PAHs in soils and estimated air-soil exchange in the Pearl River Delta, South China

Guoqing Liu · Lili Yu · Jun Li · Xiang Liu · Gan Zhang

Received: 12 June 2009 / Accepted: 25 February 2010 / Published online: 19 March 2010 © Springer Science+Business Media B.V. 2010

Abstract In this study, 74 soil samples collected from the Pearl River Delta were analyzed for polycyclic aromatic hydrocarbons (PAHs). The PAH mixture in the soils is mainly of low molecular weight compounds, with naphthalene (21.4%) and phenanthrene (21.8%) being dominant. Soil PAH levels from the Pearl River Delta are relatively low (28–711 ng/g, averaged 192 ng/g) compared to those from urban soils in temperate regions. The mean concentration of Σ PAHs generally decrease with increasing distance from the city center, with Σ PAHs of paddy soils > crop

G. Liu (🖂)

Institute of Applied Nuclear Technology, Shenzhen University, Shenzhen, 518060, China e-mail: liugq@szu.edu.cn

G. Liu · L. Yu · J. Li · X. Liu · G. Zhang State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China

L. Yu

GeoQuEST Research Centre, School of Earth and Environmental Sciences, University of Wollongong, Wollongong, NSW 2522, Australia

G. Zhang

Yantai Institute of Coastal Zone for Sustainable Development, Chinese Academy of Sciences, Yantai, 264003, China soil > natural soil. PAHs in the air were measured during a year-round sampling campaign using semipermeable membrane devices, and the transfer of chemicals between the soil and air compartments were estimated. Soil–air fugacity quotient calculations showed a highly uncertain equilibrium position of PAHs, with net volatilization of naphthalene and fluorene, whereas net deposition of phenanthrene, fluoranthene, and pyrene, indicating a capacity for the air to supply the soil with more substances.

Keywords Soil • PAHs • Air-soil exchange • Pearl River Delta • China

Introduction

Soil is the primary environmental reservoir for persistent organic pollutants (POPs) in the terrestrial environment. Once deposited, POPs may reside in the soil for many years. However, soil may not be a permanent sink for these compounds; they tend to recycle continuously between the atmosphere and the terrestrial environment over long periods of time. The soil therefore can either be a sink for POPs or become a source of POPs back into the atmosphere (Mackay 2001; Cousins et al. 1999a). Low-latitude regions may be important source regions for POPs and play an important role in the global transport and redistribution. As stated or indicated by the "global distillation" model (Wania and Mackay 1996), tropical regions tend to represent an atmospheric POPs "net emission," in contrast to their "net sink" in polar regions. Eventually, soils of tropical regions should have lower POPs concentration than those of temperate places.

Polycyclic aromatic hydrocarbons (PAHs) are widespread contaminants in the environment, originated mainly from incomplete fossil fuel combustion and biomass burning. Some PAHs are known to be mutagenic and carcinogenic and have a similar environmental behavior as POPs. Recent publications indicate that PAH concentrations in tropical soils are lower than those in temperate soils (Smith et al. 1995; Connel et al. 1999), and the PAH pattern in tropical soils is markedly different from that in temperate soils (Wilcke et al. 1999a, b; Wilcke 2000). However, the little data available on PAH concentrations in urban soils are mainly derived from tropical cities; knowledge on PAH burden in subtropical soils is scarce. Furthermore, few studies have been carried out on the airsoil exchange of PAHs in tropical to subtropical regions, such data are important if we are to assess the air-soil equilibrium position of PAHs in these regions.

Located in the subtropical monsoon region, the Pearl River Delta (PRD) in Guangdong province is one of the most prosperous regions in China. In the last two decades, the PRD region has undergone rapid urbanization and industrialization. It has a population of more than 38 million and a land area of approximately 40,000 km², contributing one ninth of the country's gross domestic production (Li et al. 2006a). Not surprisingly, this rapid economic growth has resulted in environmental problems. Recent studies have shown that organic contaminants, including PAHs, polychlorinated biphenyls, and organochlorine pesticides are presented in various environmental media in the PRD (Li et al. 2006b; Liu et al. 2005; Mai et al. 2003; Tan et al. 2006). The few studies that have been done indicate that moderate levels (42-3700 ng/g) of PAHs are present in the vegetable soils of the PRD, and the sources of PAHs are mainly the combustion of fossil fuel, coal, and biomass (Cai et al. 2007; Chen et al. 2005; Ma et al. 2008). However, the occurrence and the distribution of PAHs in paddy and natural soils of the PRD are still scarce, and no studies have been carried out on the air–soil exchange of PAHs in this region. Such studies are necessary in order to assess the current status of air–soil quality and to develop appropriate management strategies.

