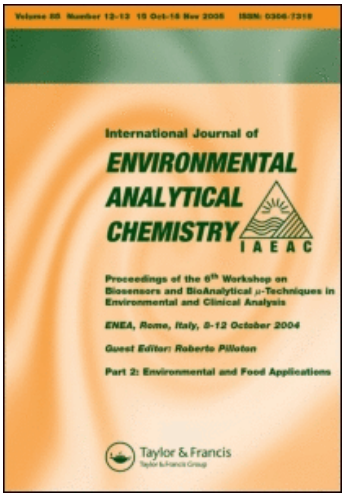

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Polycyclic Aromatic Hydrocarbon Burden in Fruit and Vegetable Species Cultivated in Allotments in an Industrial Area

Luise Wennrich[a]; Peter Popp[a]; Monika Zeibig[a]
[a] Department of Analytical Chemistry, UFZ Centre for Environmental Research, Leipzig, Germany

Online publication date: 17 September 2010

To cite this Article Wennrich, Luise , Popp, Peter and Zeibig, Monika(2002) 'Polycyclic Aromatic Hydrocarbon Burden in Fruit and Vegetable Species Cultivated in Allotments in an Industrial Area', International Journal of Environmental Analytical Chemistry, 82: 10, 667 — 690
To link to this Article: DOI: 10.1080/0306731021000075401
URL: http://dx.doi.org/10.1080/0306731021000075401

Intern. J. Environ. Anal. Chem., Vol. 82, No. 10, pp. 677–690

Taylor & Francis
Taylor & Francis Group

POLYCYCLIC AROMATIC HYDROCARBON BURDEN IN FRUIT AND VEGETABLE SPECIES CULTIVATED IN ALLOTMENTS IN AN INDUSTRIAL AREA

LUISE WENNRICH*, PETER POPP and MONIKA ZEIBIG

Department of Analytical Chemistry, UFZ Centre for Environmental Research, Permoserstrasse 15, D-04318 Leipzig, Germany

(Received 30 July 2001; In final form 16 November 2001)

The polycyclic aromatic hydrocarbon (PAH) burden of various fruit and vegetable species (strawberries, apples, tomatoes, lettuce, kohlrabi, potatoes, parsley and kale) cultivated in allotments in the industrial area of Bitterfeld-Wolfen (Germany) were determined. In addition, the garden soils of the sampling sites were analysed. The total PAH concentrations of fruit and vegetables investigated varied in the range of 1–120 μg/kg fresh weight, with the highest being found in parsley and kale. As the highest concentration of benzo(a)pyrene (BaP) was 0.55 μg/kg in a parsley sample, none of the samples exceeded the recommended BaP limit in vegetable foods of 1 μg/kg. A positive relationship between the total PAH burden and the cultivating site was only found for the more highly contaminated species parsley and kale. The total PAH concentrations in the garden soils ranged from 28 to about 7000 μg/kg dry weight.

Keywords: Polycyclic aromatic hydrocarbons, PAHs; Vegetables and fruit; Plant uptake; Soils

INTRODUCTION

The industrial region of Bitterfeld-Wolfen was once one of the most heavily polluted areas in Germany. Compounded environmental impacts – especially from lignite mining, coal-fired power stations and the concentration of various chemical industry sites – resulted in the extensive contamination of soils, groundwater and river sediment by a multitude of inorganic and organic pollutants [1]. Particularly as a result of the large-scale combustion of lignite in power stations for many decades, one of the main environmental contaminants in the region is polycyclic aromatic hydrocarbons (PAHs). PAHs are by-products from the incomplete combustion of organic material. Although they are known to be formed during natural processes in the environment such as forest fires and volcanic eruptions, the bulk of PAHs is released in the environmental compartments by human activities, e.g. the combustion of fossil fuels (coal,

*Corresponding author. Fax: +49 341 235 2625. E-mail: lwenn@ana.ufz.de

ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/0306731021000075401

lignite, crude oil), coke production, oil cracking and refining, aluminium production, incineration of industrial and domestic waste, etc. [2,3]. Traffic also plays an increasingly dominant role.

The group of PAHs is of environmental concern due to the carcinogenic and/or mutagenic effects of several of these compound [4]. These pollutants are semivolatile, lipophilic compounds, and can be accumulated by plants depending on the physicochemical properties of individual compounds (water solubility, volatility, lipophilicity [5,6]. This accumulation in plants can cause the indirect exposure of humans to PAHs by the consumption of fruit and vegetables grown in contaminated areas. In most cases, diet is the main source of human exposure to these pollutants, vegetables and cereals being important dietary sources of PAHs [7].

The occurrence of PAHs in a wide variety of plants has been demonstrated [8–10] and three possible sources of contamination have been considered: uptake as a result of atmospheric exposure, uptake from the soil (soil water), and endogenous biosynthesis. Most papers on this subject published in recent years agree that the main pathway of plant contamination is atmospheric exposure, with the other paths playing lesser, possibly negligible roles [2,11].

Several papers have investigated the PAH burden of different kinds of vegetables grown in contaminated areas [12–16]. Leaf vegetables, such as lettuce, can have particularly high contents of PAHs. Thus, a 1984 study in Finland identified PAH levels in leaf lettuce in the range of 4.8–94 μg/kg fresh weight [12]. Speer *et al.* [13] investigated samples of several vegetables (parsley, carrot, kale, kohlrabi, spinach, cabbage, lettuce, turnips). They reported increased PAH levels in kale and parsley. Kipopoulou *et al.* [16] determined PAHs in vegetables (cabbage, carrot, leek, lettuce, endive) cultivated in an industrial area in northern Greece. The highest PAH burden was observed in the leafy vegetables, lettuce ($\sum$PAH 40–294 μg/kg dry wt.) and endive ($\sum$PAH 112–239 μg/kg dry wt.).

The aim of this study was to investigate the PAH burden of various fruit and vegetable species mainly cultivated in allotments in the industrial area of Bitterfeld-Wolfen (Germany). The data should be used to assess the risk resulting from the consumption of these vegetable foods. Sampling sites (allotment parks) with different burdens were selected for the investigations. In addition, the soils of the selected sampling sites were analysed. Relationships between PAH contamination of fruit–vegetables and soils were investigated.

