RESEARCH ARTICLE

PCDD/F and dioxin-like PCB profiles in soils amended with sewage sludge, compost, farmyard manure, and mineral fertilizer since 1962

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Abstract

Background, aim, and scope Biowaste contains compounds of agricultural value such as organic carbon, nutrients, and trace elements and can partially replace mineral fertilizer (MIN) and improve the physical properties of the soil. However, the obvious benefits of land spreading need to be carefully evaluated against potential adverse effects on the environment and human health. Environmental contamination resulting from biowaste application is one of the key variables when assessing cost/benefits. This study provides data on the resulting concentration of polychlorinated dibenzodioxins and dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (DL-PCBs) in the soil column as a result of the different types of fertilizers.

Materials and methods In a long-term field experiment established in 1962, we investigated the influence of the application of biowaste-derived fertilizers such as sewage sludge (SSL), compost (COM), and farmyard manure (FYM) to a luvisol derived from loess on the contents of PCDD/Fs and DL-PCBs. Control plots amended only with MIN served as a basis to compare the biowaste-amended soils with soils affected only by atmospheric deposition, thus experimentally separating the two pathways of soil contamination. Samples of the soil column down to a depth of 90 cm were taken in 2001 and analyzed for PCDD/Fs and dioxin-like PCBs according to US-EPA methods 1613 and 1668, respectively.

Results Thirty-nine years of experimental SSL and COM applications exceeding four times the maximal amount as laid down in German legislation resulted in a doubling of the international toxicity equivalent (I-TEQ) budget for PCDD/Fs and a threefold increase for DL-PCBs as compared to test plots amended with MIN only. As compared to MIN, the application of FYM had no effect on the PCDD/F and PCB content in soil. The average contribution of the DL-PCBs to the WHO-TEQ was 19% in the MIN and FYM plots and somewhat higher in the COM (23%) and in the SSL (27%) plots.

Discussion Although the test plots received four times the maximum application of SSL as laid down in the German SSL ordinance and the investigated region represents the upper end of the topsoil concentrations typically found in Germany, the soils treated with SSL and COM were still a factor of 4 below the German guideline value of PCDD/Fs for arable land. No enhancement of translocation of PCDD/Fs and PCBs into the corresponding subsoils due to the presence of dissolved humic matter or other surfactants potentially present in the biowaste was observed. The similarity of congener patterns in all soils, irrespective of the type of fertilizer applied, points towards atmospheric deposition of PCDD/Fs and DL-PCBs as the main intake route in the soils. The higher levels in the SSL- and COM-amended soils can be explained by the fact that both biowastes are subject to atmospheric deposition occurring at their origin. In the case of COM, it is accumulation in the

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foliage, while in the case of SSL, atmospheric particulate from wet and dry deposition is collected in the wastewater treatment system via urban runoff.

Conclusions It appears that the common practice of SSL applications in Germany does not pose a current threat to the agro-environment with regard to PCDD/Fs and DL-PCBs. However, time trend data on PCDD/Fs in SSL-amended soils will be needed to obtain a prognosis about the long-term effect of biowaste applications on soil quality.

Keywords Atmospheric deposition · Compost · Congener pattern · Dioxin-like PCBs · Manure · PCDD/Fs · Sewage sludge · Soil · Translocation

1 Background, aim, and scope

There is broad agreement that land spreading of biowaste can contribute to a sustainable resource management. In addition, land spreading is a low-cost disposal option. Different kinds of biowaste such as sewage sludge (SSL), compost (COM), and farmyard manure (FYM) are spread on the land in agriculture, forestry, and land reclamation operations. Biowaste contains compounds of agricultural value such as organic carbon, nutrients, and trace elements and can partially replace mineral fertilizer (MIN) and improve the physical properties of the soil (Chambers and Nicholson 2001). Phosphorus, especially, with an expected availability of 200 years maximum from geological deposits (Sommelier et al. 1996) can be recycled from biowaste.

It is expected that land spreading of biowaste will increase worldwide following the implementation of national or transborder (e.g., European Union, EU) regulations, which restrict the disposal of organic-rich materials in landfills and sea dumping. However, the obvious benefits of land spreading need to be carefully evaluated against potential adverse effects on the environment and human health. Environmental contamination resulting from biowaste application is one of the key variables when assessing cost/benefits. The potential threat that land spreading of biowaste poses to soil quality and the food chain and, to some extent, to aquatic ecosystems resulted already in the banning of land spreading of SSL in Switzerland, for example.

In the USA and several EU member states, SSL application is under regulation for heavy metals and a series of organic pollutant classes such as polychlorinated dibenzo-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), PAHs, surfactants and their stable metabolites, softening agents, adsorbable organic halogens, and even volatile organic compounds.