The present study examines the status of PAH contaminations in the soil of Pearl River Delta and to understand its air-soil equilibrium position. The results of this study will be of particular value for understanding the environmental behavior of PAHs in subtropical regions.

Materials and methods

Soil sampling

Seventy-four soil samples, consisting of 37 crop soils, 14 paddy soils, and 23 natural soils, were collected in September 2001 (Fig. 1). The locations of the crop soils were relatively evenly distributed across the region. The majority of the paddy soils were collected in the relatively less developed areas located in the northern and eastern parts of the region. The paddy soils are for rice culture, and the crop soils are predominantly used for fruit and vegetable production. The natural soils were generally collected from uncultivated and/or remote sites, in forests or on mountaintops. The natural soils were generally thin and sandy. The crop and paddy soils consisting of three to five subsamples were collected at the depths between 0 and 15 cm, which are representative of the plough layer. Each of the natural soils that consisted of nine subsamples were obtained between 0 and 5 cm below the surface. All soil samples were collected using a hand auger and then stored in polyethylene bags. The soil samples were stored at -18°C until analysis.

Air sampling

PAHs in the air were sampled by semipermeable membrane devices (SPMDs). The sampling sites were located in forests or on mountaintops to avoid air pollution from point sources. The design





and deployment of SPMDs have been described in detail in our previous study (Liu et al. 2006). Briefly, SPMDs were exposed and collected every 3 months from April 2001 to March 2002 in the Pearl River Delta, and a total of 40 SPMD samples were collected in the ten city sampling sites, namely, Zhaoqing, Qingyuan, Dongguang, Guangzhou, Panyu, Nanhai, Shunde, Jiangmen, Zhongshan, and Zhuhai.

Analytical procedure

Organic carbon determination

Soil organic carbon analysis was done using a Carlo Erba model 1108 elemental analyzer (carbon-hydrogen-nitrogen [CHN] analyzer). Two grams of freeze-dried sediment was treated with a 10% HCl solution to remove inorganic carbon and dried overnight at 60°C. A 5- to 15-mg subsample was then placed into a tarred 5.8-mm silver capsule, which was folded and compressed with tweezers for CHN analysis. Samples were analyzed in duplicate, and an average percent of total organic carbon was determined.

Analysis of PAHs

Soil samples were thawed and freeze-dried for 24 h and pulverized and sieved through a 100meshed stainless steel mesh. Approximately 20-g spiked with subsamples were surrogates (naphthalene- d_8 , acenaphthene- d_{10} , phenanthrene d_{10} , pyrene- d_{10} , chrysene- d_{12} , and perylene d_{12}) and Soxhlet-extracted for 48 h with dichloromethane. Activated copper granules were added to the collection flask to remove elemental sulfur. Concentrated extracts were cleaned and fractionated on a 10-mm inner diameter silica/ alumina column packed, from the bottom to top, with neutral alumina (6 cm, 3% deactivated), neutral silica gel (2 cm, 3% deactivated), and anhydrous sodium sulfate (1 cm). The mixture was eluted with 60 mL of hexane/dichloromethane (6:4 v/v), and the final extract volume was reduced to 200 μ L under a gentle N₂ stream. A known amount of internal standard (hexamethybenzene) was added to all extracts prior to PAHs analysis.

PAHs were quantified on a HP-5971 gas chromatograph (GC)-mass selective detector system operating at 70 eV under full scan mode. Analytes were separated with a DB5-MS column ($30 \text{ m} \times$ 0.25 mm diameter, 0.25-µm film thickness). The GC temperature program was as follows: initially at 80°C for 5 min, increased to 290°C at 3°C/min, and held for 30 min. A 1-µL sample was injected into the split/splitless injector with a 5-min solvent delay. Peak confirmation and quantification was performed on a disk operating system-based HP ChemStation system. In this study, 16 priority pollutant PAHs identified by the US Environmental Protection Agency (EPA) were analyzed. Total PAH (Σ PAHs) was computed as the sum of the following 16 EPA PAHs: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flo), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a, h]anthracene (DiA), indeno[1, 2,3-c, d]pyrene (InP), and benzo[g, h, i]perylene (BghiP).

Quality control

The instruments were calibrated daily with calibration standards. Method blanks (solvent), spiked blanks (standards spiked into the solvent), and sample duplicates were routinely analyzed with field samples. The mean surrogate recovery for PAHs (excluding naphthalene- d_8) was 112%, ranging from 70% to 140%. The recovery of naphthalene-d₈ was 34-47%. Reported concentrations were corrected for surrogate recoveries. The levels of phenanthrene in procedure blanks were below 5% of the levels found in the soil samples, and the differences between individual chemical measurements in duplicate samples were <15%.