EXPERIMENTAL

Standards, Solvents and Reagents

EPA-PAH standard solution (in acetonitile), HPLC grade water and acetonitrile (ultra gradient grade) were purchased from Baker (Deventer, the Netherlands). Acetone, *n*-hexane, cyclohexane, petroleum benzine (boiling range 40–60°C) and dichloromethane (all for organic trace analysis) were supplied by Merck (Darmstadt, Germany). Silica gel (particle size 0.063–0.200 mm) and anhydrous sodium sulphate were also obtained from Merck. Cellulose flakes were supplied by Sigma (Deisenhofen, Germany). The HPLC method was optimised and validated with 15 of the EPA-PAHs (except acenaphthylene). Dilutions of standard solutions were prepared in acetonitrile.

Sampling Sites and Samples

The study areas comprised 4 allotment parks located in the industrial region Bitterfeld-Wolfen in Saxony-Anhalt (Germany). The sites of the allotment parks are shown in Fig. 1.

In each allotment park, 3 gardens were selected as cultivating and sampling sites for fruit and vegetables. Eight kinds of fruit and vegetables mainly cultivated in the study region were included in the investigation: strawberries, apples, tomatoes, lettuce, kohlrabi, potatoes, parsley and kale. Composite plant samples were collected at the various sites in 1999: in early June (strawberries, lettuce and kohlrabi), in mid-August (tomatoes, potatoes and parsley), and in early October (apples and kale). Composite samples of top soils were taken from the same locations at the beginning (April) and at the end of the main vegetation period (October).

Sample Preparation

After harvesting, portions of vegetable material were prepared for analysis in the way they would usually be consumed. The fruit and vegetables were thoroughly washed with fresh running water (and the potatoes brushed) to remove surface dust. Dead or yellow leaves of lettuce and parsley as well as the kohlrabi leaves were discarded, kohlrabi were peeled, and the apples had their cores removed. Then the plant materials were chopped and subsequently homogenised for 10 s at a speed of 7000 rpm using a grindomix device (Retsch, Haan, Germany). The fruit–vegetable mush obtained was frozen in small portions and stored at −18°C.

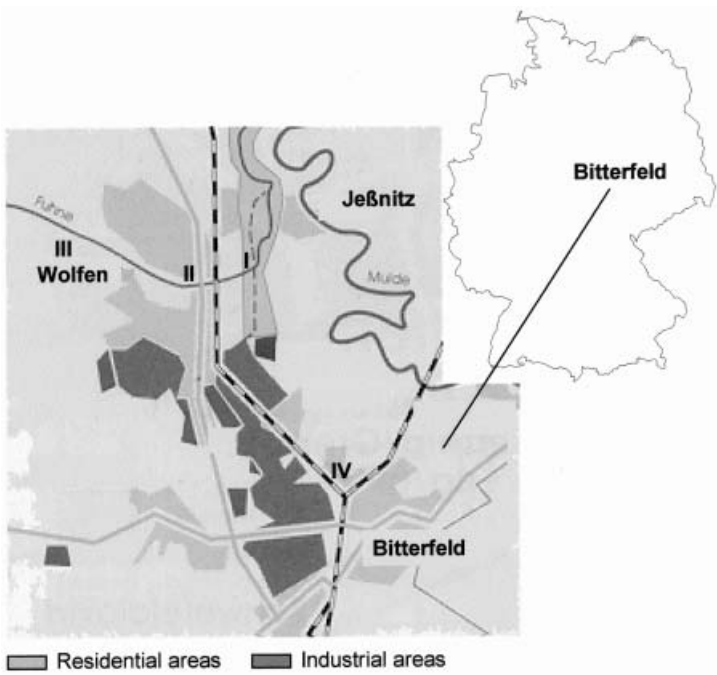

FIGURE 1 Map of the study area I, II, III, IV – cultivation and sampling sites (allotment parks) for fruit–vegetables and soils.

The soil samples were sieved to a grain size of < 2 mm, homogenised, and stored until analysis at 4°C. The water content of the soils was determined by drying parts of the material at 105°C down to a constant weight.

Solvent Extraction and Clean-up

Fruit–Vegetable Samples

The extraction of fruit–vegetable samples was carried out by pressurised liquid extraction (PLE) employing an ASE 200 accelerated solvent extractor (Dionex, Sunnyvale, USA) equipped with 22 mL stainless-steel extraction cells. For this purpose the thawed plant sample (10 g) was thoroughly mixed with 5 g cellulose flakes and then placed in the extraction cell. The samples were extracted using the following conditions: extraction solvents, *n*-hexane–acetone mixture (1:1, v/v); pressure, 10 MPa; temperature, 100°C; time, 2×5 min (2 cycles).

After phase separation assisted by adding a small volume of *n*-hexane (about 5 mL) and shaking, the organic phase was evaporated at ambient temperature nearly to dryness and the residue was taken up in 0.5 mL of a petroleum benzine–dichloromethane mixture (4:1, v/v).

Clean-up was performed in a silica gel column (20 cm × 11 mm ID) filled with 7.5 g silica gel (dried at 450°C for 4 h and adjusted with water of a humidity of 10% (w/w)) and overlaid with 3 g anhydrous sodium sulphate. The column was conditioned with 15 mL *n*-hexane. After the addition of the sample extract, the column was eluted with 50 mL of a petroleum benzine–dichloromethane mixture (4:1, v/v). The eluate was carefully concentrated at ambient temperature to dryness and the residue was taken up in 0.2 mL of acetonitrile.

Soil Samples

The extraction of the soil samples was also carried out by PLE. For extraction, 5 g of the soil sample was triturated with 5 g anhydrous sodium sulphate and placed inside an 11 mL extraction cell. The sample was extracted using the following conditions: extraction solvents, cyclohexane–acetone mixture (1:1, v/v); pressure, 14 MPa; temperature, 150°C; time, 3×5 min (3 extractions). The combined extracts were concentrated at ambient temperature to about 0.5 mL.

Clean-up was done on a silica gel column (Baker, Spe, 6 mL) filled with 2.5 g silica gel (dried at 450°C for 4 h) and overlaid with 1 g anhydrous sodium sulphate. The column was conditioned with 10 mL of *n*-hexane. After the addition of the sample extract, the column was first eluted with 6 mL of n-hexane, this eluate then being discharged. Subsequently, the column was eluted with 18 mL of a *n*-hexane–dichloromethane mixture (3:2, v/v). The eluate was carefully concentrated at ambient temperature to dryness and the residue was taken up in 1 mL of acetonitrile.

