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Polycyclic aromatic hydrocarbons (PAHs) and their polar derivatives (oxygenated PAHs, azaarenes) in soils along a climosequence in Argentina



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HIGHLIGHTS

- PAC concentrations were among the lowest ever reported.
- OPAHs occurred in all soils at similar or even higher concentrations than PAHs.
- The influence of anthropogenic PAC sources decreased from N to S.
- Atmosphere–soil partitioning was the main PAC source of the studied soils.
- Global distillation and biological production explained most of the PAC patterns.

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ABSTRACT

We evaluated the effects of soil properties and climate on concentrations of parent and oxygenated polycyclic aromatic compounds (PAHs and OPAHs) and azaarenes (AZAs) in topsoil and subsoil at 20 sites along a 2100-km north (N)–south (S) transect in Argentina. The concentrations of $\Sigma 29$ PAHs, $\Sigma 15$ OPAHs and $\Sigma 4$ AZAs ranged 2.4–38 ng g⁻¹, 0.05–124 ng g⁻¹ and not detected to 0.97 ng g⁻¹, respectively. With decreasing anthropogenic influence from N to S, low molecular weight PAHs increasingly dominated. The octanol–water partitioning coefficients correlated significantly with the subsoil to topsoil concentration ratios of most compounds suggesting leaching as the main transport process. Organic C concentrations correlated significantly with those of many compounds typical for atmosphere–soil partitioning. Lighter OPAHs were mainly detected in the S suggesting biological sources and heavier OPAHs in the N suggesting a closer association with parent-PAHs. Decreasing alkyl-naphthalene/naphthalene and 9,10-anthraquinone (9,10-ANQ)/anthracene ratios from N to S indicated that 9,10-ANQ might have originated from low-temperature combustion.

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1. Introduction

The priority pollutant group of polycyclic aromatic hydrocarbons (PAHs, e.g., US EPA, United States Environmental Protection Agency, 2008) has been extensively studied since their first detection in soil by Blumer (1961) because of their potential harmful effects on ecosystems and humans. However, their oxygen-containing (OPAHs) and N-heterocyclic derivatives (e.g., azaarenes, AZAs) have not although OPAHs and AZAs may be similarly or even more toxic than the parent-PAHs (Bleeker et al., 2002; Machala et al., 2001; Lundstedt et al., 2007; Lübcke-von Varel et al., 2011). At least some

OPAHs have been shown to occur at higher concentrations in soils than their related parent-PAHs (Lundstedt et al., 2007; Bandowe et al., 2010, 2011). Primary PAHs, OPAHs and AZAs are formed in any incomplete combustion process of organic matter and fossil fuels (Sims and Overcash, 1983; Warshawsky, 1992; Wilcke, 2000; Bleeker et al., 2002; Lundstedt et al., 2007). In the environment, soil is the largest reservoir of PAHs (Wild and Jones, 1995) and presumably also of OPAHs and AZAs.

Polycyclic aromatic hydrocarbons have been ubiquitously detected in soils even at sites far from industrial activity such as the polar regions pointing at long-range transport of PAHs (Hoyou et al., 1996; Wania and Mackay, 1996). According to the “Global Distillation” hypothesis of Wania and Mackay (1996) this should result in a fractionation of the PAH pattern according to the volatility of the individual compounds. In a study of soils along a climosequence in the North American prairie,

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indications for such a fractionation were found for naphthalene (NAPH) – the most volatile PAH – but not for any other PAH. The contribution of NAPH to the sum of the concentrations of 20 PAHs increased with decreasing mean annual temperature (Wilcke and Amelung, 2000). Nam et al. (2008) found a larger contribution of <4-ring PAHs in Norwegian background soils than in the UK which they interpreted as the result of fractionation during long-range transport. Recently, von Waldow et al. (2010), however, postulated that the latitudinal distribution of persistent organic pollutants may be mainly driven by differential removal of individual compounds because of compound-specific degradation and/or deposition and put forward the “Differential Removal” hypothesis. Neither the “Global Distillation” nor the “Differential Removal” models, however, take into consideration the fact that there might be natural in-situ production (e.g., biological sources of PAHs and azaarenes) of some organic pollutants (Kaiser et al., 1996; Wilcke, 2000, 2007; Michael, 2008; Cabrerizo et al., 2011). The results of Wilcke (2007) revealed that there is a close negative correlation between the contributions of the sum of NAPH and phenanthrene (PHEN) concentrations with the sum of eight high-molecular weight, presumably mainly anthropogenic PAHs. Furthermore, NAPH + PHEN usually contribute the more to total PAHs concentrations, the lower the total PAHs concentrations are, i.e. the less contaminated a soil is.