At the EU level, the current regulatory framework for contaminants in biowaste spread on land is limited to heavy metals in SSL (Council 1986) and nitrates from agricultural sources including FYM (Council 1991). However, a revision of Directive 86/278/EEC (Council 1986) is envisaged, as an element of the actions proposed by "The Thematic Strategy on the prevention and recycling of waste", and the extension to some organic parameters including PCDD/Fs and PCBs is under discussion. The land spreading of COM is currently not regulated at EU level but will be tackled through the establishment of technical and environmental quality criteria for COM that has been recovered from waste and is traded as a product. These criteria will be established through the "end-of-waste" procedure the Commission has envisaged in its proposal to revise the Waste Framework Directive COM (2005)667 (European Commission 2005).

Today's biowaste is generated or at least processed within the "technosphere" and may consequently contain traces of a variety of "urban" pollutants (Bright and Healey 2003). Among the critical compound classes, which, in addition to their toxic properties, tend to persist after their introduction into the environment are heavy metals and persistent organic pollutants such as PCDD/Fs and PCBs. The half-life of PCDD/Fs in soil is estimated to be at least 10 years (Jackson and Eduljee 1994; Rappe et al. 1999). A comprehensive literature overview on exposure to PCDD/Fs as a consequence of recycling of sewage biosolids on land was prepared by Rideout et al. (2002) and Rideout and Teschke (2004).

Elevated PCDD/F concentrations after SSL application on soil have been reported (McLachlan and Reissinger 1990; McLachlan et al. 1996; Wilson et al. 1997; Eljarrat et al. 1997; Molina et al. 2000), and it has been demonstrated that the elevated concentrations in SSL-amended soils persist over time. Using archived soil samples of a plot that received a single SSL application, McLachlan et al. (1996) demonstrated that 59% of the PCDD/F burden was still present after 18 years.

Compared to SSL, literature data on the potential impact of FYM and related fertilizers on soil quality are scarce. The data available from Welsch-Pausch and McLachlan (1998) and Stevens and Jones (2003) on cattle manure indicate maximum PCDD/F concentrations in manure (dry matter) at the lower end of the range typically found in SSL. However, due to higher application rates, the PCDD/F burden in soil resulting from cattle manure application may be equal or may even exceed the burden resulting from SSL application (Stevens and Jones 2003).

Another potentially adverse effect of the application of SSL and other organic-rich material to soil is the potential enhancement of leachability and translocation of PCDD/F due to the presence of dissolved humic matter (DHM) or synthetic surfactants like linear alkyl benzene sulfonate (LAS). Kim and Lee (2002) assumed on the basis of

calculations based upon octanol/water partition coefficients ($K_{o/w}$) that specifically higher chlorinated PCDD/Fs were subject to solubility enhancement in the presence of DHM: A DHM concentration of 5 mgl^{-1} in water would enhance the solubility of octachlorodibenzodioxin (OCDD) by a factor of 450 and for octachlorodibenzofuran (OCDF) by a factor of more than 700 when compared to water without DHM. The effect on lower chlorinated PCDD/Fs would be less, but the solubility of 2,3,7,8-tetrachlorodibenzodioxin (TCDD) would still increase by a factor of 35.

Laboratory-scale experiments conducted earlier by Lee et al. (2000) demonstrated enhanced leachability of highly chlorinated compounds extracted with DHM, and Schramm et al. (1995) observed an enhancement of PCDD/F leachability from soil and fly ash after adding LAS to the eluent. Similar observations were made at laboratory scale by Payá-Pérez et al. (1996) for hexachlorobenzene in soil after the addition of sodium dodecyl sulfate. In how far these observations are reproducible under field conditions remains to be assessed, although Schramm et al. (1995) recommended on the basis of their findings that wastes containing dioxins should not be co-disposed with organic wastes such as SSL and other biowastes.

Only few publications refer to the accumulation of dioxin-like PCBs (DL-PCBs) in biowaste-amended soils. However, DL-PCBs are present in considerable amounts in SSL as shown by Eljarrat et al. (2003) who found contributions from DL-PCBs to the combined toxicity of PCDD/Fs and DL-PCBs ranging from 13% to 50% (World Health Organization toxic equivalent, WHO-TEQ) in various domestic and industrial sludges from Catalonia (Spain).

The present paper intends to supplement the existing information on accumulation of PCDD/Fs and DL-PCBs in SSL-amended soils and to widen the scope to other kinds of biowastes such as COM and FYM. In addition, the significance of potential solubility enhancement of PCDD/Fs and DL-PCBs through the presence of DHM or surfactants in biowaste will be addressed.

