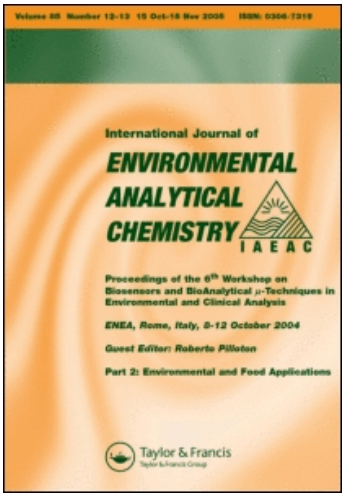

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Diercxsens, P. and Tarradellas, J.(1987) 'Soil Contamination by some Organic Micropollutants Related to Sewage Sludge Spreading', International Journal of Environmental Analytical Chemistry, 28: 1, 143 — 159
To link to this Article: DOI: 10.1080/03067318708078406
URL: http://dx.doi.org/10.1080/03067318708078406

Intern. J. Environ. Anal. Chem., 1987, Vol. 28, pp. 143–159
0306-7319/87/2802-0143 $18.50/0

Printed in Great Britain

Soil Contamination by some Organic Micropollutants Related to Sewage Sludge Spreading†

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The aim of the present publication is to give some information on soil contamination by 4 different micropollutant classes due to sewage sludge spreading.

The soil under research shows an accumulation of light molecular weight PAHs and PCBs, DEHP and 4-NP just after spreading, but one month later the concentration of these micropollutant groups fall to the concentration detected just before the sludge spreading.

As far as the soil concentration is concerned, only PAHs and PCBs are precipitation dependent.

Some test plots, enriched during 10 years with fertilisers, pig-dung or sewage sludges show only an increase of the PAH concentrations of the plots amended with sludges. In the same way, the sewage sludge is chiefly responsible for the increase of PCBs in the soils, but pig-dung seems to contain quantities of these micropollutants which have to be taken into consideration.

KEY WORDS: PAH, PCB, 4-nonylphenol, Di-ethyl-hexyl-phthalate, soil pollution, sewage sludge.

INTRODUCTION

The sewage sludge disposal methods most frequently used and adopted by the E.E.C. countries are, the utilisation of liquid or

†Presented at the 16th Symposium on the Analytical Chemistry of Pollutants, Lausanne, Switzerland, March 17–19, 1986.

dehydrated sludge in agriculture and the disposal on land or at sea.[2]

Among the problems concerning the contamination effect of sewage sludge spreading we shall discuss in the present paper the behaviour of the micropollutants of the sewage sludge, before, during and after the spreading, associated with the detection of other micropollutant sources in the soils.

The purpose of the research can be summarized in two questions:

—In what conditions is the micropollutant concentration of the soil of a cultivated farmland influenced by sewage sludge application?

—How does the concentration of the previously cited micropollutants of the improved farmland vary 1 month and 3 months after the sewage sludge has been applied?

TABLE I

List of abbreviations for PAHs studied

Abbrev.	Organic micropollutant	MW.
	The 11 selected PAH	
Phe	Phenanthrene	178
An	Anthracene	178
Ft	Fluoranthene	202
Py	Pyrene	202
B(a)A	Benxo(a)anthracene	228
B(e)P	Benzo(e)pyrene	252
B(b)F	Benzo(b)fluoranthene	252
B(k)F	Benzo(k)fluoranthene	252
B(a)P	Benzo(a)pyrene	252
DBA	Dibenz(a,h)anthracene	278
BP	Benzo(g,h,i)perylene	276
4-NP	4-Nonyl-phenol	230
DEHP	Di-ethyl-hexyl-phthalate	391

EXPERIMENTAL

Sample handling

PAH and PCB recovery All the sludge and soil samples were treated in the same way, as illustrated in Figure 1.

