BSAF for the various plant parts covers a range of 0.08 to 0.0008 for carrot peels and corn grain, respectively. Despite the very large rates of sludge application used in this study, the findings clearly indicated that uptake of PCB in crops grown on sludge treated land is very limited.

White et al. (2006) conducted a series of small and large pot trials in greenhouse and outdoors to assess the uptake of PCB in three cucurbits plant species and earthworms exposed to (weathered) PCB in soil at a concentration of 105 ± 7.8 µg/g Arochlor 1268. Regarding the small pot trials, measurable PCB-quantities were detected in all tissues of three plant species, with the highest concentration in the roots and decreasing amounts present in the stems and leaves. Within a specific tissue type, the PCB-content was not significantly different among the various plants. The PCB-content of the roots, stems, and leaves were 210 ± 79, 11 ± 0 4.3 and 7.0 ± 2.3 µg/g, respectively. When exposing the vegetables to PCB-contaminated soil in larger 70 kg bins, a different uptake pattern was observed. Zucchini accumulated significantly greater levels of PCB than all other species, with 430 µg/g in the roots and 22 µg/g in the stems. The study shows that under specific condition, BSAF higher than one may be observed for some vegetables, in this case zucchini.

Gosselin et al. (1986) studied PCB uptake in potatoes grown on sewage sludge soil (containing 1.52 ± 0.71 µg PCB/kg). Potato plant leaves and tuber pulp contained less than the detectable level (<0.007 µg/g), whereas potato peels contained 0.04 µg/g PCB, which corresponds to a BSAF of maximum 0.03.

Ye et al. (1991) studied the uptake of PCBs from soil in barley and tomato plants. The results indicated a lack of active transport of these compounds. However, plants readily trap airborne PCBs escaping from soil, and a good correlation between vapour pressure of PCBs and their concentration in plant tissue was observed. The concentrations were found to be highest in the leaves and lowest in the fruits, but as the soil PCB concentration was not provided, the BSAF cannot be calculated.

Dorn et al. (1996) observed the uptake of PCB in rye plants cultivated in pots with field soil artificially polluted by PCB. The rye plants grown in the PCB contaminated soils had accumulated higher levels of PCB compared to plants grown in the non-spiked field soil. The concentration of PCB in the roots, straw and grain of exposed and non-exposed was 0.78/0.06 mg/kg, and 1.04/0.85 and 0.29/0.27 µg/kg, respectively. Hence, a significantly increased uptake of PCB was only observed in the roots with a BSAF of 2.6 (0.78:0.3). The BSAF in the part of the rye plants that are edible for humans or husbandry was significantly below 1, i.e.0.003 for straw and 0.001 for grains.

Gan and Berthoex (1994) studied the crop uptake of PCBs from sludge-amended farmland in a five year field experiment. Eight different treatments with PCB contaminated sludge were included in the experiment. Four repeated plots received a one-time only application of PCB-contaminated sludge in the spring of 1986. Four other repeated plots received annual applications of contaminated sludge at the specified loading rates in each spring season from 1986 to 1990. Two levels of PCB concentrations in spiked sludge (25 and 75 mg/kg) were used. The low level PCB sludge was applied at two different rates, 2.5 and 7.5 t dm/ha/year, whereas the high level PCB sludge was applied at 0.8 and 2.5 t dm/ha/year. Data on the accumulation of PCB in corn grain and corn stover were available for the years 1986, 1988, 1989, and 1990. The PCB concentrations were higher for the stover than for the grain. This could be due to foliar adsorption of PCB, dust that was not washed off the stover, or sampling and analytical interferences. However, data shows that the crops grown on sludge treated plots did not have higher PCB concentrations than crops grown on the control plots. Data also showed that there were no differences due to PCB sludge concentration, sludge loading rate, sludge application pattern, or year. Hence, it was concluded that there was practically no uptake of PCBs into either corn grain or corn stover.

Javorska et al. (2011) studied the distribution of PCB in root vegetables grown in two different soil types spiked equally with seven PCB congeners to a nominal concentration of 100 µg/kg (700 µg PCB_7/kg). The experiment was carried out with carrot, parsley and red beet. Chemical analyses showed that the initial PCB_7 concentration of 643 and 616 µg/kg decreased to 340-389 and 347-398 µg/kg in the two soil types. The majority of accumulated PCB was found in the peels of the vegetables with the highest root concentration of 2,164 µg/kg found in parsley with PCB_{28} being the dominating congener. The concentration in the shoots of the vegetables ranged from 114 to 279 µg/kg. The percentage of the total PCB_7 found in the peel of the roots varied from 75% for red beet to 93 % for carrots. The observed uptake in parsley corresponds approximately to a BSAF of 3-4 in the peel of the roots and a BSAF of 0.19 for the shoots when based on the initial soil concentrations.

Kacálkova et al. (2011) investigated the accumulation of PCBs by the willow (*Salix* x *smithiana*), poplar (*Populus maximowiczii*), maize (*Zea mays* L.) and sunflower (*Helianthus annuus*) in a field experiment. The trees/plants were planted and grown on-site in contaminated urban soil in the vicinity of a former waste incineration plant in the Czech Republic. The concentration of PCB_7 was determined in soil from 11 sites in the area and ranged from 23.9 to1530 µg/kg. Two sites were chosen for plant growth studies, one with high PCB concentration (1530 µg/kg) and one with a much lower concentration (76.4 µg/kg). During the study period, the PCB content in the plants ranged from less than 5 to 129.5 µg/kg. The highest PCB amount was found in the roots of maize (49.5 µg/kg) and sunflower (129.5 µg/kg). The concentrations in stalks and leaves of maize were below the detection limit, whereas approximately 20µg/kg was detected in the leaves of sunflower. The aboveground parts of willow did not show detectable amounts of PCBs. Recalculated to BSAF, the highest was found in the roots of sunflower and maize (0.09 and 0.03), whereas the highest non-root BSAF was observed in leaves of sunflower (0.01).

Pavlíková et al. (2007) studied the composition of native vegetation on a PCB contaminated dumpsite in the Czech Republic. Furthermore, species variability in the accumulation of PCBs was investigated. The soil PCB content in the most contaminated part of the dumpsite reached 153,000 µg/kg dry soil. Low diversity of plant species was found on the dumpsite. Results showed that three different grass species comprised more than 90% of the total aboveground biomass at the most contaminated part of the dumpsite. The PCB content in *Festuca arundinacea* was the highest among the tested grasses (813.2 μg/kg dw, BSAF = 0.006), with PCB_{28} making up 69% of total PCB. PCB uptake by the two other dominating grass species was only 48.5 and 37%, respectively, of the PCB content found in *Festuca.* The BSAF for ten plant species and two tree species found in the highly polluted area ranged from 0.002-0.006.

Javorska et al. (2007) studied the accumulation and distribution of the seven PCB congeners (28, 52, 101, 118, 138, 153 and 180) in carrots grown in various soils types all spiked with 100 µg of each PCB congener per kg. Results showed that the PCBs were significantly higher in the edible parts of carrots compared to shoots. The highest concentration in carrot roots

(1280±130 µg PCB_7 kg^{-1}) was observed in the soil with the lowest organic matter content. These values can be recalculated to a BSAF of 1.8 when based on the sum of all seven PCBs.

5.5.2 Bioaccumulation by invertebrates

Beyer and Stafford (1993) monitored the uptake of PCBs in earthworms in nine confined disposal facilities bordering the Great Lakes, US. Earthworm species included in the study were *Lumbricus rubellus*, *Dendrodrilus rubidus*, *Eiseniella tetraedra*, *Aporrectodea trapezoides*, *Aporrectodea tuberculata*, *Lumbricus terrestris*, and *Allolobophora chlorotica*. Soil PCB concentrations, estimated as Aroclor 1254, ranged from below the detection limit of 100 to 1000 µg/kg dw, while earthworm concentrations in 15 out of 18 samples were below the detection limit. In the three remaining samples, tissue concentrations up 1800 µg/kg dw were measured, which corresponded to an average BSAF of approximately 3. Although these data were collected from species taken from contaminated soil and not from agricultural land, they may demonstrate the bioaccumulation potential of PCB in earthworms.

Krauss et al. (2000) studied the uptake of 12 PCBs from 25 field-contaminated soils by the earthworm *Lumbricus terrestris L.* The sum of the 12 PCBs in the collected soils ranged from 1.1 to158 µg/kg. After 30 days of exposure in the laboratory, the low chlorinated PCBs (8, 20, 28, and 52) showed average BSAF of 10, whereas the BSAF for the high-chlorinated was 1. The relatively low BSAFs of the high-chlorinated PCBs are confirmed by e.g. Hendriks et al. (1995), who found BSAF of 0.75 in field-sampled *L. rubellus* and by (Belfroid et al. 1995ab), who found BSAF well below one in the compost worm *Eisenia Andrei*, when exposed to either contaminated food or PCB polluted field soils.

Blankenship et al. (2005) conducted a series of field studies to determine the bioaccumulation of PCB congeners in the terrestrial food web of the Kalamazoo River flood plain in the US. Samples included soils, plants and several un-specified taxa of above-ground terrestrial invertebrates from two locations, a contaminated location and a close-by reference area. Mean concentrations of total PCB in samples from the contaminated area were 6.5 mg/kg (d.w.) for soils and 0.023, and 1.3 mg/kg (w.w.) for plants and depurated earthworms. The study reports the following range of biota-to-soil accumulation factors at the two locations: soil to plants 0.016-2.5, soil to terrestrial above-ground invertebrates 0.022-2.0, and soil to depurated earthworms 0.48-2.4, where the lower BSAFs were found at the contaminated location and the higher at the reference area.

White et al. (2006) conducted a series of small and large pot trials in greenhouse and outdoors to assess the uptake of PCB in earthworms exposed to (weathered) PCB in soil at a concentration of 105 ± 7.8 µg/g Arochlor 1268. Two separate species of earthworms, *E. foetida* and *L. terrestris*, were maintained in the PCB-contaminated soil for 14 days. After exposure, the PCB concentration of the whole organism tissues of *E. foetida* and *L. terrestris* were 13 and 16 µg/g, respectively. This corresponds to BSAF of approximately 0.1.

