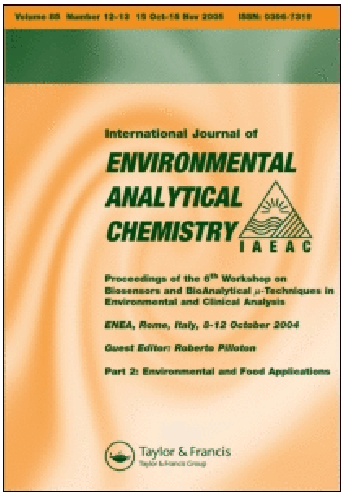

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Organic Micropollutants in Swiss Agriculture: Distribution of Polynuclear Aromatic Hydrocarbons (PAH) and Polychlorinated Biphenyls (PCB) in Soil, Liquid Manure, Sewage Sludge and Compost Samples; a Comparative Study

J. D. Berset[a]; R. Holzer[a]
[a] Swiss Federal Research Station for Agricultural Chemistry and Hygiene of the Environment (FAC), Liebefeld-Berne, Switzerland

To cite this Article Berset, J. D. and Holzer, R.(1995) 'Organic Micropollutants in Swiss Agriculture: Distribution of Polynuclear Aromatic Hydrocarbons (PAH) and Polychlorinated Biphenyls (PCB) in Soil, Liquid Manure, Sewage Sludge and Compost Samples; a Comparative Study', International Journal of Environmental Analytical Chemistry, 59: 2, 145 — 165

To link to this Article: DOI: 10.1080/03067319508041324

URL: http://dx.doi.org/10.1080/03067319508041324

Intern. J. Environ. Anal. Chem., Vol. 59 pp. 145–165
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ORGANIC MICROPOLLUTANTS IN SWISS AGRICULTURE: DISTRIBUTION OF POLYNUCLEAR AROMATIC HYDROCARBONS (PAH) AND POLYCHLORINATED BIPHENYLS (PCB) IN SOIL, LIQUID MANURE, SEWAGE SLUDGE AND COMPOST SAMPLES; A COMPARATIVE STUDY

J. D. BERSET and R. HOLZER

Swiss Federal Research Station for Agricultural Chemistry and Hygiene of the Environment (FAC), CH-3097 Liebefeld-Berne, Switzerland

(Received, 1 November 1993; in final form, 10 April 1994)

This report aims to give a general view of the present state of contamination of agricultural soils and manures like sewage sludge, liquid manure and compost in Switzerland with two groups of organic micropollutants: polynuclear aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB). Overall PAH concentrations for soils ranged between 60–575 μg Σ PAH/kg dw (mean value 175 μg/kg dw). The corresponding values for the other matrices were: cattle slurries 87–309 μg/kg (165 μg/kg), pig slurries 66–339 μg/kg (143 μg/kg), sewage sludge 1.7–15 mg/kg (6.3 mg/kg) and compost 0.8–2.7 mg/kg (2 mg/kg). PCB levels for soils averaged 14 μg Σ PCB/kg dw and represented typical background concentrations. PCB values in cattle slurries were slightly higher (20 μg/kg) and significantly higher in pig slurries and compost (37 and 32 μg/kg). The highest PCB concentrations were found in sewage sludges (0.4 mg/kg). Application of these sludges onto soils at rates normally used in Switzerland (0.5 tons dw/ha.y) does however not represent a serious contamination problem. A qualitative analysis of the environmental samples showed that besides the 16 EPA PAHs frequently used for quantification mainly alkylated derivatives as well as N-S-and-O-PAHs were detected. These compounds, although usually found in low quantities, should be considered more seriously when estimating the toxicity of PAHs in the environment.

KEY WORDS: PCB, PAH, soil, sewage sludge, liquid manure, compost, quantitative and qualitative analysis.

INTRODUCTION

Organic micropollutants (xenobiotics) are widespread in the environment as a result of human activities (industry, agriculture and traffic). In recent years numerous studies have been published dealing with the methodology and analytical techniques necessary for determining these trace compounds in various compartments of the biosphere. Scientists have expressed increased concern about the state of contamination of soils and different manures (sewage sludge, liquid manure, compost) in the agricultural milieu. In Switzerland soils are therefore analysed in more detail in some cantons in order to gain information about background concentrations or to study the immissions caused e.g. by traffic.

Sewage sludge is known to be contaminated with a wide array of xenobiotics[1,2]. Approximately 50% of the sludge produced in Switzerland is applied to agricultural land as fertilizer[3,4]. This amount corresponds to 10^5 tons of dry solid sludge per year[4]. Agriculture therefore still remains an important domain for sludge disposal. At present Swiss authorities have set no legal restrictions for xenobiotics occurring in sludges except an AOX value of 500 ppm as a global parameter for adsorbable organic halogens[5]. Yet the fate, behaviour and health significance of xenobiotics in sludges are still attracting research interest as well as public concern since studies have shown the occurrence of polychlorinated dioxins (PCDD) and furans (PCDF) in German sewage sludges[6].

Liquid manure is mostly used as a plant fertilizer in agriculture. There is, however, virtually no information about organic contaminants in this matrix. One Swiss study has been performed on the distribution of PCBs and PAHs in farm yard manures (FYM)[7]. A recent English study has shown an increase in PAH content in FYM amended soils[8]. Both studies indicate that liquid manures might contribute significantly to pollution of agricultural soils with xenobiotics.

Presently over 10^5 tons (fresh weight) of compost per year are produced in Switzerland. Composting reduces the amount of waste and produces a manure rich in organic matter, approx. 40% of which is used in agriculture[9]. Although these amounts do not yet play an important role as a fertilizer composting might increase in the near future. Little is known about organic micropollutants in composts. A recent American study about various types of compost (yard waste, municipal solid waste) has measured relatively high levels of PCDD/PCDF, PCBs, chlorophenols and chlorobenzenes[10].

For the present study two groups of ubiquitous, hydrophobic and partly highly persistent organic contaminants have been chosen: PCBs and PAHs. PCBs were widely used in industry including transformers and capacitors in the electrical industry as well as in inks, paper and paints. Due to their hydrophobicity they adsorb onto organic particles. PCBs are hardly degradable, accumulate in higher organisms and represent a considerable risk of chronical ecotoxicity. PAHs are produced naturally only in small amounts (e.g. through forest fires and possibly microbiological synthesis). The main input into the environment originates however from anthropogenic activities by means of incomplete combustion of fossil fuels. Some PAHs are well known carcinogens and/or mutagens and are listed by the U.S. Environmental Protection Agency and the European Community as priority pollutants. It is clearly important to investigate PAH levels and the fate of these compounds in agricultural compartments, especially in sewage sludge, where relatively high concentrations are found. Only few data on contemporary PCB and PAH contents of Swiss soils and sewage sludges as well as of liquid manures and composts are available. The aim of this study was to establish new information on the range and concentration of PCBs and PAHs in these matrices (quantitative aspects) and to perform a qualitative analysis in order to identify further xenobiotics which might become important in future investigations.

MATERIALS AND METHODS

General comments

For the analysis of soils samples from sites of the Swiss Soil Monitoring Network (NABO) were chosen[11]. Soil characteristics are described in Table 1. Soils had not been treated with the liquid manures analyzed in this study. However liquid manures had

Table 1 Soil characteristics.