In several studies, a close correlation between PAHs and OPAHs concentrations in soils was reported (Lundstedt et al., 2007; Bandowe et al., 2010, 2011) suggesting similar sources (i.e. combustion processes, Ramdahl et al., 1982; Oda et al., 1998; Shen et al., 2011) and/or the production of OPAHs by transformation of PAHs in the atmosphere (photochemical and biological, Atkinson and Arey, 1994; Cerniglia, 1992) and in soil (biological and abiotic, Cerniglia, 1992; Lundstedt et al., 2006; Jonsson et al., 2007; Wilcke et al., 2014). In the atmosphere, OPAHs and azaarenes are to a larger extent bound to atmospheric particulates than their related parent-PAHs because of the lower vapor pressure of OPAHs and AZAs than PAHs. Because of the stronger association to atmospheric particulates and the higher water solubility of OPAHs and AZAs than of PAHs, the polar PACS should be faster removed from the atmosphere by deposition (Bidleman, 1988; Chen and Preston, 1997; Albinet et al., 2008). If secondary (photo)chemical and biotransformation sources played important roles, the OPAH to related parent-PAH concentration ratios should increase with increasing transport distance from the source in the atmosphere. In soil, microbial transformation of PAHs to OPAHs should be related with biological activity which is driven by climate and soil fertility (mainly pH, nutrient availability, organic matter concentration [Okere and Semple, 2012]). The higher the biological activity is, the higher should be the OPAH/PAH concentration ratios in soil. In a short-term incubation experiment of a fertile soil, it has been shown that microbial turnover of parent-PAHs produced some OPAHs resulting in increasing OPAH/PAH concentration ratios (Wilcke et al., 2014). The higher water solubility of OPAHs and azaarenes than of their related PAHs usually results in a faster vertical leaching in soils (Weigand et al., 2002; Lundstedt et al., 2007; Schlanges et al., 2008; Bandowe et al., 2011) although OPAHs could also interact more closely with soil solid phase because of their polar functional groups retarding transport in soil (Huang and Weber, 2004). Up to now, OPAH and AZA concentrations in soils were almost exclusively reported for urban or industrial soils and only a few studies reported the concentrations of OPAHs and AZA in background soil of Manaus (Brazil) and Sweden (Meyer et al., 1999; Lundstedt et al., 2003; Lundstedt et al., 2007; Biache et al., 2008; Bandowe and Wilcke, 2010; Brorström-Lundén et al., 2010; Bandowe et al., 2011). Our objectives were to (i) determine OPAHs, AZAs and PAHs concentrations in remote soils of Argentina to establish background concentration levels, (ii) determine the effects of varying soil properties and (iii) climate on the composition of the OPAHs, AZAs, and PAHs mixtures, concentration ratios of selected OPAHs to parent-PAHs, and OPAHs and AZAs leaching along a climosequence.

2. Materials and methods

2.1. Sampling and soil characterization

Samples of the uppermost topsoil and the first subsoil horizons were collected at 20 sampling sites along a 2100-km N–S transect from the Argentinean Pampas to the Patagonian Steppe in March and April 2010 (Fig. S1, Table S1). The sampling sites were located at distances of 70–160 km from each other at the Atlantic side of Argentina. The transect covers a large climate gradient, from warm humid subtropical conditions in the N to warm semiarid and arid conditions in the central part, and warm humid temperate conditions in the S. Mean annual temperature and precipitation at the sampling sites range from 11.4 °C to 18.0 °C and 185 mm a⁻¹ to 1100 mm a⁻¹, respectively. From N to S, the humid Pampa grasslands border sharply to the semiarid Espinal steppe and scrublands which form a narrow transition zone to the arid Low Monte semidesert scrublands. Further south, the xerophytic grasslands of the semiarid Patagonian steppe form a large, comparatively homogeneous ecoregion. Elevation ranged from 20 to 950 m above sea level (a.s.l.).

For basic characterization, all samples were pre-dried in air during the sampling campaign and later dried at 50 °C in a laboratory drying furnace while for PACs analysis we froze the samples and stored them at –20 °C during transport and storage in the laboratory until analysis. Dried samples were ground in a ball mill. Concentrations of C and nitrogen were determined with an Elemental Analyzer (EA) (vario EL III, Elementar Analysensysteme, Germany). Carbon concentrations measured after combusting the soil samples for 4 h at 550 °C in a muffle furnace were assumed to be inorganic (C_{inorg}) and organic C (C_{org}) concentrations were calculated as the difference of the total C and C_{inorg} concentrations. We did not detect C_{inorg}. Soil pH was determined with a glass electrode in 1 M KCl at a soil:solution ratio of 1:2.5. Texture was determined with the pipette method after destruction of carbonates with HCl and organic matter with H₂O₂, and wet sieving of the >0.50 µm fraction.