Paine et al. (1993) used laboratory and field studies to investigate bioaccumulation of PCBs in crickets exposed to contaminated soil. A 14-d laboratory soil bioassay with the house cricket *(Acheta domesticus)* showed that the mean whole body concentrations of Aroclor 1254 in exposed crickets were 11, 48, 92, 149, and 144 mg/kg when exposed to soil test concentrations of 100, 250, 500, 1,000, and 2,000 mg/kg, respectively. This corresponds to BSAF of 0.11, 0.19, 0.18, 0.15 and 0.07.

Matscheko et al. (2002) analysed soils from five Swedish agricultural sites, three research sites, and two privately owned farms for PCB. For each plot, a suitable reference site was chosen. The impact of adding 1 to 3 tonnes of sludge (DM) per hectare per year over a twenty-year period on the soil concentrations of PCB was studied at the three research sites. No information about the level of PCB in the used sludge was available. In soils that had not received sludge (reference soils), the sum of six different penta- and hexa-PCBs ranged from 0.45 to 1.4 µg/kg DM, compared to 0.45 to 3.0 µg/kg DM in the sludge treated soils. Accumulation of PCB in earthworms from the five sites was also investigated. The BSAF varied for the various PCB congeners from 0.4 to 11 at the reference sites, and between 0.6 and 18 at the site receiving sewage sludge.

Jager et al. (2005) studied the accumulation of PCB in two species of earthworms in the laboratory and in field collected earthworms. They collected soils from three different plots within a contaminated site in Rotterdam, The Netherlands. Site 1 is the reference-site located within a polder, but with clean soil being put on top. Sites 2 and 3 are within the most polluted part of the polder. Site 2 and 3 are comparable in their metal, PCB, and PAH content, but site 2 has much higher levels of hexachlorobenzene and, especially, dieldrin. The concentration of the 8 PCBs measured ranged from below the detection limit to 0.7 µg/kg at the reference site, to 14-120 µg/kg at site 2, and 15-110 µg/kg at site 3. It is, therefore, relatively unlikely that the strong adverse effects observed in earthworms exposed to soil, especially from site 2, could be attributed to the PCB level. The BSAF for the surviving earthworms was generally shown to fall within the range of approximately 0.5-3.0 for the various PCB congeners, earthworm species and locations, with one exception among the 20 data points, where the BSAF reached approximately 8.

Larsen et al. (1992) studied the 48 h uptake of PCB in the earthworm (*Lumbricus rubellus*) from a soil contaminated with a commercial PCB formulation (Askarel at 150 mg kg^{-1}) and their elimination over 60 days in a low contaminated soil (15 mg kg^{1}). 17 individual congeners were monitored. The uptake and the elimination rate were similar for all PCB congeners notwithstanding their different chloro-substitution pattern, which suggested that bioaccumulation of PCBs in earthworms is governed by passive, possibly diffusion controlled processes. The equilibrium state in the three-phase system, soil/soil water/earthworm was reached with a half-time around 3-4 days. The soil to earthworm bioaccumulation factor ranged from 4 to 20 for the tetra- to octa-chlorinated biphenyls and was (weakly) correlated to the octanol-water partition coefficient (K_{OW}).

Wågman et al. (2001) studied the dietary uptake and elimination of 20 PCBs in earthworms. The PCBs were selected to cover a wide range of physicochemical properties. The uptake efficiencies from the contaminated food applied to the worms were between 10 and 68%. The PCBs that were eliminated fastest contained few chlorine atoms, had more polar characteristics, and were sterically hindered. Slowest was the elimination for less polar PCBs with six or seven chlorine atoms. Elimination half-lives varied between 6 and 25 d. The BSAF for the PCBs averaged 0.1 (range: 0.05-0.22) when based on lipids and 0.04 (range: 0.02-0.08) when based on weight.

Wågman et al. (1999) used three indoor household composts and their native earthworms to study the uptake of PCB. The levels of PCBs found in the composts were 32, 120 and 440 µg/kg (dry weight), whereas the mean concentrations of three earthworms collected from each of the three composts were 23, 129 and 290 µg/kg (wet weight). As the water content of the three composts was given as 67, 74 and 69%, the concentrations in the compost can be recalculated to wet weight basis, i.e. 97, 462 and 1,419 µg/kg wet weight. Hence, on a wet weight basis the compost-to-earthworm bioconcentration factors were all below 1, i.e. 0.33, 0.26 and 0.31.

Vermeulen et al. (2010) investigated the bioaccumulation of PCB in a terrestrial food chain, i.e. a soil–earthworm-hedgehog food chain, in a number of Belgian residential parks. Concentrations of 10 PCB congeners were measured in soil and earthworms collected in grassland and open woodland and in hair and blood of hedgehogs foraging in two parks. The background concentrations in soil ranged from 2.3 to 6.5 µg/kg for PCB, and the BSAF for earthworms ranged from 0.78-2.76. The BSAF decreased with increasing soil concentrations, suggesting that steady-state equilibrium was not reached in soil or earthworms. Hair from hedgehogs was used as a potential biomonitoring tissue for animals higher up in the food chain. However, no significant relationship between PCB concentrations in earthworms and hair or blood from hedgehogs was established, possibly due to variation in individual foraging behaviour and uptake rates.

5.5.3 Conclusion on bioaccumulation

Numerous studies covering a wide span of wild plants, crops, vegetables and trees have almost exclusively demonstrated a plant-to-soil accumulation ratio typically one or two orders of magnitude lower than one. An exception to this may be peels of root vegetables like carrots, where higher BSAF may be observed under certain conditions. Furthermore, vaporisation of the lower chlorinated PCB from the soil surface to plant leaves has been observed as well. The translocation of PCB within the plants to e.g. grains or fruits will, however, be inferior.

The accumulation of PCB in earthworms are somewhat higher than for plants, with biota-to-soil accumulation ratios typically found in the range of less than one to maximum 20 in rare cases. There are a few studies available, which may indicate a potential for accumulation of PCB in terrestrial food chains like earthworms-rodents-raptors, although the magnitude of biomagnification is far from the scenarios reported in marine food chains.

5.6 Ecotoxicity of PCB to plants and soil fauna

Compared to the relatively large attention paid to the environmental properties of PCB, a limited set of soil-relevant ecotoxicity data is available. Furthermore, a major part of the data is of older age.

5.6.1 Soil dwelling species

Weber and Mrozek (1979) studied the effects of PCB residues in soybean and fescue plants grown in the greenhouse in contaminated soil. Analytical grade PCB (Aroclor 1254) was thoroughly mixed with sand at rates 0, 1, 10, 100, and 1000 mg/kg. PCB applied to the soil significantly inhibited height and fresh top weight of soybean plants with up to 27 % and fescue with up to 16 % at the high application rates (100 and 1000 mg/kg). Malformation (twisting and curling) of newly developing leaves was also observed on plants grown in soil with 1000 mg/kg. The two lowest rates of PCB were seemingly stimulatory for fescue, but slightly inhibitory for soya (3-11% reduction), although the effects were not significantly different from the untreated controls.

Strek et al. (1981) continued the work of Weber and Mrozek (1979) by studying the phytotoxicity and uptake of PCB's in a wider set of crop plants, i.e. soybean (*Glycine max*), beet *(Beta uulgaris*), corn *(Zea mays*) and sorghum (*Sorghum bicolor*). Effects on growth parameters were followed at soil concentrations from 1 to 1000 mg PCB/kg. Growth parameters evaluated at harvest showed no apparent inhibition of corn *(Zea mays*) and sorghum (*Sorghum bicolor*) by PCB. Soybean was harvested two times with differences in response between the two harvests. The first cropping revealed no significant difference due to PCB treatment in any of the treatments, although the growth reduction was 22% at the highest test concentration. In the last cropping, soybean heights were significantly lower at all levels of PCB, with effects levels between 18 and 29%. However, no clear dose-response was observed, as the lowest effect was observed at the highest test concentration. The effects on beets were more pronounced. By 14 days, beet foliage height was inhibited by 63% at the 1000 mg/kg rate, increasing to 73% by 28 days and finally to 100% with the death of the plants between 28 and 56 days. Top fresh weight was reduced to nearly 100% after 28 days of growth in 1000 mg/kg with only one plant out of six surviving. Based on these results, a no-effect level for crop plants could be established at 10 mg/kg.

Fries and Marrow (1981) showed that the average heights and weights of soybean plants exposed to PCB concentrations ranging from 2.08 to 3.69 mg/kg did not differ significantly from the controls.

Dorn et al. (1996) observed the effects of PCB on rye plants cultivated in pots with field soil artificially polluted with various pollutants (PCB, PAH and heavy metals). No effects on the yield of rye were observed in pots artificially contaminated with PCB 52 at a concentration of 0.3 mg/kg.

Paine et al. (1993) used laboratory and field studies to investigate toxicity and bioaccumulation of PCBs in crickets exposed to contaminated soil. A 14-d laboratory soil bioassay with the house cricket *(Acheta domesticus)* yielded an LC50 of 1,200 mg/kg of Aroclor 1254. LOEC and NOEC were 100 and 500 mg/kg, respectively. A whole body concentration of about 150 mg/kg appears to be a threshold concentration above which acute mortality is likely to be observed. Mean whole body concentrations of Aroclor 1254 in exposed crickets were 11, 48, 92, 149, and 144 mg/kg for soil test concentrations of 100, 250, 500, 1,000, and 2,000 mg/kg, respectively. This results in BSAF between 0.072 and 0.19.

Parmelee et al. (1997) used soil microcosms to investigate the toxicity of Aroclor 1254 to trophic groups of soil nematodes and to the microarthropod community. Aroclor 1254 had a greater negative impact on microarthropods than on nematodes. Total microarthropod abundance declined by 87% at a nominal test concentration of 2,500 mg/kg (extractable concentration of 1,496 ± 127 mg/kg at day 7 when samples were taken). The prostigmatid and oribatid mites showed the highest sensitivity among the microarthropods. No significant effects were observed at an exposure concentration of nominal 500 mg/kg (extractable concentration of 385 ± 22 mg/kg at day 7 when samples were taken). Effects on nematodes were not statistically significant, although a 25% reduction was observed at the highest exposure concentration.

Leupromichair et al. (2002) studied the contribution of earthworms to bioremediation of PCB contaminated soil using the earthworm *Pheretima hawayana* alone or in combination with the PCB-degrading bacteria. The test cylinders contained 100 mg/kg of Aroclor 1242, and the test duration was 9 weeks of treatment. The results suggest that earthworms facilitate PCB bioremediation by enhancing the dispersal of PCB-degrading bacteria in the columns as well as providing environmental conditions that favour the growth and activity of indigenous PCB-degrading bacteria. Although not a toxicity study, the publication shows that earthworms apparently are tolerant of up to 100 mg/kg of PCB, as no mortality was reported.

