The Influence of Sewage Sludge Fertilization on the PCDD/F Concentration in Soil

An Example from Northeastern Bavaria

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Introduction

Sewage sludge is an excellent fertilizer and serves to improve soil structure. Agricultural use of sewage sludge is also often viewed as an economic and ecological disposal method, in part because the alternatives are costly and fraught with environmental costs. This concurrence of the farmer's and the municipality's interests has led to the widespread use of sewage sludge fertilization in West Germany. In 1988 607,500 tonnes (dry weight) of sewage sludge, 25% of the total German production, was spread on 360,000 hectares of farmland (UBA, 1988).

In the last few years elevated concentrations of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) have been reported in sewage sludge. A survey of 43 samples from 28 German wastewater treatment plants (WWTP) found concentrations between 28 and 1560 ng 2,3,7,8-Cl_4DD toxicity equivalents (TE) per kg dry sludge (Hagenmaier et al., 1988). This compares with the German recommendation for unlimited agricultural use of soil of 5 ng/kg. Food is the primary pathway of PCDD/F to humans (Environment Ontario, 1988) and there is concern about the toxic effects at current exposure levels. Therefore, it would seem prudent to investigate possible increases in PCDD/F levels in food arising from sewage sludge fertilization.

The first issue to be addressed is: Do PCDD/F accumulate in soil that is treated with sewage sludge? We analysed several soil samples from northeastern Bavaria with different sludge fertilization histories.

Sampling

The Department of Agricultural Ecology at the University of Bayreuth collected 4 soil samples on a farm where sewage sludge had been extensively used. The farm lies in a rural area, well removed from known significant PCDD/F sources such as incinerators or major roads. The core depths and fertilization histories are summarized in Table 1. Unfortunately, the exact amount of sludge applied could not be determined. A sludge sample from the WWTP where the farmer had obtained his sludge was also analysed.

TABLE 1 Description of the Soil Samples

Sample	Bore Depth	Fertilization History
Field 1	30 cm	No sludge in the last 20-30 a.
Field 2	30 cm	Sludge regularly in the last 10 a.
Field 3	30 cm	Sludge regularly in the last 30 a.
Meadow	20 cm	Sludge regularly in the last 30 a.

Analysis

The soil samples were dried, dosed with labelled standards and soxhlet extracted for 48 hours in toluene and then for 24 hours in n-hexane/acetone (2:1). The sludge sample was centrifuged. The solid fraction was dried and then soxhlet extracted for 48 hours in toluene, while the supernatent was shaken with toluene (3 repititions). The extract was subjected to an acid silica/basic silica cleanup, followed by an alox chromatographic column. The analysis was conducted on a Finnigan MAT 8230 mass spectrometer at a resolution of 1700.

