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Landesanstalt für Umweltschutz, Baden-Württemberg

Bodenschutz 16

Contaminants in arable soils in Baden-Württemberg fertilised with sewage sludge

Concise Report

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1 Summary

Rationale for the study

One focus of current discussions in Germany on the application of sewage sludge to soil, and the forthcoming amendment of the corresponding legislation (Klärschlammverordnung AbfKlärV), is the anticipated long-term accumulation of contaminants in agricultural soils. The presence in the soil of a large number of organic substances that give cause for concern in terms of toxicology, and that are not covered by the German sewage sludge legislation, gives rise to unquantifiable risks. The resolutions adopted at the joint conference of Agriculture and Environment ministers in June 2001 were intended to avoid any increase in the concentrations of contaminants in the soil as a result of agricultural activities. The presence of a wide range of organic contaminants in sewage sludge has been demonstrated in recent studies, including studies carried out in the German states of Baden-Württemberg and Nordrhein-Westfalen. However, there is insufficient data available on their fate in arable land to which sewage sludge has been applied.

Study aims

The aim of this study was therefore to establish if the entry of contaminants into the soil through the application of sewage sludge may lead to a demonstrable increase in their levels in the soil. Attention was focused both on the ubiquitous contaminants (heavy metals, PAH, PCBs, PCDD/PCDF) and on further organic compounds, such as organotin compounds, that have been associated with endocrine effects (e.g., hormonal actions). These have been found in sewage sludge in recent studies, but have been studied to only a minor extent in soils.

Results

The main outcome of this study has been a demonstration of an accumulation of contaminants in the soil at 3 out of 11 agricultural field locations and 2 experimental study locations as a consequence of many years of application of sewage sludge. Higher concentrations of organotin compounds and polycyclic musks, as well as copper and zinc, were found at the 2 field locations to which the highest quantities of sewage sludge had been applied. The concentrations of organotin compounds and dioxins (PCDD/PCDF) were significantly elevated at 1 further agricultural field location. The experimental study locations were found to have higher levels of the above substances and, in addition, of cadmium, lead and mercury, as well as PCBs, PAH and DDT. The heavy metal concentrations at the experimental study locations lay both above and below the precautionary values laid down in Bundes-Bodenschutz- und Altlastenverordnung BBodSchV. The values for the agricultural field locations were below the precautionary values. On the basis of extrapolations carried out for continued fertilisation with sewage sludge (assuming a further 70 years of such application), it is likely that the precautionary values will be reached and exceeded in the long term.

Assessment of results

As far as we are aware, this is the first analytical demonstration of an accumulation of non-ubiquitous organic compounds in soils of agricultural field locations as a result of the application of sewage sludge. The presence of organotin compounds and polycyclic musks in soils to which sludge has been applied, with elevated levels of heavy metals and dioxins/furans at the same time, is of particular note. A further point is the apparent high persistence of the organic compounds in the soil over a relatively long period of time since the last sludge application – up to 14 years.

The results presented here should be viewed in the context of the aims to prevent the accumulation of contaminants in agricultural soils. For substances with a ubiquitous presence the following technical action options are suitable for the limitation of substance inputs into soil, as given in the "Principles and Measures for a Prevention-oriented Limiting of Contamination of Farmland" (Umweltbundesamt UBA Text 59/01, 2001). Action option 1: "similar quality to similar quality" (limitation of harmful substance discharges to a content level that corresponds to that of the cultivation site; i.e., with respect to substance concentrations in the waste) or action option 2 "input = output" (limitation of harmful substance discharges to a balance level with tolerable discharge; i.e., with respect to substances loads brought to the soil). The action option 3 "avoidance of harmful substance inputs to soils" is primarily targeted on non-ubiquitous organic substances. The elevated concentrations of copper and zinc and the presence of different organic compounds typical of sewage sludge in the soils investigated here show that the requirements that result from the above action options are, overall, not being adhered to in the current practice of sewage sludge recycling in agriculture. A predominant problem appears to be the wide range of organic compounds present in sewage sludge with their insufficiently investigated risks for humans and the environment.