Paine et al. (1993) cited Rhett et al. (1988) for mortality data published in an internal report. Rhett et al. reported an LC50 of 240 mg/kg in soil (wet weight) for the earthworm, *Eisenia foetida,* following 14 d of exposure to Arochlor 1254. The LC50 was associated with whole-body concentrations of 930 mg/kg PCB in earthworm tissue (ww.), whereas the tissue related NOEC for growth was below 520 mg/kg ww.

Debus and Hund (1997) studied the toxicity of PCB 52 in soils using tests with several representative soil organisms (plants, nematodes, soil algae, microorganisms). The test concentrations were 50 and 500 mg/kg. At the lowest test concentration, no significant effects were observed on days 0 and 14. On day 56, however, an effect was registered on the plants and on one nutrient type of nematodes. At the highest test concentration, effects on the microorganisms occurred at all three sampling points, and on day 56 an adverse effect was also demonstrated in the plants and in one nutrient type of nematodes.

Wilke and Braütigam (1992) studied the effects of the PCB congeners 5, 8, 29 and 77 as well as two technical (Arachlor) PCB formulations on soil microbial activity. Microbial toxicity was measured by means of long-term respiration (CO_2-evolution) and short-term respiration (CO_2-evolution 12 h after addition of glucose). One mg/kg of PCB_5 and PCB_8 reduced the long-term and short-term soil respiration after 35 and 28 days, respectively, whereas 10 times more of PCB_{20} was needed to obtain the same effect. PCB_{77} did not adversely affect the soil respiration. The technical PCB mixtures reduced the long-term respiration only after high additions of 50 mg/kg or 100 mg/kg, with Arochlor 1242 being more toxic than Arochlor 1260.

5.6.2 Aquatic and sediment species

As relatively few terrestrial ecotoxicity studies are available, a recent study regarding the toxicity of PCB to sediment dwelling species has been included in this review.

Fuchsman et al. (2006) conducted an in-depth evaluation of PCB aquatic toxicity and organic carbon partitioning in order to predict sediment effect concentrations using the equilibrium partitioning (EqP) approach. This evaluation was limited to invertebrate toxicity data because PCBs toxicity to invertebrates and fish was expected to occur via different toxicological mechanisms. As a result of differences in organic carbon partitioning among PCBs of differing chlorination levels, the estimated EqP benchmarks increased with increasing degree of chlorination for various PCB mixtures. They, therefore, suggested the following sediment benchmarks based on organic carbon:

Arcolor 1242: 210 ug/g OC,
Arcolor 1248 490 ug/g OC,
Arcolor 1254 1500 ug/g OC,
Arcolor 1260 3800 ug/g OC,

Assuming that the sediment dwelling invertebrate species (or actually pelagic invertebrates, as the sediment benchmarks are based on toxicity data from this group of species) have the same sensitivity as soil dwelling invertebrates and that the organic carbon content of soils is 2 %.(20g OC/kg soil), then the following soil-related benchmarks can be estimated:

Arcolor 1242: 4.2 mg/kg
Arcolor 1248 9.8 mg/kg
Arcolor 1254 30.0 mg/kg
Arcolor 1260 76 mg/kg

5.6.3 Summary of ecotoxicity data

Ecotoxicity data has been identified for at least three trophic levels in soils, i.e. microorganisms, plants and invertebrates. Effects of specific single congeners have been observed down to 1 mg/kg, whereas effects of mixtures of PCB start at least one order of magnitude higher.

5.7 Provisional risk assessment of PCB in sludge

Based on the data presented in Sections above, a provisional risk assessment for the terrestrial environment can be conducted.

The risk is assessed by comparing the predicted soil exposure (predicted environmental concentration – PEC) with the predicted level in soil where no effects are observed or anticipated (No Observed Effect Level – NOEL). The ratio between PEC and NOEL indicate the so-called margin of safety, which essentially is the reverse of the more common “risk quotient” utilised in many risk assessments. As all exposure scenarios cannot be foreseen and all soil dwelling species cannot be tested, a certain margin of safety is needed in order to conclude that significant effects of PCB in sewage sludge would be unlikely. Based on the amount of data available, the margin of safety should fall within a range of at least 10 to 1000 in order to be in line with the use of assessment factors in the REACH programme in the European Union and described in the Technical Guidance Document for risk assessment of new and existing chemicals.

5.7.1 Predicted soil concentration

The PEC_{soil} at steady state, i.e. the time where input equals out-put, is calculated according to the guideline outlined in the REACH programme (see chapter 1 for details) using the following input parameters:

Load of sludge = 3 t dm/ha/y
Sludge concentration = 0.071 mg/kg [13]
Log Koc = 5.3 (Hansen et al. 1999)
Half-live = 10 years
Initial background concentration in soil = 0.37 µg/kg [14]

Based on the assumptions above, the following PEC values can be calculated:

PECss = 6.8 µg PCB/kg

A steady state based PEC_{soil} of 6.8 µg/kg is at the upper range of what is reported in EU for soils outside specific contaminated areas, and especially for agricultural soils (see Section 5.4.3), which have normal application rates of sewage sludge.

5.7.2 No Observed Effect Level (NOEL)

The number of ecotoxicity studies with PCB are relative sparse and primarily published a decade or two ago. Most of the plant studies show no significant adverse effects of PCB mixtures at test concentrations up to approximately 10 mg/kg. Earthworms and other soil dwelling invertebrates are apparently relatively insensitive to PCB, with LC50 values or lowest observed effect concentration in the range of 100 mg/kg. Regarding microorganisms or microbial processes, effects of individual congeners have been observed down to 1 mg/kg, whereas 50 or 100 times more were needed in order to obtain the same effect if PCB was dosed as a mixture in a technical formulation. As no PCB congeners are likely to be found alone, 50 mg/kg would be considered a realistic exposure concentration of PCB causing (transitional) effects on the microbial community. Based on these results, a no observed effect level for PCB for soil microorganisms would be 50 mg/kg.

5.7.3 Margin of Safety

The lowest soil concentration where no effects on soil dwelling biota (plant growth) were observed is 10 mg/kg. From the available studies, this soil concentration does not seem to cause effects on soil fauna or soil microorganisms and is, therefore, adopted as a NOEL for all soil dwelling species. This correspond relatively well with the ecotoxicological benchmark for soils (4.2-76.0 mg/kg) recalculated from published benchmark for sediments presented above (Fuchsman et al. 2006).

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[13] The 95% Percentile from a recent Danish dataset of 62 sludge samples (see above)

[14] The concentration measured in a Danish agricultural soil after 25 years of normal sludge application (Vikelsø et al 2002)

Based on a comparison between the predicted concentrations in soils after sewage sludge amendment and the lowest test concentration where no significant effects were observed,a margin of safety (PEC/NOEL) can be estimated as follows:

PEC = 6.8 µg/kg
NOEL = 10,000 µg/kg
MoS = 1,470

In light of the current use of uncertainty factors, i.e. in the REACH risk assessment framework, a margin of safety exceeding 1,000 would be sufficient to conclude that that the current level of PCB in Danish sludge is most likely of no risk to soil dwelling organisms.

5.7.4 Comparison with established soil quality criteria and soil screening levels

A wide number of countries have established soil quality criteria (SQC), a.k.a. soil screening levels, soil quality objectives or benchmarks for PCB. These are typically based on human health considerations and include for example the risk for direct intake of soil by soil-ingesting children. Hence, these are not directly usable for an evaluation of potential environmental risks. For comparison, however, some of these are listed in Table 5.7. A comparison of these SQCs for PCB in soils reveals that the estimated soil steady state concentration after repeated sludge application of 6.8 µg/kg approaches the lowest SQC in Sweden and Norway, but is significantly below those reported for the other countries and WHO.

Table 5.7. A list of published soil quality criteria, a.k.a. soil quality objectives, maximum permissible soil concentrations, target values etc. for a wide set of countries.

Country	SQC (µg/kg)	Subset of PCB	Land use
Canada[15]	500	Total	Agricultural land
Finland[16]	100	PCB_7	Not land-use specific
Germany[17]	200	PCB_6	Grassland
Norway[18]	10	PCB_7	Clean soil for all uses
Sweden[19]	8	PCB_7	Sensitive land uses
The Netherlands[20]	20	PCB_7	Not land-use specific
WHO[21]	890	Not specified	Agricultural land

5.8 Summary and Conclusions

There are no indications that the current level of PCB identified in Danish or most European sludge would pose a risk to soil ecosystems even after numerous applications of sewage sludge to farm land if dosed at normal rates to fulfil the nutrition need of the crop systems. PCB levels in soils high enough to cause ecotoxicological concern for soil dwelling invertebrate species or plants have only been observed in cases where massive application of contaminated sludge has taken place for decades. The low potential for PCB in soil to move to the edible part of most crops has been demonstrated in numerous studies. PCB may, to some extent, move from the soil into the peels of the roots of e.g. carrots and sugar beets, but translocation within the plants has been found to be insignificant. However, even in roots the biota-to-soil ratios are typically below 1. Soil ingesting earthworms may accumulate some PCB congeners with biota-to-soil ratios that may reach 20. Evaporation from the surface of the soil of some of the less chlorinated PCB to above ground parts of plants has been observed as

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[15] CCME 1999
[16] Statsrådet (The Assemply of the Finnish Constitution) 2007
[17] BBodSchV (1999)
[18] Langedal 2007
[19] Naturvådsverket. 2009
[20] VROM 2000
[21] Chang et al (2002) for the World Health Organisation (WHO)

well, but agricultural practises like those in Denmark with mandatory incorporation of sewage sludge into the soil shortly after spreading will help to minimise this.

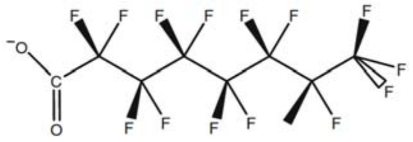
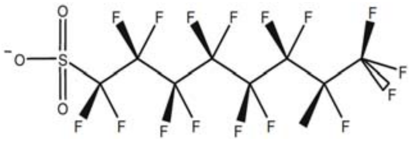
The provisional risk assessment presented in this report, therefore, shows that the current level of PCB found in Danish sludge is very unlikely to pose any long term risk to the terrestrial ecosystems in agricultural soils.