NABO site no	*land utilization*	*depth (cm)*	*org. C content (% g/g)*	*soil texture*
1	permanent grassland	0–20	3.8	clay loam
21	agriculture	0–20	1.7	sandy loam
25	agriculture	0–20	2.4	clay
33	permanent grassland	0–20	3.8	silty clay loam
36	agriculture	0–20	2.4	loam
38	agriculture	0–20	2.0	loam
39	agriculture	0–20	5.5	loam
48	agriculture	0–20	16.5	organic soil
54	agriculture	0–20	1.3	sandy loam
55	vine growing	0–20	1.1	loam
56	dairy farming	0–20	3.6	silty loam
57	dairy farming	0–5, 0–20	4.1/5.8	clay loam
58	coniferous forest	0–5, 0–20	19/6.6	loam
59	vegetable gardening	0–20	2.9	loam
61	city park	0–20	2.2	loam
62	deciduous forest	0–20	3.7	silty clay loam
69	permanent grassland	0–20	3.3	loam
98	permanent grassland	0–20	4.6	sandy loam

probably been applied to some or all soils according to local farming practice in the period before this study was performed. Sampling and storage were carried out according to the Ordinance Relating to Pollutants in Soils[12]. All soils were freeze dried and ground with a porcelain pestle and mortar to pass a 0.63 mm mesh sieve. Samples were subsequently filled into brown glass jars which had been previously rinsed with hexane and acetone and had been sealed with a similarly rinsed aluminium foil protected cover before use. The covered jars were finally stored in the dark at –20°C until extraction. Liquid manures were taken from the pits on the farm located at NABO sites after stirring for at least 30 min using steel tools (Table 2). One to two liters were brought into glass

Table 2 Liquid manure data.

NABO site no	*slurry type*	*solid content (%)*
1	c,p	
25	c	2.8
33	c,p	c: 9.1, p: 3.8
36	c	6.3
38	c,p	c: 5.3, p: 2.2
39	c	4.3
48	c	3.5
54	p	0.9
69.1	c	7.1
69.2	c	3.9
98	c	2.9
Grangeneuve	c	4.5

c: cattle slurry
p: pig slurry
69.1: liquid manure produced by dairy cows
69.2: liquid manure produced by fattening bulls

jars precleaned as described above. Freeze drying occurred in portions of 200 ml for 70 to 80 hours at a temperature of –55 to –60°C. After grinding them with a hammer mill samples were stored as already mentioned. Sludge samples were collected from waste water treatment works of three major cities (Berne, Zurich and Geneva) and two rural sites (Kiental, Niederried). They covered a range of catchment sizes in rural/domestic through the urban and industrial areas and represented sludges containing varying amounts of industrial waste waters (Table 3). Following collection the sludge samples were prepared and stored in the same way as liquid manures. Finally three compost samples were prepared by collecting several subsamples from compost pits and mixing them thoroughly (Table 4). Laboratory samples were freeze dried and stored in the same way as soil.

Table 3 Sewage sludge details.

Location	*Sewage treatment work*	*Catchment characteristics*	*Population equivalent (× 1000)*	*Current sludge disposal*	*Solid content (%)*
Zurich	digested sludge	urban/much industrial wastew.	340	agriculture, landfill incineration	4.8
Berne	digested sludge	urban/moderate industrial wastew.	> 200	agriculture	7.5
Geneva	digested sludge	urban/much industrial wastew.	400	landfill	3.6
Kiental	digested sludge (Imhoff tank)	rural/domestic no industrial wastewater	0.2	agriculture	6.2
Niederried	digested sludge	rural/domestic no industrial wastewater	0.25	agriculture	0.6

Table 4 Compost data.

Location	*Compost Origin*
Lostorf (canton of Solothurn)	rural/organic waste from kitchen and garden of a private houshold
City of Solothurn (Werkhof)	urban/park and garden waste
City of Solothurn (Stadtpark)	urban/garden and houshold waste

Compound selection for quantitative analysis

PCBs

As proposed by the Community Bureau of Reference in Brussels (BCR)[13] the following 7 PCB congeners were determined in all matrices:

BZ* 28: 2,4,4' - Trichlorobiphenyl ($C_{12}H_7Cl_3$)
BZ 52 : 2,5,2',5' - Tetrachlorobiphenyl ($C_{12}H_6Cl_4$)
BZ 101: 2,4,5,2',5' - Pentachlorobiphenyl ($C_{12}H_5Cl_5$)
BZ 118: 2,4,5,3',4' - Pentachlorobiphenyl ($C_{12}H_5Cl_5$)
BZ 138: 2,3,4,2',4',5' - Hexachlorobiphenyl ($C_{12}H_4Cl_6$)
BZ 153: 2,4,5,2',4',5' - Hexachlorobiphenyl ($C_{12}H_4Cl_6$)
BZ 180: 2,3,4,5,2',4',5' - Heptachlorobiphenyl ($C_{12}H_3Cl_7$)
BZ*: Ballschmitter-Zell numbers

These congeners occur in many environmental samples, are frequently measured in countries of the European Community and can be separated from the matrices rich in organic matter and coeluting congeners by analytical techniques described in the sample analysis section. BZ 118 was included because it is the most abundant of the toxic PCBs. Σ PCB refers to the sum of these 7 congeners.

Although several hundreds of PAH compounds exist, this study limits its scope to the 16 better known EPA PAHs which are part of the US EPA Priority Pollutants List:

NAP : Naphtalene
ANY : Acenaphtylene
ANA : Acenaphtene
FLU : Fluorene
PHE : Phenanthrene
ANT : Anthracene
FLT : Fluoranthene
PYR : Pyrene
BaA : Benzo(a)anthracene
CHR : Chrysene
BbF : Benzo(b)fluoranthene
BkF : Benzo(k)fluoranthene
BaP : Benzo(a)pyrene
IPY : Indeno(1,2,3-cd)pyrene
DBA : Dibenzo(a,h)anthracene
BPE : Benzo(g,h,i)perylene

Some of these compounds have a mutagenic or carcinogenic potential[14] (e.g. benzo(a)pyrene) and therefore need to be monitored carefully. Σ PAH refers to the sum of the 16 EPA PAHs enumerated above.

Sample analysis for quantitative determination of PCBs and PAHs

Extraction and clean up

Glassware, solvents and chemicals were pesticide grade or cleaned as usual for trace analysis. Samples (typically 10 g of soil or cattle/pig slurry, 5 to 10 g of compost and 1 to 2.5 g of sewage sludge) were saponified in 2 M KOH in methanol (MeOH) for 2 hours at 70°C (Figure 1). Tetrachloronaphtalene for PCB analysis and 3,6-dimethylphenanthrene for PAH determination were added at the initial extraction. After liquid-liquid partition with hexane the non polar phase was reduced in volume and

