



Polycyclic aromatic hydrocarbons (PAHs) and their oxygen-containing derivatives (OPAHs) in soils from the Angren industrial area, Uzbekistan

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Concentrations of oxygen-containing PAHs are strongly correlated with those of PAHs and trace metals in soils from Angren industrial region, Uzbekistan indicating a common industrial source.

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ABSTRACT

We measured the concentrations and depth distribution (0–10, 10–20 cm) of 31 PAHs and 12 OPAHs in soils at eleven equidistant sampling points along a 20-km transect in the Angren industrial region (coal mine, power plant, rubber factory, gold mine), Uzbekistan to gain an insight into their concentrations, sources, and fate. Concentrations of all compounds were mostly much higher in the 0–10 cm than in the 10–20 cm layer except in disturbed soil close to the coal mine. Proximity to one of the industrial emitters was the main determinant of PAH and OPAH concentrations. The $\sum 31$ PAHs concentrations correlated positively with the $\sum 7$ carbonyl-OPAH ($r = 0.98$, $p < 0.01$), $\sum 5$ hydroxyl-OPAH ($r = 0.72$, $p < 0.05$), and with industrially emitted trace metals in the topsoil, identifying industrial emissions as their common source. Concentrations of several OPAHs were higher than their parent PAHs, but their vertical distribution in soil suggested only little higher mobility of OPAHs than their corresponding parent PAHs.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are persistent and toxic, because of which 16 of them are included in the USEPA list of priority pollutants (Keith and Telliard, 1979). PAH concentrations in soil have been extensively studied in the temperate zone (mainly Europe, North America, and Japan) but little outside the temperate zone such as in the semi-arid regions of Central Asia (Wilcke, 2000, 2007). Central Asia hosts several former Soviet industrial hubs where the environment is likely to be heavily contaminated by a range of pollutants including PAHs and heavy metals. One example is the Angren industrial area near Tashkent in Uzbekistan. Previous studies conducted in this area demonstrated that soil, vegetation, surface, and groundwater are polluted with heavy metals and sulfur and nitrogen compounds, and that this pollution has negatively affected plants, soil nematodes, and soil microbial properties (Talipov et al., 1996; UNECE, 2002; Sanitation Country Profile, 2004; Shukurov et al., 2009).

Both, coal mining and combustion (e.g., coal-based electricity production) occur in the Angren industrial region. Besides the coal

combustion activities which emit gaseous and particle-bound PAHs, coal mining itself can emit large quantities of unburnt coal particles which can contain high concentrations of PAHs (Achten and Hofmann, 2009). Generally, concentrations of PAHs in soil decrease exponentially with increasing distance from a point source (Van Brummelen et al., 1996; Wilcke et al., 1996; Bakker et al., 2000). In the atmosphere, the fraction of a given PAH concentration sorbed to particles increases with decreasing volatility (Meharg et al., 1998). Previous studies observed that the transport distance decreases with increasing molecular weight because the proportion associated with fast settling atmospheric particles increases (Yang et al., 1991; Meharg et al., 1998; Bakker et al., 2000; Sharma and Tripathi., 2009). Gaseous PAHs, in contrast, may be distributed over longer distances.

Oxygen-containing PAH derivatives (OPAHs) including microbial metabolites may contain functional groups such as e.g., carbonyl, hydroxyl, carboxyl, anhydrides, and coumarins (Konig et al., 1983; Lundstedt et al., 2007). OPAHs are emitted together with PAHs from combustion activities (primary sources), or are post-emission degradation products (secondary sources) of PAH conversion by photooxidation, chemical oxidation, and microbial transformation processes (metabolites) (Cerniglia, 1984; Bamforth and Singleton, 2005; Lundstedt et al., 2007). OPAHs were shown

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in several studies to occur at elevated concentrations in atmospheric samples (gaseous and particulate) and soil (Moyano and Galceran, 1997; Meyer et al., 1999; Lundstedt et al., 2006; Albinet et al., 2007). Some OPAHs are known to be persistent, ubiquitous, and some are even more toxic than their parent compounds (Lundstedt et al., 2007). There is generally little available information on OPAH concentrations in soil. In particular, the relative contributions of combustion (primary source) and post-emission transformations (secondary sources), including microbial processes, photooxidation, and chemical oxidation to the OPAH concentrations in soil are unknown.

Usually, PAHs are strongly sorbed to soil organic matter and therefore little leached to greater soil depths (Wilcke et al., 1996; Wilcke, 2000). Nevertheless, PAHs frequently occur in subsoils (Guggenberger et al., 1996; Wilcke et al., 1996; Krauss et al., 2000; Ma et al., 2005). While for the low molecular weight PAHs a (minor) transport in dissolved phase may occur, the transport of high molecular weight PAHs is only possible if facilitated by colloids such as dissolved organic matter (Gauthier et al., 1987; Maxin and Kögel-Knabner, 1995; Chin et al., 1997). In contrast to PAHs, OPAHs should be considerably more mobile because of their higher water solubility as indicated by lower octanol-water partitioning coefficients (Hansch et al., 1995). It was also directly shown in soil column experiments that OPAHs are more mobile than their parent PAHs (Weigand et al., 2002; Lundstedt et al., 2007). However, we are not aware of any report on the depth distribution of OPAHs in field soils.

The objectives of our study were to (i) determine the spatial distribution of PAH and OPAH concentrations in soils along a linear transect in an industrial semi-arid region in Central Asia, (ii) explore the correlations between PAHs, OPAHs, and heavy metals (taken from the literature) as indication of possible joint sources, and (iii) assess the depth distribution of PAHs and OPAHs in soil. We

tested three hypotheses: (i) PAH concentrations are controlled by distance from industrial emission sources and correlated with heavy metal concentrations. (ii) OPAH concentrations are correlated with those of PAHs and heavy metals near emission sources while at greater distance transformation processes (microbial, photooxidation, and chemical oxidation) of PAHs play an increasing role weakening the relationship between parent PAH and OPAH concentrations. (iii) OPAHs are more water soluble than their parent PAHs and therefore more strongly leached into deeper soil layers.

2. Materials and methods

2.1. Description of study location

The study area is located at 114 km south of Tashkent, the capital of the Republic of Uzbekistan, Central Asia. This region is a semi-arid mountain valley located along the Akhangaran River between 41°01' and 40°58' N and 70°10' and 69°57' E, at 900–950 m a.s.l. The climate is continental with a temperature amplitude between –30 °C in January and +45 °C in July and an annual precipitation between 320 and 550 mm falling mostly in spring and winter. The study area is covered by grassland. Dominating plant genera include *Astragalus*, *Stipa*, *Medicago*, and *Artemisia*. The prevailing wind direction is western and north-western with thermal inversions providing cyclic circulations of air masses causing pendulum distributions of dust and gas-smoke emission from the industrial complex. Because this area is surrounded by a chain of mountains air circulation is poor. The soils are Haplic Calcisols (IUSS Working Group WRB, 2006) with low organic matter concentrations. A detailed description of the site is given by Shukurov et al. (2009).

2.2. Soil sampling and properties

Soil samples were collected at two depths (0–10 cm and 10–20 cm) from 11 locations along a 20-km transect downwind of the industrial complex. The soils were air-dried, sieved over stainless steel sieves (< 2 mm), and stored at 4 °C until analysis. The sampling locations are shown in Fig. 1, and the land use and physico-chemical properties of the soils listed in Table 1. Soil pH, total organic carbon (C_{org}), and trace metal concentrations were determined as described earlier (Shukurov