HPLC Analysis

All fruit–vegetable and soil extracts were analysed by high performance liquid chromatography (HPLC) employing an HP1050 system with an HP 1046A programmable fluorescence detector (Hewlett Packard, Palo Alto, CA, USA). A 250×3 mm ID

TABLE I Investigated polycyclic aromatic hydrocarbons, abbreviations, excitation (λ_{ex}) and emission wavelengths (λ_{em}), log octanol–water partition coefficients (log K_{OW}) and water solubilities

Compound	*Abbreviation*	λ_{ex}(nm)	λ_{em}(nm)	*log* K_{OW}[a]	*Water solubility*[b](mg/L)
Acenaphthene	Ace	227	315	3.98	3.470
Fluorene	Flu	227	315	4.18	1.980
Phenanthrene	Phe	252	372	4.45	1.290
Anthracene	Ant	252	372	4.45	0.070
Fluoranthene	FLU	237	440	4.90	0.260
Pyrene	PYR	237	440	4.88	0.140
Benzo(a)anthracene	BaA	277	393	5.61	0.014
Chrysene	CHR	277	393	5.16	0.002
Benzo(b)fluoranthene	BbF	258	442	6.04	0.0012
Benzo(k)fluoranthene	BkF	266	415	6.06	0.00055
Benzo(a)pyrene	BaP	266	415	6.06	0.0038
Dibenzo(a,h)anthracene	DBahA	295	425	6.84	0.0005
Benzo(g,h,i)perylene	BghiP	295	425	6.50	0.00026
Indeno(1,2,3-cd)pyrene	INP	251	510	6.58	0.062

[a]Obtained from US Dept Health Human Services USDHHS [24]; [b]Koch [25].

LiChroCART column from Merck (Darmstatt, Germany) filled with LiChrospher PAH (5 µm) was used. The mobile phase was acetonitrile–water with a initial content of 50% (v/v) acetonitrile. The acetonitrile content was linearly increased to first 60% (0–3 min) and then to 100% (3–14 min). This level was held constant for 24 min until the end of the analysis. The flow rate of the mobile phase was 0.5 mL/min. An injection volume of 10 µL was used. HPLC analysis was performed at 20°C. The excitation and emission wavelength programme used is shown in Table I. The PAH levels in the extracts were quantified using external calibration.

RESULTS AND DISCUSSION

PAH Concentrations in Fruit and Vegetables

The results of the PAH analysis of the fruit and vegetable samples are summarised in Table II. The concentration ranges (minimum and maximum values) and the mean values of the individual PAHs in the various fruit–vegetable species investigated are listed. In all samples, 14 of the 16 EPA-PAHs were quantified (see Table I). Acenaphthylene and naphthalene were not included in the investigations, because acenaphthylene showed no response using the fluorescence detector, and naphthalene losses occurred during the sample preparation procedures.

As shown in Table II, the total contents ($\sum$PAH) of the 14 PAHs in the fruit and vegetable species are in the range of 1–120 µg/kg fresh weight. The concentrations (mean values of all sites) decrease in the following order: parsley > kale > apples > potatoes > strawberries > tomatoes > kohlrabi > lettuce. In Fig. 2 this decrease in the total PAH contents of the fruit–vegetable species is illustrated for the most burdened Site IV (mean values of the 3 gardens investigated).

Increased PAH levels ($\sum$PAH > 15 µg/kg) were detected in some kale samples and in all parsley samples (see also Table III). These findings tally with the results of Speer *et al.* [13]. That means vegetables with a large leaf surface area exposed to the atmosphere such as parsley are liable to increased PAH uptake. This was confirmed

TABLE II Concentrations[a] of polycyclic aromatic hydrocarbons (PAHs) in fruit and vegetables (μg/kg fresh wt.)

PAH	*Strawberries (n = 8)*	*Apples (n = 6)*	*Tomatoes (n = 12)*	*Lettuce (n = 12)*	*Kohlrabi (n = 12)*	*Potatoes (n = 12)*	*Parsley (n = 11)*	*Kale (n = 12)*
Ace	0.04–0.21 (0.13)	0.26–1.62 (0.54)	n.d.–0.03 (0.01)	n.d.	0.05–0.09 (0.07)	0.02–0.23 (0.10)	p.i.	0.10–0.40 (0.20)
Flu	0.06–0.22 (0.14)	0.21–2.26 (0.62)	0.03–0.13 (0.07)	0.11–0.15 (0.13)	0.01–0.13 (0.05)	0.05–0.31 (0.15)	0.51–15.52 (3.87)	0.02–0.95 (0.35)
Phe	0.96–2.69 (1.72)	1.92–8.01 (3.33)	0.88–1.83 (1.39)	0.21–1.07 (0.51)	0.41–2.30 (1.12)	0.52–4.76 (2.24)	8.48–73.86 (22.37)	1.40–10.75 (4.92)
Ant	0.04–0.24 (0.10)	0.09–0.78 (0.22)	0.06–0.15 (0.09)	0.06–0.10 (0.08)	n.d.–0.27 (0.09)	0.03–0.38 (0.11)	0.34–2.86 (0.85)	n.d.–0.29 (0.03)
FLU	0.23–0.89 (0.48)	0.40–0.85 (0.59)	0.37–0.79 (0.56)	0.09–0.82 (0.26)	n.d.–0.67 (0.06)	0.08–0.74 (0.48)	2.07–14.26 (5.59)	n.d.–8.02 (3.14)
PYR	0.10–0.34 (0.21)	0.15–0.25 (0.21)	0.14–0.32 (0.21)	0.07–0.39 (0.15)	0.03–0.29 (0.08)	0.07–0.39 (0.23)	0.82–8.91 (3.08)	n.d.–3.71 (1.69)
BaA	0.05–0.16 (0.10)	0.09–0.20 (0.14)	0.13–0.21 (0.15)	0.14–0.23 (0.18)	n.d.–0.19 (0.03)	0.06–0.35 (0.20)	0.17–0.48 (0.27)	0.13–0.70 (0.45)
CHR	0.29–0.87 (0.57)	0.58–1.04 (0.74)	0.68–0.97 (0.82)	0.71–1.10 (0.87)	0.47–1.07 (0.81)	0.37–1.01 (0.77)	1.02–3.05 (1.65)	0.49–1.87 (1.31)
BbF	0.02–0.16 (0.07)	0.05–0.10 (0.07)	0.07–0.11 (0.09)	0.08–0.18 (0.11)	0.05–0.15 (0.10)	0.02–0.13 (0.07)	0.14–0.87 (0.34)	0.04–0.52 (0.23)
BkF	0.01–0.07 (0.04)	0.02–0.04 (0.03)	0.04–0.05 (0.04)	0.03–0.07 (0.05)	0.03–0.05 (0.04)	0.01–0.04 (0.02)	0.07–0.45 (0.19)	n.d.–0.16 (0.05)
BaP	0.03–0.15 (0.07)	0.04–0.09 (0.06)	0.04–0.08 (0.05)	0.04–0.11 (0.06)	n.d.–0.04 (0.04)	0.03–0.06 (0.04)	0.07–0.55 (0.23)	0.01–0.31 (0.11)
DBahA	n.d.–0.03 (0.01)	n.d.–0.03 (0.01)	n.d.	n.d.–0.04 (0.02)	n.d.–0.04 (n.d.)	n.d.–0.02 (0.01)	n.d.–0.11 (0.04)	n.d.–0.05 (0.02)
BghiP	0.03–0.13 (0.07)	0.05–0.08 (0.06)	n.d.–0.07 (0.05)	0.06–0.12 (0.07)	0.05–0.07 (0.06)	0.03–0.08 (0.05)	0.09–0.52 (0.22)	0.05–0.25 (0.12)
INP	n.d.–0.08 (0.04)	0.02–0.04 (0.03)	n.d.–0.06 (0.03)	0.05–0.10 (0.06)	0.04–0.05 (0.04)	n.d.–0.04 (0.02)	0.08–0.54 (0.21)	0.05–0.28 (0.13)
$\sum$PAH	1.89–5.92 (3.73)	3.99–14.83 (6.64)	2.47–4.68 (3.55)	2.03–4.04 (2.54)	1.22–4.09 (2.60)	1.29–8.41 (4.47)	15.12–119.47 (38.91)	3.78–27.52 (12.75)
$\sum$carcPAH	0.42–1.34 (0.89)	0.81–1.48 (1.08)	0.95–1.49 (1.18)	1.09–1.66 (1.34)	0.64–1.58 (1.11)	0.49–1.63 (1.13)	1.54–6.05 (2.93)	0.73–3.67 (2.30)

