Environmental Chemistry

APPLICATION OF SEWAGE SLUDGE TO ARABLE LAND—SOIL CONCENTRATIONS OF POLYBROMINATED DIPHENYL ETHERS AND POLYCHLORINATED DIBENZO-\(p\)-DIOXINS, DIBENZOFURANS, AND BIPHENYLS, AND THEIR ACCUMULATION IN EARTHWORMS

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(Received 9 November 2001; Accepted 2 April 2002)

Abstract—Soils from five agricultural sites, three research sites, and two privately owned farms were analyzed for polychlorinated dibenzo-\(p\)-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), and polybrominated diphenylethers (PBDEs). In soils that had not been treated with sludge (reference soils), the international toxic equivalents (I-TEQs) were 0.6 to 1.5 pg/g dry matter (DM) for the PCDD/Fs, which are low compared to generally reported background soil levels in Europe. The concentrations of sum of six penta- and hexa-PCBs were 450 to 1,400 pg/g DM. The PBDEs 47 and 99 dominated among the tri- to hepta-PBDEs analyzed (8–80 pg/g DM). The impact of adding 1 to 3 tonnes of sludge (DM) per hectare per year on the concentrations was studied at the three research sites by calculating ratios of the compounds in sludge-treated soil to reference soil (S/R ratio). The concentrations of I-TEQs did not increase in the sludge-treated soil, whereas the S/R ratios for PBDEs were greater than one. Also, although the PCB contents were higher in the sludge-treated soils, the background sources were more important for the concentrations of PCBs than of PBDEs. The largest increase in the S/R ratios was found at a private farm where large amounts of sludge had been used in the past. Accumulation of the compounds in earthworms from the sites also was investigated. The biota–soil accumulation factors (BSAFs) of the tested compounds declined in the following order: ortho-PCBs > non-ortho-PCBs > 2,3,7,8-substituted PCDD/Fs. The average BSAF for ortho-PCBs was five (organic matter/lipids), and the lowest BSAFs (0.1–0.8) found were for octachlorodibenzo-\(p\)-dioxin. To our knowledge, accumulation of PBDEs in earthworms has not been published previously.

Keywords—Sewage sludge Soil Earthworms Accumulation Organohalogens

INTRODUCTION

Hydrophobic organic environmental contaminants such as polychlorinated dibenzo-\(p\)-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), and polybrominated diphenylethers (PBDEs) are ubiquitous and can enter the soil through atmospheric fallout via dry and wet deposition, or through accumulation in vegetation that eventually reaches the ground in falling foliage. Another potential source is sludge used as fertilizer in agriculture. However, the levels of PCDD/Fs in sewage sludge have been decreasing in many countries during recent years, probably because emissions from industry and households have been falling [1–3]. Few data on PBDEs in sewage sludge have been published to date [4,5]. However, comparisons from different years indicate that environmental levels may be increasing. The highest concentrations are found in the vicinity of industrial sites where the compounds have been used. Analogously, heavily populated areas have higher concentrations of PBDEs than areas with fewer inhabitants [4].

Earthworms constitute an important link in the transport of environmental pollutants from the soil to organisms higher up in the terrestrial food web. For this reason, earthworms are used as model organisms in standardized toxicity tests for chemicals in the soil [6]. Accumulation factors are calculated to estimate the amounts of specific pollutants that organisms could be exposed to [7]. The biota–soil accumulation factor (BSAF) is the ratio between the concentration in the organism and the concentration in soil. Large molecules (cross section > 0.95 nm) have been suggested not to be able to penetrate membranes because of their size [8], and would therefore not be accumulated in organisms. However, other studies have shown some sizeable compounds to be readily taken up by various organisms [9,10].

In this study, soils that have received sewage sludge applications and soil from a field flooded by a river were analyzed for PCDD/Fs, PCBs, and PBDEs. Concentrations in soil in rural and urban areas in Sweden, without known sources other than background, were used as reference sites. To study accumulation of environmental pollutants, some of them large in molecular size, earthworms were collected from all the fields and starved. They were then analyzed and BSAFs were calculated.

MATERIALS AND METHODS

Chemicals

All solvents used were of glass-distilled grade from Burdick and Jackson (Muskegon, MI, USA) or of chromatographic quality from Merck (Darmstadt, Germany). The glassware, which was of high quality, was machine washed with alkaline detergent and rinsed with glass-distilled solvents before use. [9]

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The PCBs and PBDEs were numbered according to International Union of Pure and Applied Chemistry standard nomenclature. Artificial soil was prepared by Pelagia (Umeå, Sweden) according to Organization for Economic Cooperation and Development guidelines for testing chemicals [6].

