Personal care compounds in a reed bed sludge treatment system

Chen, Xijuan; Pauly, Udo; Rehfus, Stefan; Bester, Kai

Published in:
Chemosphere

Publication date:
2009

Document Version
Publisher's PDF, also known as Version of record

Link to publication from Aalborg University

Citation for published version (APA):
1. Introduction

Sludge (also referred to as biosolids) has long been used as fertilizer on agricultural land. The usage of sludge as fertilizer is controversial because of possible high concentration of xenobiotic compounds, heavy metals as well as pathogens. In this study, the fate of the xenobiotic compounds triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol), OTNE (1-(2,3,8,8-tetramethyl-1,2,3,4,5,6,7,8-octahydro-naphthalen-2-yl)ethan-1-one), HHCB (1,3,4,6,7,8-hexahydro-4,6,6,7,8-hexamethylcyclopenta-(g)-2-benzopyran), HHCB-lactone, AHTN (7-acetyl-1,3,4,4,6 hexamethyl-1,2,3,4 tetrahydrophthalene), and DEHP (bis(2-ethylhexyl)phthalate) in advanced biological treatment of sludge was determined.

During 13 months of field-incubation of the sludge in reed beds, the xenobiotic compounds were analysed. The bactericide triclosan was reduced to 60%, 45%, and 32% of its original concentration in the top, middle, and bottom layer. The fragrance OTNE was decreased to 42% in the top layer, 53% in the middle layer, and 70% in the bottom layer, respectively. For DEHP a reduction of 70%, 71%, and 40% was observed in the top, middle, and bottom layer, respectively. The polycyclic musk compounds HHCB, AHTN, and the primary metabolite of HHCB, i.e., HHCB-lactone showed no degradation in 13 months during the experimental period in this installation. Tentative half-lives of degradation of triclosan, OTNE and DEHP were estimated to be 315–770 d, 237–630 d, and 289–578 d, respectively.
mainly used in domestic purpose as well as OTNE (1-(2,3,8,8-tetramethyl-1,2,3,4,5,6,7,8-octahydro-naphthalen-2-yl)ethan-1-one), triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol), DEHP (bis(2-ethylhexyl)phthalate) have recently been identified as major anthropogenic organic contaminants in sewage sludge (Simonič et al., 2002; Kinney et al., 2006).

Triclosan is currently used as an antimicrobial agent in toothpaste, mouthwash, and in functional clothing such as sport shoes and underwear and as a stabilizing agent in a multitude of detergents and cosmetics (Adolfsson-Erici et al., 2002). Additionally, it is used as an antimicrobial agent in polymeric food cutting boards. Approximately 1500 tonnes are produced annually worldwide, and approximately 350 tonnes of those are applied in Europe (Singer et al., 2002). Triclosan has a low water solubility and very high potential of bio-accumulation (Coogan et al., 2007). Studies have increasingly linked triclosan to a range of health and environmental effects, skin irritation, allergy susceptibility, and ecological toxicity to the aquatic and terrestrial environment (Coogan et al., 2007). In sludge from North Rhine-Westphalia, triclosan is widespread and the concentration is in the range of more than 2000–8000 ng g⁻¹ (dry mass) (Bester, 2005a). In Table 1 the structural formula and other details on the compounds are presented.

Polycyclic musk compounds such as HHCB and AHTN are used frequently as fragrances in washing softeners, shampoos, and other consumer products. More than 2000 tonnes are used annually in Europe (Balk and Ford, 1999). The structural formulas of both
compounds are given in Table 1. After application, most of these materials are released to the sewer. Thus, they have been identified in sewage treatment plants (Eschke et al., 1994, 1995) and in sewage sludge (Reiner and Kannan, 2006). Both of them have very low water solubility and high potential of bioaccumulation, thus they can cause ecological toxicity to the aquatic and terrestrial environment (Brunn and Rimkus, 1997). The musk compounds are not mineralized in sewage treatment processes and sorption is their main elimination path in waste water treatment plants, although transformation to other compounds may occur (Bester, 2005b). Elimination rates of fragrance compounds in 17 different plants in US and Europe were compared by Simonich et al. (2002). Removal rates of 50%–90% were determined for HHCB and AHTN. Concentration of HHCB for 3100 ± 240 ng g⁻¹ and AHTN for 1500 ± 150 ng g⁻¹ in digested, dewatered sludge was determined from one STP in North Rhine-Westphalia (Bester, 2004).