[a]Minimum–Maximum (mean) values; $\sum$carcPAH = BaA + CHR + BbF + BkF + BaP + DBahA + INP; n.d. below detection limit; p.i. peak interference.

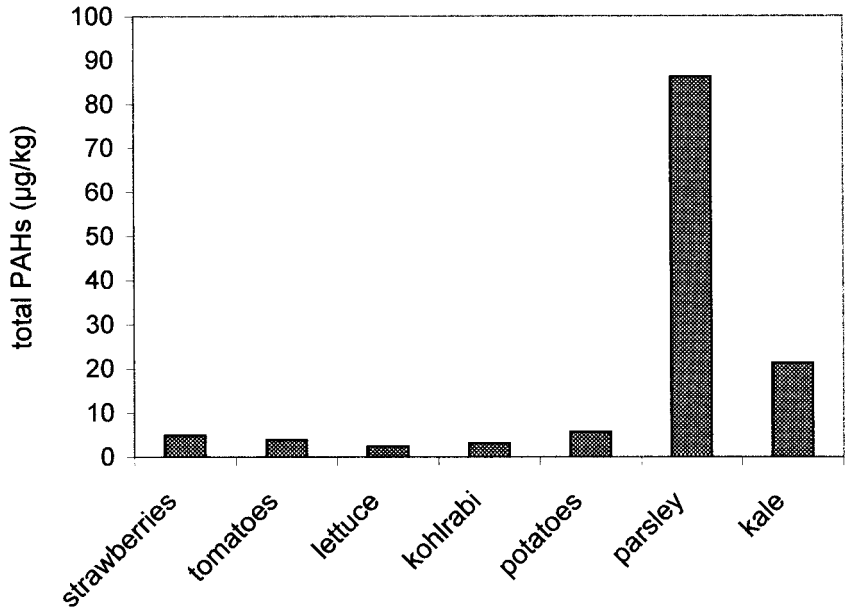

FIGURE 2 Comparison of the total PAH contents of the fruit and vegetable species cultivated on Site IV (mean values of the 3 allotments).

by comparative studies [17,18] of the PAH burden of air depositions, soil and plants with large leaf surface area (poplars, kale, parsley) resulting in a dominated PAH uptake from atmosphere. In this context, the comparatively low PAH burden of the lettuce samples is surprising. With a mean burden of 2.5 µg/kg, these samples had the lowest PAH contents of all the species investigated. Reasons for the low PAH contents of lettuce compared with parsley and kale are the substantially shorter exposure time of lettuce (about 7 weeks in contrast to about 16 weeks for parsley) and the smaller leaf surface area.

Leaf lettuce samples cultivated in southern Finland in 1984 [12] had total PAH concentrations in the range of 5–94 µg/kg fresh weight. These burdens are approximately one order of magnitude higher than those found in the present study. Kipopoulou *et al.* [16] investigated (along with other vegetable species) lettuce samples grown in an industrial area in Greece and determined a mean PAH contents of 161 µg/kg dry weight. Assuming a fresh weight/dry weight factor of 10, these values are also higher than the burden in Bitterfeld-Wolfen.

Popp *et al.* [19] investigated kale samples cultivated in various urban and rural sites in Saxony-Anhalt (Germany) in summer 1997. For the urban site of Halle, a total PAH burden of 34 µg/kg was determined.

The kohlrabi samples show PAH contents which are similarly low to lettuce. Of the fruit species investigated, the apples with a mean value of 6.6 µg/kg had slightly higher PAH contents.

The burden of fruit–vegetables with carcinogenic PAHs (see Table II, $\sum$carcPAH, mean values) varied in the range from 0.9 (strawberries) to 2.9 µg/kg (parsley). Apart from parsley and kale, the species investigated show a low level of carcinogenic PAHs of about 1 µg/kg. What is remarkable is the existence of such a low underground

TABLE III Concentrations[a] of polycyclic aromatic hydrocarbons (PAHs) in parsley and kale samples (μg/kg fresh wt.)