2.2. PAHs, OPAHs and AZAs analyses

For PACs analysis, frozen soil samples were thawed and extracted in moist state to avoid volatilization during sample drying. We determined the concentrations of 29 PAHs and alkyl-PAHs: naphthalene (NAPH), 2-methylnaphthalene (2-MNAPH), 1-methylnaphthalene (1-MNAPH), 1,3-dimethylnaphthalene (1,3-DMNAP), acenaphthylene (ACENY), acenaphthene (ACEN), fluorene (FLUO), phenanthrene (PHEN), anthracene (ANTH), 1-methylphenanthrene (1-MPHEN), 3,6-dimethylphenanthrene (3,6-DMPHEN), fluoranthene (FLUA), pyrene (PYR), 1-methyl-7-isopropylphenanthrene (RET), benz[a]anthracene (B(A)A), chrysene + triphenylene (CHRY), benzo[b + j + k]fluoranthenes (B(BJK)), 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)), coronene (COR) and additionally 1,2,3,4-tetrahydronaphthalene (THNAPH) and biphenyl (BP) which strictly seen do not belong to the PAHs; 15 carbonyl-OPAHs: 1-indanone (1-INDA), 1,4-naphthoquinone (1,4-NQ), 1-naphthaldehyde (1-NLD), 2-biphenylcarbox-aldehyde (2-BPCD), 9-fluorenone (9-FLO), 1,2-acenaphthylene-dione (1,2-ACQ), 9,10-anthraquinone (9,10-ANQ), 4H-cyclopenta[d,e,f]phenanthrene-4-one (CPHENone), 1,8-naphthalic anhydride (1,8-NAA), 2-methyl-9,10-anthraquinone (2-MANQ), benzo[a]fluorenone (B(A)FLUone), 7H-benz[d,e]anthracene-7-one (BANTone), benzo[a]anthracene-7,12-dione (7,12-B(A)A), 5,12-naphthacenequinone (5,12-NACQ), 6H-benzo[c,d]pyrene-6-one (BPYRone), and 4 azaarenes: quinoline (QUI), benzo[h]quinoline (BQI), acridine (ACR), and carbazole (CBZ). About 15 g of each soil sample was mixed with inert bulk sorbent (Isolute HMN, Biotage, Uppsala, Sweden), placed in a 33 ml accelerated solvent extraction (ASE) cell and spiked with a mixture of 7 deuterated PAHs (NAPH-D₈, ACEN-D₁₀, PHEN-D₁₀, PYR-D₁₀, CHRY-D₁₂, PERY-D₁₂

and B(GHI)-D₁₂: 70 µl of 5 µg ml⁻¹ in toluene), benzophenone-D₅ (70 µl of 5 µg ml⁻¹ in toluene) as internal standards for the parent + alkyl-PAHs and carbonyl-OPAHs + AZAs, respectively. After spiking the soil samples and blanks (made of 100% inert bulk sorbent) with the internal standards, extra space in extraction cells was filled with more inert bulk sorbent and extracted twice using ASE (ASE 200, Dionex, Sunnyvale, CA, USA). The ASE instrumental conditions and solvents used to extract the samples and blanks were the same as in Bandowe and Wilcke (2010). After extractions, the two extracts from each sample were combined and filtered through baked Na₂SO₄ to dry the extracts. Each combined extract was rotary evaporated, solvent exchanged to hexane, transferred onto a silica gel (10% deactivated) column and fractionated into a parent + alkyl-PAH-containing fraction and an OPAHs + AZAs-containing fraction using a series of solvents with increasing polarity as previously described (Bandowe and Wilcke, 2010). A few drops of toluene (as keeper) were added to the parent + alkyl-PAH-containing fraction, rotary evaporated to about 0.5 ml, spiked with FLUA-D₁₀ (100 ng in toluene) and transferred to a 2 ml vial for GC-MS measurements. The OPAHs + AZAs-containing fraction from each sample was treated similarly and transferred to a separate 2 ml vial for GC/MS measurements. All samples were analyzed using an Agilent 7890 N gas chromatograph coupled to an Agilent 5975C mass selective detector. Target compounds were separated on a HP-5MS column (5% phenyl- 95% methyl-polysiloxane, 30 m × 0.25 mm × 0.25 µm film thickness) and measured with GC/EI-MS in the single-ion monitoring (SIM) mode to quantify the carbonyl-OPAHs + AZAs and parent + alkyl-PAHs. The OPAHs and AZAs were measured in one GC/MS analytical run for which the conditions reported by Bandowe et al. (2011) were only slightly modified to include the relevant mass spectra of target and qualifier ions for AZAs. The GC/MS conditions used for the measurement of OPAHs and parent + alkyl-PAHs were the same as specified previously (Bandowe and Wilcke, 2010). The criteria used to identify target compounds in sample extracts included the comparison of retention times, qualifying and qualifier ions and the ratios of quantifying ion to qualifier in extracts to those in standards measured together with samples. Target compounds were considered to be identified in samples when retention time was ± 0.2 min and the ratio of quantifying to qualifier ions was within ± 20% of those of the calibration standards measured together with samples within same GC/MS measurement sequence. Target compounds were quantified by the internal standard technique using calibration standards which were each spiked with a constant mass of internal standards (same mixture as spiked to the samples before extraction). GC/MS data were recorded, processed and quantified with Agilent MSD ChemStation software package.

2.3. Quality assurance and quality control

All solvents used for our analyses were of high purity pesticide residue grade (Carlo Erba, Milan, Italy). Glassware and metallic glassware were rinsed with acetone, machine-washed with soap, dried and baked at 250 °C for 24 h and further rinsed with the appropriate high purity pesticide residue grade solvents before use. The limit of detection (LOD) of our measurement was defined as the mass of the target compound that produces a mass spectrometric signal which is three times higher than the baseline noise. LODs were derived using a typical extracted soil mass of 15 g. Quantified masses of target compounds (that were higher than the LODs) were blank-corrected before their concentrations in soil were calculated. LODs of alkyl- and parent-PAHs, OPAHs and AZAs ranged 0.002–0.131, 0.031–0.235, and 0.045–0.136 ng g⁻¹, respectively. The recoveries of the seven deuterated PAHs added as internal standards averaged 92% (range: 67–126%). The accuracy of the determination of our target compounds was checked by analysis of the certified reference material ERM-CC013a-PAHs in soils (Federal Institute for Materials Research Testing [BAM], Berlin, Germany) with

the same method as described above along with the Argentinean samples. The mean recovery of PAHs from ERM-CC013a-PAHs for which certified and indicative values are provided by the BAM was 106 ± 5% (n = 2 independent extractions of the certified reference material).