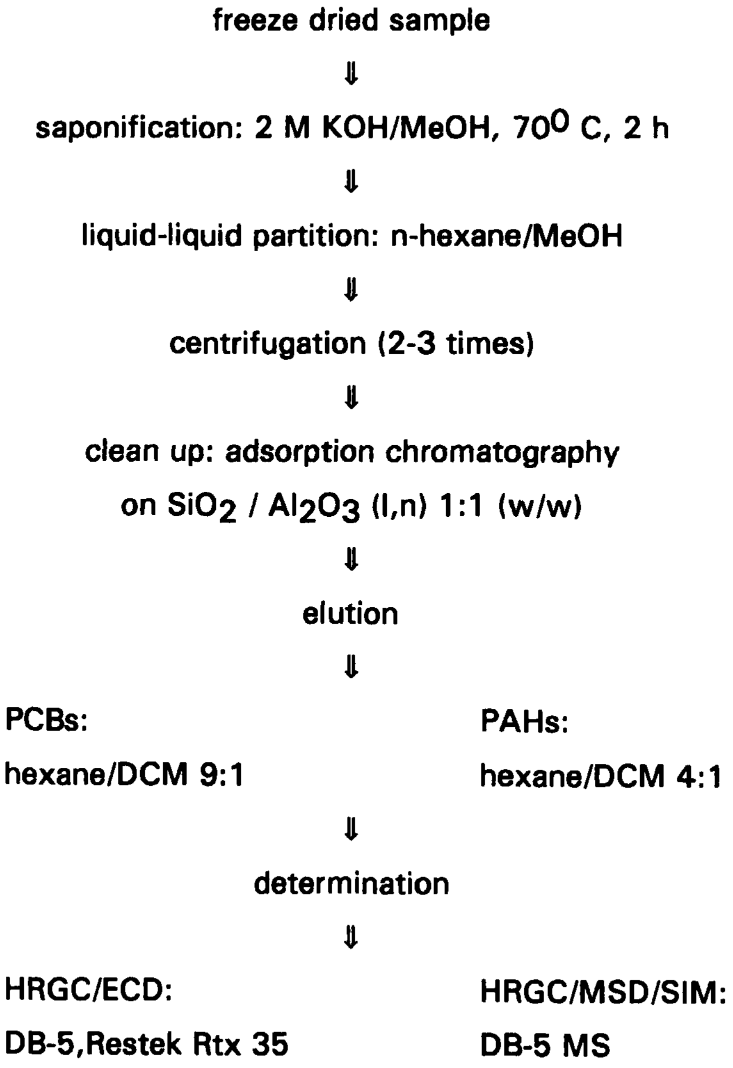


Figure 1 Method for the simultaneous isolation of PCBs and PAHs from soil, sewage sludge, liquid manure and compost samples.

further cleaned on a double layer column consisting of silica gel (bottom layer) and aluminium oxide (top layer). Two ml of sample were loaded onto an 8 g, 5% (w/w) deactivated silica gel (70–230 mesh) and 8 g, 5% (w/w) deactivated aluminium oxide (neutral, activity 1, 70–230 mesh) column (dimensions 1 × 40 cm) and eluted with 20 ml hexane/dichloromethane (DCM) 9:1 to collect PCBs and 40 ml of hexane/DCM 4:1 to isolate the PAHs. After reconcentration PCBs and PAHs were dissolved in isooctane and toluene respectively and analysed by high resolution gas chromatography (HRGC) with ECD detection for PCBs and HRGC with mass selective detection (MSD) for PAHs.

Analysis of PCBs by high resolution gas chromatography

Analysis of PCBs was completed on a Carlo Erba HRGC 5300 Mega Series GC using ECD detection (Ni^{63}, 10 mCi). For PCB separation a 50 m J&W DB-5 capillary column was used with 0.2 mm ID and 0.25 μm film thickness. The analytical column was protected with 2 m of a 0.53 mm ID deactivated precolumn. Injection volume was 1 μl of the isooctane solution on column. The temperature program was as follows: Initial oven temperature 80°C, two minutes hold; first temperature ramp to 200°C at 25°C/min; and second temperature ramp to 300°C at 2°C/min and hold for 7 min. The carrier gas was helium (He) set at 36 psi at 80°C. PCB concentrations were calculated using the internal standard procedure. PCB results were confirmed on a 60 m Restek Rt_X 35 (65% dimethyl-35% diphenyl polysiloxane) as a second column (0.25 mm ID, 0.25 μm film thickness). Temperature program: Initial oven temperature was 80°C, one minute hold; first temperature ramp to 230°C at 25°C/min; and second temperature ramp to 290°C at 2°C/min and hold for 5 min.

Analysis of PAHs by HRGC-MS

Extracts containing PAHs were quantified by gas chromatography (Hewlett Packard, 5890 Series II gas chromatograph) with mass spectrometry (Hewlett Packard 5971 A Mass Selective Detector) (GC-MSD) in the selective ion monitoring (SIM) mode. PAHs were separated on a J&W DB-5 MS column (30 m, 0.25 mm ID, 0.25 μm film thickness). A deactivated precolumn (5 m, 0.53 mm ID) was again used to protect the analytical column. 1 μl of the extract in toluene was injected on column. Temperature program: 100°C hold for 2 min; temperature ramp to 310°C at 5°C/min, hold for 5 min. The carrier gas was He set at 9.1 psi at 100°C. Analysis was carried out using the injection system in the oven tracking mode to maximize chromatographic resolution. The oven tracking mode maintains the inlet temperature three degrees higher than the oven temperature to optimize repeatibility. MS parameters: The MS was operated under electron impact (EI) ionization with a 70 eV ionization voltage. Quantification was based on SIM as follows: NAP m/z 128.15, 127.05, ANY 152.05, 151.05, ANA 154.15, 153.15, FLU 166.15, 165.15, PHE/ANT 178.15, 176.05, FLT/PYR 202.15, 200.1, BaA/CHR 228.15, 226.10, BbF/BkF/BaP 252.20, 250.1, IND/BGP 276.20, 278.20, DBA 278.20, 276.20; Electron multiplier voltage (EMV) 2400 V absolute, dwell time 200 msec., MS temperature parameters: injector: 103°C, transferline: 320°C, ion source: 208°C.

Laboratory quality control and standards

Analytical blanks (one for each 5 environmental samples) were prepared and analysed using the same procedure. Replicate injections gave an error usually <10%. To test the accuracy of the experimental procedure a certified standard reference material of sewage sludge CRM 392 from the BCR was analysed on a regular basis together with the environmental samples. Our PCB results generally agreed well with the reported values[13]. The linearity of the ECD was tested periodically by injecting PCB standard mixtures of different concentrations and determining the linear range[13]. No CRM for PAHs was available at that time for internal quality control. Recovery experiments were performed by spiking the different matrices with PCBs and PAHs at a low and a high concentration. For PCBs 70 to 90% were recovered wereas for PAH recoveries were very structure dependent: 30 to 50% for the low molecular weight PAHs (NAP, ANY, ANA, FLU), 70 to 110% for the remaining PAHs. PCB standards were obtained individually as solutions in hexane or isooctane from the Group of Ecotoxicology of the ETH Lausanne. PAH standards were purchased as a mixture in a toluene solution from ICT company Basle.

Sample preparation for qualitative analysis of the different environmental samples

For qualitative analysis matrices were extracted in DCM under reflux over night and cleaned in the same way as described in the previous section. From the chromatography five fractions were collected: hexane eluate (fraction 1), hexane/DCM 9:1 eluate (fraction 2), hexane/DCM 4:1 eluate (fraction 3), hexane/DCM 1:1 eluate (fraction 4) and DCM 100% eluate (fraction 5). The eluates were concentrated and studied by GC-MS in the full scan mode (GC conditions as mentioned above). Mass spectra acquired were compared with the Wiley spectral library integrated in the GC-MS system. For fraction 3, which contained mainly PAHs, structural proposals were additionally based on published data[15].

RESULTS AND DISCUSSION

The problem of comparing PCB and PAH values with literature data

A comparison of measured PCB and PAH concentrations with published data is often difficult to realize. The areas under study, the characteristics of the different matrices, the types of human activities, the atmospheric conditions, the analytical methods and the ways solutes are calculated differ very much from one study to another. In PCB analysis either an Aroclor mixture is used for quantification or congener specific determination with a limited amount of PCBs, that cover a wide range of chlorination, is performed. Normally in PAH quantification only Benzo(a)pyrene or part of the 16 EPA PAHs are determined. These differences should be kept in mind when comparing concentrations of these xenobiotics.