6 Perfluorinated compounds

6.1 Introduction

Perfluorinated compounds (PFC) form a group of organic compounds, which consists of a fluorinated carbon chain and at least one different atom or functional group. The most common PFCs are perfluoro-alkyl carboxylates (PFAC) and perfluoro-alkyl sulfonates (PFAS), which are characterised by a perfluorinated alkyl chain and a terminal carboxylate or sulfonate group, respectively. Thus, PFAC and PFAS comprise a wide variety of alkyl chain lengths, but there are two compounds that usually occur in higher concentrations in the environment than other PFCs. These are PFOS (perfluoro-octane-sulfonate) and PFOA (perfluoro-octanoate) (Table 6.1) and, accordingly, they dominate the available literature on PFCs in the environment and humans. See Table 6.1 for information on PFOS and PFOA. PFOS is believed to be the ultimate degradation product of several widely used PFCs (Giesy et al. 2010).

Table 6.1. Physical-chemical properties and structure of PFOA and PFOS.

Parameter	**Value**	**Reference**	**Structure**
Melting point		OECD (2002)	**PFOA**  **PFOS** 
PFOS	≥400°C		
Boiling point	n.a.		
Vapor pressure			
PFOS	3.31×10^{-4} (Pa, 20°C)		
Water solubility			
PFOS	12.4 – 570 (mg/l)		
Log K_{OW}	n.a.		
Log K_{OC}	2.1	Higgins & Luthy (2006); Johnson et al. (2007)	
PFOA	2.4 – 3.1		
PFOS			
K_D[1]	1.1 – 1.8	Enevoldsen & Juhler (2010); Beach et al. (2006)	
PFOA	2.8 – 40		
PFOS			

[1] *Depending on soil type*

Other PFCs in this group are homologues of PFAC and PFAS and derivatives such as perfluorooctanesulphonyl fluoride (POSF), amines, amides, carboxylates and perfluorooctane sulphonamide (PFOSA). Such compounds often serve as precursors for PFAC and PFAS (Gisey et al. 2010). PFOA includes the anion and salts of perfluorooctanoic acid.

PFOS has been designated as a Persistent Organic Pollutant under the Stockholm Convention. This designation requires that usage must be phased out, but some uses are allowed to continue until suitable alternative products are available.

6.2 Use and consumption

PFOS salts are a component of fire-fighting foam concentrates, while PFOA is primarily used as an emulsifier in industrial applications, for example in the production of fluoropolymers, such as polytetrafluoroethylene (PTFE). In addition, PFAC and PFAS can exhibit both lipophobic and hydrophobic properties, making them useful for stain resistance in a wide variety of products, i.e. textiles and food packing.

In 2011, the OECD (OECD 2011) published the results of a 2009 survey of the production and use of PFOS and (PFOA), as well as related substances and products/mixtures containing these substances. It was found that products containing PFOS and related chemicals are still imported and/or manufactured within the OECD, and that products containing perfluorinated chemicals continue to have a wide range of uses, including metal plating, semiconductors, anti reflective coatings for photolithography processes, tubing / pipe liners / cable insulation, lubricants, and many others (Table 6.2).

Table 6.2. Estimated use of PFOS related chemicals in the EU in 2004 (OECD 2005)

Use	**Annual Tonnage in the EU**
Metal plating	10
Photographic Industry	1
Semiconductor Industry	0.5
Aviation Industru (hydraulic fluids)	0.73
Fire Gighting Foams	122

6.3 PFC levels in sewage sludge

6.3.1 The level of PFC in Danish and Scandinavian sludge

In a Danish study, Bossi et al. (2008) reported PFOS and PFOA in sludge samples from six waste water treatment plants (WWTP) at concentrations ranging from 4.8 to 74.1 and from 3.4 to 19.7 µg/kg dry weight, respectively. PFHxS was also found in sludge samples with concentrations ranging from 0.4 to 10.7 µg/kg dry weight.

In a monitoring programme, 15 sewage sludge samples from six Nordic countries were analysed for perfluorinated alkylated substances (PFAS) (Kallenborn et al. 2004). Indications of surprisingly high variability in sewage sludge were found across and within the various Nordic countries. The lowest contaminated sewage sample was from Finland with sum concentrations of PFAS between 0.15 – 2.52 µg/kg wet weight. For the other Nordic countries, the concentrations ranges were: Sweden 0.17 – 3.79; Norway 1.05 – 1.65, Iceland ~0.23; Faroe Islands approximately 1.68, and Denmark between 0.65 and 1.50 µg/kg wet weight. PFOS and PFOA were the predominant PFAS residues in sludge samples. However, in the Finnish sludge samples, PFHxA also contributed significantly to the total PFAS burden. The highest concentrations of PFOS and PFOA in the Danish sludge samples were 1.04 and 0.68 µg/kg wet weight, respectively (Kallenborn et al. 2004).

Sweden has a national monitoring programme of hazardous substances in sewage sludge which includes PFC (Haglund and Olufson, 2010). In 2009, the average concentrations of PFOS and PFOA in sludge from eight different WWTP were 15.9 (1.6-37.4) and 4.9 (0.87-23.9) µg/kg dry weight, respectively. Generally, the concentrations had been stable over the last five years, but with a small tendency to a decline.

6.3.2 PFC in sludge across the world

As seen in Table 3, the concentrations of PFOA and PFOS observed in activated and digested sludge range from below the detection limit to 1,875 and 2,615 µg/kg, respectively.

In their supportive information, Washington et al. (2010) reported the level of PFOA in sludge from a WWTP in Alabama, US. Waste-stream sources to this WWTP included industries that work with fluorotelomer compounds. Sludge from the sampling period (2004-2006), therefore, had PFOA concentrations ranging from below the detection level to1,875 µg/kg. However, in 2007 and 2008, where the abovementioned industries no longer discharged their wastewater to the WWTP, the concentration ranges had decreased to 27-128 µg/kg.

Yoo et al. (2009) reported PFOA concentrations between 8 and 20 µg/kg in sludge samples from New York City. In the study of Loganathan et al. (2007), contamination profiles of perfluorinated compounds (PFCs), including perfluoroalkyl sulfonates (PFASs; PFOS, PFOSA, PFHxS) and perfluoroalkyl carboxylates (PFACs; PFOA, PFNA, PFDA, PFDoDA, PFUnDA), were determined in sludge samples collected at a rural WWTP in Kentucky, U.S., and an urban WWTO in Georgia, U.S. PFOS was a major contaminant in samples from the rural WWTP with concentrations ranging between 8.2–990 µg/kg dry wt followed by PFOA ranging between 8.3–219 µg/kg dry wt. In the urban WWTP, PFOA was the predominant PFC with concentrations from 7.0–130 µg/kg dry wt followed by PFOS with concentrations from <2.5–77 µg/kg dry wt. Furthermore, PFHxS, PFNA, PFDA, and PFOSA were detected in most of the samples, whereas PFUnDA and PFDoDA were detected only in very few samples.

Sinclair and Kannan (2006) measured concentrations of several PFCs in sludge from two waste water treatment plants (WWTPs) in New York State. A pattern was observed in sludge samples, in which the relative dominance of PFOA decreased compared to the wastewater composition, whereas PFDA and PFUnDA increased, suggesting preferential partitioning of longer-chain PFCAs to sludge. The median concentration and ranges in sludge from the two WWTPs were 28 (26-65) and 32 (<10-34) µg/kg for PFOS and 134 (69-241) and 80 (18-89) µg/kg for PFOA.

Generally, the highest concentrations of PFC were observed in sludge from U.S.A. as shown above, but a survey from the Baden-Württemberg region in Germany (UBW 2009) also revealed high concentrations. The mean concentration of PFOS among the 61 WWTP sampled was 271 µg/kg. Four of the 61 WWTPs had concentrations of PFOS above 1000 µg/kg. Although the concentrations are high compared to other countries, the results of this study represent a decrease in concentrations compared to previous years.

A Swiss study investigated one sludge sample from 20 different WWTPs and found a large variation in the concentrations of PFOA and PFOS, the latter being significantly higher (20 – 600 µg/kg) than the former.

6.3.3 Conclusions on PFC levels in sewage sludge

The information gathered shows that PFCs are often identified in sludge when looked for, but also that the concentrations are generally low, i.e. in the lower µg/kg range. Recent studies from Germany and USA have, nevertheless, shown higher levels up to the mg/kg range, typically in areas were PFC production occurs. The only study in Denmark (Bossi et al. 2008) showed sewage sludge concentrations comparable to other Nordic countries, i.e. in the lower µg/kg range. For risk assessment purposes in this report, the highest reported concentration in Denmark of PFOS and PFOA have been used, i.e. 74.1 and 19.7 µg/kg, respectively.

Table 6.3. International data on occurrence of PFC in sludge from WWTPs.

Country	**Region**	**Year**	**No. of samples**	**Sludge type**	**Measured compound**	**Concentration µµg/kg**		**Reference**
						Mean	Range	
Denmark	Not specific	2004 – 2005	7 WWTPs	Not reported	PFOA PFOS		3.4 – 19.7 4.8 – 74.1	Bossi et al. (2008)
Nordic	6 nordic countries	~2003	15 samples 6 countries	Not reported	Total PFC		0.15 – 3.8[2] 0.6 – 15.2[3]	Kallenborn et al. (2004)
Sweden	Not specific	2007	1 from each of 8 WWTPs	Not reported	PFOA PFOS	3.6[1] 32.6[1]	< 0.6 – 16.3 < 10 – 54.8	Haglund and Olofson (2008)
		2008			PFOA PFOS	3.5 21.3	0.86 – 13.7 3.8 – 45.8	Haglund and Olofson (2009)
		2009			PFOA PFOS	4.9 15.9	0.87-23.9 1.6 - 37.4	Haglund and Olofson (2010)
Germany		2008	1 from each of 61 WWTPs	Not reported	PFOS	271	14 – 2,615	UBW (2009)
Switzerland	Zürich	2008	1 from each of 20 WWTPs	Digested and dewatered sludge	PFOA PFOS		<LOQ – 20 20 – 600	Sun et al. (2011)
USA	New York State	2005	5 from each of 2 WWTPs	`Combined´ sludge samples	PFOA PFOS	70 – 144 25 – 37	18 – 241 <10 – 65	Sinclair and Kannan (2006)
	Kentucky, Georgia	2005	> 3 from each of 2 WWTPs	Return activa-ted sludge, Dewatered	PFOA PFOS		8.3 – 219 8.2 – 993	Loganathan et al. (2007)
	New York City	Not reported	4 from each of 3 WWTPs	Not reported	PFOA PFOS	8 – 20 32 – 77		Yoo et al. (2009)
	One WWTP, Alabama	2004 – 2006	4 – 6 samples per year	Not reported	PFOA		<LOD – 1,875	Washington et al. (2010)
		2007 – 2008			PFOA		32 – 128	

[1] In case of values below LOD (PFOA = 0.6 and PFOS = 10), LOD was used in the calculation of the mean value. [2] uµg/kg wet weight. [3] uµg/kg dry weight, assuming that sludge samples had a water content of 75%.