2 Study Concept

The study was based on a comparison of pairs of fields, one of which had sewage sludge applied to it (sewage sludge field) and the other a reference field without sewage sludge application (reference field).

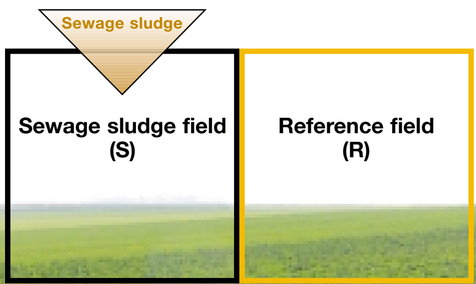
Locations

The study locations were selected on the basis of the following criteria to enable an attribution of increased substance concentrations present in the soil to the application of sewage sludge:

- The reference field without sewage sludge application was selected close to the sludge field and had soil and site characteristics that largely correspond to the sludge field.
- The soils in the sewage sludge fields have had many years of recorded application of, as far as possible, high quantities of sludge within the statutory limits.
- The sewage sludge fields should be largely uninfluenced by the usage of farmyard manure (especially liquid manure).
- The 11 agricultural field locations were distributed over different agricultural regions of Baden-Württemberg.

The selection resulted in 13 study locations distributed over Baden-Württemberg, each comprising a sewage sludge field and a reference field. There were a total of 11 agricultural field locations (Nos. 3 to 13), as well as 2 experimental locations (Nos. 1 and 2) on the campus area of the University of Hohenheim (2 plots of a former sewage sludge high-load study). The quantities of sewage sludge applied to the agricultural sewage sludge fields lay between 3.2 t/ha and 31.5 t/ha in total. The corresponding values for the experimental sewage sludge field plots were 85 and 510 t/ha (the reference field here corresponded to the zero plot). The selection of locations thus yielded only a few agricultural field locations that had high sewage sludge application over several years. Nevertheless, increases in the concentrations of various substances as a result of the application of sewage sludge were evident.

Fig. 1: Overview of the study locations



Substance groups investigated

The selection of the substance groups was based, inter alia, on a substance list elaborated by the UMK-AG (working group on behalf of the conference of Environment Ministers) titled “Reasons for the Presence of Hazardous Substances in Sewage Sludge and Action Plan” (UMK-AG, 2000). Measurements were carried out for heavy metals (and As and Sb), and for organic substance groups of “high relevance” and substances for which “more information is required”, as stated in the UMK-AG. Analysis of heavy metals was conducted using 3 parallel samples and 3 different extraction methods (aqua regia, EDTA and ammonium nitrate solution). The analysis of organic compounds (except for PAH, PCBs and CHC) was initially confined to selected locations and single samples for cost reasons. Where locations were found to have higher substance concentrations, a total of 3 parallel samples were taken and subjected to statistical analysis. A further biological test (yeast oestrogen receptor screening test) was performed to establish the presence of substances exerting oestrogenic and cytotoxic effects. The findings of that test were not suitable for evaluation.

Table 1: Overview of the substances investigated

Heavy metals
As, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Tl, Hg, V, Zn
Organic substances
- Polycyclic aromatic hydrocarbons (PAH)
- Polychlorinated biphenyls (PCBs)
- Organochloropesticides (CHCs - 3 substance groups)
- Dioxins / furans (PCDD/PCDF)
- Octyl-/Nonylphenol (AP)
- Polycyclic musks
- Phthalates (DEHP)
- Polybrominated diphenylethers (PBDE)
- Organotin compounds (OT)
- Linear alkylbenzene sulfonates (LAS)
- Bisphenol A
- (Medicinal products, investigated at one location only and not found)