HHCB-lactone is the primary metabolite of HHCB, which is an oxidation product as shown in Table 1. The ratio of HHCB:HHCB-lactone has been used to detect transformation processes of this fragrance. During the sewage treatment process about 10% of HHCB is transformed to HHCB-lactone which has been reported for balance assessment for polycyclic mask fragrances in German treatment plant by Bester (2004). The relation HHCB:HHCB-lactone varies from 3 to 130 in surface waters. This indicates that degradation processes, especially degradation/transformation efficiency, in the respective sewage treatment plants differ considerably (Bester, 2005b). Concentrations of HHCB-lactone from sludge of 20 sewage treatment plants were determined from 30 ng g⁻¹ to 36,000 ng g⁻¹ (Bester, 2005b).

### Table 1

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Name</th>
<th>Molecular formula</th>
<th>Molecular weight</th>
<th>CAS</th>
<th>Vapour pressure</th>
<th>Water solubility</th>
<th>log Kow</th>
<th>log Koc</th>
</tr>
</thead>
<tbody>
<tr>
<td>OTNE (Gautschi et al., 2001; Bester et al., 2008)</td>
<td>1-(2,3,8,8-tetramethyl-1,2,3,4,5,6,7,8-octahydro-naphthalen-2-yl)ethan-1-one</td>
<td>C₁₆H₂₆O</td>
<td>234 g mol⁻¹</td>
<td>54464-57-2</td>
<td>0.2 Pa</td>
<td>2.68 mg L⁻¹</td>
<td>5.7</td>
<td>4.64</td>
</tr>
<tr>
<td>HHCB (Balk and Ford, 1999)</td>
<td>1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[g]-2-benzopyran</td>
<td>C₁₈H₂₆O</td>
<td>258 g mol⁻¹</td>
<td>1222-05-5</td>
<td>0.0682 Pa</td>
<td>1.25 mg L⁻¹</td>
<td>5.7</td>
<td>4.80</td>
</tr>
<tr>
<td>AHTN (Balk and Ford, 1999)</td>
<td>7-acetyl-1,1,3,4,4,6 hexamethyl-1,2,3,4 tetrahydronaphthalene</td>
<td>C₁₈H₂₆O</td>
<td>258 g mol⁻¹</td>
<td>1506-02-1</td>
<td>0.0727 Pa</td>
<td>1.75 mg L⁻¹</td>
<td>5.9</td>
<td>4.86</td>
</tr>
<tr>
<td>Triclosan (Bester, 2005a; Ying et al., 2007)</td>
<td>5-chloro-2-(2,4-dichlorophenoxy)phenol</td>
<td>C₁₂H₇Cl₃O₂</td>
<td>290 g mol⁻¹</td>
<td>3380-34-5</td>
<td>0.00062 Pa</td>
<td>4.621 mg L⁻¹</td>
<td>4.2–4.76</td>
<td>4.265</td>
</tr>
<tr>
<td>DEHP (Cheng et al., 2008)</td>
<td>bis(2-ethylhexyl)phthalate</td>
<td>C₂₄H₃₈O₄</td>
<td>391 g mol⁻¹</td>
<td>117-81-7</td>
<td>0.000034 Pa</td>
<td>0.003 mg L⁻¹</td>
<td>7.5</td>
<td>5.2</td>
</tr>
<tr>
<td>HHCB-lactone (Bester, 2005b)</td>
<td>1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[g]-2-benzopyran-1-one</td>
<td>C₁₈H₂₄O₂</td>
<td>272 g mol⁻¹</td>
<td>507442-53-7</td>
<td>4.7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
OTNE is widely used in consumer products (in Table 1). It has been among the most popular compounds in fragrances in the last few years. It is marketed as Iso E Super, with 2500–3000 tonnes annually being sold (Gautsch et al., 2001). Concentrations of 7000–30,000 ng g⁻¹ OTNE in dry sludge were determined in sludge from the U.S. (Difrancesco et al., 2004), while European data indicate concentrations of 2000–4000 ng g⁻¹ (Bester et al., 2008).