2.4. Data evaluation and statistical analysis

The sum of the concentrations of all analyzed 29 parent- and alkyl-PAHs (including THNAPH and BP), 15 carbonyl-OPAHs, and 4 AZAs is reported as ∑ 29PAHs, ∑ 15OPAHs, and ∑ 4AZAs, respectively. The sum of the 21 parent-PAHs is reported as ∑ 21PAHs and that of the 6 alkyl-PAHs as ∑ 6Alkyl-PAHs. The sum of the concentrations of 4–6 ring high molecular weight, combustion-derived parent-PAHs (i.e. FLUA, PYR, B(A)A, CHRY, B(BJK), B(E)P, B(A)P, PERY, IND, DIBE, B(GHI) and COR) is ∑ 15Comb-PAHs and the sum of low (2–3 ring) molecular weight parent-PAHs (NAPH, ACENY, ACEN, FLUO, PHEN, and ANTH) ∑ LMWPAHs. The octanol–water partition coefficients (K_{OW}) of PAHs and alkyl-PAHs were taken from Neff et al. (2005) and Mackay et al. (2006), and those of OPAHs and AZAs were estimated from EPI Suite version 4.11 from US EPA (<http://www.epa.gov/opptintr/exposure/pubs/episuitd.htm>) verified on 05/12/2012. Data sets of explanatory variables (soil properties and geographical attributes) were not transformed if the skewness was < 0.5, root square-transformed if the skewness was between 0.5 and 1 and log(x + 1)-transformed if the skewness was > 1 (Webster, 2001). Concentrations of target compounds were generally log(x + 1)-transformed to approximate normal distribution before correlation and regression analyses. The influence of climatic and soil properties was assessed with the help of simple and multiple correlation and regression analyses following the least-squares method after principal component analysis (varimax normalized on the log-transformed data) to detect the interrelations of the used climatic and soil properties. All statistical analyses were conducted with STATISTICA (Statsoft, Tulsa, OK, USA). Significance was set at p < 0.05.

3. Results and discussion

3.1. Concentrations and patterns of PACs

We detected concentration ranges of 1.8–34 (mean: 8.5) ng g⁻¹ for ∑ 21PAHs 1.7–31 (7.5) for ∑ 16EPA-PAHs, 0.30–1.6 (0.72) for ∑ 6Alkyl-PAHs, 0.1–124 (17) for ∑ 15OPAHs, and n.d.–0.97 (0.24) for ∑ 4AZAs, respectively (Tables S2 and S3). The concentrations of parent-PAHs were at the lowest end of the concentration range of two published global data sets (3.6–17000 ng g⁻¹ of ∑ 16EPA-PAHs [Wilcke, 2007] and < 0.1–7836 ng g⁻¹ of ∑ 15PAHs [Nam et al., 2009]). The PAH concentrations in Argentinean soils were consistently at the lower end of those in Brazil of 4.8–347 ng g⁻¹ for ∑ 20PAHs concentrations (Wilcke et al., 2003). The difference in PAH concentrations between the remote Brazilian and Argentinean soils might be attributable to a higher microbial NAPH, PHEN and PERY production in the tropical soils of Brazil than in the temperate soils of Argentina and possibly also to a higher vegetation fire activity in Brazil than in Argentina (Wilcke et al., 2000, 2003; Wilcke, 2007). Another explanation might include a more pronounced long-distance transport from the densely populated Brazilian Atlantic coast to inland with the dominating easterly trade winds while the dominating westerly winds in Argentina might drive some PAHs emissions over the Atlantic.

The ∑ 15OPAHs concentrations showed a broader concentration range than the parent-PAHs and were higher than ∑ 21PAHs concentrations at 11 of the 20 study sites. The ∑ 15OPAHs concentrations were at the lower end of reported values (23–543,000 ng g⁻¹ of ∑ 3–18OPAHs, Bandowe et al., 2011). Our results indicate that the background concentrations of OPAHs tend to be higher than those of parent-PAHs. The AZAs were only detected in some of the study soils (each of QUI and CBZ in four soils and each of BQI and ACR in one soil, respectively) and only in one soil two AZAs were simultaneously detected.

The topsoil patterns of parent-PAHs were on average dominated by NAPH > B(BJK) > PHEN, those of alkyl-PAHs by 1-MNAPH > 2-MNAPH > 1,3-DMNAPH (Fig. 1A) and those of OPAHs by 2-MANQ > 1-INDA > BPYRone (Fig. 1B). While the high contributions of NAPH and PHEN to the $\Sigma 21$ PAHs concentrations are typical for remote locations and likely mainly of biological origin, that of B(BJK) belonging to the combustion-derived PAHs reflects some anthropogenic influence (Wilcke, 2007). Both, the biological origin of NAPH and PHEN and the combustion-derived origin of B(BJK) are supported by our finding that the contributions of NAPH + PHEN to the $\Sigma 21$ PAHs concentrations correlated significantly negatively and those of B(BJK) significantly positively with the $\Sigma 15$ Comb-PAHs concentrations as indicators of the degree of contamination (Fig. 2). In addition, we found significant negative relationships between the $\Sigma 15$ Comb-PAHs concentrations and the contributions of ACENY ($r = -0.53$, $p = 0.017$), FLUO (-0.71 ,

<0.001), and ANTH (-0.55 , 0.012) and significant positive ones for FLUA (0.45 , 0.047), CHRY (0.46 , 0.042), B(E)P (0.63 , 0.003), and COR (0.63 , 0.003) illustrating that the low molecular weight compounds had either other sources than the high molecular weight compounds, were preferentially removed by degradation, or were transported further away (as compared to co-emitted Comb-PAHs) from their emission sources (Wania and Mackay, 1996; Wilcke et al., 2000, 2007; von Waldow et al., 2010).