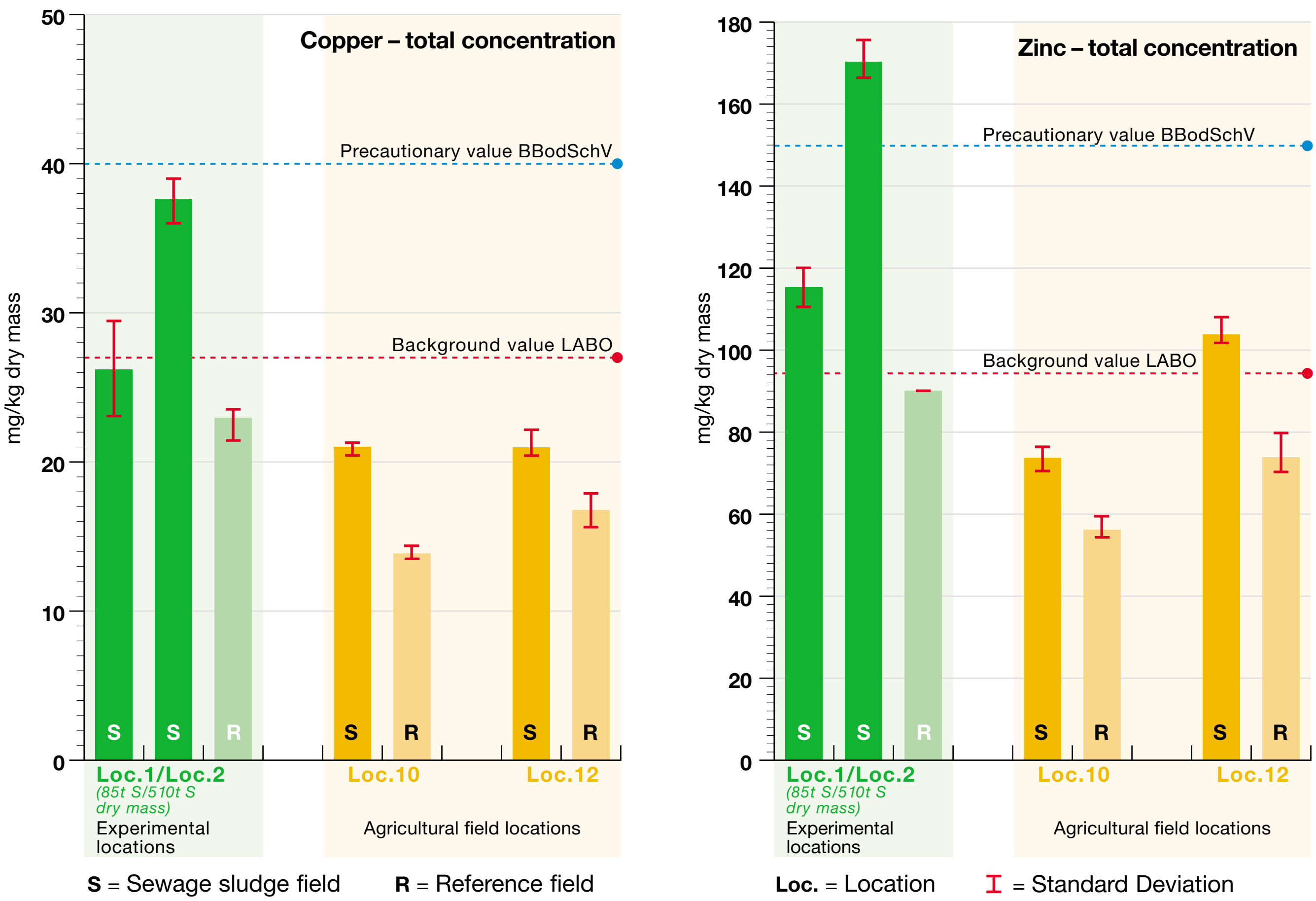
3 Results

Concentrations of soil contaminants

Heavy metals:

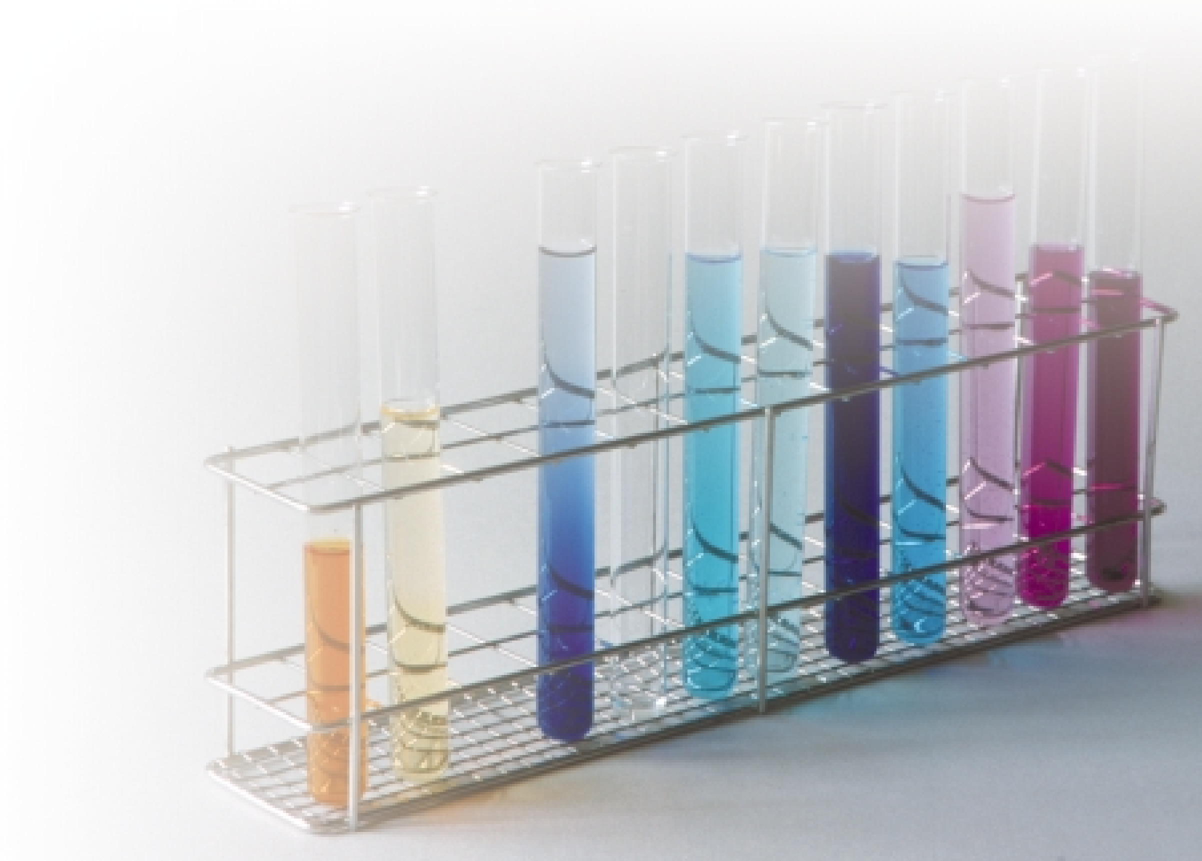
The total heavy metal concentration (extracted with aqua regia) for 3 out of the 11 agricultural field locations was significantly elevated on the sewage sludge field for at least 1 heavy metal (see Table 2 and Figures 2 and 3). At locations 10 and 12 the values were significantly higher for 4/2 heavy metals on the sewage sludge fields and yielded a clearly increased incidence of elevated concentrations. These 2 locations were those that had received the highest quantities of sewage sludge (31.5 and 19 t/ha respectively). With regard to the variety of analysed heavy metals (aqua regia extract), the values obtained for Cr (1), Cu (3), V (1) and Zinc (2) were conspicuous. Extraction with EDTA again yielded significantly higher concentrations for heavy metals from the sewage sludge fields – Nos. 10 (Zn) and 12 (Cu and Zn). Extraction with ammonium nitrate did not yield any relevant results, at least for the agricultural field locations.

The results for the experimental locations (Nos. 1 and 2) also revealed a clear relationship between the quantities of sewage sludge applied and the heavy metal concentrations. The value for Hg at location 1 (85 t/ha sewage sludge) is significantly higher. At location 2 (510 t/ha sewage sludge) the values for 7 heavy metals (Cd, Cu, Mo, Pb, Sb, Hg, Zn) were significantly higher than for the reference field (zero plot). The heavy metals Ni and Zn soluble in ammonium nitrate were significantly elevated for location 2.