PAH	*Parsley*				*Kale*			
	Site I	*Site II*	*Site III*[b]	*Site IV*	*Site I*	*Site II*	*Site III*	*Site IV*
Ace	p.i.	p.i.	p.i.	p.i.	0.19–0.27 (0.23)	0.18–0.22 (0.20)	0.10–0.15 (0.12)	0.12–0.40(0.25)
Flu	0.51–1.22 (0.86)	1.71–2.39 (2.06)	2.69–2.80 (2.74)	3.74–15.52 (9.45)	0.32–0.45 (0.43)	0.22–0.28 (0.25)	0.02–0.16 (0.11)	0.40–0.95 (0.62)
Phe	8.48–9.37 (8.84)	9.28–14.29 (11.19)	15.29–18.78 (17.04)	27.33–73.86 (50.62)	4.18–5.56 (5.22)	4.40–4.65 (4.55)	1.40–2.66 (2.23)	5.99–10.75 (7.89)
Ant	0.34–0.43 (0.39)	0.39–0.53 (0.45)	0.47–0.63 (0.55)	1.08–2.86 (1.92)	n.d.	n.d.	n.d.	n.d.
FLU	2.07–3.68 (2.71)	2.09–3.54 (2.74)	3.37–4.84 (4.11)	9.02–14.26 (12.32)	2.38–3.34 (2.97)	2.47–3.13 (2.80)	n.d.–1.78 (0.91)	4.68–8.02 (5.86)
PYR	0.82–2.06 (1.36)	0.96–1.79 (1.28)	1.80–2.80 (2.30)	5.30–8.91 (7.14)	1.29–1.76 (1.59)	1.20–1.87 (1.53)	n.d.–0.77 (0.44)	2.51–3.71 (3.21)
BaA	0.25–0.30 (0.27)	0.17–0.28 (0.22)	0.19–0.32 (0.26)	0.23–0.48 (0.33)	0.45–0.69 (0.55)	0.40–0.48 (0.44)	0.13–0.32 (0.23)	0.35–0.70 (0.58)
CHR	1.29–1.85 (1.55)	1.02–1.38 (1.20)	1.06–1.54 (1.30)	1.87–3.05 (2.41)	1.32–1.87 (1.55)	1.18–1.36 (1.27)	0.49–0.98 (0.75)	1.66–1.69 (1.67)
BbF	0.26–0.44 (0.35)	0.14–0.30 (0.21)	0.17–0.29 (0.23)	0.28–0.87 (0.55)	0.18–0.30 (0.24)	0.13–0.24 (0.18)	0.04–0.12 (0.08)	0.32–0.51 (0.42)
BkF	0.15–0.22 (0.17)	0.07–0.17 (0.11)	0.09–0.17 (0.13)	0.16–0.45 (0.31)	0.03–0.07 (0.05)	n.d.–0.05 (0.02)	n.d.	0.07–0.16 (0.12)
BaP	0.14–0.31 (0.21)	0.07–0.21 (0.12)	0.12–0.23 (0.18)	0.20–0.55 (0.39)	0.08–0.11 (0.10)	0.05–0.11 (0.08)	0.01–0.04 (0.03)	0.14–0.31 (0.24)
DBahA	0.05–0.06 (0.06)	n.d.	n.d.	0.05–0.11 (0.08)	n.d.	n.d.	n.d.	0.04–0.05 (0.04)
BghiP	0.16–0.24 (0.20)	0.09–0.22 (0.15)	0.13–0.21 (0.17)	0.17–0.52 (0.35)	0.10–0.14 (0.12)	0.06–0.13 (0.10)	0.04–0.06 (0.05)	0.13–0.25 (0.20)
INP	0.16–0.28 (0.21)	0.08–0.19 (0.12)	0.11–0.20 (0.16)	0.16–0.54 (0.36)	0.12–0.15 (0.13)	0.08–0.16 (0.12)	0.05–0.09 (0.07)	0.15–0.28 (0.22)
∑PAH	15.12–18.08 (17.18)	16.83–25.34 (19.85)	25.50–32.80 (29.17)	49.60–119.47 (86.23)	10.77–14.54 (13.18)	10.83–12.27 (11.54)	3.78–6.68 (5.02)	16.80–27.51 (21.32)
∑carcPAH	2.38–3.04 (2.82)	1.54–2.59 (1.98)	1.74–2.74 (2.26)	2.95–6.05 (4.43)	2.29–3.22 (2.62)	1.97–2.26 (2.11)	0.73–1.54 (1.16)	2.76–3.67 (3.29)

[a]Minimum–Maximum (mean) values ($n=3$); [b]$n=2$; ΣcarcPAH = BaA + CHR + BbF + BkF + BaP + DBahA + INP; n.d. below detection limit; p.i. peak interference.

level for various species irrespective of the uptake mechanism, plants' exposure times, etc. The increased concentrations of these higher molecular weight PAHs for the leafy vegetables parsley (2.9 μg/kg) and kale (2.3 μg/kg) resulted from the deposition of particle-bound PAHs on the leaves and uptake directly into the waxy leaf cuticle [20]. The percentage contribution of the carcinogenic PAHs (BaA, CHR, BbF, BkF, BaP, DBahA, INP; abbreviations are given in Table I) to total PAHs was highest in lettuce (52.8%) and lowest in parsley (7.5%).

In this context, comparing parsley (a typical leafy plant) and potatoes (a typical root vegetable) is of interest. Figure 3 shows the PAH profiles of parsley and potatoes from the same sampling Site IV-2 (the site with the highest PAH burden). In the case of parsley, the contribution of the lower molecular weight PAHs (Ace, Flu, Phe, Ant, FLU and PYR) is very high (92.5%), whereas the proportion of Phe is dominant (57.5% of total PAH). By contrast, the proportion of the more volatile PAHs in the potatoes is distinctly lower (74.7%). In principle, two pathways are possible for the uptake of the lower molecular weight PAHs with their comparatively higher water solubilities and higher volatilities: uptake from the soil via aqueous soil solution by the roots (and if necessary translocation to other parts of the plant) and/or uptake from the atmosphere (gaseous phase) through the leaves. Briggs *et al.* [21] and Ryan *et al.* [22] showed that compounds with $\log K_{OW}$ values > 3.0 (which covers all the PAHs investigated here) have a low potential for root uptake, and that these compounds are presumably retained at the root surface.

The pollutants detected in the potatoes ought only to be taken up by roots. The increased fraction of the lower molecular weight PAHs in the case parsley indicates the additional uptake of these more volatile compounds via the gaseous phase.