Results and discussion

PAH concentrations

The range and arithmetic mean of PAH concentrations in soils are presented in Table 1. Total PAH concentrations ranged from 28.0 to 710.8 ng/g dry weight, with a mean value of 191.5 ng/g. In general, soil PAH concentrations descended in the order of paddy soil > crop soil > natural soil. Geographically, PAH concentrations are higher in the center of the Delta than those in the north and west (Fig. 2). Most PAHs reach the soil via deposition from the atmosphere, and PAH concentrations in the soils tend to increase with the increasing impact of industry, traffic, and domestic heating (Jones et al. 1989). Guangzhou, Fushan, Dongguang, and Shenzhen are the most

Table 1 PAH	PAHs	Crop soil $(n = 37)$	Paddy soil $(n = 14)$	Natural soil $(n = 23)$		
from the Pearl River		$\overline{\text{Mean} \pm \text{SD} (\text{ng/g})}$	Mean \pm SD (ng/g)	$Mean \pm SD (ng/g)$		
Delta	Nap	38.2 ± 54.5	38.9 ± 33.5	30.4 ± 32.7		
	Acy	2.9 ± 2.6	1.1 ± 0.7	2.2 ± 4.8		
	Ace	0.6 ± 1.1	0.9 ± 0.5	0.6 ± 0.4		
	Flo	15.4 ± 12.3	5.9 ± 4.2	5.1 ± 3.8		
	Phe	22.0 ± 51.6	45.9 ± 25.9	23.5 ± 13.6		
	Ant	1.5 ± 3.4	2.4 ± 1.6	1.4 ± 0.8		
	Flu	23.5 ± 33.4	26.3 ± 14.9	11.1 ± 6.7		
	Pyr	10.6 ± 18.5	14.9 ± 8.5	6.7 ± 3.8		
	BaA	4.8 ± 6.1	4.7 ± 2.9	2.2 ± 1.5		
	Chry	14.4 ± 18.7	16.3 ± 8.0	8.1 ± 4.9		
	BbF	13.4 ± 15.9	12.6 ± 6.4	6.6 ± 4.6		
	BkF	4.5 ± 5.8	5.4 ± 3.4	2.3 ± 1.5		
	BaP	5.2 ± 7.2	7.0 ± 3.9	3.4 ± 2.7		
	InP	7.7 ± 8.7	16.0 ± 24.3	4.1 ± 3.1		
	DiP	3.0 ± 3.2	4.3 ± 6.0	1.5 ± 1.2		
	BghiP	8.9 ± 9.4	15.8 ± 22.9	4.5 ± 3.4		
	∑PAHs	218 ± 123	253 ± 130	114 ± 67		



Fig. 2 Spatial distribution of Σ PAH levels in the topsoils of the Pearl River Delta

developed regions in the PRD region and show high levels of PAHs in the soil. This suggests that the PAH distribution in the PRD soil is largely influenced by anthropogenic activity, such as industrial discharges and vehicular emissions.

PAHs levels in urban soils have been reported in many studies. Mielke et al. (2001) found a median concentration of 3,731 ng/g in New Orleans urban soil, and Trapido (1999) observed a mean level of 2,200 ng/g in 12 PAHs from Estonian soils. These values are much higher than those found in the current study. In addition, soil PAH levels in the PRD are also lower than those reported in Tianjin industrial soil (>1,000 ng/g, Tao et al. 2004) and suburban soil in Beijing (1,347 ng/g)average, Ma et al. 2005). PAH concentrations in soils of the PRD are comparable to those in tropical and subtropical regions, such as Uberlândia (107 ng/g average, Wilcke et al. 1999a) and Bangkok (106 ng/g average, Wilcke et al. 1999b). The works of Smith et al. (1995), Wilcke (2000), and Wilcke et al. (2003) indicate that PAH concentrations in tropical soils are, on average, lower than those of temperate soils with similar pattern of land use. This may be due to shorter accumulation times and/or enhanced biodegradation, volatilization, and photooxidation in tropical environment (Wilcke et al. 1999b).

PAH distribution pattern and source

The most abundant PAHs in the PRD soil are, on average, Nap (21.4% of the total PAHs),

Phe (21.8%), Flu (11.6%), Pyr (6.7%), and Chry (7.3%). PAH distribution patterns are similar to those found in tropical regions where soils PAH are dominated by Nap, Phe, and perylene (Wilcke et al. 1999a, b). Previous studies (Li et al. 2006b; Ma et al. 2008) have indicated that in the PRD, PAH sources are mainly of anthropogenic origin. Vehicle emissions and coal combustion are considered to be the main sources. It is interesting to note the elevated Nap concentration in the PRD soil. Industrial and vehicular sources of PAH frequently result in PAH patterns dominated by Flu, Chry, and benzo [b, j, k] fluoranthene in urban soils (Chen et al. 2005; Ma et al. 2005). The elevated Nap in the soil may suggest that there are specific sources for this compound, such as biological synthesis or plant metabolism (Wilcke et al. 2003).