**Sites and soil samples**

Table 1 presents details of the sites. Samples of soil were taken in spring and autumn 2000. Igelösa (I) and Petersborg (P) were sampled in the spring and Horred (H) and Björketorp (B) were sampled in the autumn. Site Lanna (L) was sampled in both spring and autumn. All sampling sites are situated in southern Sweden. Igelösa and Petersborg are research stations managed by the Agricultural Society of Malmöhus. Sewage sludge from the two cities Lund (I) and Malmö (P) have been applied every fourth year to soil at these sites at two dosages since 1981, with the last occasion in 1997 before sampling. The areas receiving the lower dosage were applied with 1 tonne of sludge, dry matter (DM), per hectare per year (4 tonnes every fourth year), the maximum rate earlier recommended by the Swedish Environmental Protection Agency (Stockholm, Sweden). The higher dosage areas received 3 tonnes of dry sludge per hectare per year (12 tonnes every fourth year). Other areas at these stations had not received sludge and were used as reference areas (R). The Swedish Institute of Agricultural and Environmental Engineering runs the research station at Lanna, where 2.3 tonnes of sludge (DM) originating from Ryaverken in Gothenburg was applied per hectare in 1998.

Soil from two private farms, Björketorp and Horred, also was sampled. Björketorp received a total of 614 tonnes of sewage sludge (DM) from the municipal sewage treatment plant from 1978 to 1982, spread over approximately 25 ha, that is, approximately 25 tonnes/ha during this period. At this time, a textile industry that used PBDEs in their production was connected to the sewage treatment plant. The field also was very close to a road. The adjacent river Viskan, known to contain PBDEs in its sediment [11], had flooded part of the field in Horred in the summer preceding the sampling. Reference samples also were taken from these two farms. The reference areas were another field that had not received sludge in Björketorp, and a part of the field not known to have been flooded recently in Horred.

Further information provided in Table 1 includes abbreviations, conditions of the field at the sampling occasion, the types and properties of the soils, and the amounts of sewage sludge applied. The sites with controlled application of sludge (I, P, and L) consisted of 6 × 20-m² or 5 × 20-m² plots and each soil sample was pooled from 30 to 40 collections from each type of soil, from 0 to 20 cm depth. Each sample was divided into three subsamples. For one soil, Petersborg 2 (P2), all three subsamples were analyzed, whereas for the others, one of the subsamples was analyzed. The water content in the soils was measured in parallel samples dried for 12 h at 130°C and loss on ignition (assumed to equal organic matter [OM]) was determined by heating at 500°C for 2 h.

**Earthworm samples**

Earthworms were collected by hand-sorting from the same spots that the soil samples were taken. The main earthworm species collected were *Lumbricus terrestris*, *Lumbricus* spp., *Aporrectodea caliginosa*, *A. rosea*, and *Allobowphora chlorentica* (H. Larsson, Swedish University of Agricultural Science, Alnarp, Sweden, personal communication). The worms were kept in the same soil that they were found in for 1 to 4 d and then were placed on humid filter paper in the laboratory at 22°C for 24 h to allow them to clear their guts. They were then sorted into three subsamples, with the ambition to get the same amount and size of each species with a maximum of 70 earthworms in the subsamples. Worms from LR were divided into two subsamples, and worms from LS were kept as one sample, because few specimens had been collected (minimum four individuals). The worms were then washed, gently dried, weighed, and killed by being put in a freezer (−20°C). Additional worms were collected from Horred and Björketorp, two and three weeks after the first sampling, respectively.

**Extraction and clean-up**

The soil samples (16 g) were extracted with toluene in a Soxhlet apparatus (Millville, NJ, USA) with a water separator. The extracts were spiked as described below and split into two equal parts. The worm samples (7–37 g) were homogenized with activated sodium sulfate. The lipids were extracted with 300 ml of acetone:cyclohexane (5:2, v/v) and 300 ml of cyclohexane:diethyl ether (9:1, v/v), and any residual water was eliminated by azotropic evaporation with 99.5% ethanol, after which the lipid content was weighed. The extracts were cleaned-up according to a previously described method [9]. Before the presented study, the method was validated for PBDEs in a test study that used fish homogenates that resulted in good recoveries.

The clean-up of soil and lipid extracts was continued by using a mixed acid–alkaline silica column from which the analytes were eluted with cyclohexane (worms) or n-hexane (soil). The earthworm extracts were divided (1:1), and a mixture of 13C-labeled PBDEs and PBDD/Fs was added to one half of each sample. The spiked worm and soil extracts were purified on a 9-mm inner diameter 0.5 g AX-21 carbon/celite column by using the modified U.S. Environmental Protection Agency method 1613. The eluate was concentrated to 1 ml of hexane, and PCBs and PBDEs were eluted with 40 ml of n-hexane:dichloromethane (1:1, v/v). The column was then reversed and the PCDD/Fs were eluted with 40 ml of toluene. Before each separation the column was washed with solutions of dichloromethane:methanol:toluene, dichloromethane:n-hexane, and n-hexane.