2 Materials and methods

2.1 Experimental design

Valuable environments to assess the long-term impact from land spreading of biowaste on soil are agro-environments with a well-documented history of their amendment practice. The Institute of Crop Science and Resource Conservation (INRES) at the University of Bonn (Germany) is running a long-term field experiment since 1962, where different types of biowaste have been applied, focusing on their potential for replacing mineral fertilizers. Crop rotation

until 1994 was sugar beet followed by three times bread wheat and later on sugar beet followed by three times bread wheat. The crop yield of bread wheat was positively correlated with the amount of SSL and MIN while high applications of COM resulted in lower yields, in particular for sugar beet.

Although the initial focus has been put on organic matter and nutrient supply and plant growth, the well-documented history on type and application rates of biowaste offers the possibility to evaluate pollutant transfer as well. A description of the experimental setup and data on the accumulation of trace metals were published by Werner and Warnusz (1997).

Soil properties, meteorological conditions, and the history of land use are identical for the whole test area. Consequently, all differences found between the level of pollutants and their translocation into the soil column can be related exclusively to specific properties of the different fertilizers applied.

Making use of this experimental setup, this paper expands the focus onto PCDD/Fs and DL-PCBs. The soil of the experimental site Meckenheim (50° 37′ 42″ N, 6° 59′ 14″ E), 15 km southwest from Bonn (Germany) is a luvisol derived from loess. The experimental application of biowaste started in 1962. Before starting the experiments, the different test plots were used identically under the application of FYM and MIN. At the start of the experiment, the pH of the soil was 6.4, the total organic carbon content 1.07%, and the total nitrogen content 0.108%. In a continuous rotation between hoed crops—only twice replaced by fodder crops—and cereals, SSL, COM, and FYM were applied every other year on separate plots. In control plots, only MIN was applied. MIN was applied according to the farmer's practice and the demand of the concerning crop. This plot is taken as a reference, reflecting atmospheric deposition and other diffuse input pathways to soil. A significant contamination of mineral fertilizer with PCDD/Fs and PCBs has not been reported.

The experiment is a randomized complete block design with four replications. Each plot has a size of 24.5 m^2. The plots were plowed (depth 25–30 cm) after harvest in autumn and the different organic fertilizers were applied immediately before sowing. The dosage of SSL was 15 t ha^{-1} dry weight (dw), and the dosage of COM was 58 t ha^{-1} dw every other year. These experimental dosages represent fourfold the maximum applications to soil as laid in the German SSL ordinance (BGB1 1992) and the German biowaste ordinance (BGB1 1998). The SSL was obtained from two municipal wastewater plants close to Bonn. Until 1991, the COM was derived from a composting plant, where household garbage and SSL were composted together. Since 1992, the COM applied originated from

municipal biowaste (garden and kitchen waste) only. FYM, obtained mainly from cattle farming in the vicinity, was applied in a dosage of 40 t ha^{-1} fw every other year. All biowaste-amended plots received additional MIN.

2.2 Soil sampling

In 2001, composite soil samples consisting of 10 random subsamples each were taken from the layers 0–30, 30–60, and 60–90 cm to determine potential differences in migration of the compounds investigated. The soil was freeze-dried, and the fraction <2 mm was separated for analysis.

2.3 Analytical methodology

Analysis of PCDD/Fs and DL-PCBs was based on isotope dilution using gas chromatography (GC) for separation and high-resolution mass spectrometry for quantification. The applied methodology was a combination of US Environmental Protection Agency (US-EPA) method 1613 for PCDD/Fs (where ^{13}C-labeled OCDF was added to the proposed ^{13}C surrogate mixture) and US-EPA method 1668A for the DL-PCBs. A mixture of all WHO-TEQ-relevant ^{13}C-labeled dioxin and PCB congeners was added to 30 g of soil dw prior to extraction.

Extraction was conducted in 300 ml *n*-hexane/acetone (220/30; vol/vol) using Soxhlet extractors for 48 h. The efficiency of this extraction procedure was confirmed in preliminary experiments by postextracting the soil for 48 h in toluene. The Soxhlet extractor was modified in a way to concentrate the extract to 10 ml in a final step inside the extractor. The extract was filtered through a small column containing 1 g of anhydrous sodium sulfate and was adjusted to a final volume of 10 ml in *n*-hexane.

Extract purification was executed with an automated cleanup system (Power-Prep P6, from Fluid Management Systems (FMS) Inc., Watertown, MA, USA). The chromatographic principle is based on the method proposed by Smith et al. (1984). The cleanup system consists of a computer-controlled modular valve set and a liquid chromatography pump that is programmable for preconditioning and cleanup. The extract was purified using a silica column, acidified with sulfuric acid followed by an aluminum oxide (alumina) column. A carbon column, which can be eluted in both directions, separates noncoplanar PCBs from PCDD/Fs and coplanar PCBs. Chromatographic columns were used as provided by FMS. A detailed description of the method and its performance is given by Abad et al. (2000).