Climate will modify PAH pattern in top soils. It is expected that low molecular PAHs would be less in the tropical regions and enriched in the colder regions. Figure 3 shows the PAH compositions of soils from different climatic zones. Contrary to what is expected, the PAH patterns in tropical/subtropical soils contain more of low molecular PAHs than those in temperate soils. Recent publications have indicated that there are large unknown sources of naphthalene and phenanthrene in the tropical environment, and it is likely that part of these sources is biological (Chen et al. 1998a, b; Wilcke et al. 2003).

PAH concentration patterns in the soils are influenced by not only atmospheric deposition but also land use. In the Pearl River Delta, the mean concentration of total PAHs descended in the order of paddy soil > crop soil > natural soil. The percentage of 2-3, 4, 5-6 ring PAHs in the paddy soil is 45%, 29%, and 26%, respectively. In crop soil and natural soil, the composition patterns are 54%, 29%, and 17% and 58%, 25%, and 18%, respectively. PAHs in the natural soil are mostly derived from atmospheric deposition, and these typically exhibit low molecular weights. PAHs with high molecular weights in paddy soil are likely derived from sewage sludge, which often contain high level of PAHs (Wild et al. 1990, 1991). In addition, ash from plant combustion for nutrition is thought to be another important source of PAHs in the paddy and crop soils. These processes tend to retain more of heavier PAHs.

Fig. 3 PAH profiles in soil from Pearl River Delta and other tropical and/or temperate regions. (Data for Norway was from Aamot et al. 1996; Poland from Barbara 1996; France from Motelay-Massei et al. 2004; Spain from Nadal et al. 2004; Welsh from Jones et al. 1989; Switzerland from Bucheli et al 2004: Korea from Nam et al 2003; Beijing from Ma et al. 2005; Tianjin from Tao et al 2004; Brazil from Wilcke et al. 2003)



As far as spatial variation is concerned, the high molecular weight PAHs account for 51.8% and 44.8% of the total PAHs in urban soil and rural soil, respectively, reflecting an urban influence on PAH composition profiles in this region.

Air-soil equilibrium position

It has been hypothesized that air–soil exchange is the key process that controls the levels of POPs present in the soil and air (Jones 1994). In order to gain further insight into the air–soil exchange processes, soil–air fugacity quotients for selected PAHs (Nap, Flo, Phe, Flu, and Pyr) were calculated using the air and soil concentration measured in the field experiment. For PAHs in the air, an annual average concentration was used. Fugacities (Pa) of PAHs in the soil (f_s) and air (f_a) were calculated using equations given by Harner et al. (2001) and assuming that the fugacity capacity of soil is entirely due to the organic matter fraction:

$$f_{\rm s} = C_{\rm s} \ RT/0.411 \phi_{\rm om} K_{\rm oa} \tag{1}$$

$$f_{\rm a} = C_{\rm a} \ RT \tag{2}$$

where C_s and C_a are concentrations in soil and air (moles per cubic meter), R is the gas constant (8.314 Pa m³ mol⁻¹ K⁻¹), and T is the absolute temperature (Kelvin). ϕ_{om} is the fraction of organic matter in the soil (1.7 times the organic carbon fraction); K_{oa} is the octanol–air partition coefficient of the compound. Soil residues were converted from a mass to volume concentration basis assuming a soil bulk density of 1.5×10^6 g m⁻³. Values of K_{oa} (25°C) for PAHs were taken from Harner and Bidleman (1998).

The fugacity fraction *F* is calculated from the measured air and soil fugacities:

$$F = f_{\rm s}/\left(f_{\rm s} + f_{\rm a}\right) \tag{3}$$

Soil–air equilibrium is indicated by a fugacity fraction F of 0.5. An F less than 0.5 represents net deposition, and an F above 0.5 indicates net volatilization (Harner et al. 2001; Daly et al. 2007).