6.4 Fate and behaviour of PFC in soil

6.4.1 Soil degradation

Perfluorinated compounds show high thermal, chemical and biological inertness (Parsons et al. 2006). The carbon-fluorine bond is the strongest existing covalent bond (450 kJ/mol). The strength of this bond is believed to be the main factor limiting the biodegradation of PFC. The published information on biodegradation of PFC is very limited, but although some data indicates at least a partial transformation of PFOS and PFOA, a full mineralisation has not been reported yet, which may indicate that the C-F bond is almost microbially inert in the environment. However, enzymatic hydrolysis of the C-F bond has been observed in bacteria (Murphy 2010).

Washington et al. (2010) reported the fate of PFC in agricultural soils, which had received sludge generated at a wastewater treatment plant (WWTP) in Alabama, US for more than a decade. The half life (DT50) for perfluoroalkylates disappearance (not the same as degradation) ranged from 1 year for the C6 to 3 years for the C11 alkylates.

6.4.2 Adsorption to soil and leaching

PFOS appears to adsorb to soil, sediment, and sludge with a range of distribution coefficients (*K*d) in soils between 9.7 L/kg (clay loam) and 35 L/kg (sandy loam) (Beach et al. 2006). Once adsorbed to these matrices, PFOS does not readily desorb, even when extracted with an organic solvent as illustrated by desorption Kd values ranging from 15.8 to 47.1 L/kg in three different soil types (Beach et al. 2006).

When measuring the presence of organic contaminants in tile drainage water following application of liquid and solid municipal biosolids to agricultural fields, ten different PFCs were detected (Gottschall et al. 2010). However, only PFOA and PFOS could be found in concentrations above the detection limit (10 ng/l) in the tile drains. Maximum concentrations observed were 17 and 12 ng/l for PFOS and PFOA, respectively. The expected concentrations in the applied sludge were 80 – 600 µg/kg, which is comparable to the concentrations generally observed in U.S.A., but generally higher than what is found in the Nordic countries (Table 6.3).

6.4.3 Soil concentrations

Washington et al. (2010) reported the concentration of PFC in agricultural soils, which for more than a decade had received sludge generated at a WWTP with elevated concentrations of perfluoroalkylates (PFAs) in Alabama, U.S. (Table 6.3). Soil samples from sludge-applied fields had much higher concentrations of PFAs compared to samples taken in nearby fields without sludge applications. The highest concentrations found were perfluorodecanoic acid (990 µg/kg), perfluorododecanoic acid (530 µg/kg), perfluorooctanoic acid (320 µg/kg), and perfluorooctane sulfonate (410 µg/kg).

Findings of high concentrations of PFCs in surface and drinking water in Germany (Skutlarek et al. 2006) resulted in an extensive monitoring programme to identify the source and elucidate the level of pollution in soil, surface and drinking water (LANUV, 2008 cited from Asselt et al. 2011). This monitoring programme showed that the source of the PFC contamination, in this case, was the widespread use of soil conditioner, which had been mixed with industrial waste. A situation similar to the one reported in the US by Washington et al. (2010) (see above). In the German case, the State of North Rhine Westphalia initiated a temporary soil monitoring programme including the analyses of 916 samples from fields, which were suspected to be polluted. Despite the known use of sewage sludge, the PFOA and PFOS remained below detection in 57 % of the samples (Asselt et al. 2011), whereas one third of the samples contained levels above the detection limit, but remained below 100 µg/kg. Another 8% of the samples had levels between 100 and 500 µg/kg. The highest levels (>1500 µg/kg) were found on two farms, which subsequently have been sanitized. Analyses of 199 soil samples from non-contaminated areas in Bayern in Germany all showed PFOS levels below 10 µg/ kg (LfU, 2007, cited from Asselt 2011).

6.4.4 Conclusions on fate and soil concentrations of PFC

PFOS and other PFCs adsorb strongly to the soil matrix and, consequently, leaching is limited. A number of PFCs have shown very strong persistence in the environment, with half-lives frequently reported in a time frame of years. Generally, the reported concentrations in soil are relatively low, with the exception of a few cases in for example Germany, where long term deposition of highly polluted sludge has resulted in soil concentrations above 1 mg/kg.

6.5 Bioaccumulation of PFC in soil biota

The vast majority of data regarding bioaccumulation of PFC in biota have been taken from the aquatic environment, primarily in the marine food web including fish eating mammals and birds where bioaccumulation has been documented. For the terrestrial compartment, far less information is available, as shown below.

6.5.1 Bioaccumulation in plants

Only limited data are available for uptake of PFOS into terrestrial plants or soil dwelling animals. Beach et al. (2006) summarised a study where seven plant species were exposed to soil concentrations of PFOS in the range of 3.61-278 mg/kg and plant tissues were analyzed at the end of the study. The concentration of PFOS in plant vegetative tissues varied less than 10 fold across the seven species, with the greatest concentrations being observed in soybeans, leading to a BSAF of 4.3. Most frequently, however, the PFOS concentrations in plant vegetative tissues were about 1–2 times greater than that measured in the soil, with the greatest BSAF observed at the lowest soil concentrations.

Stahl et al. (2009) studied the accumulation of polyfluorinated compounds (PFCs) in five cultivated plants (spring wheat, oats, potatoes, maize, and perennial ryegrass). The exposure concentration of PFOA and PFOS ranged from 0.25 to 50 mg/kg. As the objective of the study was to observe transfer of the two PFCs from soil to plant, the substances were applied in a mixture and not individually. The results showed that uptake of PFOA/PFOS in the plants vary greatly with twice as high PFOA uptake as PFOS. For both PFCs there was a relationship between exposure concentration and the amount detected in the vegetative parts of the plants. Comparison of the PFC content of the ears and the stalks of maize showed that the concentration was higher in the straw than in the ears for both PFCs. Straw concentration in maize reached approximately 15 mg PFOA /kg at the highest exposure concentration, which corresponds to a BSAF of 0.3. The highest BSAFs for the other crops were as follows: Oat straw 4.3; Potato peels 0.004; Wheat straw 6.8; Perennial wheatgrass 4.3. The BSAF in grains and potato tubers were markedly lower, i.e. up to several orders of magnitude.

The Ministry of Environment of the German State North Rhine-Westphalia evaluated the PFOS levels in various crops grown in agricultural fields known to be contaminated by PFC containing waste material (Asselt et al. 2011, also see above). Maize, grass, rapeseed, black salsify, and wheat were analysed for PFOS over two years. The PFOS levels in almost all samples remained below the limit of detection (1 µg/kg), except for wheat, which contained 3 µg/kg in one out of 6 samples, and maize, where a little more than one third of the 16 samples contained levels in the range from 3 to 164 µg/kg (Asselt et al. 2011). Contaminated soil from the same region was also used to perform crop growth experiments, showing a direct relationship between PFOS levels in plants and soil. Non-contaminated soil, moderately contaminated soil (levels around 300 µg/kg) and highly contaminated soil (levels around 2000 µg/ kg) were used to grow maize, wheat, potatoes, and grass. Based on these experiments, BSAFs for the various crops were all established to be well below one. The highest BSAFs were found for grass (0.078–0.255), whereas wheat showed the lowest BSAF (0.001–0.004).

6.5.2 Bioaccumulation in soil fauna

The Norwegian Pollution Authorities carried out environmental screening of PFC at four selected fire training facilities in Norway where the application of aqueous film forming foams (AFFF) containing PFC was known to be common (SFT 2008). In addition to collecting and analysing earthworms from the site, accumulation experiments using sampled soils from the four sites were performed in the laboratory. The accumulation experiment was performed over tree weeks. For the PFCs, there was a trend that the BSAF increased with increasing carbon chain length. PFOS was the only PFC quantified in all earthworm samples, with BSAFs in the range 0.7-6.4. The highest BSAF was observed at PFOS-concentrations approaching background levels. A comparison between accumulation data from the laboratory and field showed that, in general, there were only minor differences between the BSAFs, although the BSAFs for the two field samples were, to some extent, higher. The BSAFs for the sum of PFC ranged for the laboratory studies between 1.2 and 6.4 for earthworms exposed to the contaminated soils, whereas the BSAF was up to 12.2 when measured in soils from the references areas with lower PFC concentrations. In the field samples from the contaminated areas, the BSAF for the sum of PFC ranged between 3.6 and 4.9, whereas the BSAF in field samples from the reference area was 11.6.

These findings are comparable to previous findings by Stubberud (2006), who conducted accumulation experiments using the standard soil 'OECD-soil'. She showed that earthworms (*Eisenia fetida*) bioaccumulated PFOS, PFOA and 6:2 fluoroteleomer sulphonate (FTS) with BSAFs between 0.7 and 4.7 when exposed to soil concentrations of 10, 20, and 40 mg/kg. The 6:2 FTS had somewhat higher BSAFs than PFOS and PFOA with mean BSAFs of 3.2, 2.3 and 0.9, respectively.

6.5.3 Conclusion on bioaccumulation of PFC

The bioaccumulation potential of PFC in the soil environment has been shown to be significantly lower than the one observed in the marine environment. Biota-to-soil accumulation factors may, however, exceed 10, with the earthworms showing higher potential than plants. The highest BSAFs are, typically, observed at the lower soil concentrations.

6.6 Ecotoxicity of PFCs to plants and soil fauna

Although PFOS and PFOA tend to bind to certain proteins rather than to bioconcentrate in fat, they have some potential to bioaccumulate in the food chain. Accordingly, they are more likely to be found in the blood and liver rather than the fatty components of foods.