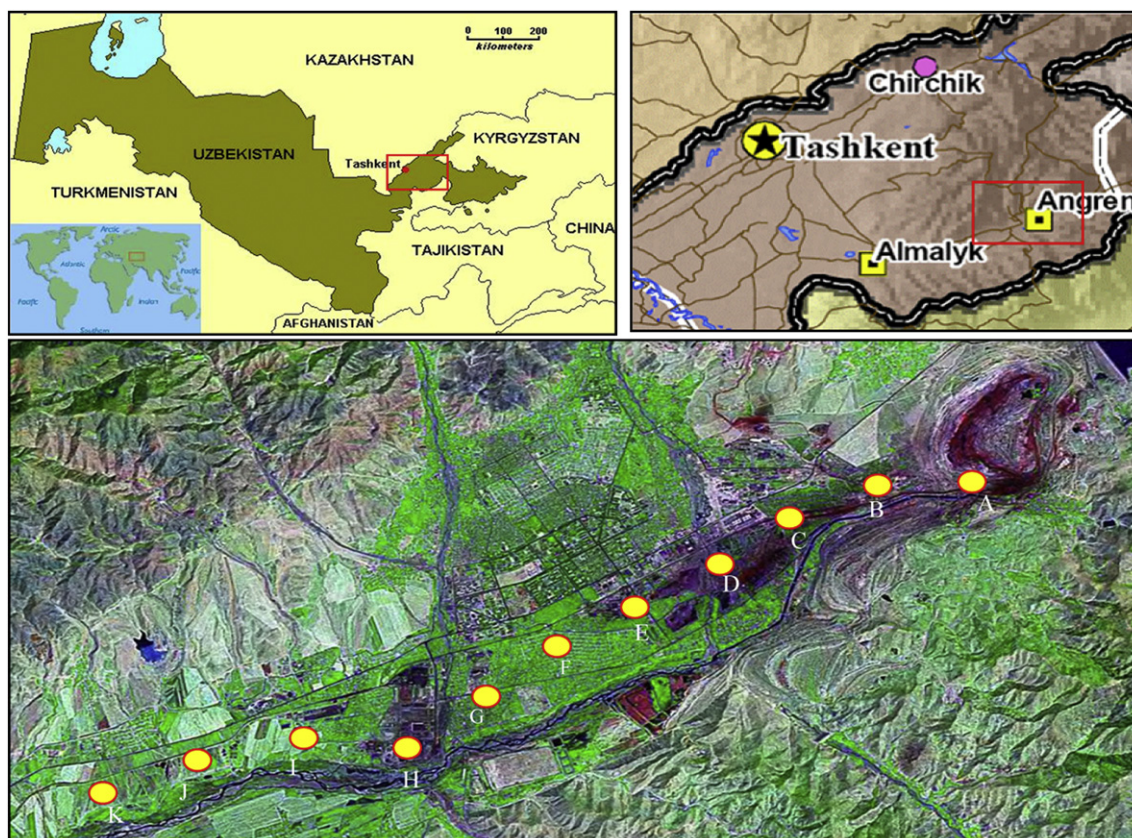


Fig. 1. Location of the study area (aerial photo is from Google Earth) with sampling sites A–K described in Table 1.

Table 1
Sampling locations, land use, and selected physico-chemical properties of soil. Sampling depth 1 is at 0–10 cm and 2 at 10–20 cm.

Site/depth	GPS Coordinates	Land use	C _{org} [g/kg]	pH	ECEC [mmol _c /kg]	Sand [%]	Silt [%]	Clay [%]
A1	41°01' N/70°10' E	Border of coal mine (0 km, grassland)	22	7.2	136	23	60	17
A2			20	7.5	100	30	54	16
B1	41°01' N/70°09' E	Near coal mine (2 km, grassland)	11	8.0	94	28	64	8
B2			7	7.8	90	25	61	13
C1	41°00' N/70° 08' E	East of Angren power plant (4 km, grassland)	20	7.8	96	37	54	9
C2			20	8.0	114	40	54	6
D1	41°00' N/70° 07' E	West of Angren power plant (6 km, grassland)	14	8.1	80	38	56	6
D2			12	8.1	79	65	31	3
E1	40°57' N/70° 05' E	Near coal ash depository (8 km, gardening area)	19	7.9	92	17	71	12
E2			19	8.2	93	27	60	13
F1	40°57' N/70° 04' E	Recreation area (10 km, gardening area)	23	8.0	101	12	71	17
F2			20	7.9	96	10	75	16
G1	40°58' N/70° 03' E	Recreation area/summer camp (12 km, grassland)	19	7.8	70	10	71	19
G2			12	8.0	66	9	73	18
H1	40°58' N/70° 02' E	Near rubber factory (14 km, industrial site)	13	7.9	52	48	44	7
H2			5	8.0	25	56	35	9
I1	41°58' N/70° 00' E	Farming area (16 km, arable land)	3	8.3	90	3	76	21
I2			2	8.0	88	4	73	23
J1	41°49' N/69° 59' E	Near gold refinery (18 km, arable land)	11	8.1	91	30	52	18
J2			7	7.8	83	40	44	17
K1	40°58' N/69° 57' E	Grazing area (20 km)	14	7.8	101	10	67	23
K2			6	7.8	95	11	63	26

et al., 2009). Soil pH was measured in H₂O (soil/solution ratio 1:2) with a potentiometric glass electrode. Total organic carbon (C_{org}) was determined by oxidation with K-dichromate with addition of H₂SO₄ without additional heating (Rowell, 1994). Effective cation-exchange capacity (CEC) was calculated as the sum of the charge equivalents of K, Na, Mg, Al, Ca, and Mn determined by flame AAS (Varian) after extraction with 1 M NH₄NO₃. Soil texture was analyzed using a pipet method after organic matter, lime, and pedogenic iron oxides were destroyed with H₂O₂, HCl, and dithionite/citrate, respectively, and after sand fractions were removed by sieving. In the earlier studies by Shukurov et al. (2009), samples were not taken from sampling sites B, F and J. For the current manuscript we additionally considered these three sampling sites and determined texture, pH, and C_{org} (with an elemental analyzer, Elementar) but not trace metal concentrations.

2.3. PAH and OPAH analyses

2.3.1. Target compounds

In all soil samples, concentrations of 31 PAHs/alkyl-PAHs were determined: naphthalene (NAPH), 2-methylnaphthalene (2-MNAPH), 1-methylnaphthalene (1-MNAPH), 1,3-dimethylnaphthalene (1,3-DMNAPH), acenaphthylene (ACENY), acenaphthene (ACEN), 2,3,5-trimethylnaphthalene (2,3,5-TMNAPH), fluorene (FLUO), phenanthrene (PHEN), anthracene (ANTH), 2-methylphenanthrene (2-MPHEN), 1-methylphenanthrene (1-MPHEN), 3,6-dimethylphenanthrene (3,6-DMPHEN), 3,5-dimethylphenanthrene (3,5-DMPHEN), 2,6-dimethylphenanthrene (2,6-DMPHEN), 1,7-dimethylphenanthrene (1,7-DMPHEN), fluoranthene (FLUA), pyrene (PYR), 1-methyl-7-isopropylphenanthrene (RETENE), benz[a]anthracene [B(A)A], chrysene + triphenylene (CHRY), benzo[b + j + k]fluoranthenes [B(B)K], benzo[e]pyrene ([B(E)P]), benzo[a]pyrene ([B(A)P]), perylene (PERY), indeno[1,2,3-cd]pyrene (IND), dibenz[a,h]anthracene (DIBE), benzo[ghi]perylene [B(GHI)], and coronene (COR); 7 carbonyl-OPAHs: 1-indanone (1-INDA), 1,4-naphthoquinone (1,4-NQ), 1-naphthaldehyde (1-NLD), 2-biphenylcarboxaldehyde (2-BPCD), 9-fluorenone (9-FLO), 1,2-acenaphthylene-dione (1,2-ACQ), and 9,10-anthraquinone (9,10-ANQ); and 5 hydroxyl-OPAHs: salicylaldehyde (SALYD), 2-naphthol (2-NAPHTHOL), 2-hydroxybiphenyl (2-PP), 1-acenaphthenol (1-ACENOL), and 9-fluorenone (9-FLUORENOL) were determined.

2.3.2. Internal standards

A mixture of seven deuterated PAHs (NAPH-D₈, ACEN-D₁₀, PHEN-D₁₀, PYR-D₁₀, CHRY-D₁₂, PERY-D₁₂, and B(GHI)-D₁₂) was used as internal standard to quantify parent and alkyl-PAHs. Benzophenone-2,3,4,5,6-D₅ was used as internal standard to quantify carbonyl-OPAHs. FLUA-D₁₀ solution at 4 µg/ml was used as syringe spike to quantify the hydroxyl-OPAHs and as recovery standard for benzophenone-2,3,4,5,6-D₅. The standards of the target PAHs, alkyl-PAHs, OPAHs, and internal standards were purchased from Dr. Ehrenstorfer (Augsburg, Germany), Ultra Scientific (North Kingston, RI, USA), Chiron (Trondheim, Germany), Acros Organics (New Jersey, USA), and the Sigma–Aldrich group (Steinheim, Germany).