Figures 2/3: Total copper concentrations (Fig. 2) and total zinc concentrations (Fig. 3) for selected locations compared to the background value given by the LABO (1998) and the BBodSchV precautionary value.

In addition to possible differences in contaminant concentrations between sewage sludge fields and reference fields, the concentrations of heavy metals were also compared to the background and precautionary values given in the federal soil protection ordinance (BBodSchV). The values found at locations 1 and 2 exceeded the precautionary values for the elements Cd, Hg and Zn, and also exceeded the background values for Cu and Zn. The value for Zn (ammonium nitrate extraction) at location 2 almost approaches the examination value for adverse effects on the growth of cultivated plants. All of the values found for the agricultural field locations were below the precautionary values given in BBodSchV. The values obtained were extrapolated on the basis of the measured data and quantities of sludge applied and assuming continued application of sludge for a further 70 years. The values obtained for locations 10 and 12 for the heavy metals showed an increase in concentrations, in particular for Cu and Zn, to values close to, or above, the precautionary values given in BBodSchV.



Organic contaminants

Significant differences were found between the sewage sludge fields and reference fields at 3 out of the 11 agricultural field locations (Nos.10, 12 and 13) for at least 1 organic parameter (see the Table on page 13). If conspicuous individual values are shown and not just the statistically significant mean values from the 3 parallel sample investigations, then the number of agricultural field locations that have apparent high values increases to 5. The concentrations of polychlorinated dioxins/furans, the organotin compounds and the polycyclic musks were significantly elevated at 3 locations (Figs. 4 - 6). At locations 1 and 2 the values for all organic parameters with concentrations above the specified limits of quantitation (8 out of 13 organic substance groups investigated) were significantly higher for the sewage sludge fields than the reference field.

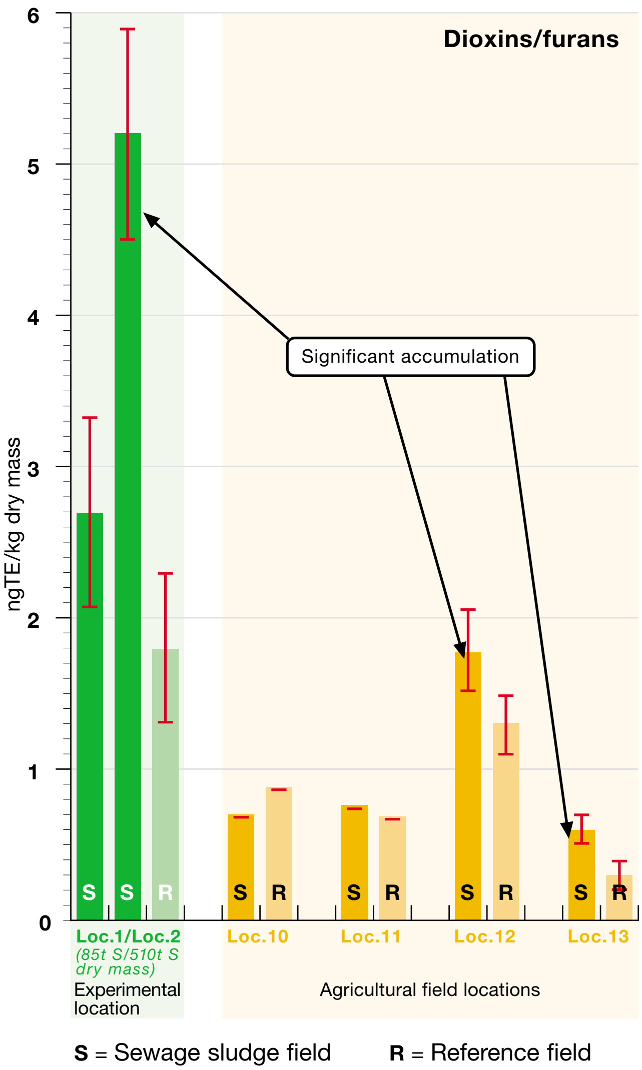


Fig. 4: PCDD/PCDF concentrations at selected locations (Values for locations 10 and 11 from single measurements)