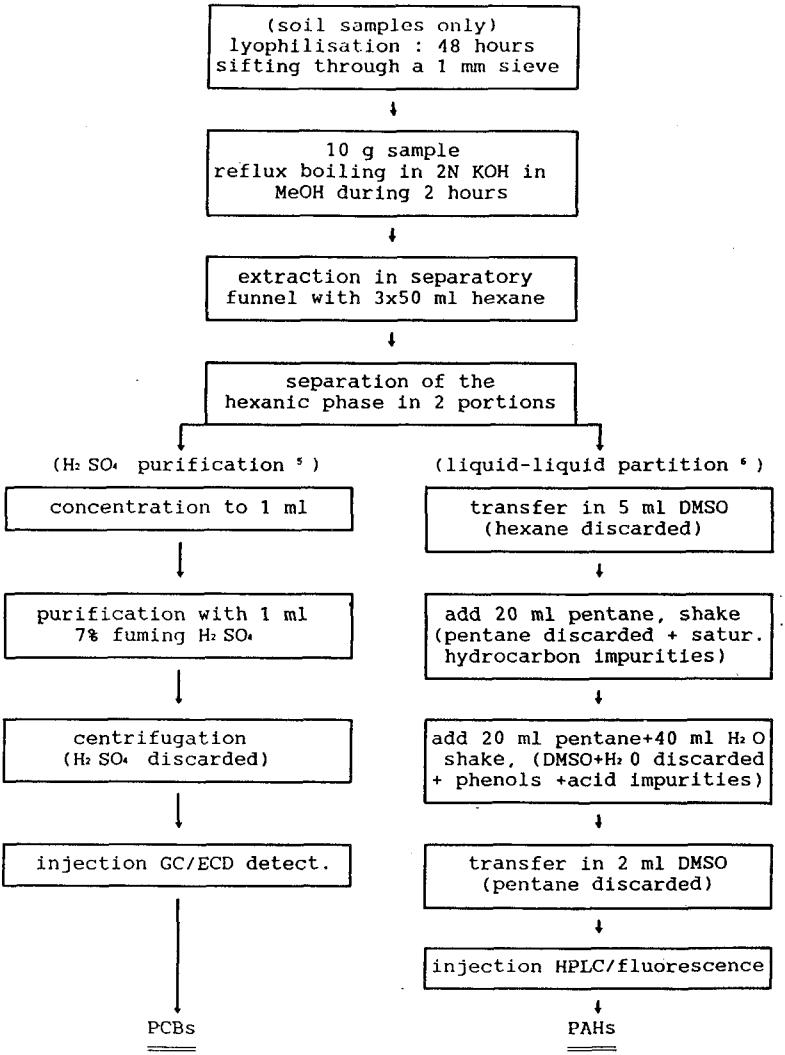

FIGURE 1 Saponification method for concentration of PAHs and PCBs from soil and sludge samples.

4-NP and DEHP recovery The analysis of 4-NP in the samples presented in this research were performed by W. Giger and coworkers according to a procedure established by themselves and already published.[3]

The analysis of DEHP was performed according to a procedure published by D. Russel and B. McDuffie.[4] However, the instrumental procedure was different and will be detailed in the following paragraph.

Instrumental

PCBs A Perkin-Elmer Sigma 2 electron capture gas chromatograph (^{63}Ni detector) coupled with a Perkin-Elmer Sigma 10B data station is used to quantify the PCBs present in each sample. A SPB 5 fused silica column from Supelco (length: 30 m, i.d.: 0.25 mm) is used in split mode. The other conditions are

Carrier gas	: N_2	Oven temperature program:	
Flow rate	: 3.75 ml/min	Initial temp.	: 130°C
Injector temp.	: 260°C	Final temp.	: 265°C
Detector temp.	: 350°C	Ramp rate	: 3.5°C/min

PAHs and DEHP A Perkin-Elmer series 4 liquid chromatograph coupled with a fluorescence detector LS-5 is used to quantify the PAHs and DEHP present in the samples. The liquid chromatograph is equipped with a Perkin–Elmer reverse phase C18 column. The solvent program is illustrated in Table II.

The PAHs are detected with accurately selected excitation and emission wavelengths as illustrated in Figure 2.

The DEHP is detected with a Coleman 55 u.v. spectrophotometer. The detection wavelength is fixed at 233 *v*m.

SEWAGE SLUDGE SPREADING AND SOIL CONTAMINATION: A CASE STUDY

The site selection

The sewage sludge application which we have studied corresponds to the average Swiss practice ($\pm$0.6 ton O.M./ha).