A comparison of the PAH burden at the 4 different sites (allotment parks) resulted in significant differences only for parsley and kale (Table III). Figure 4 shows the total PAH contents (mean values of the 3 gardens) for these two species depending on the sampling site (see Fig. 1). The highest PAH levels were found for both species at Site IV (Bitterfeld). This comes as no surprise since this allotment is located in an urban area traversed by a busy road and in the immediate vicinity of a large area containing various chemical plants. A decreasing burden in the order of Sites IV (Bitterfeld) > I (Jeßnitz), II (Wolfen-Steinfurth) > III (Reuden) was as expected. Pollution at Site III (Reuden) should be relatively low due to its position in a rural environment north-west of Bitterfeld and the low impact of road traffic. Nevertheless, our expectations were somewhat confounded by the relatively high burden of the parsley samples at Site III.

The content of BaP, the most commonly determined PAH, has been used in several papers to assess the risk resulting from the consumption of PAH-contaminated vegetable foods. A maximum BaP level of 1 μg/kg fresh weight for vegetable foods is recommended [13,23]. As the highest concentration of BaP determined in the present study was 0.55 μg/kg for the parsley samples IV-1, the recommended maximum was not exceeded in any of the samples.

PAH Levels in the Garden Soils

The concentrations of PAHs determined in the soils of the selected gardens are given in Table IV. As shown, for both sampling dates (16 April and 5 October 1999) the total PAH contents were in the range from 28 to 6968 μg/kg. These soil concentrations are comparable with those reported for background burdens of soils in industrial

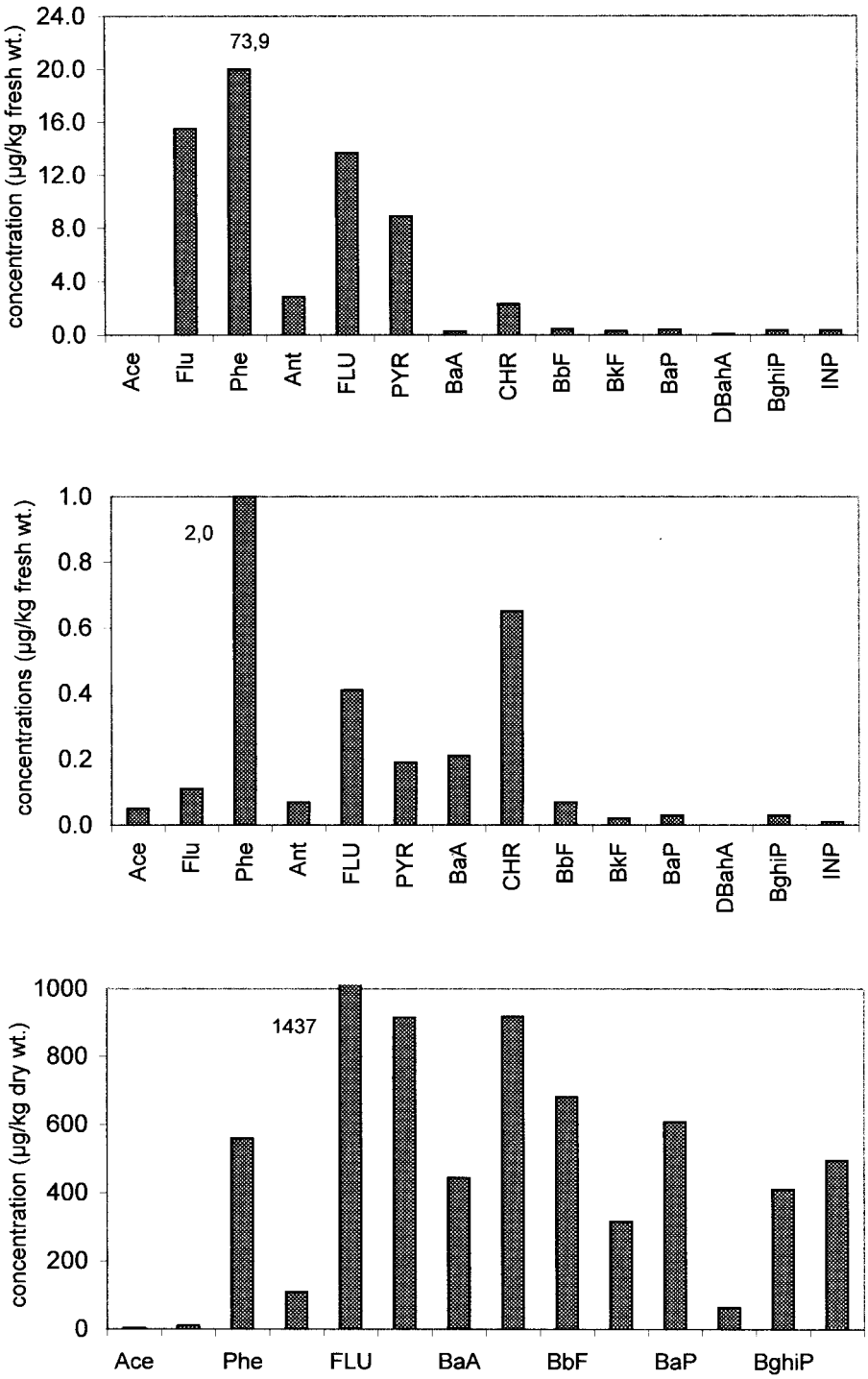

FIGURE 3 PAH profiles of parsley (upper pattern), potatoes (middle pattern) and soil (lower pattern) from Site IV-2.

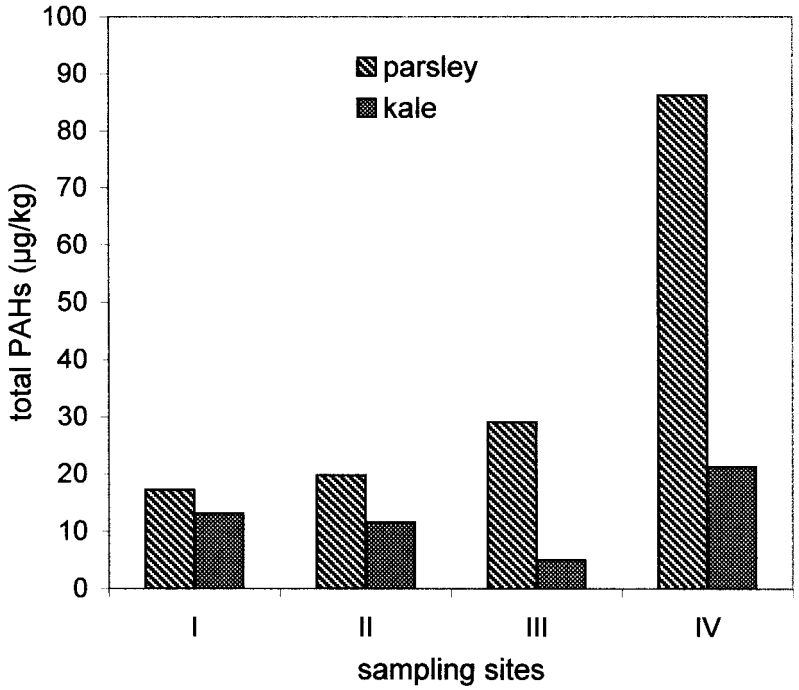

FIGURE 4 Dependence of the total PAH burden of the parsley and kale samples (mean values of the 3 gardens) on the sampling site.

areas [9,16]. In most cases, increased total PAH concentrations were found in the soil samples taken in autumn.