The whole process results in two fractions, one containing the eight mono-ortho PCBs (105, 114, 118, 123, 156, 157, 167, and 189), and the other containing all PCDD/Fs

and the four nonortho PCBs (77, 81, 126, and 169). The two fractions were collected separately and evaporated automatically under nitrogen flow (TurboVap II workstation, Zymark, Hopkinton, MA, USA) to a final volume of 1 ml.

Prior to GC injection, the final volume was adjusted under N$_2$ flow to 30 µl (PCDD/F-fraction) and 200 µl (PCB-fraction), respectively, and ^{13}C-isotope-labeled syringe standards (1,2,3,4-TCDD and 1,2,3,7,8,9-HxCDD for PCDD/F and PCB 52 and PCB 101 for DL-PCB) were added to both fractions for the calculation of the recoveries. All solvents used during extraction and extract purification were of nanograde quality (Merck, Darmstadt, Germany).

The GC system was an HP 6890 (Hewlett Packard, Waldbronn, Germany), using a split/splitless injector with borosilicate liner (4-mm inner diameter). Sample injection was done with an A200SE autosampler (CTC-Analytics, Zwingen, Switzerland). The samples were analyzed twice using two capillary columns of different polarities to detect possible coelution of TEQ relevant congeners with nontoxic congeners present in the extract.

Column 1, 60 m×0.25 mm with 0.25 µm 95% methyl–5% vinyl-polysiloxane bonded phase (DB-5MS, J&W Scientific, Folsam, CA, USA). Injector temperature, 270°C. Temperature program, 120°C, 4.5 min, 90°C/min, 130°C, 20°C/min, 240°C, 3°C/min, 262°C, 8°C/min, 300°C, 11 min.

Column 2, 30 m×0.25 mm with 0.1 µm 90% biscyanopropyl–10% cyanopropylphenyl-polysiloxane bonded phase (RTX-2330, Restek, Bellefonte PA, USA). Injector temperature, 270°C. Temperature program, 120°C, 3 min, 30°C/min, 200°C, 2°C/min, 250°C, 3°C/min, 265°C, 8 min.

The GC was coupled with a VG Autospec Ultima mass spectrometer (Micromass, Manchester, UK) operating in EI mode at 34 eV with a resolution of >10,000. Two masses in the M+ isotope cluster were monitored for each analyte and each internal standard. When interferences were encountered, more masses were monitored.

Typical recoveries of the internal standards were above 60%; samples where the recovery for TEQ-relevant congeners (> 5% contribution to the overall TEQ) was below 40% were re-extracted. The reproducibility of the analytical method was examined by a series of parallel extractions. The agreement between the parallels was very good at a variance below 5% on a TEQ basis.

3 Results and discussion

If not stated differently in the text, all results given in WHO-TEQ apply the 1998 TEF scheme (Van den Berg et al. 1998).

3.1 The contribution of biowaste-associated fluxes to the current PCDD/F and DL-PCB burden in the investigated soils

The soil profiles reveal that the main load of PCDD/Fs and DL-PCBs is aggregated in the topsoil (Fig. 1). Consequently, it can be assumed that a sampling depth down to 90 cm sufficiently represents the total burden of PCDD/Fs and DL-PCBs at present.

The amounts of PCDD/Fs and PCBs present in the soils result from atmospheric deposition only, plus the specific additional inputs from the application of the different kinds of biowaste. The plots where only MIN was applied serve as a baseline representing atmospheric deposition only, assuming that the content of PCDD/Fs and PCBs in MIN applications in the past was negligible.

For the comparison of the total amount of PCDD/Fs and DL-PCBs present in the different soils, the total amounts detected within a depth of 0–90 cm were summed up and the total PCDD/F and PCB toxicity amount per unit area was calculated based on a soil density of 1.5 g cm^{-3}. The average burdens (arithmetic mean and arithmetic standard deviation SD) from four parallel test plots[1] for each fertilizer application are displayed in Fig. 2.

The comparison shows that the COM and SSL applications between 1962 and 2002 resulted in a PCDD/F burden approximately twice as high and a DL-PCB burden approximately three times as high as found in the soil amended with MIN only. Interestingly, the burden present in soils amended with FYM did not differ significantly from the MIN reference plots (honestly significant difference (HSD)-Tukey test, 95% confidence level). This indicates that the PCDD/F and DL-PCB fluxes into the manure plots were also dominated by atmospheric deposition, and no significant contamination arose from the FYM application itself.

The average contribution of the DL-PCBs to the WHO-TEQ was 19% in the MIN and FYM plots and somewhat higher in the COM (23%) and in the SSL (27%) plots. PCDD/F and DL-PCB burdens of COM and SSL differed only slightly for the PCBs (HSD-Tukey test, 95% confidence level), but, as described above, the compost consisted of nonseparated household waste and sewage sludge until 1991. Only later on was compost exclusively derived from garden and kitchen biowaste available. Similar differences among soils amended with SSL and FYM were reported by Vives et al. (2008) from the Pavia region (Italy), where the SSL-amended soils displayed about threefold higher concentrations for PCDD/Fs.