DEHP is widely used as plasticizer in PVC construction materials, and also in varnish, paint, and cosmetics products. DEHP is used as a plasticizer because of its stability, fluidity, and low volatility (Giam et al., 1984). This plasticizer is eluted into wastewater by washing and cleaning processes, it is assumed to at least have strong ecotoxic effects on aquatic organisms (Roh et al., 2007). Because of the relatively high lipophilicity of the compounds, sorption is the main process relevant for elimination in sewage treatment plants. Beauchesne et al. (2008) investigated that sludge can represent significant sources of plasticizers in the environment. Typical concentration of DEHP in sludge was investigated in the range of 10–100 μg g⁻¹. Duplicates of the lyophilised sludge samples were extracted by means of accelerated solvent extraction (ASE) with ethyl acetate at 90°C and 150 bar. The resulting extracts were then cleaned up with 1 g silica (SPE) solid-phase extraction cartridges (silica 60 obtained from Merck, Dormstadt, Germany) by elution with ethyl acetate after adding an aliquot of 100 μL internal standard solution (IS) (containing 100 ng D₃₅, musk xylene and 100 ng TPP D₁₅).

Two hundred grams of these homogenates were immediately frozen in refrigerating room at −27°C overnight. Frozen sub-samples of 50 g wet weight were lyophilised at 2 mbar and −46°C. Duplicates of the lyophilised sludge samples were extracted by means of accelerated solvent extraction (ASE) with ethyl acetate at 90°C and 150 bar. The resulting extracts were then cleaned up with 1 g silica (SPE) solid-phase extraction cartridges (silica 60 obtained from Merck, Dormstadt, Germany) by elution with ethyl acetate after adding an aliquot of 100 μL internal standard solution (IS) (containing 100 ng D₃₅, musk xylene and 100 ng TPP D₁₅).

These resulting solutions were concentrated to 1 mL by a Büchi multivap vacuum concentrator at 80°C and 70 mbar (Büchi, Essen, Germany). The resulting extracts were injected to a GPC-column (LC-tech, Dorfen, Germany), equipped with Biorad SX-3) ID: 2.5 cm, length 30 cm, flow 5.0 mL min⁻¹ cyclohexane: ethyl acetate 1:1. The solvent eluting in the first 19:30 min was drained to waste, while the fraction 19:30–30:00 min was collected. Thus, macromolecules were separated as they elute in the first fraction, while sulphur, etc. are separated from the target compounds as they are eluted after the analyte fraction. The samples were finally transferred into toluene. The resulting extracts were finally fractionated on silica using 5% Methyl-tert-butyl ether (MTBE) in n-hexane and ethyl acetate successively as eluents. These fractions were condensed and finally analysed by gas chromatography with mass spectrometric detection (GC-MS) equipped with a programmable temperature vapouriser (PTV) injector. The PTV (1 μL injection volume) was operated in PTV splitless mode. The injection temperature of 115°C was held for 3 s, it was successively ramped with 12°C s⁻¹ to 280°C for the transfer of the analytes. This temperature was held for 1.3 min. The injector was then ramped with 1°C s⁻¹ to 300°C which was held for 7 min as a cleaning phase.