2.3.3. Analytical method

A detailed description of the analytical procedure for the measurement of PAHs and OPAHs is given in Bandowe and Wilcke (2010). Briefly, to about 10 g of soil sample, 100 µl of benzophenone-2,3,4,5,6-D₅ (5 µg/ml) and 50 µl of the mixture of the seven deuterated PAHs NAPH-D₈, ACEN-D₁₀, PHEN-D₁₀, PYR-D₁₀, CHRY-D₁₂,

PERY-D₁₂, and B(GHI)-D₁₂ (each at 5 µg/ml) were added as internal standards to the accelerated solvent extractor (ASE) cell. Samples were extracted using ASE 200 (Dionex, Sunnyvale, CA, USA) with dichloromethane in a first extraction cycle, and with CH₃COCH₃/CH₂Cl₂/CF₃COOH (1%) [250:125:1 v/v/v] in a second extraction cycle. The two extracts of each sample were combined, dried on Na₂SO₄, and cleaned up/fractionated on silica gel (10% deactivated) columns. PAHs/alkyl-PAHs were eluted with 9 ml hexane/dichloromethane (5:1 v/v), followed by 8 ml dichloromethane and 5 ml acetone to elute to the OPAHs. The PAH/alkyl-PAH fraction was rotary evaporated to about 0.5 ml and transferred to a 1.5 ml GC vial for GC/MS measurement. The OPAHs fraction was rotary evaporated and spiked with 100 ng FLUA-D₁₀ as internal standard for quantification of the hydroxyl-OPAHs and recovery standard for benzophenone-2,3,4,5,6-D₅. This fraction was split and one half measured directly with GC/MS to quantify the carbonyl-OPAHs. To the other half N,O-bis-(trimethylsilyl)-trifluoroacetamide [BSTFA:TMCS (99:1)] was added and heated for 15 min at 60 °C to silylate the hydroxyl-OPAHs followed by GC/MS measurement. Target compounds were quantified by the internal standard technique using ten calibration standards prepared from target compound standards each spiked with a constant concentration of internal standard. Hydroxyl-OPAHs were derivatized as above before GC/MS measurements. We used an Agilent 6890 N gas chromatograph coupled to an Agilent 5973 B inert mass selective detector in EI and SIM mode for our measurements. All data recording and processing was done with the Agilent MSD ChemStation software package.

2.4. Quality assurance and quality control

All glassware were rinsed with acetone, machine washed, baked at 250 °C for 12 h, and rinsed with high purity “picograde” solvents before use. All solvents used for extraction, column chromatography, and standard preparation were high purity “picograde” for residue analysis (Promochem, Wesel, Germany). To check and correct for possible contaminations during the analytical procedure, we processed three blanks made of diatomaceous earth at the beginning, middle, and end of our sample sequence. Most compounds were either not detected in the blanks or were measured in negligible quantities, significantly below those found in the samples. The measured compound concentrations in the samples were corrected by subtracting the mean blank concentration. We checked the accuracy of PAH measurements by including the certified reference material ERM[®]-CC013a (BAM, Berlin, Germany) into our analyses. The mean recovery of all PAHs for which certified values were provided was 110%. Since there is no certified reference material for OPAHs, we checked the recovery of benzophenone-2,3,4,5,6-D₅ used as internal standard for carbonyl-OPAHs. The mean recovery of benzophenone-D₅ was 80% (67–88%). The recovery of the hydroxyl-OPAHs determined previously by spike and recovery experiment with this method was 36–70% (Bandowe and Wilcke, 2010). All concentrations are reported without recovery correction.

2.5. Calculations and compound properties

The sum of the concentrations of all parent- and alkyl-PAHs is $\sum 31$ PAHs, of all parent-PAHs $\sum 21$ PAHs, of the 16 EPA-PAHs $\sum 16$ EPA-PAHs, of 1- and 2-methylnaphthalenes $\sum C1$ -NAPH, of 1- and 2-methylphenanthrenes $\sum C1$ -PHEN, and of 3,6-, 3,5-, 2,6-, and 1,7-dimethylphenanthrenes $\sum C2$ -PHEN. The octanol–water partition coefficients (K_{OW}) of PAHs and alkyl-PAHs were taken from literature (Neff et al., 2005;

Mackay et al., 2006), and those of OPAHs were taken from Hansch et al. (1995) or estimated from KOWWIN v1.67 EPI Suite™ version 4.0 (USEPA: <http://www.epa.gov/opt/exposure/pubs/episuited1.htm>). Statistical analysis was performed using SPSS 15.0 for Windows (SPSS Inc., Chicago, IL, USA). We used the Kolmogorov–Smirnov test to check normal distribution of the data. Significance was set at $p < 0.5$.

3. Results

3.1. PAH and OPAH concentrations

The $\Sigma 31$ PAHs concentrations in the 0–10 cm topsoil layer ranged from 118 ng/g at site I to 5913 ng/g at site D (Fig. 2A). The 10–20 cm subsoil layer had $\Sigma 31$ PAHs concentrations in the range from 104 ng/g (I) to 3852 ng/g (A). The $\Sigma 31$ PAHs concentrations in the topsoil were higher than in the subsoil at all sampling sites except A where the subsoil showed higher $\Sigma 31$ PAHs concentrations than the topsoil, and C and I where topsoil and subsoil had similar $\Sigma 31$ PAHs concentrations. The highest ratios of the $\Sigma 31$ PAHs concentration in topsoil to that in subsoil occurred at the sites close to industrial activities, i.e. B (3, near coal mine), D (5, near power plant), and H (8, near rubber factory).

The mixtures of the 31 parent and alkylated PAHs in topsoil were dominated by NAPH (9–35%, mean: 17%), PHEN (9–18%, mean: 15%), and B(BJK) (5–15%, mean: 10%, Fig. 3). The contribution

of the low molecular weight PAHs NAPH + PHEN to the $\Sigma 31$ PAHs ranged between 18% (site A) and 51% (site H).

The contribution of 2- and 3-ring parent PAHs to $\Sigma 21$ PAHs in topsoils was < 50% (23–49%) at sites A, B, C, D, E, G, I, and J, but > 50% (50–67%) at sampling sites F, K, and H (Fig. 4). The smallest contribution of 2- to 3-ring compounds to $\Sigma 21$ PAHs occurred at site A and the highest at site H (near the rubber factory). There was no systematic change in contribution with distance from one of the local point sources (coal mine, power plant, gold refinery, rubber factory) except a gradual increase from 37% at site D (power plant) to 50% at site F. At most sites, the contribution of 2- to 3-ring parent PAHs to $\Sigma 21$ PAHs was lower in subsoils compared to their corresponding topsoils except at sites D, J, and K.

The $\Sigma 7$ carbonyl-OPAHS concentrations showed a similar spatial distribution as those of the PAHs (Fig. 2B). The $\Sigma 7$ carbonyl-OPAHS concentrations were highest at site D (1848 ng/g) and lowest at site I (54 ng/g, Fig. 2B). The $\Sigma 7$ carbonyl-OPAHS concentrations were consistently higher in topsoil than in subsoil where they ranged between 29 ng/g (I) and 595 ng/g (C). The ratios of the $\Sigma 7$ carbonyl-OPAHS concentration in topsoil to that in subsoil were 9 (H), 8 (D), 7 (B), 4.1 (A), and 1.2–2 at all other sites. The carbonyl-OPAHS were dominated by 9-FLO and 9,10-ANQ in all samples. These compounds constituted around 40% (38–47%) each of the $\Sigma 7$ carbonyl-OPAHS. 1-INDA was also abundant and contributed with another ca. 10% on average. (Table 2).

The $\Sigma 5$ hydroxyl-OPAHS concentrations in topsoil ranged between 8 ng/g (I) and 63 ng/g (A) (Fig. 2C), and in subsoil between 7 (site A) and 23 ng/g (site C). The topsoil had higher $\Sigma 5$ hydroxyl-OPAHS concentrations than the subsoil except at site I where topsoil and subsoil had similar $\Sigma 5$ hydroxyl-OPAHS concentrations. The concentration ratio of the $\Sigma 5$ hydroxyl-OPAH in topsoil to that in subsoil were as high as 9 at site A, at all other sites (except I) in the range of 1.4–2.8, and as low as 0.9 at site I. The mixture of hydroxyl-OPAHS was clearly dominated by SALYD, with average contributions to the $\Sigma 5$ hydroxyl-OPAHS concentrations of 65% in topsoil and 64% in subsoil.