The fact that besides NAPH, the methyl-NAPHs were the dominating alkyl-PAHs suggests that methyl-NAPHs may also have biological sources although both, NAPH and alkyl-NAPH may also originate from vegetation fires (Masclat et al., 1987) and possibly volcanic exhalations. Among the three most abundant OPAHs, only 1-INDA was previously described as frequently dominating the OPAHs mixture (Bandowe et al., 2011). The 9,10-ANQ which also belonged to the dominating

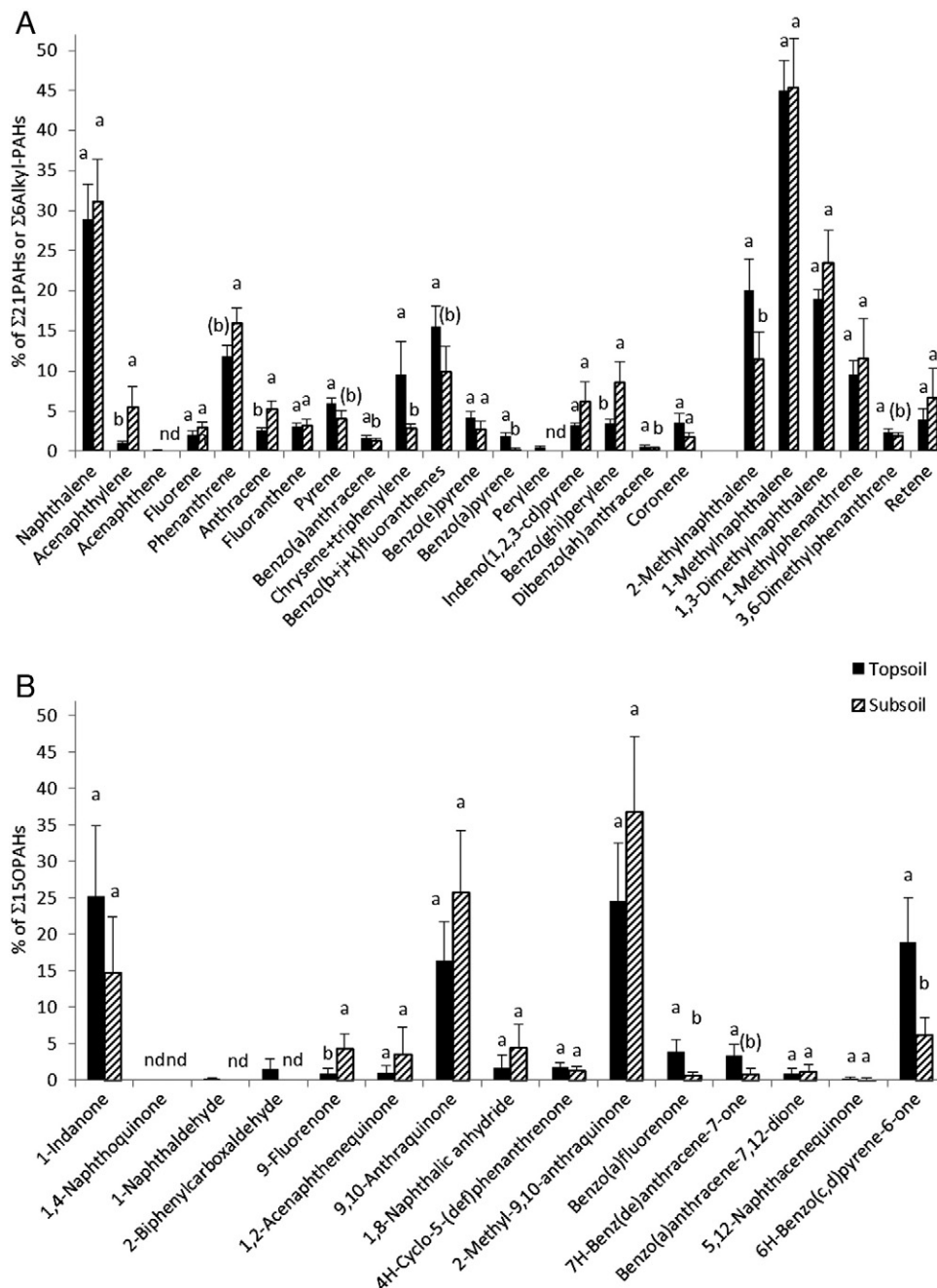


Fig. 1. Mean contributions of (A) PAHs to the $\Sigma 21$ PAHs concentrations and (B) OPAHs to the $\Sigma 15$ OPAHs concentrations in 20 topsoil and subsoil samples, respectively. Different letters indicate significant differences at $p < 0.05$ or $p < 0.10$ (in parentheses) according to the Wilcoxon matched pairs test. Error bars represent the standard errors.