The GC separation was performed with a DB-5MS column (J&W Scientific), L: 15 m; ID: 0.25 mm; film: 0.25 μm and a temperature programme of: 100°C (hold: 1 min) ramped with 30°C min⁻¹ to 130°C and with 8°C min⁻¹ successively to 220°C. Finally, the baking temperature was reached by ramping the column with 30°C min⁻¹ to 280°C which was held for 7 minutes.

The detector of the mass spectrometer (DSQ, Thermo Finnigan, Dreieich, Germany) was operated with 1281 V on the secondary electron multiplier and about 40 ms dwell time in selected ion mode (SIM) mode. The transfer line was held at 250°C, which is sufficient to transfer all compounds from the GC into the MS as the vacuum builds up in the transfer line. The ion source was operated at 230°C. Helium was used as carrier gas with a flow rate of 1.3 mL min⁻¹.

From June, 2006 to July, 2007 sludge samples were taken by using a stainless steel tube with a cutting edge for easy core removal. The samples were divided into three sub-samples according to depth. The upper third of the sample is considered to be the top layer, middle third as the middle layer and lower third as the bottom layer. Then 100 g samples were taken from 10 different points of the reed bed and a homogenate for the respective layer was produced.

Because of the relatively high lipophilicity of the compounds, sorption is the main process relevant for elimination in sewage treatment plants. Beauchesne et al. (2008) investigated that sludge can represent significant sources of plasticizers in the environment. Typical concentration of DEHP in sludge was investigated in the range of 10–100 μg g⁻¹. Duplicates of the lyophilised sludge samples were extracted by means of accelerated solvent extraction (ASE) with ethyl acetate at 90°C and 150 bar. The resulting extracts were then cleaned up with 1 g silica (SPE) solid-phase extraction cartridges (silica 60 obtained from Merck, Dormstadt, Germany) by elution with ethyl acetate after adding an aliquot of 100 μL internal standard solution (IS) (containing 100 ng D₃₅, musk xylene and 100 ng TPP D₁₅).

These resulting solutions were concentrated to 1 mL by a Büchi multivap vacuum concentrator at 80°C and 70 mbar (Büchi, Essen, Germany). The resulting extracts were injected to a GPC-column (LC-tech, Dorfen, Germany), equipped with Biorad SX-3) ID: 2.5 cm, length 30 cm, flow 5.0 mL min⁻¹ cyclohexane: ethyl acetate 1:1. The solvent eluting in the first 19:30 min was drained to waste, while the fraction 19:30–30:00 min was collected. Thus, macromolecules were separated as they elute in the first fraction, while sulphur, etc. are separated from the target compounds as they are eluted after the analyte fraction. The samples were finally transferred into toluene. The resulting extracts were finally fractionated on silica using 5% Methyl-tert-butyl ether (MTBE) in n-hexane and ethyl acetate successively as eluents. These fractions were condensed and finally analysed by gas chromatography with mass spectrometric detection (GC-MS) equipped with a programmable temperature vapouriser (PTV) injector. The PTV (1 μL injection volume) was operated in PTV splitless mode. The injection temperature of 115°C was held for 3 s, it was successively ramped with 12°C s⁻¹ to 280°C for the transfer of the analytes. This temperature was held for 1.3 min. The injector was then ramped with 1°C s⁻¹ to 300°C which was held for 7 min as a cleaning phase.

The GC separation was performed with a DB-5MS column (J&W Scientific), L: 15 m; ID: 0.25 mm; film: 0.25 μm and a temperature programme of: 100°C (hold: 1 min) ramped with 30°C min⁻¹ to 130°C and with 8°C min⁻¹ successively to 220°C. Finally, the baking temperature was reached by ramping the column with 30°C min⁻¹ to 280°C which was held for 7 minutes.