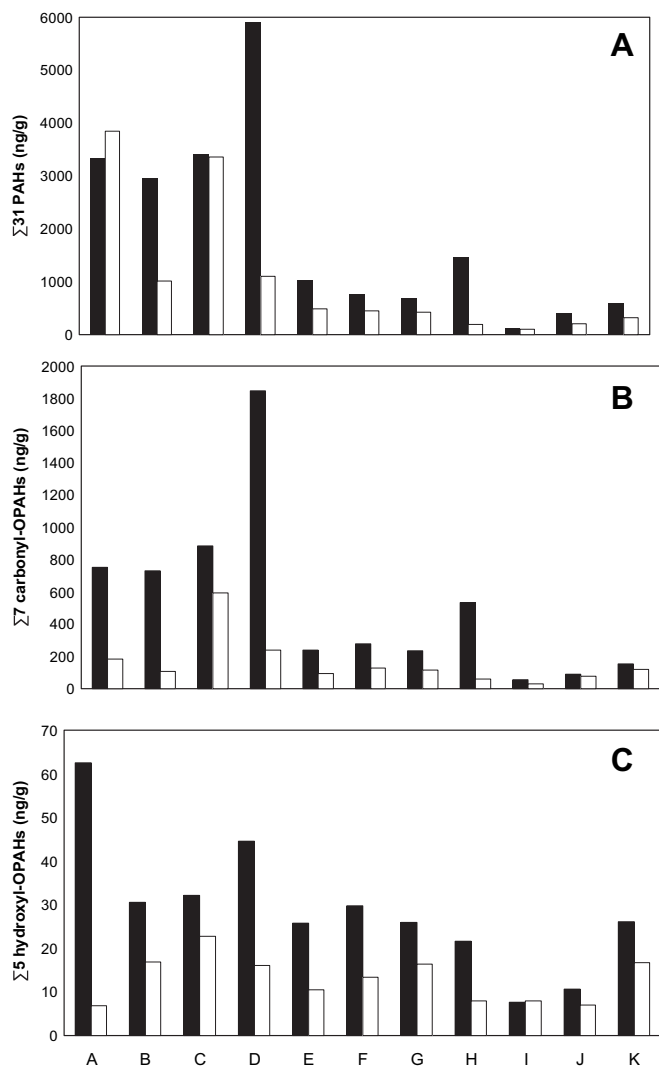


Fig. 2. Concentrations of $\Sigma 31$ PAHs (A), $\Sigma 7$ carbonyl-OPAHS (B), and $\Sigma 5$ hydroxyl-OPAHS in topsoil (0–10 cm, filled black bars) and subsoil (10–20 cm, open bars) of the 11 study sites.

3.2. Correlations among PAH, OPAH, C_{org} , and heavy metal concentrations

Prior to correlation analyses, we tested the data sets for normality. Correlations were only calculated for normally distributed data sets which was the case for most of our data sets. In topsoil, the $\Sigma 31$ PAHs concentrations correlated strongly positively with the $\Sigma 7$ carbonyl-OPAHS and the $\Sigma 5$ hydroxyl-OPAHS concentrations (Fig. 5A). The $\Sigma 5$ hydroxyl-OPAHS concentrations also correlated positively with the $\Sigma 7$ carbonyl-OPAHS concentrations (Fig. 5B). In subsoil, the $\Sigma 31$ PAH concentrations correlated significantly with the $\Sigma 7$ carbonyl-OPAH concentrations ($r = 0.72$, $p = 0.01$) but not with the $\Sigma 5$ hydroxyl-OPAH concentrations ($r = 0.11$, $p = 0.74$) while the $\Sigma 7$ carbonyl-OPAH concentrations correlated significantly with the $\Sigma 5$ hydroxyl-OPAH concentrations ($r = 0.69$, $p = 0.02$). However, the latter correlation disappeared, if site C was removed as an outlier.

Most individual PAHs correlated significantly with individual carbonyl-OPAHS in the topsoil (see supporting information). Exceptions, however, were PERY, RETENE, 1-INDA, and 2-BPCD. Correlations between individual hydroxyl-OPAHS and individual carbonyl-OPAHS or PAHs were much weaker (see supporting information). 1-NAPHTHOL correlated significantly with NAPH ($r = 0.62$, $p = 0.04$) while the concentrations of the other hydroxyl-OPAH/parent PAH pairs did not show significant correlations.

There were no significant correlations between C_{org} and any individual PAH or OPAH in the topsoil except for 1-IND ($r = 0.64$, $p = 0.04$) and SALYD ($r = 0.61$, $p = 0.048$) concentrations.

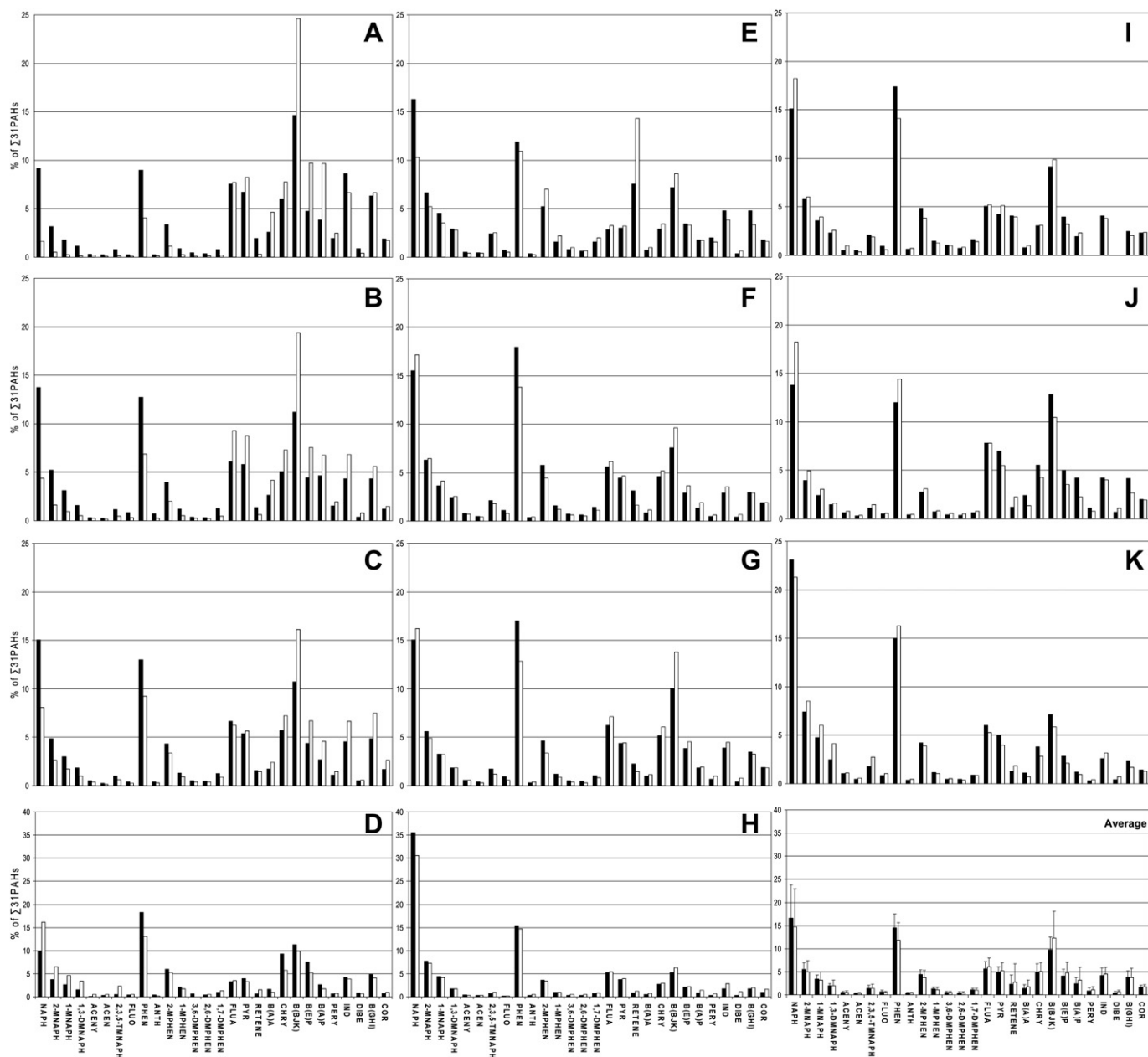


Fig. 3. Composition [%] of parent and alkylated PAH mixtures in topsoil (0–10 cm, filled black bars) and subsoil (10–20 cm, open bars) of the 11 sampling sites A–K depicted in Fig. 1.