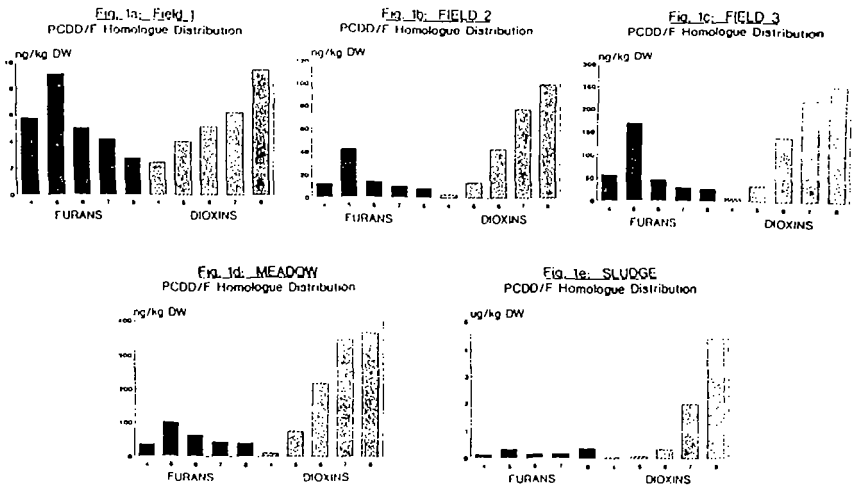
Results and Discussion

The results are presented in Table 2. They show a relationship between the length of sewage sludge use and the PCDD/F concentrations in soil. The TE level was 4.5 times higher in soil that had been fertilized for the previous 10 years than in soil that had had no sewage sludge fertilization. It was 11 times higher in the fields soil and 18 times higher in the meadow soil that had been fertilized for 30 years. The PCDD/F clearly accumulated in the soil.

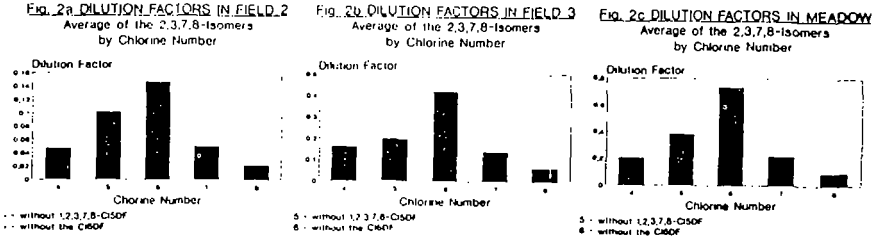
TABLE 2 PCDD/F RESULTS

Substance	Concentration (ng/kg DW) Field 1	Field 2	Field 3	Meadow	Sludge
ΣCl_4DF	5.8	13	58	39	140
ΣCl_5DF	9.1	43	170	100	350
ΣCl_6DF	5.0	15	49	66	180
ΣCl_7DF	4.2	11	32	47	190
ΣCl_8DF	2.8	9	29	43	400
ΣCl_4DD	2.4	3.2	6.8	11	64
ΣCl_5DD	4.0	14	34	76	84
ΣCl_6DD	5.1	43	140	220	340
ΣCl_7DD	6.2	78	220	350	2000
ΣCl_8DD	9.4	100	250	360	4400
2,3,7,8-Cl_4DF	0.64	0.63	2.1	2.4	12
1,2,3,7,8-Cl_5	0.72	1.6	4.2	6.4	8.2
2,3,4,7,8-Cl_5	0.88	0.89	2.7	5.9	15
1,2,3,4,7,8-Cl_6	0.57	2.0	5.4	9.7	16
1,2,3,6,7,8-Cl_6	0.45	0.94	3.2	3.8	10
1,2,3,7,8,9-Cl_6	0.058	0.19	0.70	1.1	3.3
2,3,4,6,7,8-Cl_6	0.39	0.59	1.3	1.9	15
1,2,3,4,6,7,8-Cl_7	3.0	7.4	19	31	110
1,2,3,4,7,8,9-Cl_7	0.20	0.38	1.1	1.6	10
2,3,7,8-Cl_4DD	0.040	0.047	0.16	0.24	1.1
1,2,3,7,8-Cl_5	0.14	0.47	1.1	1.9	4.9
1,2,3,4,7,8-Cl_6	0.12	0.76	2.1	3.9	4.9
1,2,3,6,7,8-Cl_6	0.28	5.0	17.	25	31
1,2,3,7,8,9-Cl_6	0.21	2.7	8.2	13	20
1,2,3,4,6,7,8-Cl_7	3.3	44	130	200	910
Toxic Equivalents (BGA)	0.84	3.7	9.4	15	42