3.2 PCDD/F concentrations in the top soils in relation to German guidelines
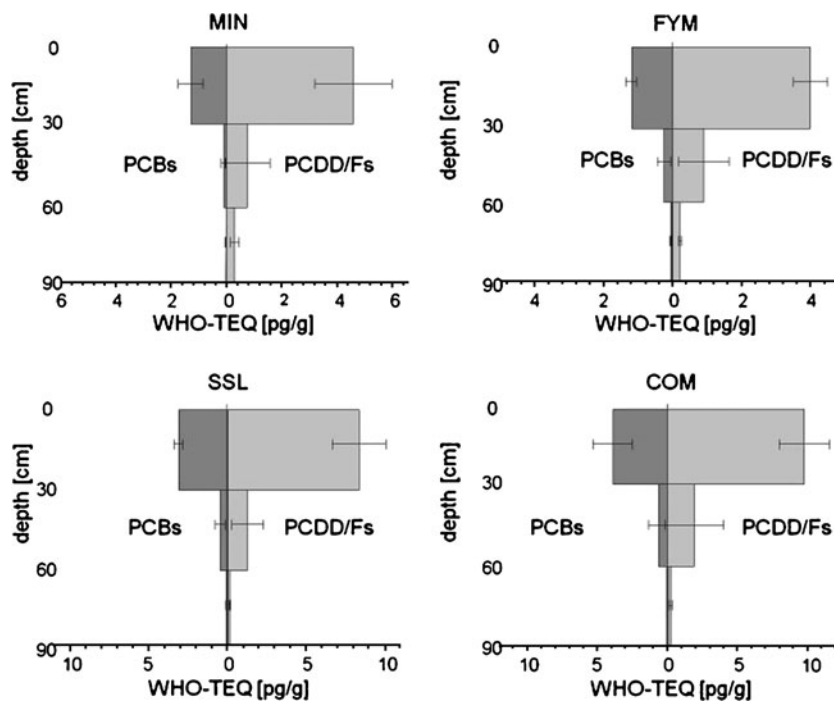
The PCDD/F concentrations in I-TEQ detected in the topsoil (0–30 cm), subject to land-use-related guidelines in Germany, are almost identical to the WHO-TEQ-based results (Table 1). In the top soils amended with MIN and FYM, the average PCDD/F concentrations were 4.7 and 4.2 pg g^{-1} dw (I-TEQ), whereas SSL and COM applications resulted in 8.9 and 10.4 pg g^{-1} dw (I-TEQ), respectively. Although the PCDD/F concentrations of the top soil amended with COM and SSL exceed the MIN and FYM plots by about a factor of 2, they are well below the German guideline limit of 40 pg g^{-1} dw (I-TEQ) for agricultural use (Federal Environmental Agency 1993).

However, in comparison with other topsoil data from Germany, the PCDD/F levels obtained during the Meckenheim experiment are in the upper range, which may be attributed to the high level of industrialization of the North Rhine Westphalia and the resulting elevated atmospheric deposition of PCDD/Fs in this region. Arable lands from other German regions measured between 1988 and 1997 show medium PCDD/F concentrations in topsoils (0–30 cm) of 1 pg g^{-1} dw (I-TEQ) with the 90% percentile of 8 pg g^{-1} dw (I-TEQ) (Federal Environmental Agency 2002).

The topsoil data of the investigated site suggest that the SSL and COM application of about 40 years resulted in an additional PCDD/F contamination of about 4 pg g^{-1} dw (I-TEQ). However, it should be noted that the application rates on the investigated biowaste plots were four times higher than the application maxima recommended by the German SSL ordinance (BGB1 1992). Consequently, the results obtained in this study overestimate the actual PCDD/F flux that would result from an application in accordance with the legislation by approximately a factor of 4.

In relation to future trends, the results presented here should be interpreted with care, since the increase of the PCDD/F and PCBs in soil observed in this experiment covers the period of maximum releases into the environment and should therefore not be used for a linear extrapolation. From the few time series available on PCDD/F and PCB concentrations in SSL, it can be assumed that SSL and other kinds of biowaste have followed the overall environmental trend. The concentrations of PCDD/Fs in Spanish SSL decreased by more than one order of magnitude since the late 1970s (Eljarrat et al. 1999). PCBs in German SSL decreased by 50% between 1989 and 1996 (UMK-AG 2000), and German PCDD/F data in SSL show a decrease of a factor 2–3 between 1990 and 1997 (Federal Environmental Agency 2002).