Figure 5 shows the PAH contamination of the soils (mean values of the 3 allotments) at the different sampling sites (allotment parks). These results show a comparable pattern to that found for kale (Fig. 4). One remarkable finding is that the soil burden of the 3 allotments within an allotment park sometimes differs significantly. For instance, the PAH contents of samples collected in two gardens in the allotment park II (taken in autumn) differ by approximately one order of magnitude.

The contribution of the carcinogenic PAH to the total PAH content was in the range from 33.7 to 61.9 µg/kg with a mean value of all sites of about 48% for the soil samples from both sampling dates. Thus, the proportion of the higher molecular weight PAHs within total PAH (mean values) in the soils is significantly higher than in the fruit–vegetable samples (about 28%) (see also Fig. 3). This is because of higher molecular weight PAHs are less water-soluble and less volatile as well as more persistent than PAHs with a lower molecular weight. Consequently, the former remain in the soil longer as they are subject to slower removal from the topsoil by vaporisation, washing out and degradation. Furthermore, those compounds with lower water solubility only have a low potential for root uptake from the soil.

To sum up, it can be concluded that the PAH burden of samples of the various fruit and vegetable species investigated in this study is rather low, despite partly increased soil contents. The exceptions are the parsley and kale samples, particularly those cultivated on Site IV (Bitterfeld), the most contaminated site.

TABLE IV Concentrations[a] of polycyclic aromatic hydrocarbons (PAHs) in soil samples (μg/kg dry wt.)

PAH	*Sampling 16.04.99*				*Sampling 05.10.99*			
	Site I	*Site II*	*Site III*	*Site IV*	*Site I*	*Site II*	*Site III*	*Site IV*
Ace	0.7–1.5 (1.0)	0.6–4.8 (2.0)	n.d.–2.5 (1.2)	0.5–2.5 (1.3)	n.d.–0.6 (0.4)	0.4–0.9 (0.7)	0.5–0.7 (0.5)	0.9–2.6 (1.8)
Flu	1.1–4.6 (2.7)	1.0–8.8 (3.7)	n.d.–2.8 (1.7)	0.7–2.6 (1.9)	1.2–3.5 (2.4)	0.4–6.2 (2.5)	n.d.–1.6 (0.9)	2.4–10.0 (6.5)
Phe	44.7–132.3 (88.2)	73.4–297.0 (161.0)	0.1–105.6 (52.4)	20.1–170.8 (72.9)	57.1–118.5 (97.7)	24.8–205.7 (91.5)	46.2–84.9 (71.7)	150.3–559.1 (371.8)
Ant	5.5–7.2 (6.3)	4.7–31.1 (14.4)	0.2–13.5 (6.5)	3.2–30.6 (13.0)	9.1–18.0 (14.2)	2.2–119.5 (42.0)	7.0–10.1 (8.6)	24.7–108.8 (63.6)
FLU	94.7–182.2 (150.0)	136.9–496.7 (265.3)	4.1–209.7 (100.2)	47.2–364.3 (159.0)	160.9–247.4 (200.9)	52.8–663.3 (265.5)	117.1–190.7 (153.9)	327.3–1436.8 (897.3)
PYR	60.6–93.8 (80.9)	6.0–320.7 (133.2)	2.3–136.1 (61.4)	32.9–234.1 (102.1)	101.2–146.1 (121.7)	22.7–505.1 (188.1)	71.6–139.7 (98.7)	178.0–915.2 (531.9)
BaA	22.7–37.9 (29.6)	20.8–126.2 (56.3)	1.3–49.4 (23.3)	14.3–116.5 (50.1)	37.5–58.8 (51.7)	7.5–213.0 (78.0)	29.1–38.3 (32.3)	90.0–443.6 (257.7)
CHR	54.4–93.8 (72.4)	61.4–239.4 (120.9)	2.8–112.7 (53.4)	31.7–220.7 (98.5)	106.2–144.8 (124.4)	24.6–465.6 (175.8)	59.0–111.4 (80.5)	188.3–918.0 (552.6)
BbF	41.5–85.2 (60.6)	46.9–167.5 (88.4)	3.5–95.3 (50.3)	33.0–182.5 (86.8)	96.5–139.5 (114.5)	26.7–289.9 (118.9)	68.1–90.3 (75.6)	185.2–681.0 (456.7)
BkF	19.1–33.3 (24.1)	17.5–80.6 (38.6)	1.4–47.5 (22.6)	16.6–86.6 (40.5)	35.3–54.9 (46.5)	8.8–140.7 (54.0)	24.6–41.1 (30.2)	77.1–315.9 (194.3)
BaP	25.1–44.6 (35.2)	23.0–146.7 (64.7)	3.0–97.1 (43.6)	31.2–171.8 (80.7)	44.6–88.9 (72.2)	10.4–278.9 (101.0)	38.1–71.4 (50.8)	131.2–607.5 (344.2)
DBahA	4.0–9.5 (6.2)	3.8–15.6 (8.0)	0.6–11.6 (5.9)	4.8–18.3 (9.3)	10.8–13.8 (12.4)	2.5–31.2 (12.3)	6.1–9.3 (7.3)	17.8–64.1 (43.6)
BghiP	26.5–70.0 (41.9)	22.7–94.3 (50.6)	4.2–78.4 (41.8)	29.8–131.8 (64.1)	77.3–91.0 (86.0)	17.7–175.2 (72.4)	45.7–91.6 (64.1)	106.3–410.2 (267.8)
INP	31.2–56.1 (40.9)	27.8–112.7 (59.4)	4.9–91.9 (46.8)	35.6–153.5 (75.1)	51.6–93.8 (79.2)	16.6–198.4 (78.6)	46.4–71.5 (56.3)	125.4–495.1 (303.7)
∑PAH	454.2–794.5 (640.0)	448.4–2142.1 (1066.4)	28.2–1054.1 (511.1)	312.5–1886.5 (855.2)	897.8–1211.2 (1024.3)	218.1–3293.6 (1281.0)	578.3–951.2 (731.3)	1604.9–6968.0 (4293.6)
∑carcPAH	220.4–360.6 (269.0)	202.9–888.7 (436.2)	17.5–505.5 (245.9)	175.1–949.9 (441.0)	382.5–587.2 (500.9)	97.0–1617.8 (618.5)	281.1–433.3 (332.9)	815.1–3525.2 (2152.9)

[a]Minimum–Maximum (mean) values ($n = 3$); ∑carcPAH = BaA + CHR + BbF + BkF + BaP + DBahA + INP; n.d. below detection limit.