The detector of the mass spectrometer (DSQ, Thermo Finnigan, Dreieich, Germany) was operated with 1281 V on the secondary electron multiplier and about 40 ms dwell time in selected ion mode (SIM) mode. The transfer line was held at 250°C, which is sufficient to transfer all compounds from the GC into the MS as the vacuum builds up in the transfer line. The ion source was operated at 230°C. Helium was used as carrier gas with a flow rate of 1.3 mL min⁻¹.

When the rain water passes through the sludge layer, some compounds can be dissolved, which can also lead to the concentration reduction of compounds. Thus, liquid samples were collected as manual grab samples in two litre glass bottles from the drainage water of the drainage canal of the reed bed during the treatment process. Two samples for out-flowing water were taken as duplicates. One litre samples were extracted for 20 min with 20 mL toluene by means of vigorous stirring with a teflonized magnetic stir bar after adding an aliquot of 100 μL internal standard solution. The organic phase was separated from the aqueous one and the residual water was removed from the organic phase by freezing the samples overnight at −20°C. The resulting extracts were then concentrated with a rotary evaporator at 80°C and 70 mbar to 1 mL. Resulting extracts were quantified by using GC-MS.
The compounds were detected by means of their mass spectral data and retention times. For quantitative measurements the method was validated, by determining recovery rates, standard deviations, and limits of quantification (see next paragraph) (Bester, 2004, 2007, 2009; Peck, 2006).

The average of the concentrations obtained from the duplicate extractions was used for further data processing. The calibrations were performed as a multi-step internal standard calibration (10–10,000 ng mL⁻¹). The recovery rates were assessed by extracting spiked manure/soil 1/1 samples. Six different concentrations (between 20 ng g⁻¹ and 10,000 ng g⁻¹) were dosed, for each concentration two samples were extracted, thus 12 extractions were performed plus extractions for blank determination. Additionally recovery rates were determined by means of standard addition by spiking sludge from this experiment with respective standard concentrations of 5000 ng g⁻¹.

2.1. Method quality assurance

The recoveries were 60–133% for the respective compounds, the relative standard deviations varying for the specific compounds from 5 to 21% (for more details see Table 2). The limit of detection was 3–30 ng g⁻¹, and the limit of quantification was 10–100 ng g⁻¹. Limits of quantification (LOQ) were calculated by two means:

(1) From the analysis of standard solutions, as the lowest concentration which gave signal to noise ratios (s/n) of at least 10 (six replicas in each series).

(2) As the lowest concentration for the respective substance that was detectable from the recovery studies with the same recovery rate as the higher concentrations. Full data are given in Table 2 (duplicates per concentration).

3. Results and discussion

3.1. Water content

During the 13 months field-incubation of the organic compounds in a technical reed bed sludge treatment the water content during time was analysed. The liquid excess sludge (used as feed for this sludge treatment) contained about 99% water. The rainfall in this treatment facility (May 2006–July 2007) was 1130 L m⁻². The lowest water content in the top layer, 76%, was found in September 2006, because of the low amount of rainfall and high temperature (and enhanced transpiration by the reed plants) at that time.

3.2. Personal care compounds

The xenobiotic compounds triclosan, HHCB, AHTN, HHCB-lactone, OTNE, and DEHP were identified by their retention times and mass spectral data in sludge samples (Table 2).

The concentration of triclosan (Fig. 2) in the beginning of the experiment was measured as 1400, 1900, and 2000 ng g⁻¹ (dry mass) in the top, middle, and bottom layer, comparable results were obtained by Bester (2005a) in sewage sludge samples from 20 WWTPs in Germany with triclosan concentration ranging from 400 to 8800 ng g⁻¹. After 13 months triclosan was reduced to less than 60% and the concentration was 800, 900 and 600 ng g⁻¹ (dry mass) in the top, middle, and bottom layer, respectively (Fig. 2). Considering a standard deviation of 12% from the method validation this change is significant.