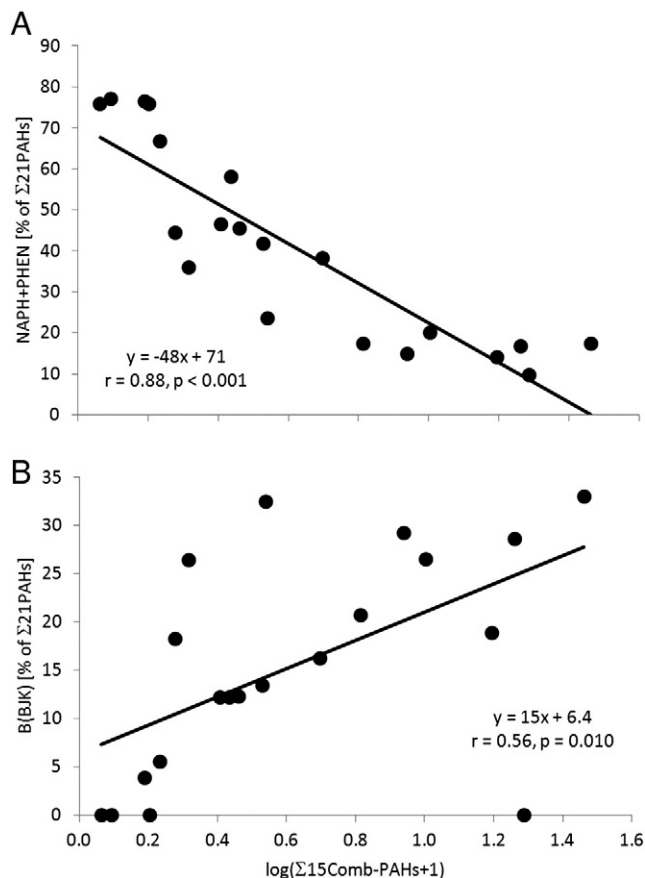


Fig. 2. Relationship between the $\Sigma_{15}\text{Comb-PAHs}$ and the contributions of (A) B(BJK) and (B) NAPH + PHEN to the $\Sigma_{21}\text{PAHs}$.

compounds in previous studies contributed on average 16% to the $\Sigma_{15}\text{OPAHs}$ and its methylated derivative was the most abundant compound (and not included in previous studies). However, 9-FLO – an abundant compound in the temperate zone of the northern hemisphere (Lundstedt et al., 2003; Albinet et al., 2007; Bandowe et al., 2011) – was only detected in two of the 20 soils at low concentrations (2.8–3.8 ng g⁻¹). The concentrations of $\Sigma_{21}\text{PAHs}$ and the $\Sigma_{15}\text{Comb-PAHs}$ did not correlate significantly with those of $\Sigma_{15}\text{OPAHs}$ ($r = 0.34$, $p = 0.132$ and $r = 0.38$, $p = 0.100$) illustrating that in remote soils other formation processes of OPAHs (photochemical, biological) during atmospheric transport or after deposition in the soils are more important than the primary sources (combustion processes).

In the subsoil, the compositions of the parent-PAHs, alkyl-PAHs, and OPAHs mixtures were similar to the topsoil (Fig. 1). However, the contributions of lower molecular weight (LMW) compounds were partly significantly higher in subsoil than in topsoil while for the higher molecular weight (HMW) compounds the reverse was true except for DIBE which showed – at a low concentration level – a significantly higher contribution to the $\Sigma_{21}\text{PAHs}$ concentrations in the subsoil than in the topsoil. The reason for this systematic shift in composition of the compound mixtures is likely the preferred leaching of LMW compounds. The latter is supported by the fact that the mean subsoil:topsoil concentration ratios (CR) of all 20 study sites were significantly negatively correlated with K_{ow} values (Fig. 3), even if the two outliers (CPHENone and B(A)FLUone) in Fig. 2 were included in the correlation ($r = 0.48$, $p = 0.005$).

3.2. Effect of soil properties on concentrations of PACs

To identify statistically independent variables we first ran a principal component analysis (PCA) on the available soil properties. The result of the PCA revealed sand, nitrogen, clay and sulfur concentrations as

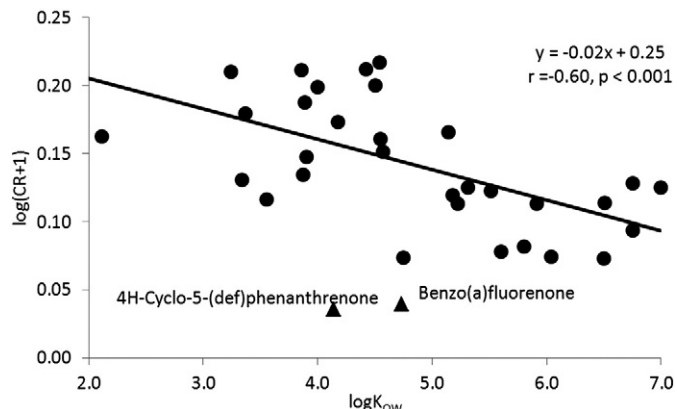


Fig. 3. Relationship between octanol–water-partitioning coefficient (K_{ow}) and mean subsoil:topsoil concentration ratios (CRs) of 18 parent-PAHs, 6 alkyl-PAHs, and 11 OPAHs. ACEN, B(A)P, PERY, 1,4-NQ, 1-NALD, 2-BPCA, and 1,2-ACNQ were not detected in the subsoil and therefore their CRs were omitted. The CRs of 4H-cyclo-5-(def)phenanthrene and benzo(a)fluorene were considered as outliers. CRs > 2 were eliminated as outliers prior to this analysis.