As some heavy metals are known pollutants emitted by industrial activity in the Angren area, we correlated PAH and OPAH concentrations with those of heavy metals taken from Shukurov et al. (2009) measured at eight sampling sites in the topsoils. Shukurov et al. (2009) identified Ba, Cu, Pb, Th, U, and Zn concentrations in soil as mainly originating from anthropogenic industrial emissions. There were significant positive correlations of $\sum 31$ PAHs and $\sum 7$ carbonyl-OPAHs with Ba, Cu, Pb, Th, U, and Zn concentrations in the topsoil (Table 3).

3.3. Concentration ratios of OPAHs to parent PAHs

Several concentration ratios of OPAHs to their parent PAHs (1-INDA/FLUO, 9-FLO/FLUO, 1,2-ACQ/ACENY, 1,2-ACQ/ACEN, and 9,10-ANQ/ANTH) were > 1 in both topsoils and subsoils, i.e. the

soils contained higher concentrations of OPAHs than parent PAHs (Table 4). The ratios of 9-FLO/FLUO and 9,10-ANQ/ANTH were higher than 10, and that of 9-FLO/FLUO even reached > 100 at site H near the rubber factory. The ratios 1,4-NQ/NAPH, 1-NLD/1-MNAPH, and 2-BPCD/PHEN were < 1 . The OPAH/parent PAH ratios were not consistently higher in the subsoil than in the topsoil. We did not see a consistent shift in OPAH/parent PAH ratios with distance except a generally higher ratio in topsoil near emission sources (Table 4).

3.4. Depth distribution of PAHs and OPAHs in relation to their hydrophobicity

To assess the mobility of PAHs and OPAHs in soil, we calculated the concentration ratio [CR] defined as the concentration of each

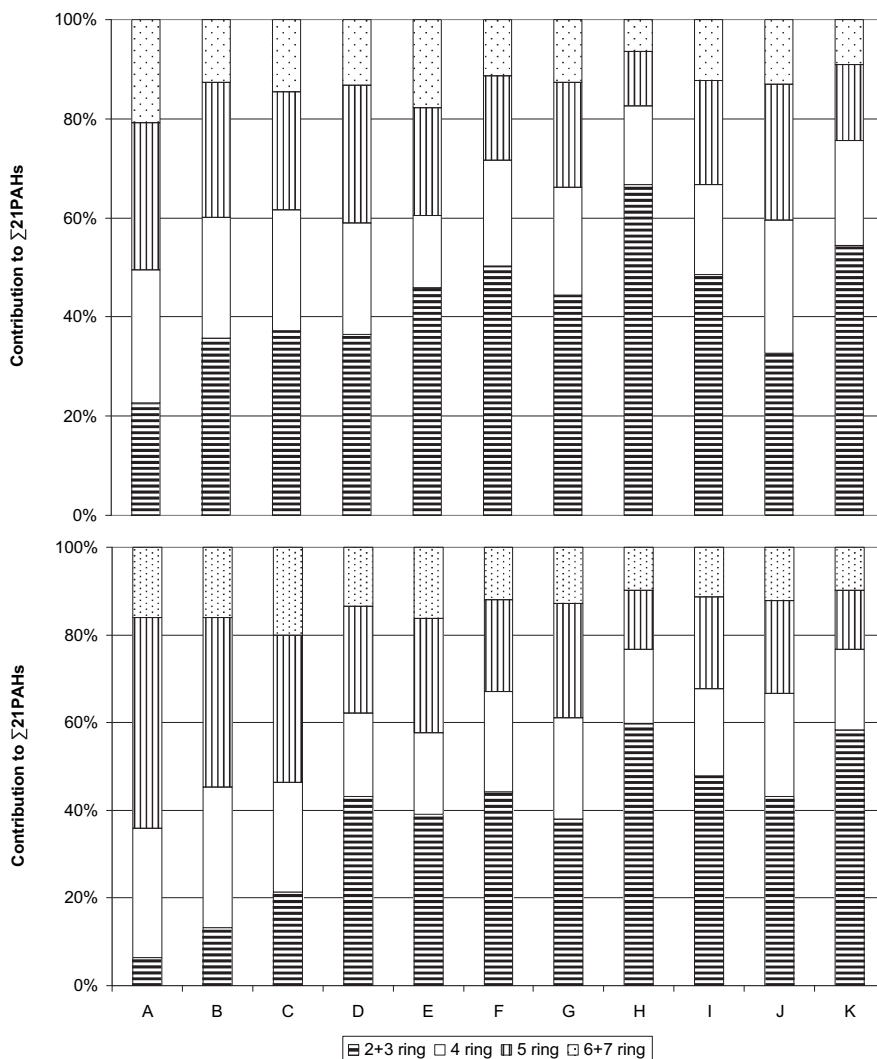


Fig. 4. Percentage contribution of 2- + 3-, 4-, 5-, and 6- + 7-ring parent PAHs to the sum of 21 parent PAHs ($\Sigma 21$ PAHs) in topsoils (upper diagram) and subsoils (lower diagram).

compound in the subsoil divided by that in the topsoil at each site (Fig. 6). The CR for most individual PAHs and OPAHs were variable among different sites but mostly < 1 illustrating that these compounds are accumulated in topsoil. The mean CRs for individual PAHs and individual OPAHs ranged 0.43–0.83 and 0.41–1.02, respectively.

CRs of several higher molecular weight PAHs at sampling sites A and C ranged 1–2.9 (Fig. 6). Mean CRs of OPAHs had a slightly higher range (0.41–1.02) than those of the low molecular weight (2–3 ring) parent PAHs; NAPH, 1-MNAPH, ACENY, ACEN, FLUO, PHEN, and ANTH (0.41–0.63, Fig. 6).

We correlated $\log CR$ values with $\log K_{OW}$ values of the carbonyl-OPAHs at each sampling site to assess factors controlling their vertical distribution (Guggenberger et al., 1996). For PAHs, there were significant positive correlations between $\log CR$ values and their $\log K_{OW}$ values at sites A, B, C, E and H ($r = 0.47$ – 0.86), a significant negative correlation at site D ($r = -0.42$) and no correlation at the remaining sites. Furthermore, there was a significant negative correlation between $\log CR$ values of carbonyl-OPAHs and their $\log K_{OW}$ values at sampling site D ($r = -0.77$). All other sites did not show correlations. We could not correlate $\log CR$ with $\log K_{OW}$ of hydroxyl-PAHs because their concentrations were too frequently below the detection limit in either topsoil or subsoil (Table 2).

4. Discussion

4.1. Spatial distribution of PAH concentrations and relationship with heavy metals

The study sites A–D, located in the immediate proximity to the Angren coal mining area and power plant, were most contaminated by PAHs and OPAHs (Fig. 2). Industrial combustion of coal for power generation and coal dust emanating from the coal mining activities are the likely main sources of PAHs and carbonyl-OPAHs at these sites. This is in line with other findings that coal dust contains high PAH concentrations (Stout and Emsbo-Mattingly, 2008; Achten and Hofmann, 2009) and combustion is a well known source of PAHs and OPAHs (Oda et al., 1998; Lima et al., 2005; Simoneit et al., 2007). The potential spread of PAHs with coal dust was also observed at a coal mine in India (Jharia coal field) where it is estimated that 9368 kg/day of coal dust is emitted because of mining activities and wind erosion of the exposed area (Ghose, 2007). The soils at all study sites contained both petrogenic PAHs including NAPH and PHEN and their alkyl-derivatives which are typical for coal dust emitted by the open-pit coal mining (Stout and Emsbo-Mattingly, 2008; Achten and Hofmann, 2009) and pyrogenic high molecular weight PAHs (Booth and Gribben, 2005; Neff et al., 2005). The PAH sources in soils can therefore be interpreted as mixtures of coal dust deposition and

Table 2
Concentration of individual OPAHs and Σ EPA-PAH and Σ 21PAHs at the 11 study sites (ng/g). Sampling depth 1 is at 0–10 cm and 2 at 10–20 cm.