TABLE II

HPLC solvent program

Elution steps	PAHs Time (min)	PAHs Flow (ml/min)	PAHs ACN/H_2O[a] (%)	PAHs ACN[b] (%)	DEHP Time (min)	DEHP Flow (ml/min)	DEHP H_2O (%)	DEHP ACN[b] (%)
equil.	30	0.5	100	0	30	0.5	80	20
1	18	0.5	100	0	0.1	0.5	50	50
2	8	0.5	0	100	14.9	0.5	0	100
3	30	0.5	0	100	17	0.5	0	100
wash	30	0.5	0	100	30	0.5	0	100

[a]ACN/H_2O = mixture of acetonitrile (Mallinckrodt, Chromar) and double distilled water (50-50%).
[b]ACN = pure acetonitrile.

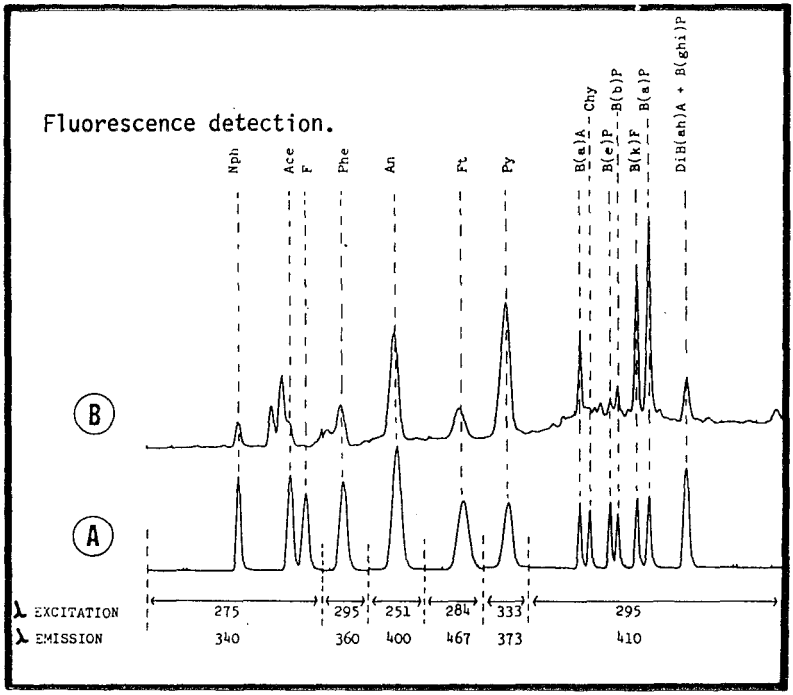

FIGURE 2 HPLC chromatograms (A) Mixture of 15 pure PAHs. (B) PAHs detected in a sludge sample.

In order to visualise clearly the effect of the sewage sludge spreading, the most important field selection criteria was to find a farmland with very low micropollutant concentrations (CB in Table IV). Edwards[7] considered that these concentrations are characteristic of very weakly polluted soils. The site selected has the following characteristics:

TABLE III

Site description

The farmland	The soil conditioner
1. Locality: Ependes, canton of Fribourg–Switzerland.	*1. Type*: 50-50% mixture of sewage sludge (95% water) and cow-dung.
2. Site description: 10 km from the center of the city of Fribourg, open country, no traffic.	*2. Origin*: water treatment plant of Fribourg–CH.
	3. Application: 3 times 0.6 tons organic matter per hectare in 1983, 1984 and 1985.

The micropollutant selection

Four micropollutant families were accurately analysed during this case study:

The polychlorinated biphenyls: are still present in the sewage sludges[8,9] and are known for their accumulative behaviour in the trophic chains.[10] They are present in precipitations.[11,12]

The polycyclic aromatic hydrocarbons: are carcinogenic[13] and are also present in sewage sludges[9,14,15] and precipitations.[16–18]

4-Nonyl-phenol: very high concentrations are found in sewage sludges.[19]

Di-ethyl-hexyl-phthalate: are present in many industrial products as plasticizers and are thus ubiquitous in the environment.[20] High concentrations are found in sewage sludges.[8]

The soil sampling method

A simple randomized strategy of sampling according to the criteria of Scherrer[21] was used.