**Analysis**

Before extracting the worms, and after each soil extraction, a surrogate standard containing a range of 13C17-labeled compounds (the seventeen 2,3,7,8-substituted PCDD/Fs [310 pg]; coplanar PCBs 77, 126, and 169 [620 pg]; and PCBs 52, 101, 118, 153, 138, 156, and 180 [15 ng]) was added to the samples. Before clean-up, the soil samples were also spiked with 13C-labeled PBDEs 28, 47, 99, 153, 154, and 183 (2 ng). A recovery standard containing 13C-labeled PCB 178 and PBDE 77 was added before gas chromatography (GC)-injection to the orthonal GC and PBDE fractions from the carbon column. The 13C-labeled 1,2,3,4-tetrachlorodibenzo-p-dioxin (1,2,3,4-TCDD) and 1,2,3,4,7,8,9-heptachlorodibenzofuran (1,2,3,4,7,8,9-HpCDF) were added to the dioxin fraction.

Analysis was performed with selected ion monitoring in a combined gas chromatography–mass spectrometer (GC-MS). For the analysis of PCDD/Fs and PBDEs, a high-resolution MS (VG 70S, VG Analytical Limited, Manchester, UK) was used, and for PCBs a low-resolution MS (Fisons MD800, Waltham, MA, USA) was used. All analyses were performed in
Table 1. Data about sites and sampling of soil

<table>
<thead>
<tr>
<th>Site and type of field in Sweden (reference or applied with sludge)</th>
<th>First, last year of sludge application</th>
<th>Total amount of sludge applied (tonnes/ha)</th>
<th>Rate (tonnes DM/ha · yr)</th>
<th>Date of sampling</th>
<th>Condition at time of sampling</th>
<th>Samples analyzed</th>
<th>Organic matter (%)</th>
<th>Clay type</th>
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<td></td>
</tr>
<tr>
<td>I1 lower sludge dosage</td>
<td>1981, 1997</td>
<td>20</td>
<td>1</td>
<td>April 6, 2000</td>
<td>Plowed autumn 1999, not harrowed or sowed</td>
<td>3</td>
<td>4.7</td>
<td>Medium clays</td>
</tr>
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<td>60</td>
<td>3</td>
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<td></td>
<td></td>
<td>4.8</td>
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<tr>
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<td>1981, 1997</td>
<td>20</td>
<td>1</td>
<td>April 6, 2000</td>
<td>Plowed autumn 1999, harrowed and sowed</td>
<td>5</td>
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<tr>
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<td>1998</td>
<td></td>
<td>2.3</td>
<td>April 3, 2000</td>
<td>Before sowing</td>
<td>2</td>
<td>3.4</td>
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<tr>
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<td>1998</td>
<td></td>
<td>2.3</td>
<td>September 19, 2000</td>
<td>3–4 d after harvest</td>
<td>2</td>
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<tr>
<td>BS sludge applied</td>
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<td>25</td>
<td>September 20, 2000</td>
<td>Ploughed grassland (BR)</td>
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<td></td>
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<td>Sediment overflow 2000</td>
<td></td>
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<td></td>
<td></td>
<td>2</td>
<td>2.6</td>
<td>Not classified</td>
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</table>

* DM = dry matter.
the electron ionization mode, at 30 and 70 eV for the high-
and low-resolution MS, respectively. The GC column used in
the PBDE-analysis, a 30-m-long DB-5 capillary column, with a
0.32-mm inner diameter and 0.25-µm-thick film, from J&W Folsom (Ranch Cordova, CA, USA), was introduced directly
into the ion source (250°C) via a heated transfer line (270°C).
A 60-m DB-5 column was used for the PCDD/Fs. For PCBs,
a 30-m DB-5 column with a 0.25-mm inner diameter and 0.25-
µm-thick film was used. The carrier gas was helium at a head
pressure of 14 psi (PBDE) or 18 psi (PCDD/Fs). Sample ali-
quots were injected, by using an autosampler, into a splitless
injector (250°C). The GC temperature started at 180°C or
200°C, which was maintained for 2 min, and then increased
to 300°C. The total time of the temperature program was
between 32 min (for PCBs) and 45 min (for PBDEs).

The two most abundant ions in the chlorine and bromine
isotope clusters were monitored for each native compound.
In addition, one ion (two ions for PBDEs) was monitored for
each of the 13C-labeled standards. The quantification standards
included the 17 native 2,3,7,8-substituted PCDD/Fs, 17 PCBs,
and seven PBDEs in addition to the internal and recovery
standards. Searches were made for all of the tetra-
to octa-
PCDD/F-congeners and three non-ortho-PCBs. Of the other
PCBs, PCB 101, 110, 118, 138/160/163/164 (hereafter denoted
138), 149, and 153/132 (hereafter denoted 153) were quantified
although tri- to deca-PCB were analyzed. The following
PBDEs were quantified in the samples: 28, 47, 66, 99, 100,
153, 154, and 183.

