PCDD/Fs and Dioxin-like PCBs in Soil after 42 Years of Bio Waste Application

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Introduction

Land spreading of bio-waste can partially replace mineral fertilisers and is a low cost disposal for waste. However, the obvious benefits of land spreading need to be carefully evaluated against potential adverse effects on soil quality. Elevated PCDD/F concentrations after sewage sludge application on soil have been reported [1-5] and it has been demonstrated that the elevated concentrations in sludge-amended soils persist over time. Using archived soil samples of a plot which received a single sludge application, McLachlan et al. [2] demonstrated that 59% of the PCDD/F concentration was still present after 18 years. The half-life of PCDD/Fs in soil is estimated to be at least 10 years [6, 7]. The key question arising is obviously whether the elevated concentrations in sludge-amended soils detected nowadays are a result of current application practice or just reflecting elevated contamination levels in sludges applied in the past. An answer to this question is crucial to create a scientifically sound basis for the decision whether or not it makes sense to include PCDD/Fs and dioxin-like PCBs (DL-PCBs) in future legislation related to bio-waste spreading on land. Another aspect of bio-waste application is the enhancement of leachability of PCDD/Fs due to the presence of dissolved humic matter (DHM) as reported by Kim & Lee [8]. In how far these observations are reproducible under field conditions remains to be assessed, although the authors recommended on the basis of their findings that dioxin abundant wastes should not be co-disposed with organic wastes such as sewage sludge and other types of bio-waste. Only few publications refer to the accumulation of DL-PCBs in bio-waste amended soils. However, DL-PCBs are present in sewage sludges as shown by Eljarrat et al. [9] who found contributions from DL-PCBs to the WHO-TEQ ranging from 13% to 50% in various domestic and industrial sludges in Catalonia (Spain). The present study intends to supplement the existing information on PCDD/F accumulation in sludge-amended soils and to widen the scope to other kind of bio wastes such as compost and cattle manure, including DL-PCBs. In addition, the significance of potential solubility enhancement of PCDD/Fs and DL-PCBs through the presence of DHM in bio waste will be addressed. An exemplary site in Germany was selected to determine the influence of a 42-years application of different kinds bio-waste on the fate of PCDD/Fs and DL-PCBs in soil. Control sites amended exclusively with mineral fertiliser were used as a reference representing the baseline pollution due to atmospheric deposition.

Methods and Materials

The Institute of Plant Nutrition in Bonn (Germany) is running a series of experimental plots amended with sewage sludge, compost (until 1988 composted municipal sewage sludge waste, later separated and composted bio waste), cattle manure and mineral fertiliser. The soil of the experimental site at Meckenheim is a luvisol derived from loess. The experimental application of bio-waste started in 1958. Before starting the experiments, the different test plots were used identically under the application of cattle manure and mineral fertiliser. Application rates were 106 t/ha sewage sludge, 98 t/ha compost, 20 t/ha cattle manure every second year. Mineral fertiliser was applied according to the farmer's practice. For each fertiliser scenario, 4 parallel plots were available. In 2002 from each set of plots pooled soil samples were taken in 3 layers (0-30cm, 30-60cm, and 60-90cm). Analysis was executed using HRGC-HRMS with quantification based on isotope dilution according to US-EPA methods 1613 and 1668A. In addition time series covering the whole application period were generated in using archived topsoil samples (0-30cm) from the plots amended with sewage sludge and mineral fertiliser.

Results and Discussion

Total PCDD/F and DL-PCB burden in soils after 42 years of bio-waste application: The amount detected within a depth of 0-90cm, summed up and calculated as the total burden in WHO-TEQ per unit area (soil density of 1.5 g/cm^3) is shown in Fig. 1. The plots where only mineral fertiliser was applied serves as a baseline, indicating atmospheric deposition only.