The fields under research (a sludge amended field and a reference field) each have a surface of 1 ha. In order to eliminate border effects, a band of 5 meters was discarded from the sampling site all around the field. The site was then subdivided into plots of 5 by 5 meters. Five of them were picked out in each of which 5 soil samples were mixed and immediately brought to the laboratory where they were lyophilised. Each micropollutant analysis was thus at a definite time, made 5 times.

The transfer of the micropollutants

Table IV shows the global concentrations of the 4 micropollutant families found in the conditioner, the soil before and after the spreading and the concentration factor (CF).

Why introduce the CF? The CF is defined by the following relation:

$$CF = \frac{CA - CB}{CC} \times 100$$

TABLE IV

Global micropollutant concentration[a] (vg/g d.m.) found in the conditioner and the sludge amended soil (0–1 cm)

O.MP.	CC	CB	CA	CF (%)	C1	C3
Date	13/03/85	11/03/85	13/03/85	—	16/04/85	14/06/85
ΣPCB	258±58	6±0.3	8±2	0.78	6±1	6±1
ΣPAH	1343±232	78±15	93±18	1.12	85±23	93±35
4-NP	49482±2740	242±542[b]	720±306	0.97	330±188	58±23
DEHP	16610±1023	ND	157±34	0.95	ND	ND

CC = the concentration of the micropollutant in the conditioner; CB = the concentration of the micropollutant in the soil just before the conditioner spreading, CA = the concentration of the micropollutant in the soil just after the conditioner spreading, CF = the concentration factor, C1 = the concentration of the micropollutant in the soil 1 month after the conditioner spreading, C3 = the concentration of the micropollutant in the soil 3 months after the conditioner spreading and ND = not detected.

[a]Mean value and standard deviation of 5 analyses.

[b]The big standard deviation of these 4-NP value is due to the fact that on 4 of the 5 plots no trace of 4-NP was detected and 1212 vg/g d.m. on the fifth plot.

Ideally the concentration factors have to be exactly the same for each of the 4 micropollutants within the same sewage sludge spreading. If this is the case, the 4 different analytical techniques selected for the recovery of the micropollutants are accurate.

The concentration factor is dependent on the conditioner spreading practices of the farmer, and is therefore of no environmental interest.

Table IV shows that the values of the concentration factor "CF" are quite similar for each of the 4 micropollutant groups. This result shows us the relevance of analysing different micropollutants simultaneously to discuss a problem of pollution.

The values of the concentration factor "CF" show that in this case the micropollutant soil concentration is enhanced by roughly 0.9% of the concentration detected in the conditioner.

The detailed analyses

PAHs and PCBs: Figures 3a, 3b and 4a, 4b show detailed results repectively for light and heavy molecular weight PAHs and PCBs. The observations are roughly the same for the 2 micropollutants:

—the conditioner spreading enhances particularly the light molecular weight micropollutants of the farmland. This type of micropollutants is more degradable,[22–24] thus more absent in the soils than the heavy molecular weight one.

—One month after the sludges have been applied, the concentrations of these light molecular weight micropollutants fall down to the concentrations recorded before the conditioner spreading.

—Something noticeable happened 3 months after the conditioner spreading. With the exception of the light molecular weight PAHs, all the PAH and PCB concentrations recorded reached higher values than those detected just after the sludge spreading, even in the amended soil, as well as in the reference soil. The farmer did not touch his fields between the dates shown on table II. The only micropollutant input was in that case supplied by wet and/or dry precipitation.

4-NP and DEHP: The behaviour of these two micropollutants, illustrated in Figures 5 and 6, is comparable. Not detected or very faintly detected before the conditioner spreading, they reached