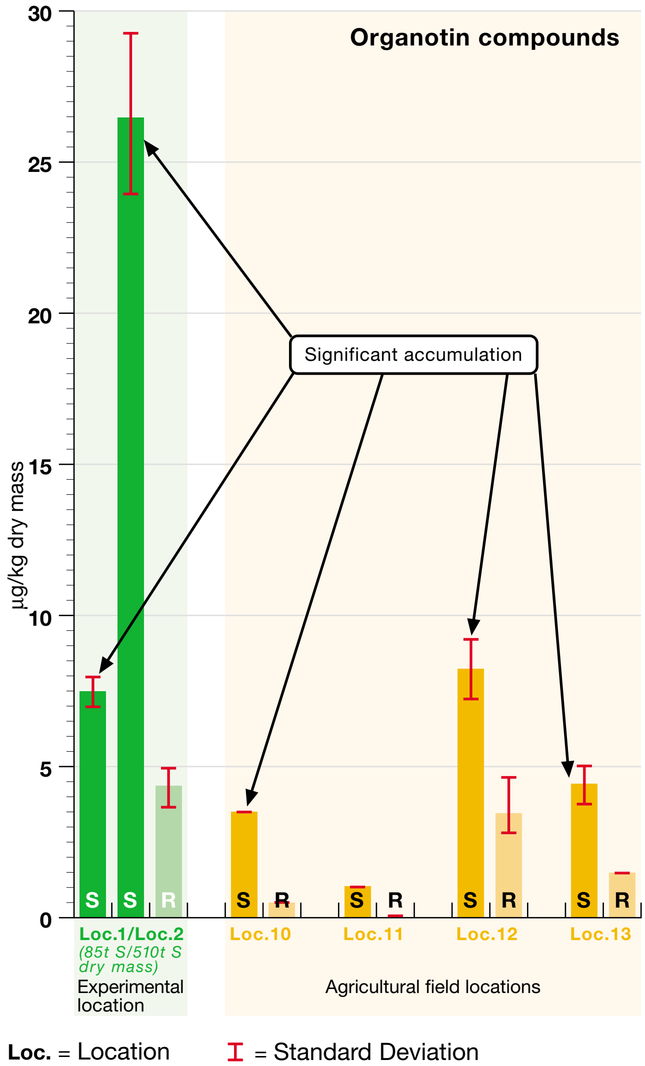
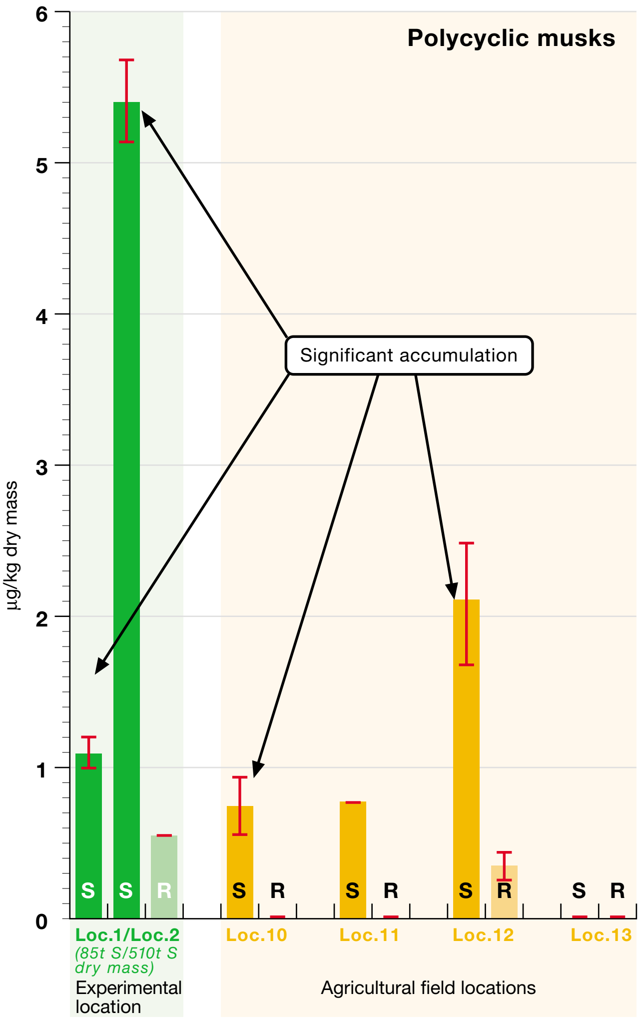