The selected PAH concentrations in the air and the soil and the calculated air-soil fugacity fractions for each of the ten sampling sites in the Pearl River Delta are listed in Table 2. Most of the

Table 2 Concentrations of selected PAHs in air and soil, the calculated fugacity fraction, and air-soil net diffusive fluxes

		ZQ	QY	DG	GZ	PY	NH	SD	JM	ZS	ZH
Air concentration (ng·m ⁻³)	Nap	2.12	2.04	2.34	2.16	3.13	3.47	8.03	3.76	1.76	2.81
	Flo	0.66	1.42	2.27	1.46	1.65	1.89	3.17	1.44	1.48	0.93
	Phe	5.41	9.09	24.19	18.04	14.47	22.18	23.40	10.50	11.69	3.98
	Flu	2.58	4.38	13.75	9.88	6.42	5.54	9.40	3.54	3.12	0.32
	Pyre	0.42	0.69	3.70	2.73	1.99	2.02	3.26	0.65	0.59	0.04
Soil concentration (ng·g ⁻¹)	Nap	17.6	5.5	16.7	11.3	18.1	14.9	7.6	9.6	101.5	31.3
	Flo	9.3	4.5	12.1	3.8	5.7	22.0	9.8	5.4	21.1	6.4
	Phe	13.6	6.5	17.8	5.6	11.5	30.5	11.8	7.9	25.8	9.4
	Flu	6.2	2.4	4.7	3.0	9.0	5.9	0.9	3.1	13.9	6.8
	Pyre	4.2	1.4	4.2	1.4	4.5	7.0	1.7	1.9	8.6	2.8
$F = f_{\rm s}/(f_{\rm s} + f_{\rm a})$	Nap	0.982	0.936	0.982	0.992	0.987	0.988	0.944	0.979	0.998	0.991
	Flo	0.996	0.98	0.992	0.995	0.992	0.998	0.994	0.995	0.997	0.995
	Phe	0.109	0.034	0.034	0.015	0.037	0.063	0.024	0.035	0.097	0.102
	Flu	0.019	0.002	0.001	0.001	0.005	0.003	0.000	0.003	0.016	0.111
	Pyre	0.010	0.001	0.000	0.000	0.001	0.001	0.000	0.001	0.007	0.078
Estimated flux (with bioturbation; $ng m^{-2} d^{-1}$)	Nap	7,809	1,992	8,269	10,894	12,424	12,764	5,895	7,883	55,774	18,371
	Flo	2,892	1,260	4,005	2,291	2,364	11,495	4,852	2,712	7,417	2,363
	Phe	-136	-283	-607	-232	-264	-308	-359	-156	-251	-79
	Flu	-153	-282	-782	-316	-290	-202	-363	-134	-166	-14
	Pyre	-24	-43	-203	-83	-86	-70	-120	-23	-30	-2
Estimated flux (without bioturbation; $ng m^{-2} d^{-1}$)	Nap	25.6	6.2	28.4	61.9	51.6	64.1	28.3	38.4	200.2	68.7
	Flo	38.7	15.0	58.8	58.7	45.7	268.5	108.9	61.8	117.4	39.8
	Phe	-1.1	-1.9	-5.2	-3.9	-3.1	-4.6	-5.1	-2.2	-2.3	-0.8
	Flu	-0.6	-1.0	-3.1	-2.2	-1.4	-1.2	-2.1	-0.8	-0.7	-0.1
	Pyre	-0.1	-0.2	-0.8	-0.6	-0.4	-0.4	-0.7	-0.1	-0.1	-0.01

ZQ Zhaoqing, QY Qingyuan, DG Dongguang, GZ Guangzhou, PY Panyu, NH Nanhai, SD Shunde, JM Jiangmen, ZS Zhongshan, ZH Zhuhai

fugacity fractions for Nap and Flo are >0.9. This suggests that the soil has become oversaturated with Nap and Flo, indicating a tendency for Nap and Flo to move from soil to air. However, the fugacity fractions for other PAH congeners are very low (~ 0.11), which indicates a tendency for the substances to remain in the soil and a capacity for the air to supply the soil with more substances.

The fugacity quotient is a useful way to study air–soil exchange of POPs, and this concept has been applied to assess the air–soil equilibrium position of POPs in a variety of regions (Cousins and Jones 1998; Bidleman and Leone 2004). However, there are several uncertainties associated with the use of the fugacity quotient approach (Hippelein and McLachlan 1998), including the measured air and soil concentrations and the temperature adjusted K_{oa} . The fine distribution of compounds within surface soils may also influence the magnitude of calculated soil–air quotients (Cousins and Jones 1998). A study by Daly et al. (2007) shows that the calculated fugacity fraction due to varied K_{oa} , T, C_s , C_a , and f_{oc} might create significant differences as much as 70%, which means that F between 0.15 and 0.85 does not represent a significant departure from equilibrium.

In this study, the calculated fugacity fractions are far from 0.5 for all PAH compounds, suggesting that most PAHs in the PRD environment are not close to equilibrium. The lighter compounds (e.g., Nap, Flo) that typically have lower log K_{oa} values show a tendency to move from the soil to the air, while the soil tends to retain more of heavy molecular weight PAHs. These results are not unexpected, due to rapid industrial development and urbanization; PAHs are still being emitted in large quantities in the PRD environment (Mai et al. 2003; Liu et al. 2005). The air–soil equilibrium position of PAHs in the PRD will change only if emissions to the atmosphere decline in the future.