PCB and PAH concentrations in soil, liquid manure, sewage sludge and compost samples

Soils

Tables 5 and 6 report Σ PAH and Σ PCB concentrations on a dry weight basis along with individual PAHs and PCB congeners. In the layer of 0–20 cm soil Σ PAHs and Σ PCBs ranged from 60 to 575 and 6.5 to 29 µg/kg respectively with means of 175 µg Σ PAH/kg and 14 µg Σ PCB/kg. These amounts are generally consistent with values reported for other Swiss soil samples[16–19]. In the UK PAH levels in soils ranged from 200–1000 µg Σ PAH/kg[20–22] whereas roughly 10 µg Σ PCB/kg were found[23]. In the

Table 5 Soil PAH concentrations (ug/kg dw). See table 1 for soil characteristics.

NABO site no	*depth (cm)*	*NAP*	*ANY*	*ANA*	*FLU*	*PHE*	*ANT*	*FLT*	*PYR*	*BaA*	*CHR*	*BbF*	*BkF*	*BaP*	*IPY*	*DBA*	*BPE*	*SUM PAH*
1																		
21	0–20	25	3	2	2	28	3	39	29	16	10	28	11	10	18	4	19	247
25	0–20	4	2	n.d	2	16	3	36	28	17	10	30	11	12	17	4	16	208
33	0–20	8	2	n.d	n.d	8	n.d	9	6	3	5	9	2	4	5	n.d	7	68
36	0–20	7	2	n.d	2	12	2	25	17	7	19	14	8	8	10	3	9	145
38	0–20	10	2	n.d	n.d	6	n.d	6	5	3	6	8	n.d	2	5	2	5	60
39	0–20	3	2	n.d	n.d	10	2	23	19	12	20	34	10	18	21	5	20	199
48	0–20	6	4	n.d	n.d	12	n.d	12	9	4	9	6	n.d	5	7	2	9	85
54	0–20	8	5	n.d	3	34	3	54	19	5	29	17	n.d	4	8	2	7	198
55	0–20	3	3	n.d	n.d	7	n.d	9	8	3	6	5	4	4	6	n.d	6	64
56	0–20	2	n.d	n.d	5	67	1	126	80	42	82	55	38	14	35	10	18	575
57	0–20	4	n.d	n.d	n.d	8	n.d	11	7	3	10	17	2	3	6	2	6	79
	0–5	6	n.d	n.d	2	8	n.d	10	6	3	7	9	3	4	6	2	5	71
58	0–20	7	n.d	n.d	n.d	10	n.d	14	8	5	9	13	3	5	8	2	7	91
	0–5	3	n.d	n.d	2	42	n.d	95	59	21	100	189	18	14	62	13	46	664
59	0–20	4	n.d	n.d	2	12	n.d	22	13	5	19	51	8	5	14	3	10	168
61	0–20	5	n.d	1	1	10	1	14	10	4	11	12	3	4	6	2	8	92
62	0–20	5	n.d	n.d	2	22	2	60	43	25	67	89	23	13	43	8	37	439
69	0–20	3	n.d	2	3	21	2	42	30	11	39	54	3	9	19	4	18	260
98	0–20	4	3	n.d	n.d	7	n.d	8	6	3	7	11	3	4	6	2	6	70
	0–20	3	3	n.d	n.d	13	2	28	22	13	24	17	14	16	23	5	25	208
Mean*		6.2	2.8	1.7	2.4	16.4	2.1	28.8	19.2	9.7	20.5	25.2	9.1	7.6	13.8	3.6	12.5	175.1
Median*		5	3	2	2	12	2	22	13	5	10	17	6	5	8	3	9	145
Min value*		2	2	1	1	6	1	6	5	3	5	5	2	2	5	2	5	60
Max value*		25	5	2	5	67	3	126	80	42	82	89	38	18	43	10	37	575

without NABO site no 58, 0–5 cm

n.d: not detected

Table 6 Soil PCB concentrations (ug/kg dw). See Table 1 for soil characteristics.

NABO site no	*depth (cm)*	*BZ 28*	*BZ 52*	*BZ 101*	*BZ 118*	*BZ 153*	*BZ 138*	*BZ 180*	*SUM PCB*
1	0–20	0.3	1.6	3.1	1.5	1.4	1.3	0.5	9.7
21	0–20	0.2	1.2	2.3	1.1	1.4	1.5	0.5	8.2
25	0–20	0.2	1.3	2.5	1.3	1.3	1.2	0.5	8.3
33	0–20	0.2	1.4	2.9	1.7	2.1	2	0.7	11
36	0–20	0.2	1	2.3	1.2	1.3	1.3	0.4	7.7
38	0–20	0.2	1.5	3	1.3	1.4	1.3	0.4	9.1
39	0–20	0.3	1	2.6	1.8	1.9	1.8	0.7	10.1
48	0–20	0.4	2.1	5.2	2.7	2.5	2.3	0.8	16
54	0–20	0.2	1.2	2	1	0.9	0.9	0.3	6.5
55	0–20	0.3	2.7	4.5	1.8	1.2	1.1	0.3	11.9
56	0–20	0.6	3.8	6.4	2.7	1.8	1.6	0.4	17.3
57	0–5	0.4	4.1	10	4.1	2.1	1.8	0.2	22.7
	0–20	0.3	4.1	7.3	2.7	1.3	1.2	0.3	17.2
58	0–5	0.6	8.1	23.8	13.5	16.2	15.2	6.7	84.1
	0–20	0.6	3	9.9	4.1	3.2	2.9	0.9	24.6
59	0–20	0.3	2.4	5.5	2.7	2	1.8	0.5	15.2
61	0–20	0.3	3.8	6.7	2.8	2.5	2.4	0.7	19.2
62	0–20	0.5	4.7	9.9	4.9	3.9	3.7	1.4	29
69	0–20	0.2	1.1	2.5	1.1	1.1	1	0.4	7.4
98	0–20	0.2	0.9	2.3	1.4	3.8	2.2	4.6	15.4
Mean*		0.3	2.3	4.8	2.2	2.0	1.8	0.8	14.0
Median*		0.3	1.6	3.1	1.8	1.8	1.6	0.5	11.9
Min.value*		0.2	0.9	2	1	0.9	0.9	0.2	6.5
Max.value*		0.6	4.7	10	4.9	3.9	3.7	4.6	29

*: without NABO site no 58, 0–5 cm

present study highest PAH concentrations were measured in a vine growing soil, a forest soil and a city park soil probably due to nearby emission sources (heating facilities, traffic). The highest PCB levels were determined in the two forest soils and the city park soil whereas PCB values tended to be higher in the coniferous forest soil compared to the deciduous forest soil. Assuming similar environmental inputs this might be explained by i) the higher content of organic matter in forest soils where accumulation of PCBs can occur (Figure 2), ii) the reduced mixing of the top soil in forests and iii) the higher specific surface of the coniferous forest in comparison to a deciduous forest. PAH and PCB patterns were similar in the different soil samples. The PAH compounds phenanthrene, fluoranthene, pyrene, chrysene, benzo(b)fluoranthene and benzo(a)pyrene were generally present at the highest concentrations, whereas naphtalene, acenaphtylene, acenaphtene and fluorene were present at the lowest. The greatest contribution to the $\sum$ PCB was provided by the penta- and hexa- chlorinated biphenyls.