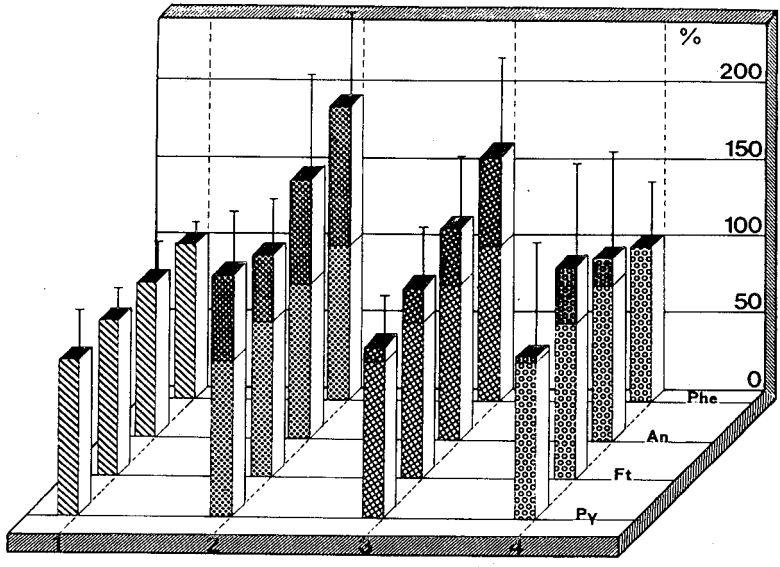

FIGURE 3a Light molecular weight PAH ($n=5$).

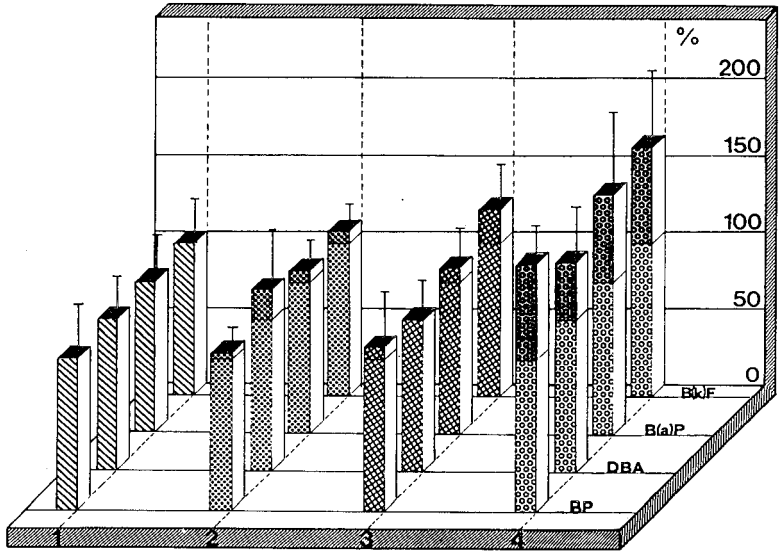

FIGURE 3b Heavy molecular weight PAH ($n=5$).

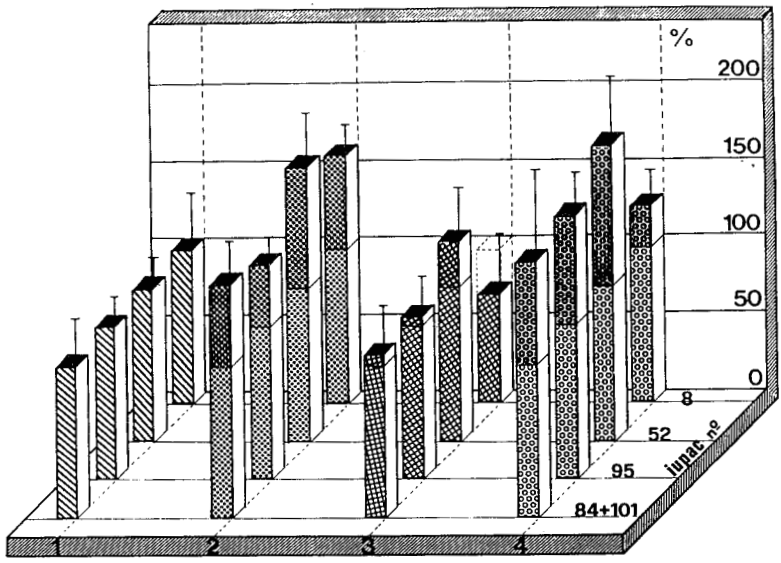

FIGURE 4a Light molecular weight PCB ($n=5$).