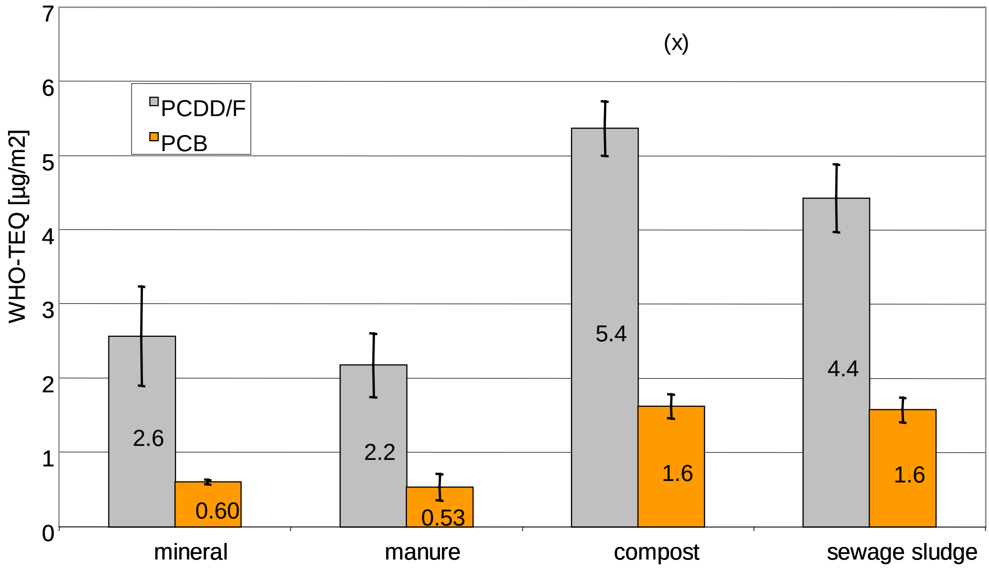


Figure 1: Total PCDD/F & PCB Burden in Soil [WHO-TEQ]

Compost and sewage sludge applications since 1958 resulted in a PCDD/F burden, approximately twice as high and a DL-PCB burden circa 3-fold higher as found in soil amended with mineral fertiliser. The application of cattle manure did not result in measurable inputs of PCDD/Fs and DL-PCBs. The average contribution of DL-PCBs to the WHO-TEQ were 19% in the mineral and manure plots, 23% in the compost and 27% in the sewage sludge amended plots.

Comparison with German guidelines: The average PCDD/F-concentrations in the topsoil of the sewage sludge and the compost plots were between 8-10 pg/g I-TEQ and are notably below the German guideline for agricultural land use of 40 pg/g I-TEQ [10]. Please note that the application rates for sewage sludge were approx. 4 times higher than foreseen in the German sewage sludge ordinance [11].

The question of DHM-induced translocation:

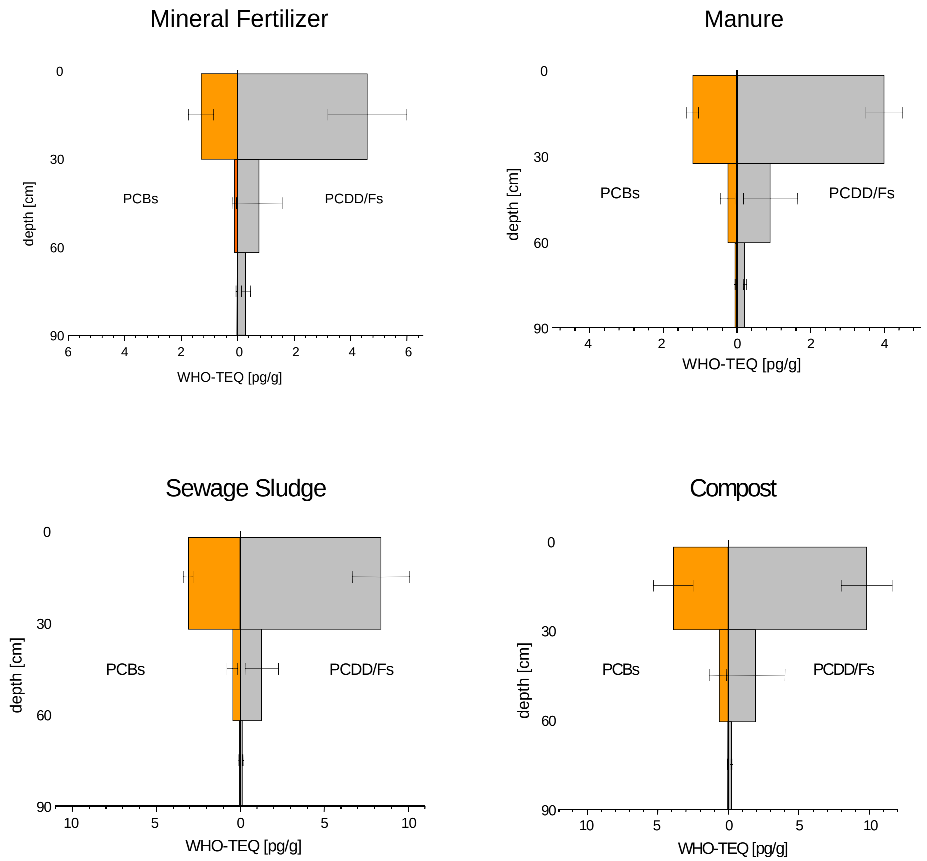
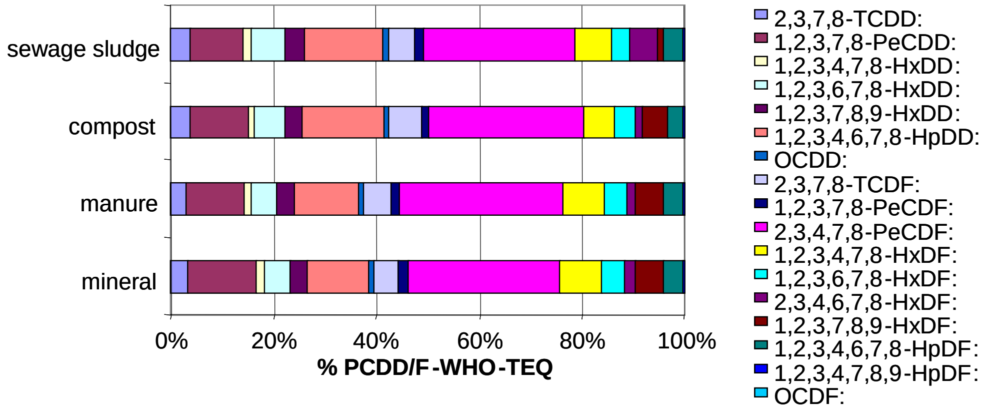