Estimated air-soil exchange fluxes

The net flux N (moles per hour) of PAHs from the soil to the air is calculated as follows:

$$N = D_{\rm v} \left(f_{\rm s} - f_{\rm a} \right) \tag{4}$$

where D_v (moles per Pascal per hour) is the overall D value for transport across the soil-air interface, and f_s and f_a are the fugacities (Pascals) in soil and air, respectively (Mackay 2001; Backe et al. 2004). D_v is calculated through:

$$1/D_{\rm v} = 1/D_{\rm e} + 1/\left(D_{\rm a} + D_{\rm w} + D_{\rm bio}\right) \tag{5}$$

where D_e is the *D* value for transport across the soil–air boundary layer (moles per Pascal per hour), D_a is the *D* value for diffusion in the soil– air (moles per Pascal per hour), and D_w is the *D* value for transport in the soil–water, and D_s is the *D* value for vertical bioturbation of soil– solids (Cousins et al. 1999b; Sweetman et al. 2002). Descriptions of the equations for estimating these *D* values are well documented (Harner et al. 1995, 2001; Sweetman et al. 2002). In this study, the soil area and the depth of incorporation were assumed to be 1 and 0.1 m, respectively.

Table 2 shows the air-soil exchange fluxes of PAHs in the PRD region. In general, the lighter PAH congeners (Nap and Flo) undergo outgassing from the soil, whereas the heavier PAH congeners are exhibiting a net absorption from the atmosphere. It is worthwhile to note that the vertical-sorbed phase transport or bioturbation has a large influence on the magnitude of the estimated air-soil net fluxes. Table 2 shows that if this transport process is excluded, the estimated net transfer of Nap and Flo from soil to air ranges from 20 to 507 ng m⁻² d⁻¹, and the net deposition flux from air to soil ranges from 2.5 to $37 \text{ ng m}^{-2} \text{ d}^{-1}$ for other PAH compounds. These fluxes are comparable to the reported net polychlorinated biphenyl air-soil fluxes in an urban site in the south of Sweden (7–17 ng m⁻² d⁻¹, Backe et al. 2004). Geographically, the air-soil fluxes of PAHs are higher in the center of the Pearl River Delta; this may due to the large industrial discharges and vehicle emissions in these regions.

The present study examined the distribution and profiles of PAHs in the topsoils of the Pearl River Delta, South China. The PAH mixture in the soil is mainly of low molecular weight compounds, with naphthalene and phenanthrene being dominant. Soil PAH levels (28–711 ng/g) are relatively low compared to those of urban soils in temperate regions and descended in the order of paddy soils > crop soil > natural soil. The sources of PAHs are largely from coal combustion and vehicle emissions. Estimated air–soil fugacity fractions showed a net volatilization of Nap and Flo and net deposition of phenanthrene, fluoranthene, and pyrene.

Acknowledgements This work was supported by the Chinese Academy of Sciences (KZCX1-YW-06), Guangdong Provincial Science and Technology Program (2006A36703003), the Natural Science Foundation of China (no. 40821003), and the Guangdong Provincial Natural Science of China (7301362). We are grateful to Ms. Paromita for reviewing this manuscript.

References

- Aamot, E., Steinnes, E., & Schmid, R. (1996). Polycylic aromatic hydrocarbons in Norwegian forest soils: Impact of long range atmospheric transport. *Environmental Pollution*, 92, 275–280.
- Backe, C., Cousins, I. T., & Larsson, P. (2004). PCBs in soils and estimated soil–air exchange fluxes of selected PCB congeners in the south of Sweden. *Environmental Pollution*, 128, 59–72.
- Barbara, M. K. (1996). Polycyclic aromatic hydrocarbons in agricultural soils in Poland: Preliminary proposals for criteria to evaluate the level of soil contamination. *Applied Geochemistry*, 11, 121–127.
- Bidleman, T. F., & Leone, A. D. (2004). Soil–air exchange of organochlorin pesticides in the Southern United States. *Environmental Pollution*, 128, 49–57.
- Bucheli, T. D., Blum, F., Desaules, A., & Gustafsson, Ö. (2004). Polycyclic aromatic hydrocarbons, black carbon, and molecular markers in soils of Switzerland. *Chemosphere*, 56, 1061–1076.
- Cai, Q. Y., Mo, C. H., Li, Y. H., Zeng, Q. Y., Katsoyiannis, A., Wu, Q. T., & Ferard, J. F. (2007). Occurrence and assessment of polycyclic aromatic hydrocarbons in soils from vegetable fields of the Pearl River Delta, South China. *Chemosphere*, 68, 159–168.
- Chen, J., Henderson, G., Grimm, C. C., Lloyd, S. W., & Laine, R. A. (1998a). Termites fumigate their nests with naphthalene. *Nature*, *392*, 558.