Recently reference values for the PAH background levels of top soils have been proposed for Germany[24]:

Reference values:		Found in our study:
FLT:	0.3 mg/kg dw	0.030 mg/kg dw
BaA:	0.2	0.010
BbF:	0.2	0.025
BkF:	0.1	0.010
BaP:	0.1	0.008
BPE:	0.1	0.012
$\sum$ 6 PAH	1	0.095 mg/kg dw

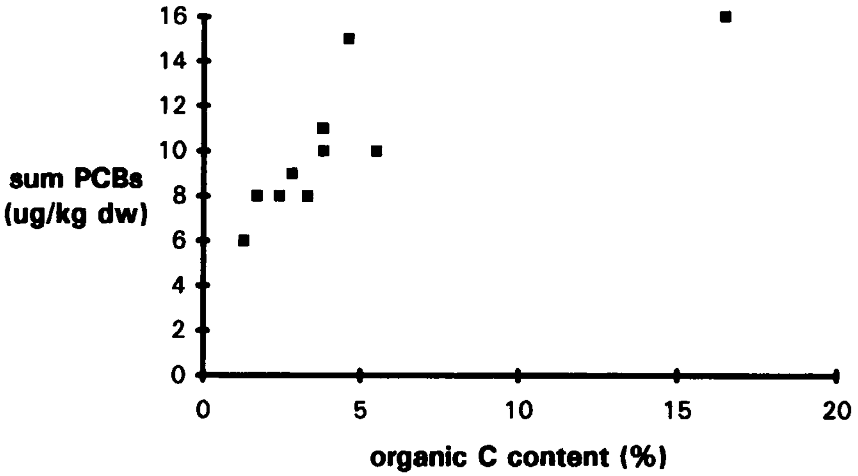


Figure 2 Correlation diagram between PCB levels and organic C content of soils.

Our soil PAH measurements proved to be approximately 10 times lower than the German reference values. For non contaminated Swiss soils these reference values seem to be much too high as Σ 16 EPA PAH frequently do not exceed 130 µg/kg. As mentioned earlier PCB background levels of approx. 10 µg/kg or lower are typical values for remote agricultural soils.

Liquid manures

PAH and PCB concentrations in cattle and pig slurry samples are displayed in Tables 7 and 8. Although slurry samples were partly taken at the same sites as the soils, these were never amended with the corresponding liquid manures so no specific correlation between the two compartments regarding PAH and PCB levels was possible. PAH contents in the different liquid manures were basically the same whereas PCB concentrations in pig slurries tended to be higher than in cattle slurries. The PAH and PCB patterns were the same as in soils. Clearly sample NABO 1 contained the highest PAH and PCB levels. An explanation of the reasons for the different amounts of PAHs and PCBs found is difficult to give at the moment, as no investigations about the environmental inputs (atmosphere, forage etc.) were performed.

Sewage sludge

As expected the sewage sludge samples showed the highest PAH and PCB concentrations of the matrices examined (Table 9). The array of sludges had a PAH content ranging from 1.7 mg Σ PAH/kg dw in a rural sludge to 15 mg/kg in a urban/industrial sludge with the mean of all sludges being 6.3 mg/kg. PCB concentrations varied from 300 to 540 µg Σ PCB/kg dw with a mean of 413 µg/kg. Contamination of sewage sludge with PAHs and PCBs is well documented in several

Table 7 PAH concentrations in pig and cattle slurry samples (ug/kg dw). See Table 2 for slurry details.

NABO site no	*NAP*	*ANY*	*ANA*	*FLU*	*PHE*	*ANT*	*FLT*	*PYR*	*BaA*	*CHR*	*BbF*	*BkF*	*BaP*	*IPY*	*DBA*	*BPE*	*SUM PAH*
Cattle slurries																	
1	29	n.d	20	7	80	8	62	38	13	20	14	3	3	5	2	5	309
25	5	3	3	6	23	2	16	12	3	3	4	n.d	3	3	n.d	3	89
33	16	n.d	6	7	46	4	33	27	8	17	11	2	5	6	n.d	6	194
36	7	n.d	6	6	26	2	10	10	3	8	3	n.d	2	2	n.d	2	87
38	3	n.d	2	5	21	2	7	7	5	9	15	4	9	7	2	7	105
39	5	n.d	5	5	24	2	23	20	13	17	23	10	11	12	4	11	185
48	9	3	3	4	20	2	19	15	7	24	23	n.d	9	10	3	9	160
69.1	4	4	2	3	16	2	28	25	12	33	29	11	13	15	3	13	213
69.2	5	n.d	5	6	43	4	37	3	11	18	16	8	8	9	3	9	185
98	9	1	13	12	39	3	17	12	3	3	2	n.d	2	2	n.d	3	121
Mean	9.2	2.8	6.5	6.1	33.8	3.1	25.2	16.9	7.8	15.2	14.0	6.3	6.5	7.1	2.8	6.8	164.8
Min. value	3	1	2	3	16	2	7	3	3	3	2	2	2	2	2	2	87
Max. value	29	4	20	12	80	8	62	38	13	33	29	11	13	15	4	13	309
Pig slurries																	
1	5	n.d	4	4	19	2	11	9	3	6	4	3	2	2	nd.	3	77
33	6	3	n.d	10	62	2	21	3	2	4	3	n.d	n.d	n.d	n.d	n.d	116
38	4	n.d	3	3	23	2	19	13	6	10	10	5	8	6	2	6	120
54	7	7	10	13	79	12	70	50	16	44	7	3	8	7	n.d	6	339
Grangeneuve	3	n.d	2	3	14	2	8	7	3	4	5	2	4	3	2	4	66
Mean	5.0	5.0	4.8	6.6	39.4	4.0	25.8	16.4	6.0	13.6	5.8	3.3	5.5	4.5	2.0	4.8	143.6
Median	5	5	4	4	23	2	19	9	3	6	5	3	6	5	2	5	116
Min. value	3	3	2	3	14	2	8	3	2	4	3	2	2	2	2	3	66
Max. value	7	7	10	13	79	12	70	50	16	44	10	5	8	7	2	6	339

Table 8 PCB concentrations in pig and cattle slurry samples (ug/kg dw). See Table 2 for slurry details.

NABO site no	*BZ 28*	*BZ 52*	*BZ 101*	*BZ 118*	*BZ 153*	*BZ 138*	*BZ 180*	*SUM PCB*
Cattle slurries								
1	0.4	2.6	8.7	7.4	4.8	5.5	1	30.4
25	0.4	2.4	6.2	5.6	4.1	5.2	1.3	25.2
33	0.6	2.1	4.3	2.9	2.8	2.8	0.9	16.4
36	0.5	2.1	4.2	2.8	2.6	2.7	0.7	15.6
38	0.6	2.6	5.2	3.3	3	2.9	0.6	18.2
39	0.3	2.6	6	4.1	3.4	3.5	0.9	20.8
48	0.4	2.4	5.6	4.5	3.3	4.1	0.9	21.2
69.1	0.2	1.4	3.1	1.9	1.5	1.4	0.3	9.8
69.2	0.7	2.6	6.2	3.8	4.1	4	1.3	22.7
98	0.4	2.6	5.1	3.6	3.2	3.3	1.1	19.3
Mean	0.5	2.3	5.5	4.0	3.3	3.5	0.9	20.0
Min. value	0.2	1.4	3.1	1.9	1.5	1.4	0.3	9.8
Max. value	0.7	2.6	8.7	7.4	4.8	5.5	1.3	30.4
Pig slurries								
1	0.7	16.6	46.8	41.4	23.3	29.2	2.4	160.4
33	0.3	2.9	6.4	4.5	5.3	6.3	1.5	27.2
38	0.6	6.5	14.7	10.9	7.6	8.1	1.3	49.7
54	0.8	6.6	16.7	8.4	8.9	7.6	1.3	50.3
Grangeneuve	0.4	2.4	6.1	4.1	3.5	3.3	1	20.8
Mean*	0.5	4.6	11.0	7.0	6.3	6.3	1.3	37.0
Min. value*	0.3	2.4	6.1	4.1	3.5	3.3	1	20.8
Max. value*	0.8	6.6	16.7	10.9	8.9	8.1	1.5	50.3