In order to estimate whether the PCDD/F trends in the investigated soils follow the decreasing trends in SSL, detailed evaluation of a time series of archived soils amended with SSL and MIN from the Meckenheim site

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[1] Except for DL-PCBs in the compost plots, where one outlier (x) was not included in the average and for PCDD/Fs in manure, where the PCDD/F fraction of one of the topsoil samples was misplaced during sample purification.

Fig. 1 Concentration profiles of PCDD/F and DL-PCB in the different plots expressed in WHO$_{98}$-TEQ

are in preparation. Preliminary results reveal stable PCDD/F concentrations (WHO-TEQ) in the Meckenheim top soil since the late 1970s and even a slight decrease of the DL-PCBs (WHO-TEQ) (Umlauf et al. 2004).

3.3 Depth profiles and the question of dissolved-humic-matter-associated translocation

DHM may principally act as a vehicle for the translocation of lipophilic compounds into deeper soil layers (Kim and Lee

2002), especially in plots where organic matter has been used as a fertilizer. In the case of SSL applications, additional effects from surfactants present in sludge may occur.

However, in this experiment, the relative vertical profiles of PCDD/F and DL-PCB concentrations of the different plots (Fig. 1) do not show remarkable differences between the plots amended with biowaste and the mineral reference plot, particularly in the layer below 60 cm. PCDD/Fs as well as DL-PCBs are located mainly in the topsoil (0–30 cm), which corresponds to the plowing depth applied.
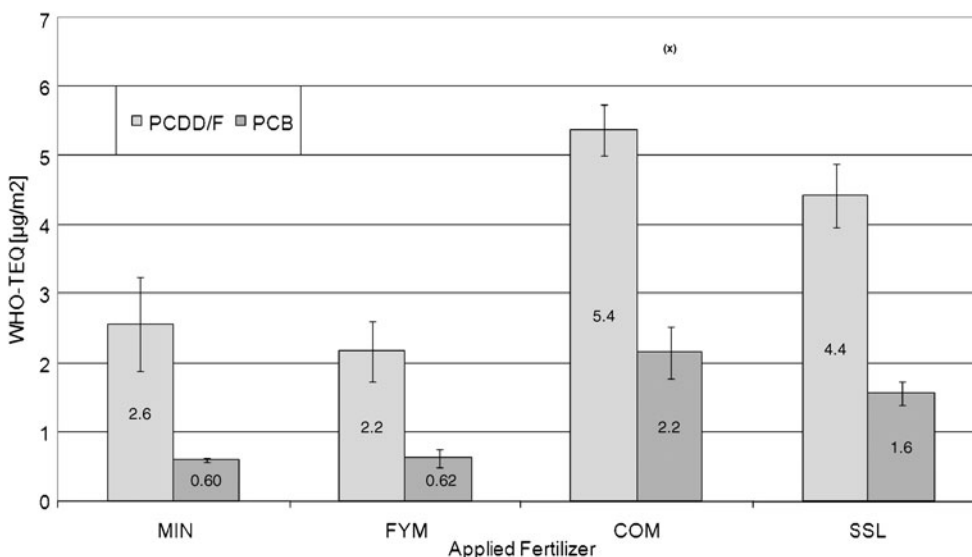

Fig 2 Total PCDD/Fs and DL-PCBs in soil (in microgram per square meter WHO$_{98}$-TEQ) calculated from the concentration detected in three horizons (0–30, 30–60, 60–90 cm) in 2001

Table 1 Toxic equivalents of PCDD/F in the topsoil of the experimental sites in Meckenheim in function of the fertilizers applied

Topsoil PCDD/F concentration in pg g^{-1} (dw)	Mineral fertilizer (MIN), $n=4$	Farmyard manure (FYM), $n=3$	Sewage sludge (SSL), $n=4$	Compost (COM), $n=4$
(I-TEQ)	4.7±1.5	4.2±0.6	8.9±1.7	10.4±1.9
(WHO$_{98}$-TEQ)	4.6±1.4	4.0±0.5	8.3±1.5	9.7±1.6