Site/depth	1-INDA	1,4-NQ	1-NLD	2-BPCD	9-FLO	1,2-ACQ	9,10-ANQ	SALYD	2-NAPHTHOL	2-PP	1-ACENOL	9-FLUORENOL	Σ EPA-PAHs	Σ 21PAHs
A1	32.0	2.0	14	0.7	316	9.1	376	44.3	7.5	10.7	n.d.	n.d.	2550	2840
A2	5.9	0.6	3.1	0.4	62	3.7	107	6.8	n.d.	n.d.	n.d.	n.d.	3180	3720
B1	6.6	4.0	4.0	n.d.	410	14	293	19.7	3.8	7.1	n.d.	n.d.	2170	2380
B2	20.6	0.4	2.4	0.4	34	3.5	44	6.7	n.d.	3.4	4.5	2.3	825	936
C1	12.3	5.0	18	8.8	466	5.6	369	20.5	4.0	7.7	n.d.	n.d.	2480	2720
C2	7.4	3.6	11	0.4	252	5.9	315	13.5	4.2	5.0	n.d.	n.d.	2530	2890
D1	27.6	6.7	20.6	15.2	810	9.6	959	29.0	4.1	11.4	n.d.	n.d.	4230	4770
D2	22.1	2.3	9.0	0.4	117	5.7	82	13.0	n.d.	3.1	n.d.	n.d.	721	799
E1	26.9	1.6	7.1	25	107	4.5	67	20.1	n.d.	5.6	n.d.	n.d.	601	675
E2	15.4	0.7	3.4	0.4	41	2.6	32	7.4	n.d.	3.1	n.d.	n.d.	251	282
F1	35.0	0.8	7.3	0.4	113	3.7	119	17.2	3.8	6.3	n.d.	2.6	511	552
F2	11.6	0.7	3.9	0.4	53	3.4	54	7.2	n.d.	3.9	n.d.	2.3	313	341
G1	30.7	0.8	5.6	0.4	105	4.2	90	17.1	3.6	5.1	n.d.	n.d.	494	538
G2	10.2	0.8	3.1	0.4	43	2.9	53	6.9	3.6	3.6	n.d.	2.2	315	346
H1	2.1	2.8	14	5.4	349	6.7	155	7.0	7.1	7.6	n.d.	n.d.	1100	1150
H2	1.6	n.d.	1.9	n.d.	34	n.d.	23	4.6	n.d.	3.4	n.d.	n.d.	139	148
I1	13.5	n.d.	2.1	0.4	20	3.2	15	4.3	n.d.	3.3	n.d.	n.d.	78	85
I2	2.3	n.d.	1.4	n.d.	14	n.d.	12	4.6	n.d.	3.4	n.d.	n.d.	70	76
J1	9.5	0.4	2.5	0.3	37	3.2	36	10.7	n.d.	n.d.	n.d.	n.d.	307	339
J2	9.4	0.3	2.2	0.4	36	3.2	25	7.0	n.d.	n.d.	n.d.	n.d.	153	166
K1	25.2	0.7	5.3	0.4	80	3.5	40	15.8	3.7	4.3	n.d.	2.4	418	445
K2	29.6	0.5	4.1	0.4	43	3.5	41	7.0	3.6	4.0	n.d.	2.2	210	222

n.d. = not detected.

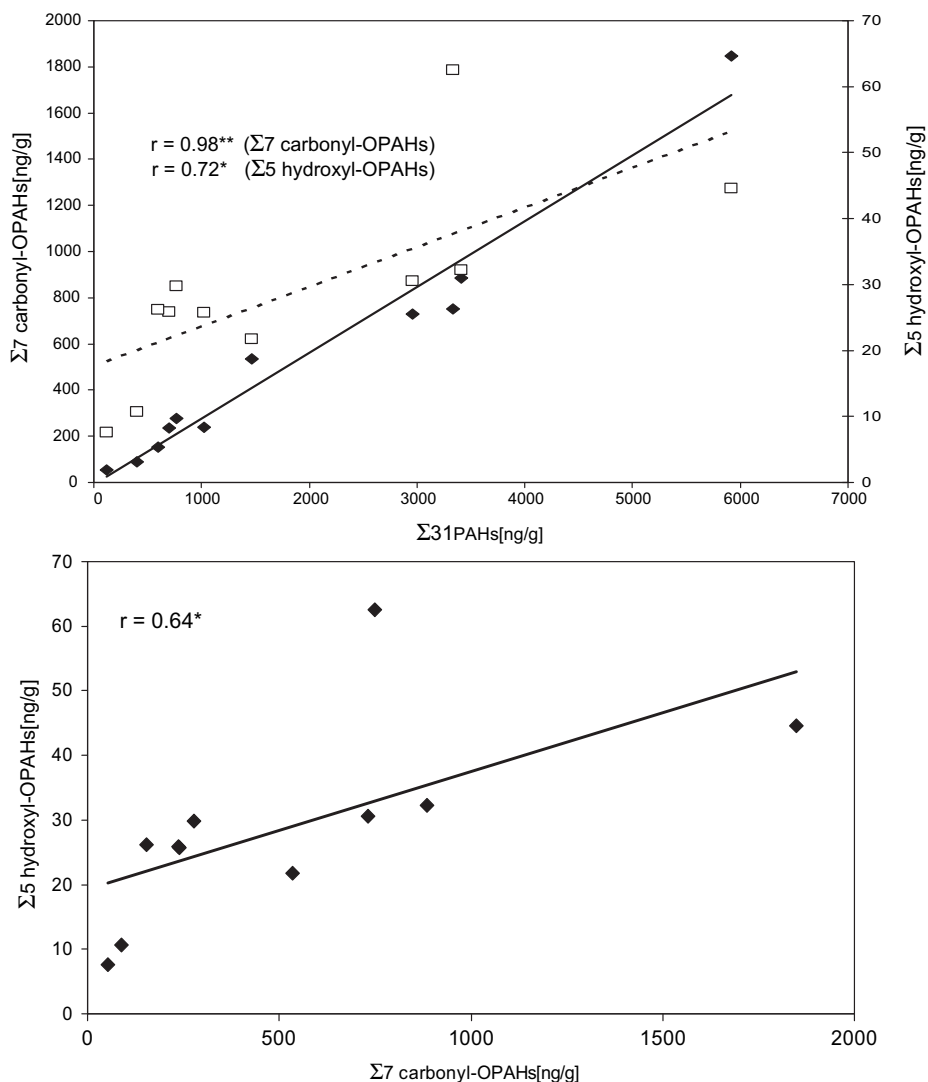


Fig. 5. Relation between concentrations of Σ 7 carbonyl-OPAHS (closed boxes), Σ 5 Hydroxyl-OPAHS (open boxes), and Σ 31PAHs (upper diagram), and between concentrations of Σ 5 Hydroxyl-OPAHS and Σ 7 carbonyl-OPAHS (lower diagram). ** Means $p < 0.01$ and * $p < 0.05$.

Table 3

Pearson correlation coefficient for $\Sigma 31$ PAHs, $\Sigma 7$ carbonyl-OPAHs, $\Sigma 5$ hydroxyl-OPAHs and selected trace metals in topsoils ($n = 8$). Correlation marked in bold are significant at $p \leq 0.05$ (two-tailed). Trace metal concentration were taken from Shukurov et al. (2009).

0–10 cm	$\Sigma 31$ PAHs	$\Sigma 7$ Carbonyl-OPAHs	$\Sigma 5$ Hydroxyl-OPAHs
Cu	0.49	0.50	0.23
Zn	0.78	0.77	0.35
Ba	0.78	0.82	0.32
Pb	0.75	0.75	0.32
Th	0.70	0.76	0.33
U	0.81	0.82	0.44

combustion-related emissions with varying mixing ratios. Between sites E and G, PAH and carbonyl-OPAH concentrations decreased with increasing distance from the main coal-related activities. At site H, the rubber factory again increased PAH and carbonyl-OPAH concentrations, while the gold refinery near site J did not seem to release significant amounts of PAHs and carbonyl-OPAHs.

According to the classification of Maliszewska-Kordybach (1996), sites A, B, C, D, and H were heavily polluted (> 1000 ng/g Σ EPA-PAHs), E contaminated (600–1000 ng/g), and the remaining sites weakly contaminated (200–600 ng/g) or not contaminated (I). Sites A–H showed comparable PAH concentrations in soil as reported for other PAH-contaminated soils (at industrial sites) in the literature while the soils at sites I–K were in the range of background soils with only diffuse ubiquitous contamination (Wilcke, 2000; Table 5).