independent variables with the highest positive or negative loadings on one of the four extracted PCs with eigenvalues > 1 (Table 1). The nitrogen concentrations were closely correlated with the OC concentrations and thus are indicative of the organic matter concentrations of the study soils which are usually represented by OC concentrations. We therefore also used OC concentrations for our further evaluation. Sand concentrations represented the soil development because sand concentrations were closely correlated with the fraction > 2 mm. Clay concentrations likely represented (together with silt concentrations) the water holding capacity of the study soils. The sulfur concentrations which were closely correlated with inorganic C concentrations likely represented the influence of salts in the study soils. There were significant correlations of nitrogen, OC, and sand concentrations with many individual concentrations of the 48 studied PACs, respectively, while there were only two significant correlations of clay and sulfur concentrations with individual compound concentrations. Sand concentrations were negatively correlated with nitrogen ($r = -0.65$, $p = 0.003$) and OC concentrations ($r = -0.57$, $p = 0.011$) and correlations of sand with individual PAC concentrations were generally weaker (with few exceptions) than those of nitrogen and OC (results not shown). We therefore conclude that nitrogen and OC concentrations are the more important drivers of compound concentrations than sand. It is interesting to note that only OPAHs with molecular weight ≥ 208 g mol⁻¹ (9,10-ANQ and heavier) showed significant correlations with OC concentrations while the lighter ones did not. Faster leaching, degradation and in-situ formation (from microbial degradation of LMWPAHs) of the lighter OPAHs could explain the observed result. The QUI concentrations correlated significantly with those of sand ($r = -0.82$, $p < 0.001$) and the BQJ concentrations with those of clay ($r = 0.80$, $p < 0.001$) suggesting

Table 1
Principal component loadings of soil properties (for transformations see text). Factor analysis was varimax rotated and only factors with eigenvalues > 1 were accepted.

	PC1	PC2	PC3
Water content	0.66	-0.27	0.07
Clay	-0.08	-0.91	-0.02
Silt	0.13	-0.89	-0.12
Sand	-0.90	0.12	0.11
Fraction > 2 mm	-0.76	0.35	0.28
pH	-0.68	0.37	0.28
Organic C	0.90	0.10	0.02
Nitrogen	0.95	0.16	0.01
Inorganic C	-0.15	-0.03	0.91
Sulfur	0.02	0.16	0.93
Eigenvalues	4.37	2.07	1.52

that for the retention of the more polar AZAs soil minerals had a larger importance than organic matter (Burgos et al., 2002; Bi et al., 2006). The correlation between organic matter concentrations and concentrations of PACs is typical of the partitioning between the atmosphere with a homogeneous PAC concentration and soil (Wilcke et al., 2000; Nam et al., 2008, 2009) and thus reflects the fact that the remote study sites were loaded by the diffuse background PAC concentration in the atmosphere but little affected by local direct sources.

Soil OC concentrations were positively correlated with CRs for a number of mainly HMW alkyl- and parent-PAHs (3,6-DMPHEN, RET, B(A)A, CHRY, B(E)P and COR, $r = 0.50\text{--}0.80$, $p = 0.033\text{--}0.018$) suggesting that at higher OC concentrations dissolved organic matter (DOM) concentrations were elevated which allowed for a more pronounced DOM-associated vertical PAC transport (Enfield et al., 1989; Johnson and Amy, 1995; Totsche et al., 1997).

3.3. Effect of geographic location and climate on concentrations of PACs

The PCA of the site and climate variables revealed that only geographic latitude and mean aridity index were independent variables (Table 2). Latitude and elevation were negatively correlated. Therefore, latitudinal and elevational effects could not be separated in our data set.

Latitude correlated weakly but significantly positively with both $\Sigma 15\text{Comb-PAHs}$ and $\Sigma 15\text{OPAHs}$ but negatively with the LMWPAHs concentrations while there were no significant correlations between latitude and $\Sigma 21\text{PAHs}$, $\Sigma 6\text{Alkyl-PAHs}$ or $\Sigma 4\text{AZAs}$ concentrations (Fig. 4). Latitude also showed significant negative correlations with the concentrations of THNAPH ($r = -0.45$, $p = 0.046$), BP (-0.77 , <0.001), and FLUO (-0.79 , <0.001) and positive ones with most other compounds (1-MPHEN, FLUA, PYR, RET, B(A)A, B(BJK), B(E)P, B(A)P, B(GHI), DIBE, and COR, $r = 0.45\text{--}0.66$, $p < 0.048$). Thus, the concentrations of combustion-derived PAHs decreased from N to S with decreasing influence of anthropogenic activities because of the decreasing population density in the same direction, while the reverse was true for the LMWPAHs (Fig. 4B). Although the dominating wind direction in most of Argentina is westerly, there are also substantial contributions of northerly wind, particularly close to the Atlantic coast where most of our study sites are located, allowing for atmospheric transport of PACs from N to S (Del Valle et al., 2008). Similar N to S trends have been reported for the concentrations of other persistent organic pollutants in the atmosphere in Chile (Shunthirasingham et al., 2011). Increasing LMWPAH concentrations can be explained by the combination of preferential atmospheric transport in gaseous form from N to S according to the “Global Distillation” hypothesis of Wania and Mackay (1996) and preferential elimination of LMWPAHs because of the higher temperature and moisture in the northern part of the study transect according to the “Preferential Removal” hypothesis of von Waldow et al., 2010 (Table S1). AZAs were detected in 13 of the 20 study sites of which eight were in the northern half and five in the southern half. While QUI

Table 2

Principal component loadings of the geographic and climatic site properties (for transformations see text). Factor analysis was varimax rotated and only factors with eigenvalues >1 were accepted.