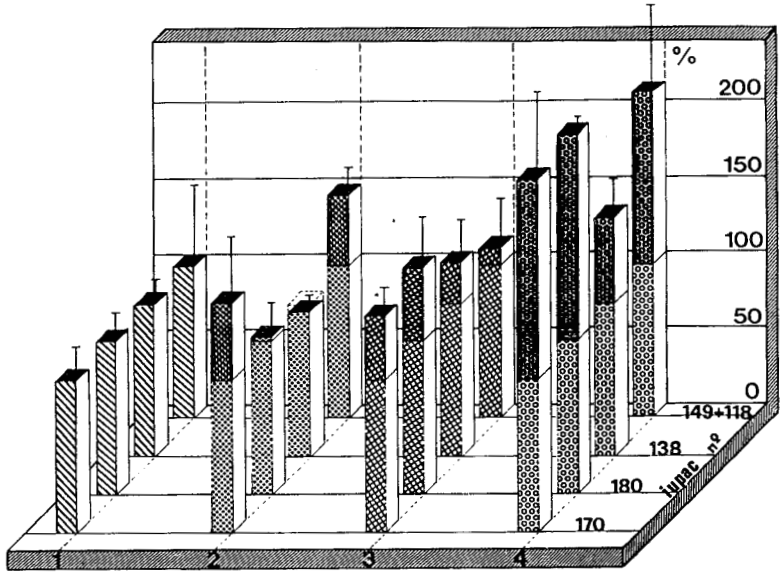

FIGURE 4b Heavy molecular weight PCB ($n=5$).

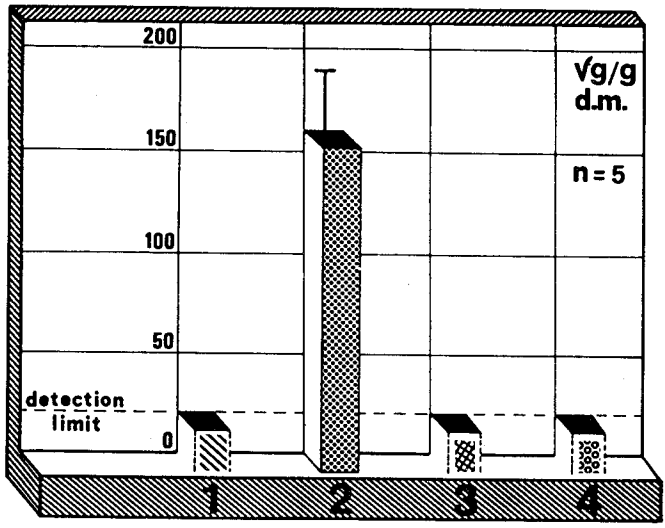

FIGURE 5 Di-ethyl-hexyl-phthalate.

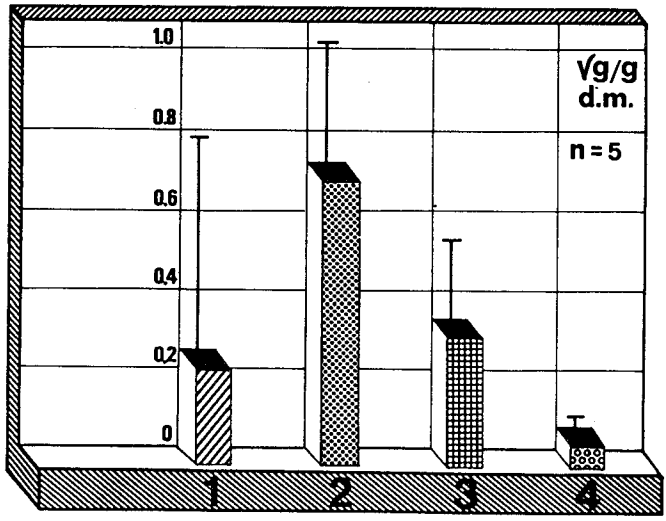

FIGURE 6 4-nonylphenol.

appreciable concentrations in the soils under research just after the spreading due to the high concentrations detected in the conditioner. Finally, they nearly completely disappeared 3 months after the spreading.

The easy degradation of these two organic micropollutants has already been underlined by Brüschweiler for 4-NP[25] and by Saeger for DEHP.[26]

SOIL MICROPOLLUTANT CONTAMINATION

Comparison of 3 soil conditioners

The previous chapter showed us that the influence of a single sewage sludge application is of limited importance on the organic micropollutant levels of an agricultural soil.