*: without NABO site no 1

countries; values for each PAH compound generally fall between 1 and 10 mg/kg[25] whereas PCBs are normally found between 100 µg and 10 mg/kg[26–28]. A recent German study determined PCBs ranging between 233 and 3456 µg/kg with a mean of 911 µg/kg[29]. PCB in digested UK sludges varied from 106 to 712 µg/kg with a mean of 292 µg/kg[30]. In our study no big differences in the Σ PAH and Σ PCB were found between rural and urban sludges except for Zurich which exhibited the highest concentrations for both groups of organic contaminants. An interpretation of these results is problematic without more information on PAH and PCB influent concentrations, point emission sources, atmospheric inputs, catchment area characteristics, sewage treatment work systems etc. Moreover spatial and temporal fluctuations in the PAH and PCB levels at a particular site might happen. To clarify some of these problems a detailed programme would be necessary concentrating on one sewage treatment plant with repeated sampling during a longer period. The samples analysed here just give a general indication of the ranges of PAHs and PCBs likely to be found in Swiss digested sewage sludges.

Since there is growing concern about the pollution of soils due to sludge amendment the increase in PAH and PCB content of soils (bulk density 1.2 g/cm^3) was calculated assuming an average sewage sludge application rate of 0.5 tons (dry weight/ha.y). It was further supposed that the sludge contained the mean Σ PAH and Σ PCB concentrations of 6.3 mg/kg dw and 413 µg/kg dw and that the soil was ploughed to a depth of 20 cm. Only a slight elevation of 1.3 µg Σ PAH/kg and 80 ng Σ PCB/kg per year would result. When highest PAH and PCB concentrations observed in our study are considered the increase

Table 9 PAH and PCB concentrations in sewage sludges (ug/kg dw). See Table 3 for sludge data

Location	*NAP*	*ANY*	*ANA*	*FLU*	*PHE*	*ANT*	*FLT*	*PYR*	*BaA*	*CHR*	*BbF*	*BkF*	*BaP*	*IPY*	*DBA*	*BPE*	*SUM PAH*
Berne	69	63	70	n.d	690	141	1196	920	296	716	455	136	263	254	77	266	5612
Zurich	48	n.d	159	n.d	1819	360	3020	2345	1124	1585	1067	718	921	821	228	826	15041
Geneva	115	n.d	102	n.d	722	171	943	819	321	292	177	88	225	210	93	254	4532
Niederried	90	n.d	n.d	n.d	350	n.d	355	278	127	126	76	88	98	96	n.d	95	1779
Kiental	34	n.d	36	n.d	709	79	1044	819	356	702	241	18	239	123	33	194	4627
Mean	71.2	63.0	91.8		858.0	187.8	1311.6	1036.2	444.8.	684.2	403.2	209.6	349.2	300.8	107.8	327.0	6318.2
Median	69	63	86		709	156	1044	819	321	702	241	88	239	210	85	254	4627
Min. value	34	63	36		350	79	355	278	127	126	76	18	98	96	33	95	1779
Max. value	115	63	159		1819	360	3020	2345	1124	1585	1067	718	921	821	228	826	15041

	BZ 28	*BZ52*	*BZ 101*	*BZ 118*	*BZ 153*	*BZ 138*	*BZ 180*	*SUM PCB*
Berne	15.5	35.4	66.6	52.8	73.5	79.5	36.2	359.5
Zurich	19.6	52	107.9	78	111.6	118.5	54	541.6
Geneva	20.8	45.9	86.7	69.8	90.5	95.2	43.9	452.8
Niederried	17	25.2	50.9	44.5	62.3	61.5	31	292.4
Kiental	31.1	36.2	72.5	55.5	88	88.6	47.3	419.2
Mean	20.8	38.9	76.92	60.12	85.18	88.66	42.48	413.1
Median	19.6	36.2	72.5	55.5	88	88.6	43.9	419.2
Min. value	15.5	25.2	50.9	44.5	62.3	61.5	31	292.4
Max. value	31.1	52	107.9	78	111.6	118.5	54	541.6

would be 3.1 µg Σ PAH/kg and 112 ng Σ PCB/kg. Therefore sludge applications to agricultural land at these typical rates should only slightly increase annual soil PAH and PCB levels.

Compost

Table 10 lists the Σ PAH and Σ PCB concentrations found in the three compost samples. The amounts of the two groups of pollutants varied between 800 to 2700 µg/kg for PAHs and 30 and 80 µg/kg dw for PCBs with a mean of 2 mg/kg and 32 µg/kg respectively. Studies about PAHs and PCBs in composts report values ranging from 300 to 1000 µg Σ PAH/kg and 10 to 140 µg Σ PCB/kg dw[31,32]. PAH and PCB values were also determined in Swiss composts[33]. The authors found a mean of 1800 µg Σ PAH/kg and 39 µg Σ PCB/kg. These results agree well with our findings. Our measurements suggest that urban composts might have higher levels of PAHs compared to rural ones. This trend does not seem to be true for PCBs as highest PCB concentrations were quite unexpectedly found in the rural compost sample. Besides emission sources the starting material used for composting might be crucial for the final PAH and PCB concentrations found.

Qualitative analysis

To get a broader view of the presence of further organic compounds in the differerent matrices some soil, sewage sludge, liquid manure and compost samples were extracted with DCM and cleaned by column chromatography. Five fractions containing increasing amounts of DCM in hexane were collected and concentrated. Qualitative analysis of the fractions was then performed by GC-MS in the full scan mode. Closest attention was given to fractions 2 and 3 containing PCBs and PAHs respectively. The compounds found in the different eluates are now briefly characterized.

Fraction 1 (hexane eluate)

All matrices essentially contained long chain linear and branched hydrocarbons, some of them being of natural origin.

Fraction 2 (hexane/DCM 9:1 eluate)

Due to their low concentrations PCBs could not be confirmed by mass spectral data. In soil samples the main compound with a molecular weight of m/z 256 turned out to be sulfur as S_8. Sewage sludge mainly contained long chain unsaturated hydrocarbons and alkylated benzenes whereas in liquid manures and composts only long chain hydrocarbons were present.