- Chen, J., Henderson, G., Grimm, C. C., Lloyd, S. W., & Laine, R. A. (1998b). Naphthalene in Formosan subterranean termite carton nests. *Journal of Agriculture* and Food Chemistry, 46, 2337–2339.
- Chen, L. G., Ran, Y., Xing, B. S., Mai, B. X., He, J. H., Wei, X. G., et al. (2005). Contents and sources of polycyclic aromatic hydrocarbons and organochlorine pesticides in vegetable soils of Guangzhou, China. *Chemosphere*, 60, 879–890.
- Connel, D. W., Miller, G. J., Mortimer, M. R., Shaw, G. R., & Anderson, S. M. (1999). Persistent lipophilic contaminants and other chemical residues in the southern hemisphere. *Critical Reviews in Environmental Science and Technology*, 29, 47–82.
- Cousins, I. T., Beck, A. J., & Jones, K. C. (1999a). A review of the processes involved in the exchange of semivolatile organic compounds (SVOC) across the airsoil interface. *Science of the Total Environment*, 228, 5–24.
- Cousins, I. T., Gevao, B., & Jones, K. C. (1999b). Measuring and modeling the vertical distribution of semivolatile organic compounds in soils. 1: PCB and PAH soil core data. *Chemosphere*, 39, 2507–2518.
- Cousins, I. T., & Jones, K. C. (1998). Air–soil exchange of semi-volatile organic compounds (SOCs) in the U.K. *Environmental Pollution*, 102, 105–118.
- Daly, G., Lei, Y. D., Teixeira, C., Muir, D. C. G., Castillo, L. E., Jantunen, L. M. M., et al. (2007). Organochlorine pesticides in the soils and atmosphere of Costa Rica. *Environmental Science and Technology*, 41, 1124–1130.
- Harner, T., & Bidleman, T. F. (1998). Measurement of octanol-air partition coefficients for polycyclic aromatic hydrocarbons and polychlorinated naphthalenes. *Journal of Chemical and Engineering Data*, 43, 40–46
- Harner, T., Bidleman, T. F., Jantunen, L. M. M., & Mackay, D. (2001). Soil–air exchange model of persistent pesticides in the United States cotton belt. *Environmental Toxicology and Chemistry*, 20, 1612–1621
- Harner, T., Mackay, D., & Jones, K. C. (1995). Model of the long-term exchange of PCBs between soil and the atmosphere in the southern U.K. *Environmental Science and Technology*, 29, 1200–1209.
- Hippelein, M., & McLachlan, M. S. (1998). Soil/air partitioning of semivolatile organic compounds. 1. Method development and influence of physical-chemical properties. *Environmental Science and Technology*, 32, 310–316.
- Jones, K. C. (1994). Observations on long-term air-soil exchange of organic contaminants. *Environmental Sci*ence and Pollution Research International, 1, 171–177.
- Jones, K. C., Stratford, J. A., Waterhouse, K. S., & Vogt, N. B. (1989). Organic contaminants in Welsh soils: Polycyclic aromatic hydrocarbons. *Environmental Science and Technology*, 23, 540–550.
- Li, J., Zhang, G., Li, X. D., Qi, S. H., Liu, G. Q., & Peng, X. Z. (2006b). Source seasonality of polycyclic aromatic hydrocarbons (PAHs) in a subtropical city, Guangzhou, South China. *Science of the Total Environment*, 355, 145–155.