What could be the "long-term effects" of sewage sludge, farm manure such as pig slurry and mineral fertilisers on the organic micropollutant levels of different soils?

In order to answer this question, we took the opportunity of using field experiments prepared 10 years ago by F. X. Stadelmann and O. J. Furrer of the Swiss Federal Research Station for Agricultural Chemistry (Liebefeld, CH).

In a field experiment in two different locations (Liebefeld: light soil, Buren: heavy soil), permanent grassland plots (clover grass) were fertilized annually for 10 years (1976–1985) with one of the 3 following conditioners:

(a) mineral fertiliser; (b) pig slurry (5 ton organic matter/ha); (c) sewage sludge (5 ton organic matter/ha).

The aim of the present research is to observe to what extent the three conditioners polluted the soil with PAHs and PCBs in 10 years. The comparison is made with a reference soil which remains untouched during that time.

All the details about the previous researches performed on these fields have already been published.[27–29]

There are two advantages of working on experimental fields: The "history" of the selected fields is perfectly known. Each quantity of fertiliser brought to the soil is strictly controlled: Two types of soil, which are pedologically very different, were selected.[27]

After 10 years of soil conditioner spreading, the ΣPAH and ΣPCB concentrations found in the different plots are the following:

TABLE V

Soil micropollutant concentrations (vg/g d.m.)

	ΣPAH		ΣPCB	
	Sandy-loam soil (Liebef.)	Clayey soil (Büren)	Sandy-loam soil (Liebef.)	Clayey soil (Büren)
Reference soil	320	240	21	43
Soil + fertilizer	321	213	15	228
Soil + pig-dung	356	272	104	116
Soil + sludge	2361	2664	273	210

The analytical details are illustrated in Figures 7 and 8 and lead to the following comments:

—The increase of PAH in the soils improved with sewage sludge is considerable compared to those improved with any of the other conditioners.

—The mineral fertilisers which were used and the pig-dung did not increase the PAH concentration of the test soils in comparison with the reference soil during the 10 years of the experiment.

—The problem is quite different for the PCBs and is illustrated in Figure 8: In the same way as PAHs, the sewage sludge is chiefly responsible for the increase of PCBs in the soils, but pig-dung seems to contain quantities of these micropollutants which have to be taken into consideration. This constatation is not surprising when we know that micropollutants can penetrate in animal tissues by the ingestion of soil contaminated with sewage sludges.[30,31]

The high PCB value recorded in the soil of Büren improved with mineral fertilisers (228 vg/g d.m.) is not explained. Is it accidental, were some fertilisers contaminated?

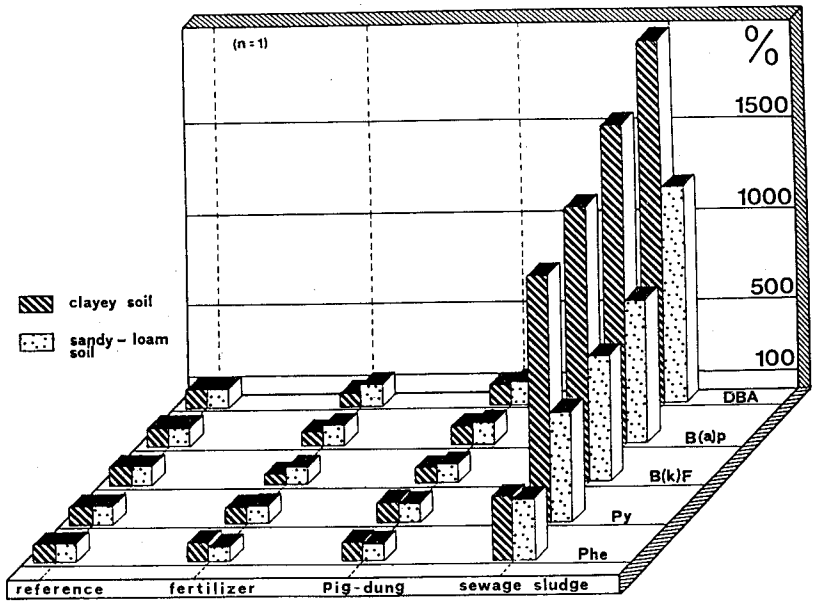

FIGURE 7 PAH and soil contamination: comparison between 3 soil conditioners.