Fig. 5: Organotin compound concentrations at selected locations (Values for locations 10 and 11 from single measurements)

The differences were smaller at location 1 since less sewage sludge was applied there. The inclusion of these experimental locations in the study has provided useful information since the high sewage sludge quantities provides data on the effects of long-term contaminant entry through application of sludge. In addition, the typical non-ubiquitous organic contaminant pattern of soils fertilised with sewage sludge was established, with the analytical limits of quantitation very clearly exceeded in some cases. Representatives of these substance groups (e.g., polycyclic musks) were still present in the soil even though the last experimental application of sludge was in 1989 (14 years ago).



S = Sewage sludge field **R** = Reference field
Loc. = location I = Standard Deviation

Fig. 6: Concentration of the polycyclic musks HHCB + AHTN in selected locations (Values for locations 11 and 13 from single measurements)

Sewage sludge as a source of elevated contaminant concentrations

Evaluation of the overall results showed a causal relationship between the application of sewage sludge and the increased concentrations of contaminants on the experimental locations 1 and 2 and the agricultural field locations 10, 12 and 13. The values were significantly elevated for Cu, Zn, PCDD, polycyclic musks and organotin compounds at the fields to which sludge had been applied. These conclusions are supported by the following observations/arguments:

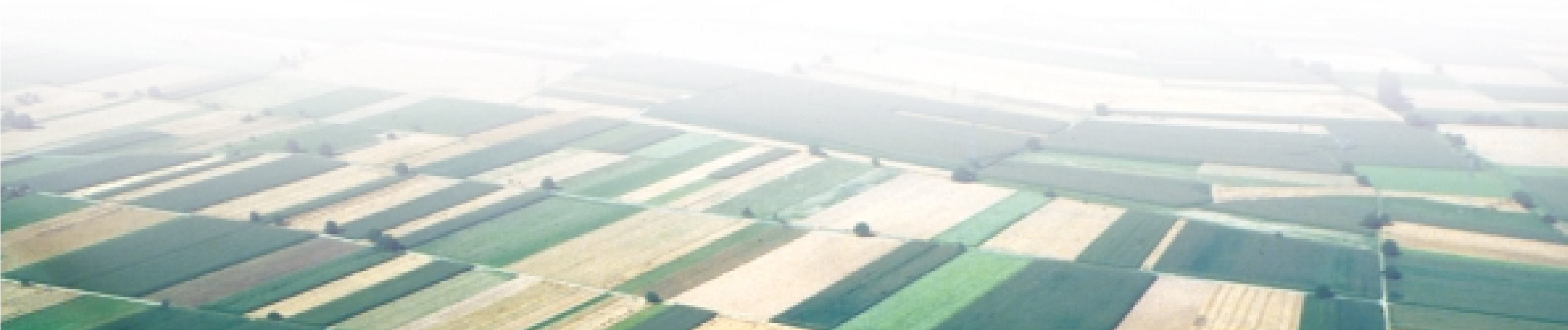
- The differences in the analytical results between sludge and reference fields were statistically significant.
- Alternative routes of entry – such as the entry of heavy metals or PCDD/PCDF through atmospheric deposition or liquid manure – and landscape/geological causes can be ruled out because of the close proximity of the sewage sludge and the corresponding reference field and their similarity in terms of soil properties. The higher concentrations of heavy metals are largely accounted for by the quantities of sludge applied to the soil.
- There was a clearly increased incidence of higher values for the samples from agricultural field locations 10 and 12 to which the highest quantities of sludge were applied, as well as a good correlation, in part, with the substance spectrum of the experimental locations 1 and 2 that had received very high quantities of sludge.
- The spectrum of organic compounds found on the sewage sludge fields is typical for sewage sludge and is in agreement with the results already obtained for sludge investigations. The concentrations of polycyclic musks are of particular interest as their pattern of usage means that their only relevant route of entry is through sewage sludge application. The presence of such compounds in the soil is virtually an indicator for the entry of substances into soils from sewage sludge.