- Li, J., Zhang, G., Qi, S. H., Li, X. D., & Peng, X. Z. (2006a). Concentration, enantiomeric composition, and sources of HCH, DDT and chlordane in soils from the Pearl River Delta, South China. *Science of the Total Environment*, 327, 215–224.
- Liu, G. Q., Zhang, G., Li, X. D., Li, J., Peng, X. Z., & Qi, S. H. (2005). Sedimentary record of polycyclic aromatic hydrocarbons (PAHs) in a sediment core from the Pearl River estuary, South China. *Marine Pollution Bulletin*, 8–12, 912–921.
- Liu, G. Q., Zhang, G., Li, J., Li, X. D., Peng, X. Z., & Qi, S. H. (2006). Spatial distribution and seasonal variations of polycyclic aromatic hydrocarbons (PAHs) using semi-permeable membrane devices (SPMD) and pine needles in the Pearl River Delta, South China. *Atmospheric Environment*, 40, 3134– 3143.
- Ma, L. L., Chu, S. G., Wang, X. T., Cheng, H. X., Liu, X. F., & Xu, X. B. (2005). Polycyclic aromatic hydrocarbons in the surface soils from outskirts of Beijing, China. *Chemosphere*, 58, 1355–1363.
- Ma, X. X., Ran, Y., Gong, J., & Zou, M. Y. (2008). Concentrations and inventories of polycyclic aromatic hydrocarbons and organochlorine pesticides in watershed soils in the Pearl River Delta, China. *Environmental Monitoring and Assessment*, 145, 453–464.
- Mackay, D. (2001). *Multimedia environmental models: The fugacity approach*. Boca Raton: Lewis/CRC.
- Mai, B. X., Qi, S. H., Zeng, E. Y., Yang, Q. S., Zhang, G., Fu, J. M., et al. (2003). Distribution of polycyclic aromatic hydrocarbons in the coastal region off Macao, China: Assessment of input sources and transport pathways using compositional analysis. *Environmental Science and Technology*, 37, 4855–4863.
- Mielke, H. W., Wang, G., Gonzales, C. R., Le, B., Quach, V. N., & Mielke, P. W. (2001). PAH and metal mixtures in New Orleans soils and sediments. *Science of the Total Environment*, 281, 217–227.
- Motelay-Massei, A., Ollivon, D., Garban, B., Teil, M. J., Blanchard, M., & Chevreuil, M. (2004). Distribution and spatial trends of PAHs and PCBs in soils in the Seine River basin, France. *Chemosphere*, 55, 555– 565.
- Nadal, M., Schuhmacher, M., & Domingo, J. L. (2004). Levels of PAHs in soil and vegetation samples from Tarragona County, Spain. *Environmental Pollution*, *132*, 1–11.
- Nam, J. J., Song, B. H., Eom, K. C., Lee, S. H., & Smith, A. (2003). Distribution of polycyclic aromatic hydrocarbons in agricultural soils in South Korea. *Chemosphere*, 50, 1281–1289.
- Smith, D. J. T., Edelhauser, E. C., & Harrison, R. M. (1995). Polynuclear aromatic hydrocarbon concentration in road dust and soil samples collected in the United Kingdom and Parkistan. *Environmental Technology*, *16*, 35–53.
- Sweetman, A. J., Cousins, I. T., Seth, R., Jones, K. C., & Mackay, D. (2002). A dynamic level IV multimedia model of emissions and environmental fate of PCBs in the U.K. over a 60-year period. *Environmental Toxicology and Chemistry*, 21, 930–940.

- Tan, J. H., Bi, X. H., Duan, J. C., Rahn, K. A., Sheng, G. Y., & Fu, J. M. (2006). Seasonal variation of particulate polycyclic aromatic hydrocarbons associated with PM10 in Guangzhou, China. *Atmospheric Research*, 80, 250–262.
- Tao, S., Cui, Y. H., Xu, F. L., Li, B. G., Cao, J., & Liu, W. X. (2004). Polycyclic aromatic hydrocarbons (PAHs) in agricultural soil and vegetables from Tianjin. *Science* of the Total Environment, 320, 11–24.
- Trapido, M. (1999). Polycyclic aromatic hydrocarbons in Estonian soil: Contamination and profiles. *Environmental Pollution*, 105, 67–74.
- Wania, F., & Mackay, D. (1996). Tracking the distribution of persistent organic pollutants. *Environmental Science and Technology*, 30, 390A–396A.
- Wilcke, W. (2000). Polycyclic aromatic hydrocarbons (PAHs) in soil—A review. *Journal of Plant Nutrition* and Soil Science, 163, 229–248.
- Wilcke, W., Lilienfein, J., Lima, S. C., & Zech, W. (1999a). Contamination of highly weathered urban soils in

Uberlândia, Brazil. *Journal of Plant Nutrition and Soil Science 162*, 539–548.

- Wilcke, W., Amelung, W., Lraiss, M., Martius, C., Bandeira, A., & Garcia, M. (2003). Polycyclic aromatic hydrocarbons (PAHs) patterns in climatically different ecological zones of Brazil. Organic Geochemistry, 34, 1405–1417.
- Wilcke, W., Muller, S., Kanchankool, C. N., Niamskul, C., & Zech, W. (1999b). Polycyclic aromatic hydrocarbons in hydromorphic soils of the tropical metropolis Bangkok. *Geoderma*, 91, 297–309.
- Wild, S. R., Berrow, M. L., McGrath, S. P., & Jones, K. C. (1991). Polycyclic aromatic hydrocarbons in crop from long-term field experiments amended with sewage sludge. *Environmental Pollution*, 76, 25–35.
- Wild, S. R., Waterhouse, K. S., McGrath, S. P., & Jones, K. C. (1990). Organic contaminants in an agricultural soil with known history of sewage sludge amendments: Polycyclic aromatic hydrocarbons. *Environmental Science and Technology*, 24, 1706–1711.