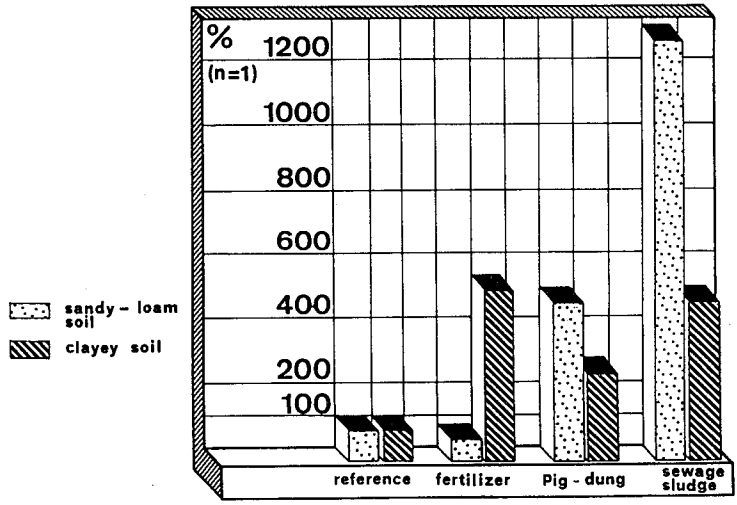

FIGURE 8 ΣPCB and soil contamination: comparison between 3 soil conditioners.

DISCUSSION

Reference 32 is directly related to the subject of this publication. The author points out that compost spreading enhances the PAH concentration of the treated soils. This observation is also underlined by Borneff.[33] The results however show that, as in this publication, a single sewage sludge application does not modify the micropollutant concentrations to a large extent.

In our point of view, the problem is much more related to duration, frequency and concentration of applications as illustrated in paragraph 4. After a certain number of years of sludge spreading, soils can accumulate PAHs and PCBs in quantities that have to be taken into consideration (Figures 7 and 8).

In the same way as for PAHs, the sewage sludge is chiefly responsible for the increase of PCBs in the soils. Three reasons could be associated to explain the concentration differences observed in Figures 7 and 8:

—Sewage sludges nearly always contain PCBs and PAHs.[8,9,34]

—Davis *et al.* observed that additional sludge applications increase the amount of detectable PCBs in the soil.[35]

—Soils, frequently improved with sewage sludges, contain more humus-like organic materials, that could increase the retention of organic micropollutants.[36] Moreover, transport by soil water of PCBs, associated with sewage sludge additions should be minimal and sewage sludge amendment should decrease the transport by soil water of the PCBs already present as soil contaminants, issued from previous sludge applications.[37]

Even if high concentrations are detected in the sewage sludge, 4-NP and DEHP are nearly completely degraded 30 days after the sewage sludge spreading.

Finally this research has shown that to evaluate the part played by the sewage sludges in the soil contamination by these micropollutants, it is necessary to consider at the same time the micropollutant contamination of different manures and mineral fertilisers and the micropollutant content of dry and wet precipitation. There are many references[11,12,16–18] on micropollutant content of dry and wet precipitation, but none of these establish a correlation between these

precipitations and the soil micropollutant content. There is a lack of information in that field.

Acknowledgement

The authors wish to thank Dr. O. J. Furrer and Dr. H. Hani from the Swiss Federal Research Station for Agricultural Chemistry of Liebefeld who kindly allowed us to work on their experimental fields. Dr. W. Giger and co-workers of EAWAG-Dubendorf for having analyzed 4-NP content of our samples. This research was supported by the PNR 7B program from the Swiss National Fund for Scientific Research.

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Appendix

The chemical names and abbreviations of the compounds mentioned in this paper are:

PCB = mixture of chlorinated biphenyl compounds having various percentages of Cl.
ΣPCB = sum of 33 PCB congeners considered for quantitation in the sample.[1]
PAH = polynuclear aromatic hydrocarbon.
ΣPAH = sum of the 11 hereafter mentioned PAHs.
OMP = organic micropollutant.