The table below gives an overview of the concentrations of the substances/substance groups for the different locations that show significant differences between the sewage sludge and reference fields.

Table 2:
Concentrations of substances and substance groups in the soil of the sewage sludge and reference fields. The values given are for soil dry mass. Those concentrations that have been derived from a single measurement are shown in brackets. The heavy metal values were derived using aqua regia extracts unless otherwise indicated. The table shows the data only for those locations that have higher concentrations of contaminants as a result of sewage sludge application.

Parameter	Units	Location 1	Location 2	Location 1/2	Location 10		Location 11		Location 12		Location 13	
		S	S	R	S	R	S	R	S	R	S	R
Cd	mg/kg		1.1	0.4								
Cd (EDTA)	mg/kg		0.8	0.4								
Cr	mg/kg				43.5	33.3						
Cu	mg/kg		37.4	22.6	21.3	15.2			21.4	16.9		
Cu (EDTA)	mg/kg		20.0	9.0					7.2	5.6		
Mo	mg/kg		1.0	0.7								
Pb	mg/kg		31.9	24.9								
Sb	mg/kg		1.0	0.6								
V	mg/kg				51.2	40.6						
Hg	mg/kg	0.8	1.7	0.5								
Zn	mg/kg		170.8	90.0	73.7	56.2			104.9	75.2		
Zn (EDTA)	mg/kg		64.8	19.0	4.9	2.6			4.8	2.5		
PCDD/PCDF	ng TE/kg	2.7	5.2	1.8					1.8	1.3	0.60	0.31
PCBs	mg/kg	0.050	0.090	0.023								
PAH	mg/kg	0.44	0.50	0.27	(0.35)	(0.08)						
OT	µg/kg	7.5	26.6	4.3	(3.3)	(0.5)	(1.1)	(n.n.)	8.3	3.6	4.4	1.4
TBT	µg/kg		1.4	0.3								
Polycyclic musks	µg/kg	1.1	5.3	0.55	0.77	n.n.	(0.80)	(n.n.)	2.1	0.3		
HCB	mg/kg		0.003	0.001								
Sum of DDT groups	mg/kg	0.006	0.008	0.003								

S = Sewage sludge field **R** = Reference field



4 List of Abbreviations

AbfKlärV	German Sewage Sludge Ordinance
AP	Alkylphenols
As	Arsenic
BBodSchV	Federal Soil Protection Ordinance
Cd	Cadmium
CHC	Chlorinated hydrocarbons (e.g., DDT)
Co	Cobalt
Cr	Chromium
Cu	Copper
DDT	Dichlorodiphenyltrichloroethane
DEHP	Di(2-ethylhexy)phthalate
EDTA	Ethylenediaminetetraacetic acid
HCB	Hexachlorobenzene
hER screen	Test method for oestrogenic effects on organisms
Hg	Mercury
LABO	Federal/State Co-operative for Soil Protection
LAS	Linear alkylbenzene sulfonates
Loc	(Study) Location
Mo	Molybdenum
Ni	Nickel
OT	Organotin compounds
PAH	Polycyclic aromatic hydrocarbons
Pb	Lead
PBDE	Polybrominated diphenylethers
PCB	Polychlorinated biphenyls
PCDD/PCDF	Polychlorinated dibenzodioxins/Polychlorinated dibenzofurans
R	Reference field
S	Sewage sludge field
Sb	Antimony
TBT	Tributyl tin
TE	Toxicity Equivalents
Tl	Thallium
UMK-AG	Joint conference of Environment Ministers
V	Vanadium
Zn	Zinc

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