The homologue distributions of the PCDD/F in the soil and sludge samples are plotted in Figure 1. The homologue pattern of the fertilized soils lies between that of the unfertilized soil and that of the sludge. One obvious difference is the much more dominant contribution of Cl_8DD in the sludge sample than in the fertilized soil samples. This sludge homologue distribution need not necessarily represent that of sludge 10 or 30 years ago. However, in 38 samples collected in 1986 from German WWTPs with no distinct industrial sources (Hagenmaier et al., 1988) the contribution of Cl_8DD to total PCDD/F was only in two cases lower than in this study (49% and 52% compared to 54%). The homologue patterns of 2 sludge samples from Sweden (Rappe et al., 1989) as well as 3 from the USA, including one from 1933 (Lamparski et al., 1984), are also dominated by Cl_8DD. We thus consider it unlikely that Cl_8DD was not just as prominent a component of the PCDD/F in the sludge from this WWTP 10 years previously. Since the PCDD/F in the fertilized soil samples comes from the sewage sludge, it would appear the Cl_8DD in the sludge was degraded.



To further evaluate this hypothesis we calculated dilution factors (defined as concentration in soil/concentration in sludge) for the 2,3,7,8-substituted isomers in the three fertilized soils. The averages of the factors in each homologue group are plotted in Figure 2 (with the exception of 1,2,3,7,8-Cl_5DF and the Cl_6DF). In a specific sample the factors increase from the Cl_4- to the Cl_6-isomers, and then decrease. We propose the following *interpretation*, based on the assumption that the isomer distribution in the sludge had not changed significantly over the previous 30 years.



1. *The Cl_7 and the Cl_8-isomers were degraded.* We cannot explain the big drop in the dilution factor for the more chlorinated isomes (Cl_6:Cl_7:Cl_8 = 1:.35:.15 for Field 2, = 1:.33:.15 for Field 3, = 1:.30:.13 for Meadow) in any other manner. Miller et al (1989) observed photodegradation of Cl_8DD on soil in less than 8 days to an effective depth of 0.06-0.13 mm. A typical sludge fertilization of 5 tonne DW/ha represents a 0.25 mm film of dry sludge on the field. Thus one could expect photodegradation under these conditions.

2. *The three Cl_6DD isomers were persistent in the soil and best reflect the amount of sludge applied.* The fact that virtually identical dilution factors were obtained for the three Cl_6DD isomers suggest that they were not degraded, as identical susceptability to degradation is unlikely. Although Miller et al. (1989) showed that Cl_6DD were formed during the photodegradation of Cl_8DD, the yield (2% of the degraded Cl_8DD) was too low to explain the concentrations measured here. Furthermore, equal amounts of the 3 Cl_6DD isomers were produced, while the isomer pattern in the fertilized soils is very different, namely the same as in the sludge.

3. *The lower accumulation of the Cl_4- and Cl_5-isomers is due to volatilization.* The good agreement between the dilution factors within the Cl_4DD/F and within the Cl_5DD/F suggests that they were subject to the same process. The increase in the dilution factor with chlorine number corresponds to a decrease in vapour pressure. Although the migration of these isomers through the soil after the sludge is plowed under is likely to be low, volatilization could be significant as long as the sludge lies exposed on the surface.

Other interpretations are also possible. The alterations in the isomer pattern could be completely due to photodegradation. The extremely high dilution factors for the Cl_6DD, that could only have been achieved through extreme fertilization, and the differences among the dilution factors for some homologue groups (1,2,3,7,8-Cl5DF and the Cl6DF) would support such an interpretation. Also, despite the thorough extraction employed for the soil samples, it is nevertheless possible that the changes in the isomer patterns are an extraction artifact.

Conclusions

1. The agricultural use of sewage sludge as a fertilizer leads to accumulation of PCDD/F in soil. Long term generous use can result in soil concentrations exceeding the recommended limit of 5 ng TE/kg DW in the FRG.

2. Photodegradation of Cl7- and Cl8DD/F and volatilization of Cl4- and Cl5DD/F are suspected of being responsible for an observed change in the PCDD/F isomer muster between sludge and soil.