The concentration of toxic equivalents (TEQs) were cal-
culated according to the international (I) and World Health
Organization (Paris, France) human toxic equivalent factors
(WHO-TEFs) [12] concept by multiplying the appropriate TEF
for PCDD/Fs with the sample concentration of the correspond-
ing congener. When the concentration was below detection
limits, one half of the detection limit was used to estimate the
TEQ. The TEQ values presented in Table 2 are the sum of
TEQs derived for each sample.

RESULTS

Soil concentrations of PCDD/Fs

As shown in Table 2, PCDD/Fs were detected and quantified
in all the soil samples. The soil from areas with controlled
applications of sludge (sites I, P, and L) contained a total of
30 to 350 pg/g DM of PCDD/Fs, corresponding with 0.6 to
2.2 pg I-TEQ and WHO-TEQ/g DM. In the sites that had
received uncontrolled applications of sludge or overflow of
sediment from the river Viskan (Sweden), the sum of PCDD/
F s was higher (8.300 and 1,900 pg/g DM). At these two sites,
the TEQs were up to 14 pg I-TEQ and 7.5 pg WHO-TEQ/g
DM. The TEQs in the reference samples from these sites were
similar to those in both the sludge-treated and untreated soils
at the sites given controlled applications of sludge.

Figure 1 shows the profiles and concentrations of the sums
of the tetra-, penta-, hexa-, hepta-, and octa-chlorinated di-
benzo-p-dioxins and dibenzofurans in the soils. The concen-
trations of the tetra-, penta-, and hexa-chlorinated congeners
are similar in the reference sample and the samples with lower
or higher amount of sludge, which is also seen in the TEQs
in Table 2. Although the concentrations of tetra-
- to hexa-chlo-
rinated congeners in the sludge-treated soil are seldom lower
than the concentrations in the reference soils, the differences
are minor, often less than 30% in I, P, and L. The river
site affected by the sediments showed generally the largest
increase in tetra- to hexa-chlorinated PCDD/F levels, by factors of 2 to 12.

Figure 2 shows the ratios between the concentrations of
compounds in sludged soil and reference soil (the S/R ratio)
for each site and sludge dosage. The PCDD homologues with
eight and, to a lesser extent, seven chlorine atoms provide
good indicators for the use of sludge in the soil from Igelösa
and Petersborg (see Fig. 1). These congeners are commonly
found in high concentrations in sewage sludge [13,14] and
the ratios of hepta- and octa-CDD contents between soils given
low loads of sludge and no sludge applications were 1.6 to
7.3 (P1/PR and 11/IR). Soils from Lanna differed less, whereas
soils from Björketropp and Horred differed significantly more.
For example, 400 times more octachlorodibenzo-p-dioxin
(OCDD) was detected in the sludge-treated soil from Björ-
ketropp and 33 times more was detected in the soil flooded by
the river Viskan, compared to the respective reference soils.
Table 2 shows that Horred had the highest concentrations of
PCDFs, 770 pg/g DM in Hsed. As shown in Figure 1, HpCDF
and octachlorodibenzofuranc (OCDF) were the dominating
PCDF congener. The ratio of sum PCDDs/
sum PCDFs was approximately one in the reference sites, and
was highest (23) in Björketropp (sewage applied to soil).

The choice of normalization base, dry matter or organic
matter, had some impact on the concentration ratios. The
sludge-treated soils (except Björketropp) contained slightly
more organic matter (see Table 1), which slightly depressed the S/R ratios based on organic matter compared to the S/R
ratios based on dry matter.

Soil concentrations of PCBs

The concentrations of the eight PCBs quantified were higher
than the total concentrations of the 136 theoretical tetra-
to octa-PCDD/F congeners except for BS (see Table 2). The
reference sites at Lanna and Horred had the lowest levels of
individual ortho-PCB congeners (0.02–0.14 ng/g DM), and
sludge-treated Björketropp soil had the highest levels (up to 1.2
ng/g DM). The PCBs 153 and 138 were present in the highest
concentrations (tri- to deca-chlorinated congeners were ana-
lyzed, and figures for penta and hexa congeners are presented).
The levels of the ortho-PCBs were at least 10 times higher
than those of the non-ortho-PCBs 126 and 169. Levels of PCB
77 are not shown because of the presence of the compound
in the soil blanks.

The concentrations of PCBs were lowest in the soil that
received no sludge, higher in the soil with the lower sludge
dose, and highest in the soil given the highest load of sludge,
as reflected in the S/R ratios shown in Figure 2. At Lanna, the
site that recently has received sludge, the ratio is closer to 1.
Again, the concentrations were highest, relative to the corre-
sponding controls, in soil from Björketropp and Horred. How-
ever, both Horred and Björketropp reference soils had lower
concentrations than the reference sites of I and P (Table 2).
At all sites, the S/R ratios for the two non-ortho-PCBs were
generally lower than those of the ortho-PCBs.