The concentrations of the polycyclic musk compounds HHCB, AHTN, and the primary metabolite of HHCB, i.e. HHCB-lactone showed no reduction in 13 months during the experimental period. The concentration varied from 8000 to 12,000 ng g⁻¹ (dry mass) for HHCB, from 1500 to 2300 ng g⁻¹ (dry mass) for AHTN and from 1400 to 2100 ng g⁻¹ (dry mass) for HHCB-lactone. These are corresponding to the results obtained by Reiner and Kannan (2006) who found concentrations ranging from 7230 to 108,000 ng g⁻¹ (dry mass) for HHCB, 809 to 16,800 ng g⁻¹ (dry mass) for AHTN and 3160 to 22,000 ng g⁻¹ (dry mass) for HHCB-lactone. Nevertheless, a few studies indicated that polycyclic musks can be degraded in sludge-amended soils. Litz et al. (2007) investigated aerobic dissipation of HHCB and AHTN in soil/sewage sludge mixtures is very slow with half-lives of 10–17 months for HHCB and 2–24 years for AHTN. Similarly, Difrancesco et al. (2004) also found a particularly slow dissipation for HHCB and AHTN in sludge-amended soils. Information on degradation of HHCB-lactone is rare, only some mass balance measurement have been carried out that indicate HHCB-lactone is developed during HHCB transformation process (Bester, 2004; Berset et al., 2004; Reiner and Kannan, 2006).

Fig. 2 shows the OTNE concentration as a function of time. The highest amount was determined in the beginning of the project. The measured concentrations were 2500 ng g⁻¹, 2500 ng g⁻¹, and 2400 ng g⁻¹ (dry mass) in the top, middle, and bottom layer, this is somewhat lower than what is found for sludges form the US by Difrancesco et al. (2004). After 13 months OTNE was reduced by 42% in the top layer, 53% in the middle layer, and 70% in the bottom layer, respectively.

Similar to OTNE, the highest concentration of DEHP was detected in the beginning of the project. The respective concentrations were 11,500, 10,500, and 7200 ng g⁻¹ (dry mass) in the top, middle, and bottom layer. Comparable results were obtained by Beachesne et al. (2008) ranging from 15,000 ng g⁻¹ to 346,000 ng g⁻¹ in sewage sludge in Canada. After 13 months DEHP was reduced by 70%, 71%, and 40% in the top, middle, and bottom layer, respectively.

The processes that contributed to the dissipation of the studied compounds in sludge may include volatilization, plants uptake, leaching, and biological transformation (aerobic and anaerobic). Considering their generally low volatility (Table 1), the tendency of these compounds to volatilize is low. Therefore it is expected that only a small fraction of these compounds was volatilized into the atmosphere, where they can photolyze (Aschmann et al., 2001; Difrancesco et al., 2004; Chen et al., 2008). To quantify the uptake of xenobiotic compounds by plants, reed samples were analysed by using the same procedure as sludge. In these samples none of the compounds were detected, except small amounts of DEHP (13,000 ± 2000 ng g⁻¹). As less than 1 kg reeds were growing in

Table 2

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Analytical ion (amu)</th>
<th>Verifier ion (amu)</th>
<th>Recovery (%)</th>
<th>RSD (%)</th>
<th>LOQ (ng g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OTNE</td>
<td>191</td>
<td>219</td>
<td>60</td>
<td>6</td>
<td>30</td>
</tr>
<tr>
<td>HHCB</td>
<td>243</td>
<td>258</td>
<td>77</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>AHTN</td>
<td>243</td>
<td>258</td>
<td>69</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Triclosan</td>
<td>288</td>
<td>290</td>
<td>133</td>
<td>12</td>
<td>100</td>
</tr>
<tr>
<td>HHCB-lactone</td>
<td>257</td>
<td>272</td>
<td>65</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>DEHP</td>
<td>279</td>
<td>167</td>
<td>87</td>
<td>21</td>
<td>10</td>
</tr>
</tbody>
</table>

Author's personal copy
1 m² sludge reed bed, it can be assumed that less than 0.01% of DEHP was ingested by reeds. This is in agreement with the results of Litz et al. (2007) who studied uptake of HHCB and AHTN by lettuce and carrots and found HHCB and AHTN were taken up only by the carrot roots to some small extent. Phyto-remediation (considering only plant uptake) is thus not relevant for this system.