PAHs are mostly accumulated in the topsoil because of strong sorption to soil organic matter or other adsorbing materials such as coal or soot (Table 2, Krauss et al., 2000; Cornelissen et al., 2005). Exceptions were sites A, C, and I. At sites A and C the soils likely have been disturbed so that a more contaminated material with elevated PAH concentrations reached greater soil depth by burial with other less contaminated soils. We observed that at site A, the uppermost soil layer (0–5 cm) was completely covered with dark-colored coal dust originating from the coal mine while at site C the uppermost soil layer (0–8 cm) was covered with particulates emitted from the stack of the Angren power plants. Other studies

from coal-impacted soils also demonstrated that the most polluted layer is sometimes not the topsoil (Pies et al., 2008; Yang et al., 2008). Contaminated subsoil at both locations is dominated by high molecular weight PAHs (Fig. 3A and C) which is typical of pyrogenic sources. At the agricultural site I, mixing of the top 20–30 cm of the soil by agricultural plowing might explain similar PAH and OPAH concentrations in topsoil and subsoil.

Some studies have suggested that higher molecular weight PAHs are deposited near emission sources because of their stronger association with particulates as a consequence of lower vapor pressure, while the more volatile lower molecular weight PAHs are deposited far from emission sources because they mainly occur in the gas phase (Yang et al., 1991). Such a trend appears to be visible between sites D and F (Fig. 4).

Further indication of industrial activity in the Angren area as source of PAHs and carbonyl-OPAHs is the close correlation with a number of heavy metals previously identified by Shukurov et al. (2009) as resulting from emissions of the industrial plants (Table 3). This is consistent with the lack of correlation of the concentrations of PAHs and carbonyl-OPAHs with those of C_{org} . Correlations between PAH concentrations and C_{org} can be considered as indication of the partitioning between a homogeneous background concentration in the atmosphere and soil (Wilcke and Amelung, 2000).

4.2. Spatial variation of the relationship of OPAHs with PAHs and heavy metals

The $\Sigma 7$ carbonyl-OPAHs concentrations in the contaminated Angren soils were higher than the 170 ng/g observed in a botanical garden topsoil of the German city of Mainz but lower than in soil at a former gasworks site in Berlin, Germany (15681 ng/g, Bandowe and Wilcke, 2010), and other contaminated soils including wood preservation sites in Sweden ($\Sigma 3$ carbonyl-OPAHs concentrations of 2870–134000 ng/g, Lundstedt et al., 2007), or creosote contaminated sites from northern Germany (6100–21800 ng/g for $\Sigma 2$ carbonyl-OPAHs; Meyer et al., 1999). The compounds 9-FLO and 9,10-ANQ dominating in Angren soils were also identified as major components of carbonyl-OPAHs mixtures in both particulate fractions of

Table 4

Concentration ratios of selected OPAHs to their corresponding parent PAHs (from which the OPAH may be derived by chemical or microbial transformation) in the study soils. Sampling depth 1 is at 0–10 cm and 2 at 10–20 cm.

Site/depth	1-INDA/FLUO	1,4-NQ/NAPH	1-NLD/1-MNAPH	2-BPCD/PHEN	9-FLO/FLUO	1,2-ACQ/ACENY	1,2-ACQ/ACEN	9,10-ANQ/ANTH
A1	3.40	0.01	0.24	0.00	34	0.82	0.95	44
A2	1.30	0.01	0.28	0.00	14	0.47	1.21	17
B1	0.27	0.01	0.04	0.00	17	1.39	1.63	13
B2	6.31	0.01	0.25	0.01	10	1.34	2.47	16
C1	0.85	0.01	0.17	0.02	32	0.31	0.57	27
C2	0.87	0.01	0.19	0.00	30	0.41	1.04	31
D1	1.11	0.01	0.13	0.01	33	1.01	0.51	37
D2	3.51	0.01	0.17	0.00	19	0.92	0.95	32
E1	3.53	0.01	0.15	0.20	14	0.82	0.91	17
E2	5.93	0.01	0.20	0.01	16	1.26	1.33	25
F1	4.15	0.01	0.26	0.00	13	0.59	0.99	41
F2	3.29	0.01	0.21	0.01	15	1.03	1.71	28
G1	4.75	0.01	0.25	0.00	16	1.02	1.46	42
G2	4.22	0.01	0.23	0.01	18	1.15	2.18	31
H1	0.77	0.01	0.21	0.02	126	1.08	1.29	35
H2	3.12	0.00	0.24	0.00	66	0.00	0.00	24
I1	11.82	0.00	0.50	0.02	18	5.10	5.46	20
I2	3.94	0.00	0.34	0.00	24	0.00	0.00	16
J1	4.61	0.01	0.25	0.01	18	1.21	2.36	22
J2	8.22	0.01	0.34	0.01	31	1.99	4.47	24
K1	5.08	0.01	0.19	0.00	16	0.57	1.20	17
K2	8.93	0.01	0.22	0.01	13	0.97	1.89	26
Average 1	3.67	0.01	0.22	0.03	31	1.27	1.58	29
Average 2	4.51	0.01	0.24	0.00	23	0.87	1.57	25

Numbers in bold indicate values > 1 .

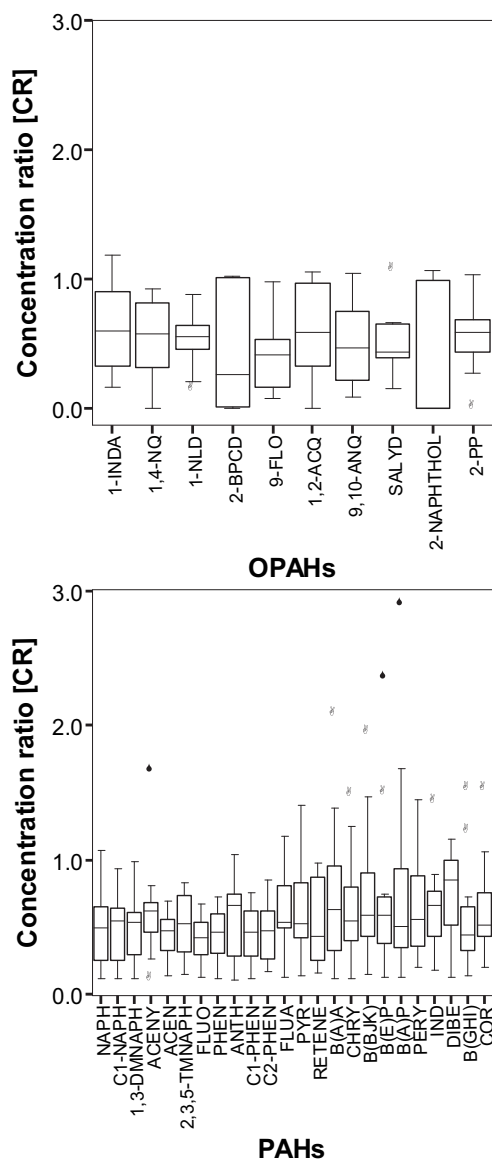


Fig. 6. Box plots of mean concentration ratios [CR] of PAHs and OPAHs of the 11 sampling points. CR is concentration ratio of individual PAH or OPAH in the subsoil to that of same compound in topsoil. Boxes define the range, the central line represents the median. Outliers (open circles) and extreme values (stars) are also shown.

atmospheric aerosol samples and in impacted soils (Lundstedt et al., 2003; Albinet et al., 2006, 2007, 2008; Liu et al., 2006).

The $\sum 5$ hydroxyl-OPAH concentrations were in the range or even lower than those in little contaminated topsoils in Germany and Brazil (9–26 ng/g), and clearly lower than in soil at a former gasworks site from Germany (383 ng/g, Fig. 2, Bandowe and Wilcke, 2010). The dominating hydroxyl-OPAH SALYD is one of the end products of all metabolic PAH degradation paths (Bamforth and Singleton, 2005). It can therefore also be produced during the biodegradation of other organic matter components in soil.

The close correlations between the $\sum 31$ PAHs concentrations and those of the $\sum 7$ carbonyl-OPAHs and $\sum 5$ hydroxyl-OPAHs (Fig. 5), and the close correlations among the individual PAHs and carbonyl-OPAHs except for PERY, RETENE, 1-INDA, and 2-BPCD concentrations in the topsoil and partly also in the subsoil, suggests that PAHs and carbonyl-OPAHs are jointly produced by combustion processes and coal mining activities and deposited together from the atmosphere to the study soils. The contribution of post-emission physico-chemical/microbial transformation processes might be limited because of the short travel distances and high soil contamination in the study area. This was already previously shown to negatively affect several indicators of biological activity in soil (Shukurov et al., 2009). However, the lack of correlations of PERY, RETENE, 1-INDA, and 2-BPCD with other PAHs/OPAHs indicates that these compounds have different sources. For PERY it is known that it can be produced biologically (Venkatesan, 1988), and RETENE was found in needles of coniferous trees (Sims and Overcash, 1983). 2-BPCD is a product of photooxidation of PHEN in water, a process enhanced by hydrogen peroxide and fulvic substances (Wang et al., 1995) and 1-INDA a microbial metabolic product of FLUO (Casellas et al., 1997).