Soil concentrations of PBDEs

The PBDEs were detected in all soil samples (see Table 2).
The dominating congeners among tri- to hepta-PBDEs were
the tetra-brominated PBDE 47 and penta-brominated PBDE
99. Besides the congeners for which there were corresponding
internal standards in the samples, levels of two other tetra-
and penta-bromo congeners were estimated, namely PBDE 66,
<table>
<thead>
<tr>
<th></th>
<th>IR</th>
<th>I1</th>
<th>I2</th>
<th>PR</th>
<th>P1</th>
<th>P2</th>
<th>LR</th>
<th>LS</th>
<th>LR</th>
<th>LS</th>
<th>BR</th>
<th>BS</th>
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<td>300</td>
<td>27</td>
<td>90</td>
<td>80</td>
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<td>26</td>
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* Meanings of designations are given in Table 1.
+ ND = not detected.
+ PCDD/Fs, human (WHO = World Health Organization; I = international).
Fig. 1. Profiles of sums tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins/dibenzofurans (-CCDs/CDFs) in soil (pg/g dry matter [DM]). Meanings of the designations for the sites are given in Table 1; see Table 3 for definitions. TCCD = tetrachlorinated dibenzo-p-dioxin; PeCDD = pentachlorinated dibenzo-p-dioxin.

and PBDE 100 (Table 2). These estimations suggest that the congener found in the third highest levels, of those measured, is PBDE 100. The recoveries of the six internal PBDE standards averaged 60 to 90% and the relative standard deviation of the concentrations in the soil sample triplicates was less than 25% DM. A common problem in analysis of PBDEs is detectable amounts PBDEs in blanks [15]. Note that for the reference soil samples, the blank values of PBDEs 47, 99, and 100 are significant, because the amounts found were only two or three times higher than in the blanks. The reference soils from Lanna contained levels similar to the blanks. The soil concentrations are not compensated for blank values.

Although the concentrations in the reference samples could be overestimated according to the blanks, the S/R ratios of PBDEs shown in Figure 2 were higher than the ratios for PCBs. The lower load of sludge in the controlled sites gave ratios ranging from two to six, with two exceptions in Lanna. The ratio I2/I1 was higher than one, which means that the field given 3 tonnes of sludge per hectare had higher concentrations of PBDEs than the field given 1 tonne per hectare. In Peterborg, the P2/P1 ratio was approximately one, that is, the concentrations in the sludge-treated soils were similar. In Björketorp, the S/R ratios were 2,000 to 12,000. The flooded soil had an average 20 times higher concentrations than the soil further away from the river Viskan.

Because of the high levels of PBDEs in the soil with sludge from Björketorp and the low levels in the reference soils, the concentration varies by a factor of approximately 400,000. None of the soils from the research sites had concentrations of PBDEs above 1 ng/g DM, whereas the lowest concentration in Björketorp soil was 0.8 ng/g (for PBDE 28). All congeners searched for were found in this soil.

Concentrations of PCDD/Fs, PCBs, and PBDEs in earthworms

As shown in Table 3, PCDD/Fs, PCBs, and PBDEs were detected in the earthworms. In most of the worm samples, the concentrations of PCB congeners were highest of all the compounds, at up to 0.1 ng/g lipid, but in the worms from Björketorp, the PBDEs dominated. In sites I, P, and L, the highest concentrations of PCDD/Fs, PCBs, and PBDEs were, in general, found in the worms from I2 and P2, whereas worms from LR had the lowest concentrations. The extraction and cleanup experiment performed before the presented study resulted in recoveries of PBDEs of 80% or more. The recoveries of PCDD/Fs and PCBs were high and consistent, averaging 90%, and the average recoveries of PBDEs from worms ranged from 70 to 130%. The relative standard deviations of the triplicates (from eight sites) were generally 15% for PBDE concentrations in the earthworms, with higher relative standard deviations in worms from site P2 because of interferences. Relative standard deviations for PCBs and PCDD/Fs were 10%. The lipid content in the earthworms averaged 1.5 % (range 1.2±1.8%) with respect to fresh biomass.

Biota-soil accumulation factors of PCDD/Fs, PCBs, and PBDEs

Normalized to fresh or dry weight, PCB and PBDE concentrations in worms generally exceeded those in soil. As
Table 3. Biota–soil accumulation factors (BAFs) of detected polybrominated diphenylethers (PBDEs), polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (PCDDs), and dibenzofurans (PCDFs) in earthworms in the soil from the sampling sites. The BAFs are the ratios of concentration in worm lipids and soil organic matter.

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a Meanings of designations are given in Table 1. ND = not detected or interference; TCDF = tetrachlorodibenzo-p-dioxin; PeCDF = pentachlorodibenzo-p-dioxin; HxCDF = hexachlorodibenzo-p-dioxin; HxCDD = hexachlorodibenzo-p-dioxin; HpCDF = heptachlorodibenzo-p-dioxin; HpCDD = heptachlorodibenzo-p-dioxin; OCDF = octachlorodibenzo-p-dioxin; OCDD = octachlorodibenzo-p-dioxin.

showed in Table 3, this was also true when the normalization was based on lipids in the earthworms and organic matter in the soil. The concentrations generally reflected the soil concentrations, although the accumulation factors differed to some degree between the compounds, as described below.