3.3. Mass balance studies

The amount of compounds in leachate can be calculated based on the concentration of effluent and amount of rainfall (water flow through the system). The concentration of xenobiotics in the effluent from this reed bed in November 2006 is shown in Table 3. The rainfall during the experimental period (from June 2006 to July 2007) was 1130 mm (Table 3) (1 mm = 1 L m⁻²). Table 3 shows mass fraction of compounds which were leached by drainage water in comparison to the mass fraction in sludge in 1 m² reed bed. Since 0.010–0.048% of the mass fraction of the xenobiotics contained in the sludge is leached by drainage water during the experimental period, it seems that biological transformation was the main dissipation mechanism for these compounds.

3.4. Kinetic analysis of dissipation data

Biological degradation of organic compounds at low concentrations usually follows first-order kinetics, thus an elimination rate constant (k) for sludge removal in reed beds can be calculated from the concentrations from a log c = c₀ e⁻ᵏᵗ plot (Fig. 3) using Eq. (1). For the triclosan degradation process the respective k values are 0.0009, 0.0021 and 0.0022 in the top, middle, and bottom layer.

\[ k = \frac{\ln(\frac{c}{c_0})}{t} \]  

With Eq. (2), the half-life can be assessed:

\[ T_{1/2} = \frac{\ln 2}{k} \]  

Fig. 2. Triclosan and OTNE concentration from the bottom layer (40–60 cm from surface) as a function of time. Error bars are from the stated uncertainty from the method development.

Fig. 3. Kinetics of triclosan degradation in log form in the bottom layer of a sludge reed bed.

| Compounds | C1 Drainage water (ng L⁻¹) | Rainfall (L m⁻²) | M1 Drainage water (mg) | C2 Sludge (mg g⁻¹) | Depth of the reed bed (m) | M2 Sludge (mg) | M1/M2 (%)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>OTNE</td>
<td>130</td>
<td>1130</td>
<td>0.147</td>
<td>2370</td>
<td>0.6</td>
<td>1140</td>
<td>0.013</td>
</tr>
<tr>
<td>HHCB</td>
<td>310</td>
<td>1130</td>
<td>0.35</td>
<td>9150</td>
<td>0.6</td>
<td>4390</td>
<td>0.0080</td>
</tr>
<tr>
<td>AHTN</td>
<td>50</td>
<td>1130</td>
<td>0.057</td>
<td>1220</td>
<td>0.6</td>
<td>586</td>
<td>0.010</td>
</tr>
<tr>
<td>Triclosan</td>
<td>270</td>
<td>1130</td>
<td>0.305</td>
<td>1330</td>
<td>0.6</td>
<td>638</td>
<td>0.048</td>
</tr>
<tr>
<td>DEHP</td>
<td>170</td>
<td>1130</td>
<td>0.192</td>
<td>11,600</td>
<td>0.6</td>
<td>5570</td>
<td>0.0034</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Tentative half-life</th>
</tr>
</thead>
<tbody>
<tr>
<td>OTNE</td>
<td>630 d (R² = 0.7361)</td>
</tr>
<tr>
<td>HHCB</td>
<td>239 d (R² = 0.6047)</td>
</tr>
<tr>
<td>AHTN</td>
<td>277 d (R² = 0.4716)</td>
</tr>
<tr>
<td>DEHP</td>
<td>770 d (R² = 0.4858)</td>
</tr>
<tr>
<td>Triclosan</td>
<td>770 d (R² = 0.4822)</td>
</tr>
<tr>
<td>HHCB-lactone</td>
<td>330 d (R² = 0.7338)</td>
</tr>
<tr>
<td>M1/M2 (%)</td>
<td>770 d (R² = 0.4822)</td>
</tr>
</tbody>
</table>

∞ means half-lives larger than 3 years.