Fraction 3 (hexane/DCM 4:1 eluate)

This fraction was dominated by the presence of PAHs. Most of the 16 EPA PAH used for quantification could be confirmed by MS and were clearly the main compounds in soils, sewage sludges and liquid manures. A summary of the PAHs and their derivatives found

Table 10 PAH and PCB concentrations of compost samples (ug/kg dw). See Table 4 for compost data

Location	*NAP*	*ANY*	*ANA*	*FLU*	*PHE*	*ANT*	*FLT*	*PYR*	*BaA*	*CHR*	*BbF*	*BkF*	*BaP*	*IPY*	*DBA*	*BPE*	*SUM PAH*
Lostorf	16	9	1	4	46	4	121	90	51	129	128	52	33	62	15	66	827
Werkhof	5	4	1	6	97	10	357	283	195	309	362	154	269	210	38	192	2492
Stadtpark	4	4	3	10	132	22	380	312	217	291	358	158	358	216	35	198	2698
Mean	8.3	5.7	1.7	6.7	91.7	12.0	286.0	228.3	154.3	243.0	282.7	121.3	220.0	162.7	29.3	152.0	2005.7
Median	5	4	1	6	97	10	357	283	195	291	358	154	269	210	35	192	2492
Min. value	4	4	1	4	46	4	121	90	51	129	128	52	33	62	15	66	827
Max. value	16	9	3	10	132	22	380	312	217	309	362	158	358	216	38	198	2698

	BZ 28	*BZ52*	*BZ 101*	*BZ 118*	*BZ 153*	*BZ 138*	*BZ 180*	*SUM PCB*
Lostorf	2.9	5.1	12.7	9.9	19	20.1	10	79.7
Werkhof	0.5	1.5	5	3.7	8.8	9.8	5	34.3
Stadtpark	0.9	2.1	5.1	3.9	7	7.5	3.3	29.8
Mean*	0.7	1.8	5.1	3.8	7.9	8.7	4.2	32.1
Min. value*	0.5	1.5	5	3.7	7	7.5	3.3	29.8
Max. value*	0.9	2.1	5.1	3.9	8.8	9.8	5	34.3

*: without data of Lostorf

is presented in Table 11. Soils contained mainly monomethylated derivatives of the priority pollutant PAHs and high molecular weight PAHs (m/z 300 and 302) among them coronene, a heptacyclic system often found. The highly carcinogenic PAH benzo(a)pyrene was usually accompanied by the biologically inactive PAH benzo(e)pyrene the ratio varying between 0.6 and 1 (BaP/BeP). The compost samples turned out to have a highly complex PAH pattern (Figure 3 A–C). The main PAHs could easily be identified by comparison with the standard mixture (Figure 3D). The chromatograms of the different compost samples all showed a similar fingerprint. Much to our surprise the abundances of two compounds, eluting at the end of the chromatographic run, partly exceeded those of the priority pollutants (Figure 3 A–C, signals in frame). The upper mass spectrum presented in Figure 4 A clearly indicated the presence of an alkylated PAH with the molecular weight of m/z 324. The Parametric Retrieval Search (PRS) shown in Figure 5 contained basically the same fragment ions although in different abundances: m/z 309 due to the cleavage of M^+- 15 (M^+- CH_3), followed by m/z 294 (M^+- $2CH_3$) and m/z 279 (M^+- $3CH_3$) due to successive loss of an additional methyl group. Depending on where alkylation in the molecule takes place and

Table 11 Qualitative GC/MS analysis of Fraction 3 of the different environmental samples containing mainly PAHs.

Molecular Weight	*Soil*	*Sewage Sludge*	*Liquid Manure*	*Compost*	*Structure Proposal*	*Comment*
128	+	+	+	+	NAP	
142	+	+	+	+	C1-NAP	several isomers
152	+	+	–	+	ACY	
154	+	+	+	+	biphenyl	
156	–	–	+	+	C2-NAP	several isomers
166	+	+	+	+	FLU	
168	+	+	+	–	dibenzofurance	
170	–	+	–	–	C3-NAP	several isomers
178	+	+	+	+	PHE/ANT	+ other isomers
182	–	–	–	+	tetrahydro-ANT?	
190	–	–	–	+	cyclopenta (d,e,f)-PHE	
192	+	+	+	+	C1-PHE/ANT	several isomers
202	+	+	+	+	FLT/PYR	
204	+	–	–	+	phenyl-NAP?	
206	–	+	–	+	C2-PHE/ANT	several isomers
216	+	+	+	+	C1-FLT/PYR	several isomers
226	+	–	–	+	benzo(g,h,i)FLT?	
228	+	+	+	+	BaA/CHR	+ other PAHs: triphenylene e.g
234	+	–	–	+	benzonaphtothiophene?	
242	+	+	–	+	C1-BaA/CHR	several isomers
252	+	+	+	+	Bb, kF	several isomers
252	+	+	–	+	Ba, eP	+ other PAHs
256	–	+	+	–	elemental sulfur	as S8
266	–	+	–	–	C1-benzofluoranthene?	
276	+	+	–	+	IPY/BPE	
278	+	+	–	+	DBA	+ other PAHs
300, 302	+	+	–	+	coronene, dibenzo-FLT/PYR	+ other PAHs
324 !!	–	–	–	+	pentacyclic, C4-PAH	$C_{25}H_{24}$ two compounds

C 1 - n: $(CH_3)_{1-n}$ +: detected and identified by MS, –: not detected

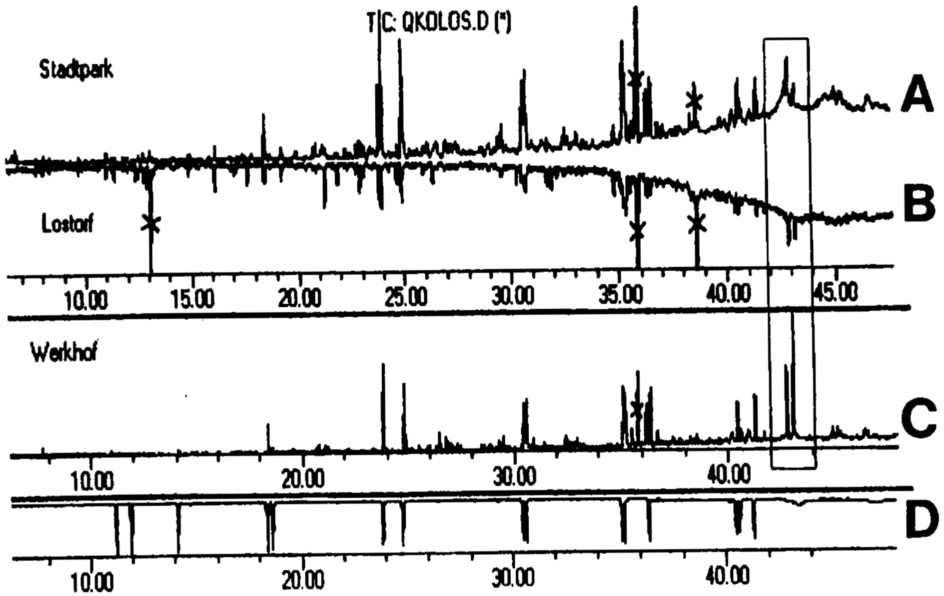


Figure 3 A-C: Total ion current chromatograms of the PAH fraction of the compost samples.
D: Standard mixture of the 16 EPA PAH compounds.