PCDD/Fs. Table 3 shows that the 2,3,7,8-substituted tetra- and penta-chlorinated PCDD/Fs were generally accumulated two to three times more than was OCDD/F. For instance, in the chromatogram (not shown) for the tetrachlorodibenzo-p-dioxins (TCDDs), some early eluting congeners of the homologue accumulate to greater degrees than later eluting congeners, and the early eluting homologues also show a tendency to accumulate more than later eluting homologues. Similarly, in most worm samples only the first two TCDD congeners (1,3,6,8-TDCD and 1,3,7,9-TDCD) to elute were found in the worms, whereas more congeners were found in the soils. Nevertheless, the BSAFs (not shown) were higher for these two TCDDs than for the 2,3,7,8-substituted congeners presented in Table 3, and similar results were found for pentachlorodibenzo-p-dioxin (PeCDD). The BSAFs for all detected 2,3,7,8-substituted PCDD/Fs at all sites ranged from 0.1 to 1.2 and no differences in this respect were found between PCDDs and PCDFs.

PCBs. Accumulation factors for eight PCBs are given in Table 3. The accumulation factors of ortho-PCBs ranged from 1 to 10, whereas non-ortho-PCB 169 had BSAF values of 0.4 to 1.5. The PCB 149 (2,2′,3′,4′,5′,6′) accumulated in many worms more than the other PCBs. The mono- and non-ortho-PCBs 118, 126, and 169 were less accumulated than the other congeners.

PBDEs. The tetra- and penta-BDEs were accumulated to the same degree as the PCBs, and their accumulation factors ranged for all sites, apart from LS in the autumn, between 1 and 10 (see Table 3). In LS AUTUMN, the three BSAFs were greater than 10. The hexa- and hepta-BDE data for the earthworms were not used because blank levels for these congeners were high in earthworm blanks, but not in the soil blanks prepared in another laboratory. The BAF values for PBDE 28 were calculated only for worms from the flooded soil and sludge-treated soil from Björketropp because the concentrations in these soils (15 and 82 pg/g DM, respectively) were clearly higher than the levels in the soil blanks. The calculated BSAF values were 1 and 2, respectively.

Discussion

Background levels

Long-range transport has a profound influence on global distribution patterns of persistent organic pollutants. For instance, PCDD/Fs, PCBs, and PBDEs have all been detected in air samples [16–18] and long-range transport and deposition are likely to be responsible in large part for the levels of these compounds found in soils that are located far from source regions. Although differences in air profiles are found, the profiles in the reference samples (Fig. 1) are more similar to those found in background air [16] than the profiles usually seen in sewage sludge [13,14].

The TEQs calculated in this study for PCDD/Fs were in the lower range of a compilation summarizing TEQs for the compounds in arable soils from some European countries (Italy: 1.9–3.1 pg I-TEQ/g DM; Germany: <1–25 pg I-TEQ/g DM) [19]. Therefore, high background levels are not masking use of sewage sludge at the study sites of the present study. The concentrations of PCBs in the soils were low, in level with the concentrations found by Andersson and Nilsson [20] in 1999 in the soils from Igelösa and Petersborg. As a comparison, the level of PCB 101 in indoor worm compost

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Lanna were 100 to 400 times higher than in the reference soils (on DM).

Many of the current data on PBDEs apply to the aquatic environment. Until data on background soil concentrations of PBDE are available, comparisons are made to sediment data. The concentrations of PBDEs 47 and 99 in sediments upstream of an industrial site were 4.2 and 8.8 ng/g OM [4], which is about 10 times higher than the levels found in the reference soils. Based on dry matter contents, the difference is even larger.

Effects on concentrations of sludge application and river sediment

PCDD/Fs. The air is a possible source of PCDD/Fs to the soils, especially in cases where concentrations in the sludge-treated and untreated soils are similar, which applies to most of the PCDD/F-congeners in this study (Table 2). Rappe et al. [14] analyzed PCDD/Fs in PR, P1, IR, and II soil from 1993 and 1994 and found that the contributions from the sewage sludge did not affect the I-TEQs. In other studies where sewage sludge was applied at different rates, or with different concentrations of organic compounds, increased levels of PCDD/Fs and PCBs have been found in the sludge-treated soils [22,23]. The sludge from 1993 used in Igelösa and Petersborg had lower levels of I-TEQs than the sludge used in the previous application in 1989 [3]. During the same period, decreases in PCDD/F concentrations were observed in sludge from Spain and Switzerland [1,2]. The decrease in PCDD/Fs in sludge and the similar levels of TEQs in sludge and nonsludged soil indicate that the S/R ratios of TEQs will continue to be similar.