3. The discussion shows how little is known about the behaviour of PCDD/F on and in soil, with the exception of 2,3,7,8-Cl4DD. This isomer was responsible for only 1-2% of the toxicity equivalents in the soil samples. In order to get a handle on the sewage sludge problem, more research on the other isomers is needed.

Acknowledgements

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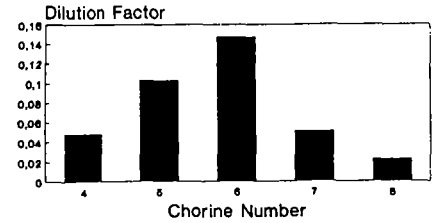
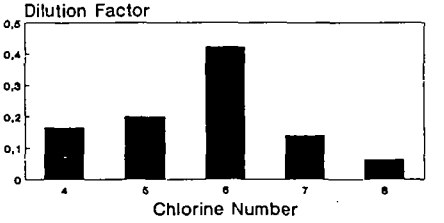
Fig. 2a DILUTION FACTORS IN FIELD 2
Average of the 2,3,7,8-Isomers
by Chlorine Number



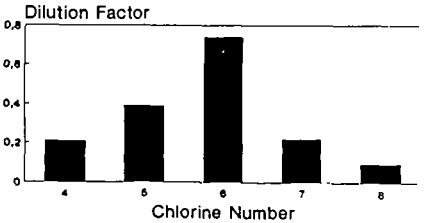
5 - without 1,2,3,7,8-Cl5DF
6 - without the Cl6DF

Fig. 2b DILUTION FACTORS IN FIELD 3
Average of the 2,3,7,8-Isomers
by Chlorine Number



5 - without 1,2,3,7,8-Cl5DF
6 - without the Cl6DF

Fig. 2c DILUTION FACTORS IN MEADO\
Average of the 2,3,7,8-Isomers
by Chlorine Number



5 - without 1,2,3,7,8-Cl5DF
6 - without the Cl6DF

Fig. 1a: Field 1
PCDD/F Homologue Distribution

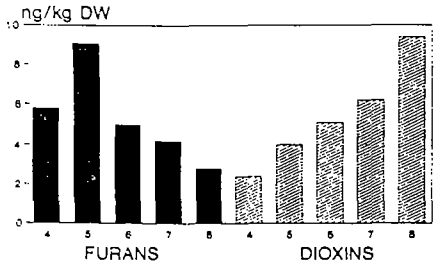


Fig. 1b: FIELD 2
PCDD/F Homologue Distribution

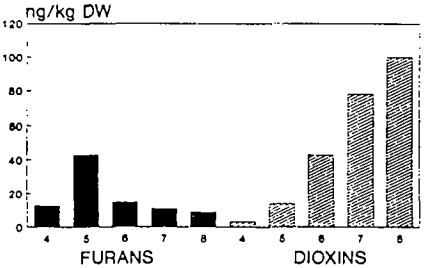


Fig. 1c: FIELD 3
PCDD/F Homologue Distribution

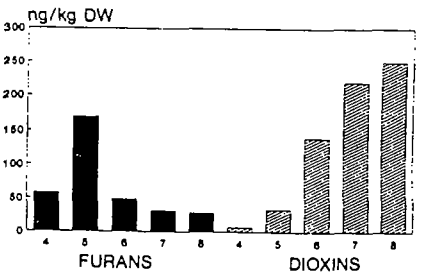


Fig. 1d: MEADOW
PCDD/F Homologue Distribution

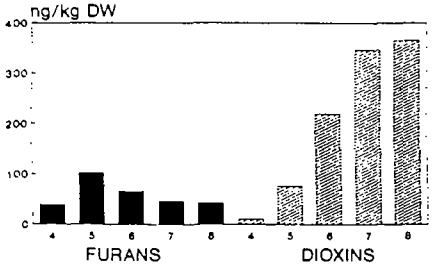


Fig. 1e: SLUDGE
PCDD/F Homologue Distribution