Table 3

Tentative half-lives for triclosan can be calculated as 770, 330, and 315 d in the top, middle, and bottom layer, respectively (Table 4). This is corresponding to the results which were gained by Ying et al. (2007) by spiking triclosan into loamy soil with a concentration of 1 mg kg⁻¹ (i.e. 1000 ng g⁻¹), 18 d half-life was calculated under aerobic conditions within this 70 d experiment. Tentative half-lives of OTNE degradation were calculated as 630, 239, 277 d in the top, middle, and bottom layer, respectively (Table 4), which indicate OTNE degraded faster in the middle and bottom layer than in the top layer. Comparable half-lives were observed by Difrancesco et al. in 2004 with OTNE dissipation half-lives of 30–100 d in sludge-amended soils.

Table 4

Tentative half-lives of the compounds during the experimental period in a sludge reed bed. The R² refers to the regression line in the log plots to gain the half-life values.

C1: Concentration in the drainage water (ng L⁻¹).
C2: Concentration in the sludge (ng g⁻¹) (start of experiment).
DEHP was eliminated with half-lives as 315, 289, and 578 d in the top, middle, and bottom layer, respectively. These can be compared with results obtained by Madsen et al. (1999) who found that more than 41% of DEHP in a sludge-amended soil was still not mineralization after 1 year incubation and in this study a half-life for DEHP in soils with sludge aggregates was estimated to be higher than 3 years.

3.5. Comparison of layering

Triclosan and OTNE degraded very similar concerning the layers of sludge, i.e., faster in bottom layer than in the top layer.

This might be influenced by different age, compactness or oxygen supply in the different layers. The oxygen regime in the different layers that can be quite diverse, as reed is known to pump oxygen from the leaves to the rizome into the surrounding medium (sludge) (Armstrong et al., 2000). This can be accounted for 29–60 ng m⁻² min⁻¹ (Armstrong et al., 2000). However the surrounding sludge can consume the oxygen rapidly especially if it is partially aerobically stabilized sludge as in this experiment. During the experiment, the reed bed was monitored in intervals for aerobic and anaerobic areas. The reed bed was usually patchy, thus aerobic areas occurred as well as anaerobic ones. Additionally air could have entered from the drainage basin. The main result at this moment is, there is indeed an effect of the different layers future research will show what might be the reason for this.

By the way of contrast DEHP degraded faster in the top layer, which suggesting the highest reduction of DEHP was achieved at the highest temperature (Cheng et al., 2008). Possibly the degradation of the different compounds is preferred at different oxygen levels (aerobic and anaerobic processes).

4. Conclusions

In the 13 months of this experiment, the concentrations of some compounds such as OTNE, triclosan, and DEHP in this sludge reed bed treatment were decreased. However, the concentrations of other compounds such as polycyclic musk compounds HHCB, AHTN, and HHCB-lactone did not change during this experiment. OTNE and triclosan degraded faster in the bottom layer while DEHP degraded faster in the top layer, which is indicating different regimes in the different layers and different degradation processes in the respective layers.

Considering half-lives of 300–900 d, this sludge reed bed can eliminate considerable amounts of some of the pollutants in its 10 years production cycle. If the sludge is to be used as fertilizer in agriculture the use of reed bed treatments can help considerably to decrease the contamination of sludge.

Acknowledgements

The authors acknowledge the support of Prolino/AIF and xenobiotic groups of university of Duisburg-Essen as well as Thomas Groß and Enno Pieper for sampling. Additionally the authors are indebted to the water board Stadtwerke Meppen for the possibility to sample their sludge reed plant.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2009.04.023.

References