Regarding health related toxicity, OECD concludes that PFOS and PFOA are widely present in humans and the environment, have long half-lives in humans, and can cause adverse effects in laboratory animals, including cancer and developmental and systematic toxicity (OECD 2002). PFOS and PFOA precursors (chemicals which degrade or may degrade to PFOS and/or PFOA) are also present worldwide in humans and the environment and, in some cases, might be present at higher concentrations than PFOS and PFOA as well as be more toxic. Higher PFC homologues are chemicals with carbon chain lengths longer than PFOA and PFOS, and available data suggest that toxicity and bioaccumulation appear to increase with increasing carbon chain length.

6.6.1 Soil invertebrates

Sindermann et al. (2002, cited from Beach et al. 2006) studied the acute toxicity of PFOS to earthworms (*Eisenia fetida*) exposed to five concentrations for 14 days in an artificial soil substrate. The 14-d LC50 was determined to 373 mg/kg soil, whereas the NOEC based on survival was determined to 77 mg/kg soil.

Stubberud (2006) found that PFOS and PFOA significantly affected earthworm reproduction at soil concentrations of 80 and 150 mg/kg, respectively. The NOEC, EC10 and EC50 values for reproduction was 40, 80 and 25 mg/kg for PFOS and 80, 213 and 94 mg/kg for PFOA. Growth apparently was a more sensitive endpoint as significant reduction in the biomass of juveniles was observed when exposed to 20 mg/kg of both substances. The NOEC values were 10 mg/kg. The PFC 6:2 fluorotelomer sulfonate (6:2 FTS) was less toxic to earthworms, with the lowest NOEC found at 150 mg/kg and EC50 and EC10 values at 253 and 30 mg/kg. The ecotoxicity data presented above is based on nominal concentrations, but chemical verification of the test concentrations showed that these were comparable to the nominal concentrations.

Thus, the data from Stubberud (2006) indicate that PFOA is expected to have a lower toxicity to soil invertebrates than PFOS.

6.6.2 Plants

Brignole et al. (2003, cited from Beach et al. 2006) reported the toxicity of PFOS to seven species of crop plants (onion, ryegrass, alfalfa, flax, tomato, soybean, and lettuce). Seeds were planted in artificial loam soil mixed with different concentrations of PFOS and endpoints, such as emergence, survival, and shoot height and weight were determined after 21 days. The EC50 value for survival across all plant species ranged from 57 to more than 1,000 mg/kg. The 21-d NOEC based on emergence ranged from 62.5 to 1,000 mg/kg. The NOEC based on growth ranged from less than 3.91 to 62.5 mg/kg. In general, onion was the most sensitive plant species, whereas soybean was the least sensitive.

Stahl et al. (2009) studied the accumulation of polyfluorinated compounds in five cultivated plants (spring wheat, oats, potatoes, maize, and perennial ryegrass). The concentration level of PFOA and PFOS ranged from 0.25 to 50 mg/kg. As the objective of the study was to observe transfer of the two PFCs from soil to plant, the substances were applied in a mixture and not individually. The results show that uptake of PFOA/PFOS in the plants vary greatly with twice as high PFOA uptake as PFOS. Oats, potatoes, ryegrass, and spring wheat, but not maize, were one way or the other visibly affected at soil concentrations of 25 mg/kg (PFOA/PFOS), whereas only spring wheat was visibly damaged at a dose of 10 mg/kg. Significant growth reduction, but not yield, was observed for spring wheat at concentrations of 10 mg/kg. The yield was significantly reduced for potatoes at 25 mg/kg, whereas for the other crops either no effect on yield was observed or only at 50 mg/kg. As no significant effects were observed for any crop species at 1 mg/kg, this can be considered as a NOEC value for plant species.

Li (2009) investigated the toxicity of PFOS and PFOA on a set of three terrestrial plant species exposed to a test solution containing PFC. Endpoints were seed germination and root elongation of three test plants: lettuce, cucumber and pakchoi. Root elongation was the most sensitive endpoint. Here, EC50 values ranged from 99 to 200 mg PFOS/L and 263 to 1254 mg PFOA/L. EC10 values of PFOS for lettuce and pakchoi were 24 and 71 mg/L, whereas the EC10 values of PFOA for three test species ranged from 5 to 812 mg/L. The observed toxicity for the aquatic tests with terrestrial plants was in the same range as with four aquatic invertebrate species reported in the same study (Li 2008). Although not directly useful for a risk evaluation of the soil environment, the study by Li may indicate that no markedly differences between the toxicity of PFOS and PFOA towards plants and invertebrates is anticipated.

In another study exposing terrestrial plants to PFOS via solutions, Qu et al. (2010) reported toxicity to wheat (*Triticum aestivum L.*), using the growing and developmental indexes of wheat, including length and biomass of roots and leaves, chlorophyll, soluble protein, peroxidase (POD), superoxide dismutase (SOD) in the seedlings, and permeability of root cells. The results showed that PFOS had significant ($p < 0.05$) effects on the growth of wheat seedlings under the experimental conditions. At concentrations below 10 mg/ L, PFOS slightly stimulated the growth of wheat seedlings, whereas at 10 mg/ L, PFOS treatment significantly inhibited the elongation and biomass of roots and leaves by approximately 10% and also caused damage to chlorophyll accumulation and soluble protein synthesis.

Although not directly useful in a risk assessment of PFCs in sludge, the two studies above indicate that terrestrial plants show similar toxic responses and sensitivity to PFOS or PFOA as aquatic species (see below).

6.6.3 Aquatic toxicity of PFC

Very limited information regarding the terrestrial ecotoxicity of PFCs exists, as seen in the sections above. However, data from the aquatic compartment may give indications of the intrinsic toxic properties of PFCs, which may be useful for a qualitative assessment of sludge borne PFC and the potential risk to terrestrial ecosystems.

Ji et al. (2008) determined the toxicity of PFOS and PFOA to several freshwater organisms, including two cladocerans, *Daphnia magna* and *Moina macrocopa*, and the fish *Oryzias latipes*. In general, PFOS was found to be approximately 10 times more toxic than PFOA in these organisms, with a minimum LC50 of 17.95 and 199.5 mg/L for PFOS and PFOA, respectively. Li (2009) showed the same order of toxicity for the two PFCs, with a 48-h and 96-h LC50 of PFOS ranging from 27 to 233 mg/L and 10 to 178 mg/L, respectively, for four different fresh water invertebrate species. The 48-h and 96-h LC50 of PFOA ranged from 181 to 732 mg/L and 337 to 672 mg/L, respectively.

The same conclusion can be made on the basis of the review by Beach et al. (2006), where all but one of the lowest reported EC50 value for a wide set of aquatic invertebrates ranged from 3.5-169 mg/L. MacDonald et al. (2004), however, observed a significantly higher sensitivity of the sediment associated midge *Chironomus tentans* to PFOS. A preliminary range-finding test generated median EC50 estimates of 45.2 mg/L and 27.4 mg/L for survival and growth, respectively, whereas a 10-d exposure up to 100,000 mg PFOA/L did not affect the survival and growth of *C. tentans*. Because of the lack of response, no further tests with PFOA were conducted. In their definitive tests with PFOS, MacDonald et al. (2004) found EC50 for growth at 87.2 µg/L in a 10 day test, whereas the corresponding EC10 was 49.2 µg/L. In a 20 day life-cycle test, the EC50 for survival was 92.2 µg/L, with corresponding EC10 and NOEC values of 86.4 µg/L and 21.7 µg/L, respectively. The EC50 for growth was 93.8 µ/L, with corresponding EC10 and NOEC values of 88.2 µg/L and 21.7 µg/L, respectively. Rosal et al. (2010) tested the toxicity of several PFCs on two aquatic bacteria and algae. The toxicity studies with PFOS, PFOA, perfluorobutane sulfonate (PFBS) and PF-656 revealed that all PFCs had relatively low toxicity, i.e. EC50 values from approximately 35 to more than 20,000 mg/L.

Based on the information above, it seems reasonable to assume that PFOS would be the most relevant PFC to assess in sludge from an ecotoxicological perspective. Furthermore, according to the criteria specified in the REACH programme of EU none of the investigated PFCs would be classified as very toxic based on their aquatic toxicities, as the observed acute LC50 values all are above 1 mg/L.

6.6.4 Conclusion on the ecotoxicity of PFC

Suitable ecotoxicity data for soil invertebrates only included effects on earthworms, while no toxicity data for soil microorganisms was identified. The NOEC for earthworms was 77 mg/kg. For plants, the lowest NOEC value was observed for spring wheat at 1.0 mg/kg in a mixture experiment with PFOS/PFOA. For risk assessment purposes, the lowest reported NOEC of 1 mg/kg will be used. This is in line with the conclusion by Beach et al. (2006), who suggested a screening benchmark for terrestrial plants to be 1.5 mg PFOS/kg soil dw, whereas their suggestion for a benchmark value for soil invertebrates was 39 mg PFOS/kg dw.

6.7 Provisional risk evaluation of PFCs in sludge

Based on the data presented in the sections above, a provisional risk assessment for the terrestrial environment can be conducted for PFC. However, for the following reasons only the potential risk of PFOS will be evaluated in this report:

1. The highest concentration of PFC are, typically, reported for PFOS,
2. Aquatic toxicity data has revealed that PFOS is more toxic than PFOA,
3. The majority of data exist for PFOS compared to the other PFCs.

The risk is assessed by comparing the predicted environmental exposure (predicted environmental concentration – PEC) with the predicted level in soil where no effects are observed or anticipated (No Observed Effect Level – NOEL). The ratio between PEC and NOEL indicate a so-called margin of safety (MoS), which essentially is the reverse of the more common “risk quotient” utilised in many risk assessments. As all exposure scenarios cannot be foreseen and all soil dwelling species cannot be tested, a certain margin of safety is needed in order to conclude that significant effects of PFCs in sewage sludge would be unlikely. Based on the amount of available data, the MoS should fall within a range of at least 10 to 1000 in order to be in line with the use of assessment factors in the REACH programme in the European Union and described in the Technical Guidance Document for risk assessment of new and existing chemicals.