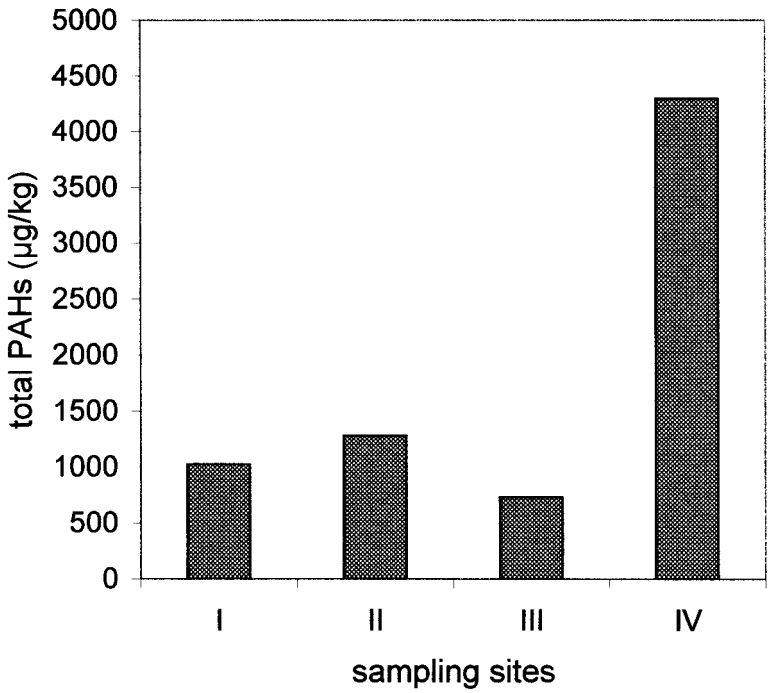

FIGURE 5 Dependence of the total PAH burden of the soil samples (mean values of the 3 gardens) on the sampling site (sampling: October 1999).

Acknowledgement

This work was kindly funded by the Ministry of the Education and the Arts of Saxony-Anhalt (Germany).

References

[1] *Umweltreport Bitterfeld 96*. Landkreis Bitterfeld, Saxony-Anhalt, Germany (1996).
[2] N.T. Edwards, *J. Environ. Qual.*, **12**, 427–441 (1983).
[3] S.R. Wild and K.C. Jones, *Environ. Pollut.*, **88**, 91–108 (1995).
[4] *Evaluation and Estimation of Potential Carcinogenic Risks of Polynuclear Aromatic Hydrocarbon*. Carcinogen Assessment Group, Office of Health and Environmental Assessment, Office of Research and Development, US Environmental Protection Agency, Washington DC (1985).
[5] K.C. Jones, *Environ. Pollut.*, **69**, 311–325 (1991).
[6] S.R. Wild, K.C. Jones and A.E. Johnston, *Atmos. Environ.*, **26A**, 1299–1307 (1992).
[7] D.H. Phillips, *Mutation Res.*, **443**, 139–147 (1999).
[8] M.D. Guillen, P. Sopelana and M.A. Partearroyo, *Rev. Environ. Health*, **12**, 133–146 (1997).
[9] A.A. Meharg, J. Wright, H. Dyke and D. Osborn, *Environ. Pollut.*, **99**, 29–36 (1998).
[10] M.I. Bakker, B. Casado, J.W. Koerselman, J. Tolls and C. Kollöffel, *Sci. Total Environ.*, **263**, 91–100 (2000).
[11] S.R. Wild and K.C. Jones, *J. Environ. Qual.*, **21**, 217–225 (1992).
[12] K. Wickström, H. Pyysalo, S. Plaami-Heikkilä and J. Tuominen, *Z. Lebensm. Unters. Forsch.*, **183**, 182–185 (1986).
[13] K. Speer, P. Horstmann, E. Steeg, T. Kühn and A. Montag, *Z. Lebensm. Unters. Forsch.*, **191**, 442–448 (1990).
[14] M. Lodovici, P. Dolara and C. Casalini, *Food Addit. Contam.*, **12**, 703–713 (1995).
[15] D. Voutsa and C. Samara, *Sci. Total Environ.*, **218**, 203–216 (1998).
[16] A.M. Kipopoulou, E. Manoli and C. Samara, *Environ. Pollut.*, **106**, 369–380 (1999).

[17] B. Niehus, L. Brüggemann, G. Peklo, P. Popp and C. Schiller, *Leipziger Geowissenschaften*, **12**, 49–56 (2000).
[18] H.W. Zwanziger, B. Niehus, G. Peklo, A. Rühle and P. Popp, *UFZ Report* (In Preparation).
[19] P. Popp, B. Niehus, G. Peklo and M. Zeibig, *UFZ Report No. 8/1999*. ISSN 0948-9452, Leipzig (1999).
[20] K.C. Jones, G. Grimmer, J. Jacob and A.E. Johnston, *Sci. Total Environ.*, **78**, 117–130 (1989).
[21] G.G. Briggs, R.H. Bromilow, A.A. Evan and M. Williams, *Pestic. Sci.*, **14**, 492–500 (1983).
[22] J.A. Ryan, R.M. Bell, J.M. Davidson and G.A. O'Connor, *Chemosphere*, **17**, 2299–2323 (1988).
[23] W. Fritz, *Zbl. Mikrobiol.*, **138**, 605–616 (1983).
[24] *Toxicological Profile for Polycyclic Aromatic Hydrocarbons*. US Dept. Health Human Services, Georgia, USA (1995).
[25] R. Koch, *Umweltchemikalien*. VCH Verlagsgesellschaft, Weinheim (1991).