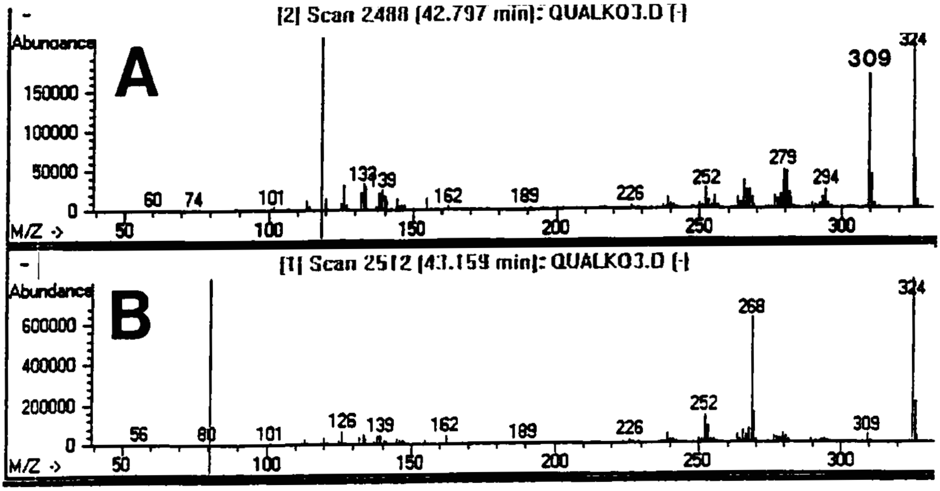
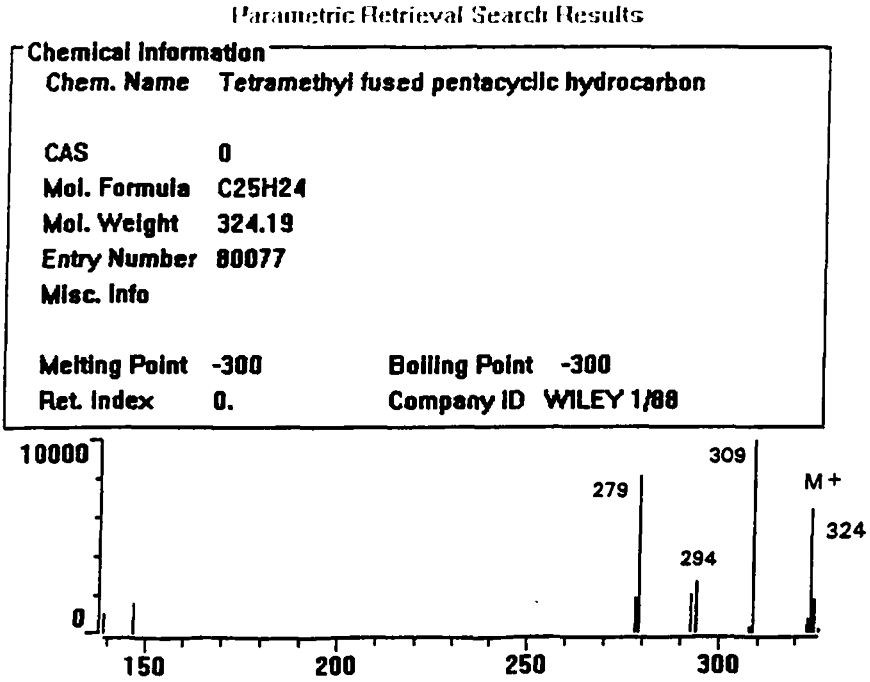


Figure 4 A: mass spectrum of signal at t_R 42.8 min. (Scan 2488)
B: mass spectrum of signal at t_R 43.2 min. (Scan 2512)

how long alkyl chains are fragment ion abundances will be quite different. As a result PRS suggested a tetramethylated pentacyclic hydrocarbon. The bottom mass spectrum (Figure 4B) showed the same fragment ions in low abundances however, assuming again an alkylated PAH with a different substitution pattern. The interpretation of the ion at m/z 268 is not obvious. A second compound with a M^+ of m/z 268 might be present



Parametric Retrieval Search Results

Chemical Information

Chem. Name ***Tetramethyl fused pentacyclic hydrocarbon***

CAS 0
Mol. Formula C25H24
Mol. Weight 324.19
Entry Number 80077
Misc. Info

Melting Point -300 **Boiling Point** -300
Ret. Index 0. **Company ID** WILEY 1/88

Figure 5 Parametric Retrieval Search of mass spectrum shown in Figure 4A.

overlapping with the first spectrum or a branched alkyl chain might be attached to the aromatic system. Apart from the alkylated PAHs sulfur containing PAHs (benzonaphtothiophene, dinaphtothiophene) were found. Finally further unsubstituted isomeric compounds like cyclopenta(c,d)pyrene, triphenylene, benzo(j)fluoranthene and dibenzophenanthrene/anthracene were detected.

Fraction 4 (hexane/DCM 1:1 eluate)

All samples analysed mainly contained end chain oxidized hydrocarbons like aldehydes or esters (e.g. hexadecenal or butylesters of hexadecane) as well as matrix specific substances as methylated indoles found in sewage sludge, liquid manure and composts.

Fraction 5 (100% DCM eluate)

The different matrices contained a variety of organic compounds part of them being of anthropogenic origin: PAH carboxylic acids (phenanthrene carboxyacids, anthropogenic) in soils and composts, phtalate esters (anthropogenic) in sewage sludge and composts, indole and alkylated indoles (natural), oxidized PAHs in liquid manures and composts (e.g. benzo(a)anthracene-one and naphtacene-dione, anthropogenic) and nitrogen containing PAHs (benzo(a)carbazole, anthropogenic) in composts. Finally vitamin E (tocopherol), which has numerous biological functions (antioxidant, stimulating agent in prostaglandin synthesis, disease resistant compound)[34], was identified as the main compound in liquid manure. This observation can be explained by the fact that substantial amounts of this compound are added to animal feed and partly recovered in feces[34].

CONCLUSIONS

Soil, sewage sludge, liquid manure and compost samples were analysed for PAHs and PCBs. PAH levels in soils and liquid manures were essentially the same. A value of 160 μg Σ PAH /kg dw was found for these two matrices. Composts contained 2 mg/kg Σ PAH/kg dw as the mean concentration. Soil Σ PCB contents reached an average of 14 μg/kg dw and represent typical background concentrations. PCB levels in cattle slurries were only slightly higher but significantly higher (Wilcoxons two sample test) in pig slurries compared to soils. The amounts of PCBs found in composts averaged 32 μg/kg dw and were very similar to those found in pig slurries. The highest PAH and PCB concentrations were determined in the sewage sludge samples (mean of Σ PAH 6.3 mg/kg and Σ PCB 413 μg/kg). A simple calculation showed that amendment of these sludges to agricultural soil at rates generally used in Switzerland would only result in a slight elevation in annual PAH and PCB levels. In order to be able to compare more accurately PAH and PCB concentrations a standardization in the choice of the priority pollutants would be highly desiderable.

A qualitative analysis of the different matrices showed that besides the EPA PAHs, which are normally quantified in environmental analysis, high molecular weight PAHs (m/z 300, 302), N-S-O-PAHs and especially alkylated PAHs were present. Some alkylated PAHs in composts were found in high amounts assuming similar response factors for these compounds. In future investigations this group of PAHs will have to be considered more seriously as it is known that some of them (e.g. 3- and 5- methylchrysenes) are strong mutagens[35] and might therefore play an important role in soil microbiology.

Acknowledgements

The authors wish to thank the Swiss Federal Office of Environment, Forests and Landscape (FOEFL) for partial financial support for this work. Thanks also to T. Candinas and Dr. H. Menzi for sampling composts, sewage sludges and liquid manures, Dr. W. Stauffer for grinding of the samples (all FAC Liebefeld) and the Swiss Federal Research Station for Animal Production (FAG), Grangeneuve, for freeze drying them. Moreover the authors are grateful to the "mpo" Group of the FAC (Dres R.Daniel, J. M. Besson, H. Häni and R. Frossard) for their helpful discussions and for critically reviewing this manuscript (Dres R. Frossard and H. Häni). Finally the Group of Ecotoxicology of the ETH Lausanne (supervisor Prof. J. Tarradellas) is greatly acknowledged for the highly estimated cooperation with this project.

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