For some OPAHs/corresponding parent PAHs, the concentration ratios were greater than 1, showing that the OPAHs were present in higher concentrations than their corresponding parent PAHs (Table 4). This was particularly evident for 9-FLO/FLUO and 9,10-ANQ/ANTH, and is in line with previous findings (Lundstedt et al., 2007; Bandowe and Wilcke, 2010). We attribute this to differences in vapor pressures between carbonyl-OPAHs and their parent PAHs. OPAHs have lower vapor pressures than their parent PAHs. Therefore, a larger part of the emitted carbonyl-OPAHs will be particle-associated and hence deposited nearer to the emission source than their parent PAHs (Yang et al., 1991; Allen et al., 1997; Albinet et al., 2006, 2007, 2008). Because of the high abundance of some OPAHs relative to their parent PAHs, it is necessary that OPAHs are included in monitoring programs given the high toxicity of some OPAHs compared to their parent PAHs.

Ratios of OPAHs/corresponding parent PAHs can be useful in several ways. For example, it is suggested that ratios of hydroxylated quinolines to parent-quinolines in tar oil contaminated sites

Table 5
PAHs concentrations (ng/g) in soils from other industrial areas in the world (ranges or means \pm standard deviations).

Region	Number of PAHs	Concentration [ng/g]	Reference
West Macedonia, Greece	16	55–359	Stalikas et al. (1997)
Eordaia basin, Greece	13	300–1600	Voutsas et al. (2004)
Ziar, Central Slovakia	20	151–2485	Wilcke et al. (1996)
Eastern Slovakia	21	53–1389	Wilcke et al. (2003)
Seine River basin, France	14	1670–5650	Motelay-Massei et al. (2004)
Taragona County, Spain	16	166–1002	Nadal et al. (2004)
Kohtla-Järve, Estonia	12	12390 \pm 9810	Trapido (1999)
El Paso, Texas (USA)	16	6–2226	De la Torre-Roche et al. (2009)
Tangu-Hangu industrialized zone, Tianjin, China	16	2430 \pm 1780	Zuo et al. (2007)
Agra (semi-arid region), India	14	13720 \pm 11900	Masih and Taneja. (2006)
Balaju industrial district, Kathmandu, Nepal	20	184–6899	Aichner et al. (2007)
Mosel and Saar river bank soils, Germany	45	12000–50000 ng/g	Pies et al. (2008)
Angren industrial region, Uzbekistan	31	118–5913 (0–10 cm) 104–3852 (10–20 cm)	This study

might be useful indicators of biological natural attenuation (Reineke et al., 2007). McKinney et al. (1999) suggested that the 9,10-ANQ/ANTH ratio could be used for source apportionment in sediments because sediments affected by point sources will have ratios < 1. On the other hand, those affected by long-range transported depositions will have ratios > 1 because of the advanced transformation of ANTH to 9,10-ANQ by photochemical reactions during atmospheric transport. However, at our study site, we did not observe a consistent direct relationship between distance from the emission source (i.e., the industrial works) and the 9,10-ANQ/ANTH or any other tested ratio. We attribute this to the short considered distance which does not allow for much transformation in the atmosphere and the joint continuous emission of OPAHs and PAHs. There were also no indications that with decreasing contamination the carbonyl-OPAH/corresponding parent-PAH ratios increased because of enhanced microbial degradation. On the contrary, the ratio was generally high at locations with higher PAH contamination (e.g. 9-FLO/FLUO at site H). This again is probably related to the dominance of carbonyl-OPAH deposition from the atmosphere over microbial production.

The significant positive correlation between $\sum 7$ carbonyl-OPAHs and trace metals identified to be produced from industrial emissions further indicate the common source of PAH, carbonyl-OPAH and these trace metals (Table 3). The lack of significant correlation between $\sum 5$ hydroxyl-OPAHs and these trace metals might be attributable to the fact that the concentrations of several hydroxyl-OPAHs were below the detection limit or that these hydroxyl-OPAHs might have additional sources such as degradation of other organic compounds in soil resulting in SALYD.

4.3. Mobility of OPAHs as compared to PAHs

Mean concentration ratios (CR, i.e. subsoil/topsoil concentration ratios) of OPAHs were sometimes higher than those of PAHs with similar number of fused rings (Fig. 6). Our results therefore suggest that in the sampled soils, OPAHs were only slightly (but not consistently) more mobile than their parent PAHs. The solubility differences between OPAHs and parent PAHs as well as previously reported column leaching experiments in the laboratory suggest a much bigger difference in mobility between OPAHs and corresponding parent PAHs than observed in our study (Weigand et al., 2002; Lundstedt et al., 2007). Log CR values of parent PAHs and carbonyl-OPAHs were only significantly negatively correlated with log K_{OW} values at sampling site D indicating that leaching of parent PAHs and carbonyl-OPAHs as dissolved solute occurred at this site. The small differences in CR between OPAHs and their parent PAHs, and the lack of negative correlation between log CR values of carbonyl-OPAHs/parent PAHs and their log K_{OW} values (except at site D) might in part be related to the prevalent semi-arid conditions providing little water for leaching. Small leaching rates also provided little opportunity for differential leaching of PAHs and OPAHs. Other reasons for these observations may be that not only the water solubility controls the transport of OPAHs in soil, but a range of interactions with the soil solid phase including hydrophobic interactions, anion sorption, ligand exchange, and complexation with Al and Fe oxides (Weigand et al., 2002). It has also been observed previously that the K_{OW} alone is unable to reliably predict the adsorption (and hence leaching) behavior of naphthalene and its oxygen-containing derivatives in soil, and that the electrostatic potential played a major role (Novosiad et al., 2005). Higher degradation rates of the more water soluble OPAHs, containing more labile and reactive functional groups compared to their parent PAHs might additionally affect the vertical distribution of OPAHs in relation to parent PAHs. It is e.g., possible that the faster OPAH than PAH degradation in the biologically more

active topsoil increase CR values of OPAHs relative to those of parent PAHs without a contribution of leaching which would even cause an overestimation of the small OPAH leaching rates at our study sites. Furthermore, some of our study sites are likely disturbed as indicated by higher PAH concentrations in the subsoil than in the topsoil at these sites (Fig. 2).

At sampling site D, the significant negative correlation between log CR values of PAHs and their log K_{OW} is consistent with other studies. This indicates that leaching as truly dissolved solute is the main mechanism of transport at this site leading to an enrichment of the less hydrophobic compounds in the subsoil layer. Positive relationships between log CR values of PAHs and their log K_{OW} values at the sites near the industrial works, and particularly near the open-pit coal mine were in contrast to findings reported for less contaminated and undisturbed sites (Guggenberger et al., 1996; Wilcke et al., 1996; Krauss et al., 2000). This might be attributable to a faster enrichment of petrogenic low molecular weight PAHs via deposition of coal dust than transport to the subsoil which decreases the log CR values of the low molecular weight PAHs, or burial of higher molecular weight PAHs in the subsoil at disturbed sites.

5. Conclusion

Our results support the hypothesis that PAH concentrations in soils are mainly controlled by distance to industrial activities with exception of the gold refinery that does not release significant amounts of PAHs.

The similarity in the spatial distribution of PAHs, carbonyl-OPAHs, and heavy metals suggests that these pollutants all result from combustion processes and emissions of coal dust and reached all study soils via deposition from the atmosphere. Exceptions were PERY, RETENE, 1-INDA, and 2-BPCD, for which biological and photochemical oxidation sources are more likely.

The mobility of OPAHs in the study soils was only marginally higher than that of low molecular weight parent PAHs which is likely attributable to the more complex interactions of OPAHs than of PAHs with soil. The subsoil/topsoil concentration ratios of PAHs and carbonyl-OPAHs were negatively correlated with K_{OW} values at the site with the highest PAH and carbonyl-OPAH concentrations near the power plant (site D). This indicates that leaching was an important transport mechanism at this site. Positive correlations of subsoil/topsoil concentration ratio of PAHs with K_{OW} values at several sites are attributable to different reasons including enrichment of low molecular weight PAHs in surface soil via deposition of coal dust, and burial of higher molecular weight PAHs in deeper soil.

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Appendix. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.envpol.2010.06.012.

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