Figure 2: Depth-Profiles of PCDD/F and DL-PCB in Soil [WHO-TEQ]

The vertical soil profile of the analyte-concentrations does not show any remarkable difference between bio-solids and the mineral reference plot (Fig.2). The PCDD/Fs & PCBs are mainly located in the topsoil (0-30cm). This suggests that the presence of dissolved humic matter in the bio wastes does not result in any notable translocation of the investigated compounds. The minor concentrations found below the plough horizon may be rather a result of differences in soil turbation than due to translocation with the aqueous phase.

Congener distributions of PCDD/Fs and DL-PCBs:



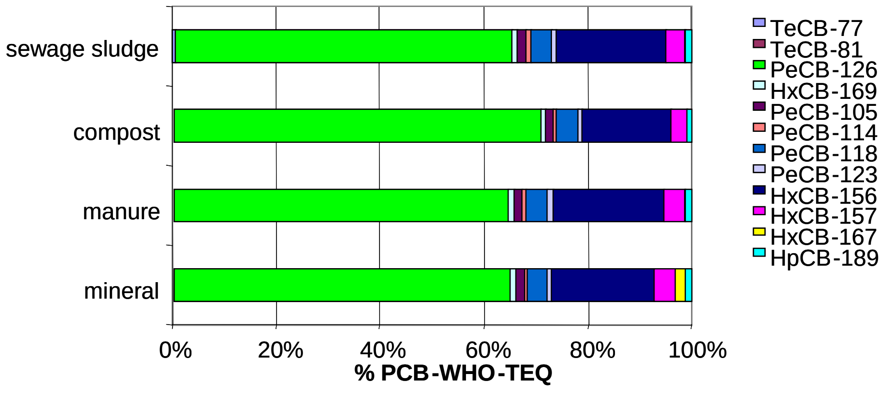


Figure 3: Congener-specific contribution to the WHO-TEQ of PCDD/Fs and DL- PCBs in soil

In the topsoil (0-30cm) no differences between the 4 scenarios were found (Fig. 3). The main TEQ-contributors among the PCDD/Fs are 2,3,4,7,8-PeCDF, 1,2,3,4,6,7,8-HpDD & 1,2,3,7,8-PeCDD). The PCB-TEQ is dominated by PCB126 & PCB156. The similarity of the PCDD/Fs and DL-PCBs profiles in the 4 scenarios indicates similar sources. In the mineral plots direct atmospheric deposition on the soil is only possible source. The similar congener distributions in the sewage sludge and in the compost plots indicate that the additional contamination results from atmospheric deposition into sewage sludge and compost before land spreading.

Time trends of PCDD/Fs and DL- PCBs in sewage sludge amended soil:

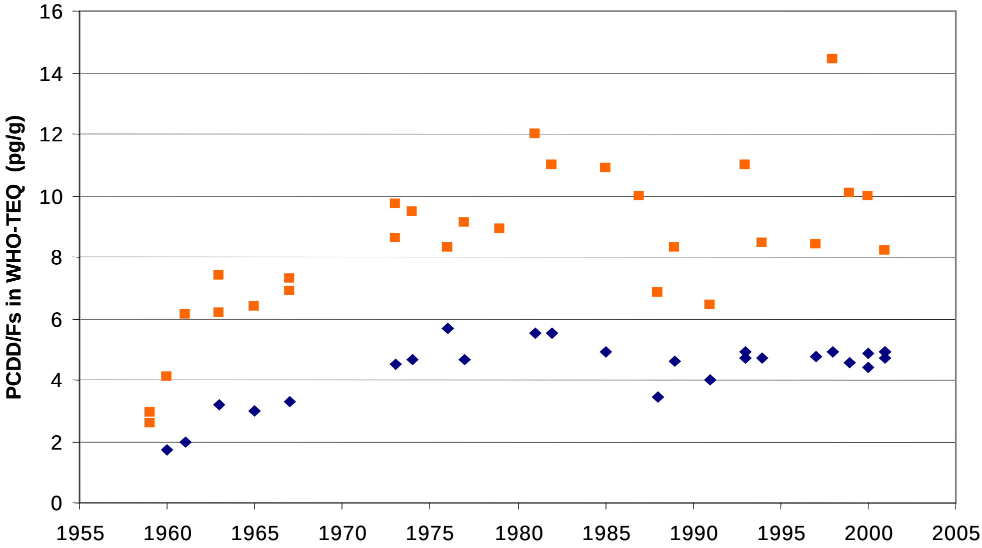


Figure 4: Time trends of PCDD/Fs in sewage sludge amended soil compared to the soil amended with mineral fertiliser.

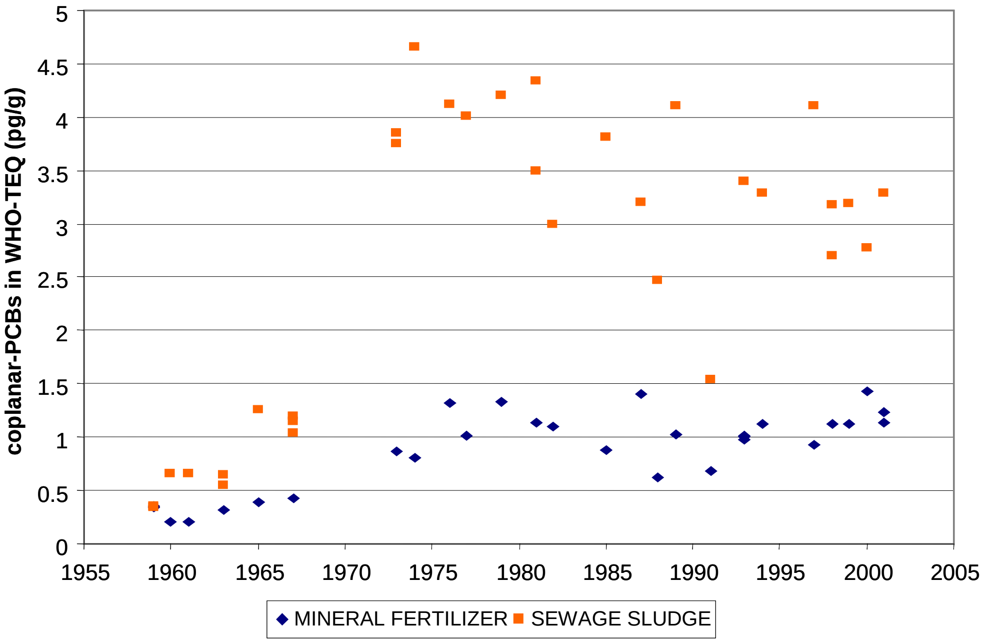


Figure 5: Time trends of coplanar PCBs in sewage sludge amended soil compared to the soil amended with mineral fertiliser

In figure 4 and 5 the temporal development of PCDD/Fs and coplanar DL-PCBs is displayed on a WHO-TEQ base. Between 1958 and the mid seventies PCDD/F-TEQs in soil show a steady increase in for both fertiliser scenarios, with a more expressed increase in the sludge-amended soil. From the mid seventies on, the concentrations in both scenarios remained rather constant. The DL-PCB-TEQs in the mineral fertiliser plots show a similar trend. However, the PCB trend in the sludge-amended soils differs considerably from the PCDD/F data: The major increase there appeared in the late sixties, a maximum can be seen during the mid seventies and from 1980 onwards a slight decrease is visible on a TEQ base. Obviously the more volatile PCBs show more tendency to equilibrate between the sewage sludge amended soils and the atmosphere, which nowadays is considerably less polluted than in the seventies.

Conclusion:
The use of manure in agriculture revealed no measurable effect on the contamination with PCDD/Fs and DL-PCBs when compared to mineral fertiliser. In the soils amended with sewage sludge and compost elevated levels were detected after 42 years of application. However, these elevated levels seem to reflect higher contamination levels in sludge and compost applied in the past. This is indicated by the observation that PCDD/F levels in these soils remained constant during the last 20 years and PCB levels were slightly declining. For the investigated site can be concluded that the continuation of the current practice of sewage sludge and compost application does not lead to additional accumulation with of PCDD/Fs and DL-PCBs. Since the current levels of PCDD/Fs were clearly below the German recommendations for agricultural land use, no restriction concerning the use of sewage sludge and compost seems indicated at the Meckenheim site.

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