The OCDD, the congener most strongly correlated to use of sludge, has a low TEF, and therefore the TEQs are not influenced to any great extent by the increase in OCDD concentration in the soil associated with sludge treatment, except at Björketorp, where the increase in OCDD was pronounced. The TEQs in the soil flooded by the river Viskan also increased, but the sediments are likely to have contributed more lightly chlorinated PCDD/Fs as well, because the abundance of these congeners also increased in the flooded soil. The PCDD/Fs were analyzed in an investigation of sediment from sites along the river Viskan [24]. The PCDF profile in the present study and the Golder Teknik report [24] were very similar. The PCDF profiles of the flooded soil differed substantially from the profiles at other sites. The reference soil at the site by the river also differed, but less strongly. Therefore, the conclusion can be made that the reference soil at this site has also probably been flooded by the river in the past. This river is situated in a region with extensive textile production. In a previous study, a textile industry was found to be the probable source of elevated levels of heptachlorodibenzo-p-dioxin (HpCDD) and OCDD in sewage sludge [25]. Sodium hypochlorite used for bleaching of raw cotton cloth was found to be contaminated with pentachlorophenol. The PCDD/Fs are known contaminants in pentachlorophenol, with OCDF or OCDD dominating the PCDD/F profile, depending on the technical mixture used, and high concentrations of OCDD and OCDF have been found in cotton textiles [26].

PCBs. The II/IR and P1/PR ratios are 1.1 and 2.3, respectively, in the soil. The higher S/R ratios for the I2 and P2 and their corresponding reference soils indicate that the PCB concentrations were slightly affected by the addition of sludge. The ortho-PCB concentrations in the sludge (DM) used at Lanna were 100 to 400 times higher than in the reference soils (O. Palm, Swedish Institute of Agricultural and Environmental Engineering, Uppsala, Sweden, personal communication). The dilution factor in Lanna between the sludge and soil was estimated to be 1:2,000 (estimating that the upper 0- to 30-cm soil layer weighed ~4.200 tonnes, according to Andersson and Nilsson [20] and the sludge applied weighed 2.3 tonnes). This means that the sludge contributed at most 20% of the PCB in the dry soil in site L, according to our findings.

PBDEs. Figure 2 demonstrates that PBDE contents increased more than those of the other two groups of compounds studied in sludge-treated soils. Although soil samples from P2 did not contain higher PBDE concentrations than soil samples from P1, the corresponding worms did. The relative standard deviations for PBDE concentrations in soil were higher for PBDEs than for PCBs based on dry matter, by approximately 25%, which could in part explain the lower concentrations in soil samples from P2, than expected from the S/R ratios from the other sites. Heterogeneity in the samples could not be ruled out although 30 to 40 subsamples were collected.

The PBDEs have been detected in air from background areas in Sweden, at concentrations (for the sum of PBDEs 47, 99, and 100) ranging from 1 to 8 pg/g m³ [18]. According to Nylund et al. [27], washout from the atmosphere had no influence on the levels in sludge and the main sources of the compounds in sludge are therefore expected to be households, industrial plants, or communities connected to the sewers. The levels of PBDE congeners in recent sewage sludge were higher or comparable to the levels of PCB congeners [4]. This is in accordance with the higher S/R ratios found for PBDEs than for PCBs in soil noted in the present study. The PBDEs 47 and 99 were present at similar concentrations in the soil and similar proportions were also seen in sewage sludge and the technical PBDE product Bromkal 70-5DE [5,18].

Sludge application seems to influence concentrations of the PCDD/Fs, PCBs, and PBDEs in soil in different ways. Substances such as PBDEs that have been introduced relatively recently and are still in use are collected from various parts of the community via the sludge, and their dispersal into the environment may not yet have equilibrated to the proportions being used. Emissions of PCDD/Fs, on the other hand, are nowadays restricted in many ways, although this group of compounds also accumulates in sludge. The PCBs are still present in our surroundings. They are, for instance, present in some types of elastic plastic sealants in buildings, and old capacitors [28]. Thus, emissions continue although PCBs were banned in Sweden in the 1970s. The ratios between the sludge-treated and untreated soils shown in Figure 2 show the impact of sludge in relation to background levels.

The results from the two areas that have been overflowed by sediment and received sludge between 1978 and 1982 show that these events had considerably greater impact on the soil concentrations than the controlled applications. Both such sites analyzed in this study are situated in a part of Sweden where the textile industry is important. This industry used flame-retardants (e.g., PBDEs) from the mid-1970s to the mid-1990s, and also handled contaminated bleaching agents [25]. To our knowledge, PBDEs are not used by the textile industry in Sweden today.