6.7.1 Predicted soil concentration

As PFCs are persistent compounds in the environment with half-lives exceeding one year, it is necessary to calculate the long-term plateau or steady state level in soil after repeated sludge applications. The PEC_{soil} at steady state (PEC_{ss}) is calculated according to the guideline outlined in the REACH programme (see Chapter 1 for details) using the following input parameters:

Load of sludge = 3 t dm/ha/y
Sludge concentration = 0.074 mg/kg[22]
Log Koc = 2.57[23]
Half-life = 1.2 years[24]
Initial background concentration in soil = 0.01 mg/kg[25]

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[22] The highest concentration in Danish sludge reported by Bossi et al. (2008). This concentration is higher than the concentration in Danish sludge reported in Kallenborn et al (2004), of 1.0 µg/kg, although the latter is reported on wet weight basis.

[23] Higgins and Luthy, (2006)

[24] The DT50 of PFOS in the field reported by Washington et al (2010)

[25] The maximum soil concentration in 199 German soil samples from non-contaminated areas (Asselt et al 2011)

Based on the assumptions above, the following PEC value can be calculated:

PECss = 30.2 µg PFOS/kg

A steady state based PEC_{soil} of 30.2 µg/kg is markedly lower than what was reported by for example Washington et al. (2010) in soil from sludge amended sites. They observed soil concentrations up to 320 µg/kg. However, this observation was from a site that for more than a decade had received large amounts of sludge from WWTP handling effluents from industries that conducted electrochemical fluorination and fluorotelomerization, as well as industries that worked with a variety of fluorotelomer compounds (FTCs) and perfluoroalkylates (PFAs). In a similar German case, where highly PFC-polluted sludge was used for a long period, soil concentrations above the calculated PECss were also observed. The sludge used in both cases is, however, expected to have contained markedly elevated levels of PFC relative to Danish sludge and this data is, therefore, less relevant in a Danish context.

6.7.2 No Observed Effect Level (NOEL)

Based on the relatively limited amount of data reviewed for PFOS, the lowest concentrations where no effects on the tested species have been observed are 1 mg/kg. Accordingly, this value is suitable as a conservative NOEL value for PFOS for soil dwelling species.

6.7.3 Margin of safety and potential risk

Based on a comparison between the NOEL value and the estimated steady state PEC_{ss}, a margin of safety (MoS) can be estimated.

PECss = 30.2 µg/kg
NOEL = 1,000 µg/kg
MoS = 33.1

As only toxicity studies with two trophic levels (plants and earthworms) have been found for PFOS, a MoS of 33 is at the lower end of what is required according to the outline of the REACH programme in the European Union, i.e. 50 or 100. Thus, more information is required in order to strengthen conclusions on the potential long-term risk to the soil environment induced by PFOS applied with sewage sludge.

6.8 Summary and conclusions

The concentrations of PFC in sewage sludge are generally low, with PFOS and PFOA as the most dominant PFCs. There are, however, published data that show relatively high local PFOS concentrations in sewage sludge, typically in areas with industries that produce or use PFCs. PFCs are persistent in the soil environment with half-lives longer than one year. Elevated soil concentrations have, therefore, been observed at areas receiving large quantities of PFC-contaminated sludge. PFOS and other PFCs may accumulate in plants and soil invertebrates, although the biota-to-soil accumulation ratios are typically in the range of 0.1-10, with the highest ratios found in low-contaminated soils. Relatively limited information regarding the toxicity to soil organisms and plants is available for most of the PFCs. Most information is available for PFOS, where significant adverse effects have been observed in the lower mg/kg range, with plants apparently being more sensitive than earthworms. A comparison of the lowest test concentration, where no significant effects were observed, and the predicted concentrations in soils after sewage sludge amendment, reveals a margin of safety which is on the borderline of what would be accepted according to the risk assessment procedure outlined in the REACH programme of the European Union.

Therefore, based on the collected information it cannot be excluded that the PFOS levels observed in Danish sludge may pose a long term risk to soil ecosystems. Thus, more information on the fate and effects of PFC is needed. In 2009, PFOS and related derivatives were listed under the Stockholm Convention due to their demonstrated toxicity, bioaccumulation, persistence in the environment and ability to travel long distances from the point of release or application. This has already led to restrictions in the use of PFOS in for example Denmark and the EU, which is likely to result in lower environmental load, including the concentration in sewage sludge, in the future.

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Appendix A

Aquatic toxicity of pharmaceuticals

It is beyond the scope of this report to evaluate the potential toxic effects and risk of sewage sludge associated with pharmaceuticals to aquatic species. However, as the effects to terrestrial species are poorly elucidated, it has been decided to include a brief data collection of aquatic toxicity data in order to qualitatively assess the intrinsic toxic properties of various pharmaceuticals.

The intrinsic toxic properties to aquatic species are used in combination with the occurrence of pharmaceuticals in sludge and their fate in WWTPs and soils to identify potential substances that could pose a long term hazard to soil dwelling species.

The toxicity of various pharmaceuticals often indentified in WWTPs is listed in Table A2. Useful toxicity data has not been identified for all substances. Various reviews and risk assessment papers have taken similar approaches.

In the absence of sufficiently extensive toxicological data, Sanderson et al. (2003) scanned all the pharmaceutical compounds reported to have been observed in the environment for toxicological properties by (Quantitative) Structure Activity Relationship ((Q)SAR). The predicted toxicity to fish, daphnia, and algae of more than 70 substances were evaluated. Among these, only few were identified to be very toxic according to the criteria for classification and labelling of hazardous substances in the European Union, i.e. with an acute EC50 or LC50 equal to or below 1 mg/L. The QSAR identified the following substances as potentially very toxic to aquatic species: clofibrate (algae); dextropropoxyphene (algae); fenofibrate (fish, daphnid, algae); gemfibrozil (fish); methaqualone (algae); propyphanazone (fish, algae); 3,4,5,6-tetrabromo-o-cresol (fish, daphnid, algae); tolfenamic acid (fish), and fluoxetine (daphnid, algae). Fent et al. (2006) evaluated the ecotoxicology of human pharmaceuticals. They identified aquatic toxicity data for 24 different pharmaceuticals. Among these, only two, i.e. propranolol and fluoxetine, could be identified as very toxic to aquatic species with EC50/LC50 values below 1 mg/L. Among the remaining 22, only ibuprofen, metroprolol, clofibrate, and diazepham had EC50/LC50 below 10 mg/L.

Webb (2001) conducted a large review of the acute toxicity data for macro-invertebrates, fish, and algae. The resulting database covered more than 350 endpoints for over 100 human pharmaceuticals. Among the 107 evaluated pharmaceuticals, the following distribution of the acute data was observed:

EC/LC50 < 0.1 mg/L	1.9 %
EC/LC50 > 0.1 – 1.0 mg/L	7.5 %
EC/LC50 > 1.0 – 10 mg/L	20.3 %
EC/LC50 > 10 – 100 mg/L	29.0 %
EC/LC50 > 100 mg/L	41.1 %

The following pharmaceuticals, excluding hormones, were identified as being very toxic according to criteria for classification and labelling of hazardous substances in the European Union: amitriptyline (shrimp); carvedilol (fish); fluticasone propionate (daphnid); fluoxetine (daphnid, algae); fluvoxamine (clam); midazolam (daphnid); oxytetracycline (algae); thioridazine (daphnid, shrimp, rotifer).

Screening Process

As shown in Chapter 4 on pharmaceuticals, the fate and effect data on pharmaceuticals is, generally, insufficient for a solid risk assessment for the terrestrial compartment. Instead, a qualitative assessment of risk, based on data regarding the fate of the substances, the presence in sewage sludge, and the intrinsic ecotoxicological properties of the substances, is made. A decision tree is created to aid the identification of such substances. All data are taken from Table A2.

Step 1.
Has the substance been reported in sewage sludge in concentrations exceeding 1.0 mg/kg and/or is the log $K_{ow} > 4$? If NO, stop the assessment. If YES, continue to step 2.

Step 2.
Is there any information showing a rapid degradation, i.e. DT50 < 21 days in soil or sludge and/or relatively low adsorption (Kd < 5), of the substance in sewage sludge and/or soil? If YES, stop the assessment. If NO, continue to step 3.

Step 3.
Is the substance very toxic to aquatic species according to criteria for classification and labelling of hazardous substances in the European Union, i.e. with an acute EC50 or LC50 equal to or below 1 mg/L. If NO, stop the assessment. If YES, the substances may need further evaluation in order to fully elucidate the potential risk to soil dwelling species.

STEP 1.
The following substances have been identified to continue to step 2:

Sludge criteria (Table A2)
Carbamazepine, Cimitidine, Ciprofloxacin, Diphenhydramine, Doxycyclin, Fluoxecine, Minocycline, Norfloxacin, Oflaxacin, Roxithromycin, Salicylic acid, Tetracycline

Log K_{ow} criteria (Sanderson et al. 2003)
Benzafibrate, Fenofibrate, Fenofibric acid, Fluoxetine, Gemfibrizil, Gemfibrozil, Indomethacine, Methaqualone, Tolfenamic acid

STEP 2 and 3

Table A1. The outcome of Step 2 and 3 for the substances passing the criteria in Step 1.

	DT50 criteria – Stop?	**Kd criteria – Stop?**	**Ecotoxicity – Stop?**
Benzafibrate	--	--	--
Carbamazepine	N	N	Y/N[§]
Cimitidine	--	--	Y
Ciprofloxacin	N	--	--
Diphenhydramine	--	--	--
Doxycyclin	N	--	--
Fenofibrate	--	--	--
Fenofibric acid	--	--	--
Fluoxetine	N	N	N
Gemfibrizil	--	--	--
Gemfibrozil[+]	--	--	--
Indomethacine	--	--	--
Methaqualone	--	--	--
Minocyclin	--	--	--
Norfloxacin	N	--	--
Ofloxacin	--	N	N

	DT50 criteria – Stop?	**Kd criteria – Stop?**	**Ecotoxicity – Stop?**
Roxithromycin	--	--	--
Salicylic acid	--	--	Y
Tetracycline	N	--	N
Tolfenamic acid	--	--	--

[+] Selected to Step 2 on the basic of its $logK_{ow}$, *however, reported sludge concentrations are well below 1 mg/kg*

[§] All reported EC/LC50 values are above 1 mg/L, however, significant adverse effects (LOEC) have been reported below 1 mg/L.