Apart from an overall enhancement of the translocation of lipophilic compounds in the presence of DHM, Kim and Lee (2002) postulated substantial differences between DHM-induced mobility between TCDD and OCDD. This should become visible in different depth profiles of the relative PCDD/F congener distributions when comparing topsoils and subsoils of the plots amended with bio-waste with those amended with mineral fertilizer. In the
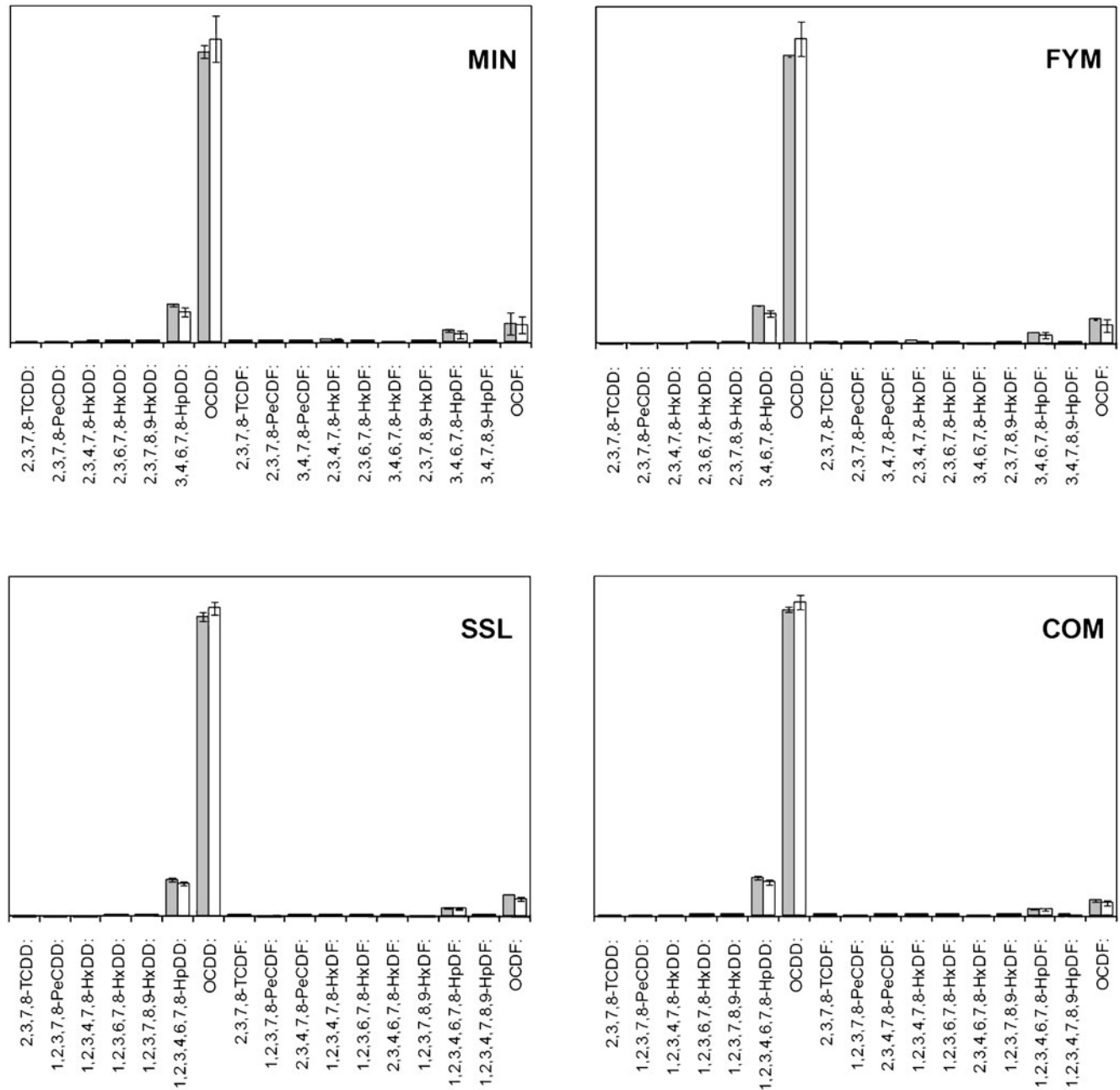
Fig. 3 Pattern of the 2,3,7,8-substituted PCDD/F in topsoils (0–30 cm, *gray signature*) and subsoils (30–60 cm, *white signature*)

case of our experiment, again, no such variations appeared (Fig. 3).

Both the similar depth profiles in TEQ as well as the homogeneous congener patterns in the plowing layer and the underlying soils with and without biowaste application suggest that the presence of DHM in the biowaste did not result in any notable translocation of the PCDD/Fs. The minor concentrations found below the plowing horizon are most probably a result of bioturbation and of variations of the plowing depth rather than DHM-associated translocation along with the aqueous phase.

3.4 Congener distributions of PCDD/Fs and DL-PCBs in the plowing horizon and the underlying soil

The similarity of the congener profiles in all soils, regardless of which fertilizer had been applied, indicates that no particular sources contributed to contamination with PCDD/Fs and DL-PCBs in SSL- and COM-amended soils. The PCDD/F congener distribution in all fertilizer scenarios is dominated by heptachlorodibenzodioxins and octachlorodibenzodioxins (Fig. 3), which points towards atmospheric deposition as the main vector of contamination in all soils at the Meckenheim site. This, together with the higher concentrations found in COM and SSL plots, suggests that the amendment with COM and SSL augments an additional contribution of atmospheric deposition into the soils. COM

and SSL seem to be loaded with off-site contamination through atmospheric deposition onto the surfaces of their origin. In the case of SSL, bulk deposition followed by surface runoff and subsequent focusing in the sewage system is obvious. In the case of COM, foliar gas exchange with the atmosphere and particle scavenging can be assumed. But since the COM applied in our field experiment included SSL in the early phase as well, no further differentiation between these phenomena is possible.