Biotas–soil accumulation factors

The accumulation factors shown in Table 3 reveal that large molecules such as PBDE 99 and OCDD were accumulated in the earthworms. Examination of the data also shows that the
BSAFs varied within compound classes because the tendency of the compounds to sorb to soil matrices increased, and differed between groups of compounds. The BSAFs for PCBs were similar to those found in earlier studies.

**BSAFs.** The BSAFs derived for the PCBs shown in Table 3 were in the same range as those found for *Eisenia* exposed in the laboratory to soil from P2 (5.1–7.0, day 10, OM/lipids, ortho-PCBs, unpublished results) or to field-contaminated soil (5.3–7.4 OM/lipids, penta- to hepta-chlorinated PCBs [10]). Reported BSAFs for PCBs in earthworms from forest soil are lower, whereas corresponding figures in worms from compost are higher [7, 21]. Accumulation of 2,3,7,8-TCDD from spiked lower, whereas corresponding figures in worms from compost (5.3±7.4 OM/lipids, penta- to hepta-chlorinated PCBs [10]).

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Accumulation of 2,3,7,8-TCDD and OCDD loads via ingested sediment [32]. Hendriks et al. [35] recently revised their model for accumulation of PCBs and PBDEs in soil applied with 1 tonne of sludge per hectare per year for more than 15 years, and soil given no sludge, was approximately 1, that is, no increase in concentrations of these compounds due to sludge application was seen. In contrast, PBDEs, a class of compounds still in use in the society, are being dispersed in the environment by the spread of sludge. This was evident from the comparisons of the soils, where the S/R ratios of PBDEs 47 and 99 were generally three or higher. Although longer depuration periods could have been used (24 h is fairly short for large worms such as the *L. terrestris* present in some of the worm samples), the BSAFs for PCBs seem reliable, as shown above. Therefore, the period on filter paper is assumed not to have distorted the accumulation factors of the compounds studied.

**Structural features influencing BSAFs.** The BSAFs of PCBs in worms from most sites showed dependence on the planarity of the congeners, which is also correlated with the organic carbon–water partition characteristics of the congeners [37]. The PCBs studied had two levels of chlorination (five and six), and four degrees of ortho-substitution (none to three ortho substituents). In most studies, the situation is reversed, in that the PCBs usually differ more in number of chlorine atoms than in substitution pattern. This may partly explain the differences in accumulation seen in the present study.

If the water phase is the most important for uptake, deviations in the strength of sorption to soil from estimates derived from octanol–water partition coefficient (\(K_{oc}\)) values could account for the differences in BSAFs. It has been shown that the organic carbon–water partition coefficient (\(K_{oc}\)) for many substances is underestimated when modeled from \(K_{oc}\), that is, their availability to organisms is overestimated by this method [38]. This is especially true for planar compounds with a weak tendency to partition into the water phase. Further BSAFs of PCBs and PAHs from the same soil can differ significantly, for example, an eightfold difference was found in a floodplain area studied by Ma et al. [39] and Hendriks et al. [7], whereas 10- to 100-fold differences were found in 25 field-contaminated soils by Krauss et al. [40]. Earthworms are used as a terrestrial test organism in toxicity tests [6] and mortality and changes in weight and are used as test parameters. According to our results, earthworms are able to survive in soil with high concentrations of PBDEs, but whether or not they are harmed in any way by such exposure was not established.

**CONCLUSIONS**

In the environment, decreasing levels of old pollutants (pollutants long known to be harmful and present in the environment) are found [1, 2], indicating that earlier efforts to limit their use and emissions have been effective. The levels of TEQs in the Swedish soils studied here were low compared to those reported for other countries. The ratios between concentrations of tetra- to hexa-PCDD/Fs in soil applied with 1 tonne of sludge per hectare per year for more than 15 years, and soil given no sludge, was approximately 1, that is, no increase in concentrations of these compounds due to sludge application was seen. In contrast, PBDEs, a class of compounds still in use in the society, are being dispersed in the environment by the spread of sludge. This was evident from the comparisons of the soils, where the S/R ratios of PBDEs 47 and 99 were generally three or higher. It would have been of benefit to know sewage contents of the discussed compounds. However, well-defined soils with corresponding reference areas are both very useful for studies such as these. Extensive use of sludge occurred during the years before controls were imposed on the release of organic pollutants from industrial sites to municipal sewage treatment plants. The effects of the sludge applications are still reflected in the high levels of PBDEs and OCDD in the soil at one of the private
farms. The earthworms living in these soils make the compounds available for birds, moles, and hedgehogs. This occurs via uptake in the worms and subsequent predation by animals on the earthworms. The accumulation of PCBs was similar to those seen in earlier investigations, and in addition we now know that large molecules such as penta-PBDEs are also accumulated in worms. Strongly sorbing congeners were accumulated less strongly than ortho-PCBs, probably being less bioavailable than the latter compounds.

Acknowledgement—Financial support by the Swedish Environmental Protection Agency and the assistance of Gunilla Söderström with sampling are gratefully acknowledged.

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