Table A1 above shows that generally far too little information is available for a solid evaluation of the potential risk of many pharmaceuticals, even if using aquatic ecotoxicity data. Besides the theoretical risk of the most persistent antibiotics, e.g. tetracycline and ofloxacin, toward a specific group of species, i.e. bacteria, only fluoxetine seems to pose a potential risk, when based on information about its fate in the environment and WWTPs as well as its intrinsic toxicity to a wide range of aquatic species. Carbamazepine has fate properties that may indicate persistence in the soil environment and has occasionally been identified in relatively high levels in sewage sludge. Furthermore, effects (although not up to the level of 50%) on aquatic species have been observed below 1 mg/L.

In conclusion, a screening of pharmaceuticals using aquatic toxicity data to identify the substances that may pose a potential risk to the soil environment does not show any likely candidates that are not already covered by the provisional risk assessment of pharmaceuticals to soil dwelling organisms in Chapter 7.

Table A2. A collection of sludge concentration, fate data and soil and aquatic ecotoxicity data fro a wide set of pharmaceuticals. It must be emphasised that this data collection by no means covers all of the vast amount of data available in the open literature.

Substance	**Exposure** Maximum conc. in sludge/soil mg/kg	**Fate** (Sorption, Persistence and DT50)	**Soil Ecotoxicity**	**Aquatic ecotoxicity**[*]
Atenolol	E sludge: ~0.08[31] D sludge: 0.002[32] CA sludge: 0.009[33]	K_D values for four sludge types from 5.9-95[31] K_D values for six sludge types up to ~9[32]		Low to moderate toxicity[24,34]
Carbamazepine	US sludge: 6.0[1] US sludge: 0.24[2] E sludge: 0.128[19] E sludge: ~0.08[31] CA sludge: 0.67[33]	No elimination in sludge over 77 d[7] K_D values in two soils from 0.49-37[10] K_D values for four sludge types from 135-314[31] In a semi-field study, 50% the applied dose was detected in soil, 35% in plants and the rest is assumed mineralised after 3 months[14]	NOEC for ryegrass of >0.032 mg/kg[14]	Low toxicity[21, 26, 30] (LOEC values observed below 1 mg/L[29])
Cimetidine	DK sludge: 1.2[4] US sludge: 8.3[1]			Low toxicity[21]
Ciprofloxacin	S sludge: 4.8[5] US sludge: 40.8[1]	No elimination in sludge over 77 d[7] Limited degradation and mobility observed in sludge amended soils after 21 months[15]		
Citalopram		K_D values in three soil from 17,540 - 42,579[12]		

Substance	**Exposure** Maximum conc. in sludge/soil mg/kg	**Fate** (Sorption, Persistence and DT50)	**Soil Ecotoxicity**	**Aquatic ecotoxicity**[*]
Clofibrate/ Clofibric acid	E sludge: <LOQ[19]	DT50 in agricultural soils < 20 days[9] K_D values in two soils from <5.4[10]		Moderate to low toxicity[21, 26, 30] (LOEC values observed below 1 mg/L[29])
Dextropropoxyphene				Low to moderate toxicity[25]
Diazepam		K_D values in two soils from 13-20[11]		Moderate to low toxicity[21, 25]
Diclofenac	E sludge: 0.087[8] US sludge: 0.035[6] S sludge: 0.039[20] E sludge: ~0.21[31]	DT50 in agricultural soils < 21 days[9] K_D values in two soils from 0.45-165[10] K_D values in two soils from 8-10[11] K_D values for four sludge types from 118-321[31] 13% fully mineralised and 72% non-extractable in soil after 102 days[11]		Low to moderate toxicity[21, 26, 29, 30]
Diphenhydramine	US sludge: 1.7[2] US sludge: 5.7[1] US sludge: 173[6]			
Doxycyclin	S sludge: 1.5[5] US sludge: 5.1[1]	DT50 in sludge > 53d[7]		
Fluovoxamnine		K_D values in three soil from 60-649[12]		
Fluoxetine	US sludge: 3.1[1] E sludge: ~0.12[31] CA sludge: 0.08[33]	K_D values in three soil from 992-12,546[12] Almost no biodegradation in soils after 270 days[13]		High toxicity[21]
Furosemide	DK sludge: 0.18[4]			
Gemfibrozil	E sludge: <LOQ[19] E sludge: ~0.12[31]	K_D values for four sludge types from 18.7-27.8[31]		

Substance	**Exposure** Maximum conc. in sludge/soil mg/kg	**Fate** (Sorption, Persistence and DT50)	**Soil Ecotoxicity**	**Aquatic ecotoxicity**[*]
Ibuprofen	DK sludge: <LOD[4] US sludge:0.36[2] E sludge: 0.11[8] E sludge: 5.1[19] S sludge: 0.122[20] E sludge: ~0.55[31]	DT50 in agricultural soils < 10 days[9] K_D values in two soils from 6-18[11] K_D values for four sludge types from 0.0-9.5[31]	Reproductive EC10 for springtails of 169 mg/kg[18] NOEC for ryegrass of >0.49 mg/kg[14]	Low to moderate toxicity[21, 26, 27]
Ketoprofen	S sludge: 0.029[20] E sludge: ~0.21[31] E sludge: <LOQ[19]	K_D values for four sludge types from 16-226[31]		Low toxicity[27]
Metroprolol	D sludge: 0.095[32]	K_D values for six sludge types up to ~90[32]		Low to moderate toxicity[28]
Minocycline	US sludge: 2.6[2]			
Naproxen	E sludge: 0.043[19] S sludge: 0.138[20]	DT50 in agricultural soils < 20 days[9, 35]		Low to moderate toxicity[21, 26, 27]
Norfloxacin	S sludge: 4.2[5] US sludge: 0.42[2]	Limited degradation and mobility observed in sludge amended soils after 21 months[15]		
Norfluoxetine	US sludge: 0.43[6]			
Ofloxacin	S sludge: 2.0[5] US sludge: 58.1[1] E sludge: ~0.07[31]	K_D values in two soils from 1,192-3,554[10]		High toxicity to bacteria, medium toxicity to algae and low toxicity to other species[30]
Oxytetracyline (oxycyclin)	DK sludge: < LOD US sludge:0.11[2]		ED_{10} SIR, in two different soil types ranged from 0.81 to 31.2 mg/kg[16] NOEC for 3 species of soil invertebrates were > 1000 mg/kg[17]	High toxicity to cyanobacteria and low to moderate toxicity to other species[22]
Paracetamol	DK sludge: 2.0[4] E sludge: 0.42[8]	K_D values in two soils from 36-46[11]		Low toxicity[21, 22, 25]
Paraxetien		K_D values in three soil from 355-6,386[12]		
Paroxetine	E sludge: <0.1[31]	Low sorption potential[23]		Low toxicity[23]
Propranolol	E sludge: 0.004[19] E sludge: ~0.05[31]	K_D values in two soils from 16.3-199[10]	Reproductive EC10 for springtails of 832 mg/kg[18]	Moderate to high toxicity[21, 26, 28, 30]

Substance	**Exposure** Maximum conc. in sludge/soil mg/kg	**Fate** (Sorption, Persistence and DT50)	**Soil Ecotoxicity**	**Aquatic ecotoxicity**[*]
	D sludge: 0.025[32]	K_D values for four sludge types from 298-641[31] K_D values for six sludge types up to ~500[32]		
Roxithromycin	E sludge: 1.45[8] CH sludge: <0.003[34]			
Salicylic acid	DK sludge: 2.8[4] E sludge: 0.13[19]			Low toxicity[21]
Sertraline		K_D values in three soil from 149-787[12]		
Sulfamethizole	DK sludge: 0.11[4]			
Sulfamethoxazole	E sludge: < LOQ[19] E sludge: ~0.02[31] CA sludge:0.004[33] CH sludge: 0.068[34]	K_D values in two soils from 0.23-37.6[10] K_D values for four sludge types from 3.2-77[31] K_D in activated sludge of 256[34]		High toxicity to algae and low toxicity to invertebrates and fish[30]
Sulfapyridine	CA sludge: < LOD[33] CH sludge:0.028[34]	K_D in activated sludge of 295[34]	ED_{10} SIR, in two different soil types ranged from 0.05 to 6.2 mg/kg[16]	
Tetracycline	DK sludge: 0.5[3] US sludge: 5.3[1]	DT50 in sludge > 37d[7]		High toxicity to cyanobacteria and low to moderate toxicity to other species[22]
Trimethoprim	DK sludge: 0.076[4] US sludge: 0.061[2] E sludge: < LOQ[19] E sludge: ~0.05[31] CH sludge: 0.041[34]	K_D in activated sludge of 208[34]		

[1] (US EPA 2009); [2] McClellan and Halden 2010; [3] Andersen (unpublished); [4] Mogensen et al. 2007; [5] Lindberg et al. (2005); [6] Chenxi et al. (2010); [7] Chenxi et al. (2008); [8] Nieto et al. (2010); [9] Xu et al. (2009); [10] Drilla et al. 2005; [11] Kreutzig al 2003; [12] Kwon and Ambrust (2008); [13] Redshaw et al. (2008); [14] Winker et al. (2010); [15] Golet et al. 2003; .[16] Thiele and Beck (2001, cited from Thiele-Bruhn 2003); [17] Baguer et al. 2000; [18] Jensen et al. personal communication; [19] Martin et al. 2010; [20] Sagrista et al. 2010; [21] Fent et al. (2006); [22] Carlsson et al. (2006); [23] Cunningham et al. 2004; [24] Pascoe et al. 2003; [25] Calleja et al. 1994; [26] Cleuvers 2003; [27] La Farré et al. 2001; [28]Huggett et al. 2002; [29] Ferrari et al. 2003; [30] Ferrari et al. 2004; [31] Radjenovic 2009; [32] Scheurer et al. 2010; [33] Lapen et al. 2008; Göbel et al. 2005; [34]Kuester et al. (2010). Topp et al. (2008)

Summary

This report is an attempt to prioritise and select five groups of chemicals commonly found in Danish sludge and to assess the potential risk to soil organisms. The following groups of chemicals have been evaluated: Brominated Flame Retardants, Musk substances, Pharmaceuticals, Polychlorinated Biphenyls and Perfluorinated compounds. For the first four groups of substances it was concluded that it was very unlikely that the levels found in Danish sludge should pose a significant risk to the soil dwelling. For the perfluorinated substances it could not be excluded that the PFOS levels observed in Danish sludge may pose a long term risk to soil ecosystems. Thus, more information on the fate and effects of PFC is needed.

Danish Ministry of the Environment
Environmental Protection Agency

Strandgade 29
DK - 1401 København K
Tlf.: (+45) 72 54 40 00

www. mst.dk