The congener distribution of the DL-PCBs differs slightly between topsoil and subsoil of all applications, especially in the soils amended with MIN (Fig. 4): The more volatile PCBs show less abundance in the congener patterns of the top soils. This indicates selected evaporative losses from the topsoil layer, which did not affect the congener profiles of the PCBs in the subsoil layer. An overall decrease of the PCB concentrations in the soils from the Meckenheim site since the mid-1970s, supporting the hypothesis of evaporative losses, can be seen from the time series of the topsoil (Umlauf et al. 2004). The observation that the congener shift towards less volatile PCBs in the topsoil is more pronounced in the MIN-amended plots suggests a reduced adsorption potential there and—as a consequence—in higher evaporation rates of the more volatile PCBs deposited during the 1970s. This might be due to a lower content of organic in the MIN-amended soils.
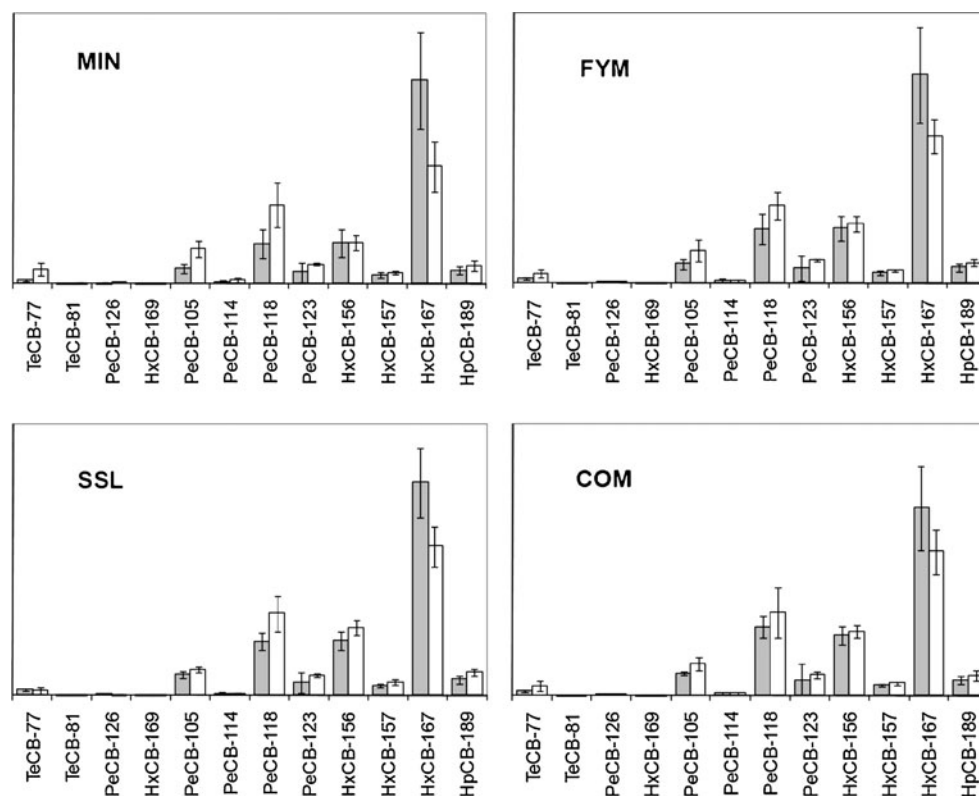
Fig 4 Pattern of the dioxin-like PCB in topsoils (0–30 cm, *gray signature*) and subsoils (30–60 cm, *white signature*)

4 Conclusions

Although the test plots received four times the maximum application of domestic SSL as laid down in the German SSL ordinance, and the investigated region represents the upper end of the topsoil concentrations typically found in Germany; soils under SSL and COM application were approximately a factor of 4 below the PCDD/F guidelines value for arable land in Germany. Increased translocation of PCDD/Fs and DL-PCBs into deeper soil layers did not appear in the biowaste-amended soils, so an enhanced risk for the groundwater quality can be excluded.

It is concluded that the common practice of SSL applications in Germany does not pose a current threat to the soil or groundwater quality with regards to PCDD/Fs and DL-PCBs. However, more detailed time trend data on PCDD/Fs and similar compounds in SSL-amended soils will be needed to evaluate the long-term effect of biowaste applications on soil quality.

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