	PC1	PC2
Latitude	0.76	0.64
Longitude	0.68	0.70
Elevation	-0.84	-0.41
Mean annual precipitation	0.38	0.92
Mean annual maximum temperature	0.94	0.31
Mean annual minimum temperature	0.86	0.37
Mean annual temperature	0.93	0.35
Mean annual relative humidity	0.40	0.90
Mean annual potential evapotranspiration	0.88	0.38
Mean annual aridity index [P/PET]	0.25	0.96
Eigenvalues	8.33	1.18

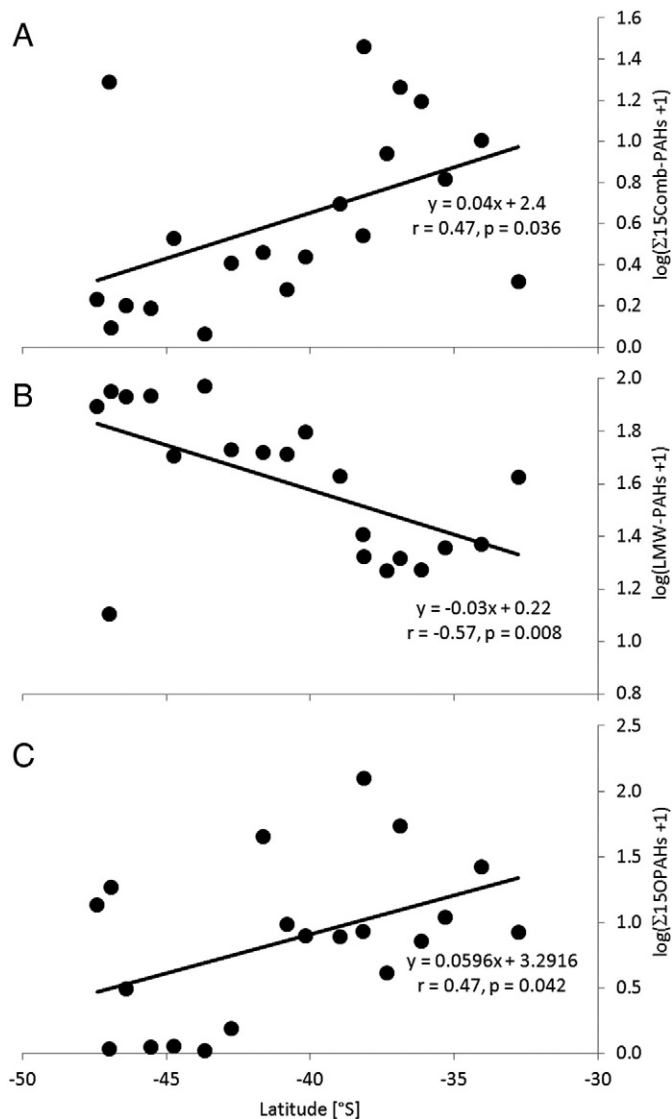


Fig. 4. Relationships between latitude and (A) $\Sigma 15\text{Comb-PAHs}$, (B) LMWPAHs, and (C) $\Sigma 15\text{OPAHs}$ concentrations in topsoil.

mainly occurred in the northern half, the other three compounds were not detected in the eight northernmost sites. The fact that the most volatile AZA mainly occurred in the northern part while the less volatile AZAs occurred (occasionally) in the southern part which is in contrast to the distribution of LMW and HMW compounds of the other groups suggests that there were specific sources of QUI perhaps associated with combustion processes and of BQI, ACR, and CBZ more likely associated with in-situ biological processes (emissions from plants and/or microbes and local vegetation fires (Table 2, Kaiser et al., 1996; Michael, 2000; Michael, 2008)).

There were significant negative correlations between latitude and contributions of a compound to the $\Sigma 21\text{PAHs}$ and $\Sigma 6\text{Alkyl-PAHs}$, respectively, for several LMWPAHs including NAPH (Fig. 5A), 1-MNAPH ($r = -0.59$, $p = 0.006$), FLUO (-0.69 , 0.001), PHEN (-0.69 , 0.006) and significant positive correlations for many HMWPAHs including FLUA (0.57 , 0.009), PYR (0.62 , 0.003), RET (0.46 , 0.041), B(A)A (0.54 , 0.013), B(BJK) (Fig. 5B), B(E)P (0.84 , 0.001), B(A)P (0.59 , 0.006), B(GHI) (0.63 ; 0.003), and COR (0.67 , 0.001). These results can either be explained by increasing influence of in-situ natural sources of these PAHs and local vegetation fires with decreasing PAH

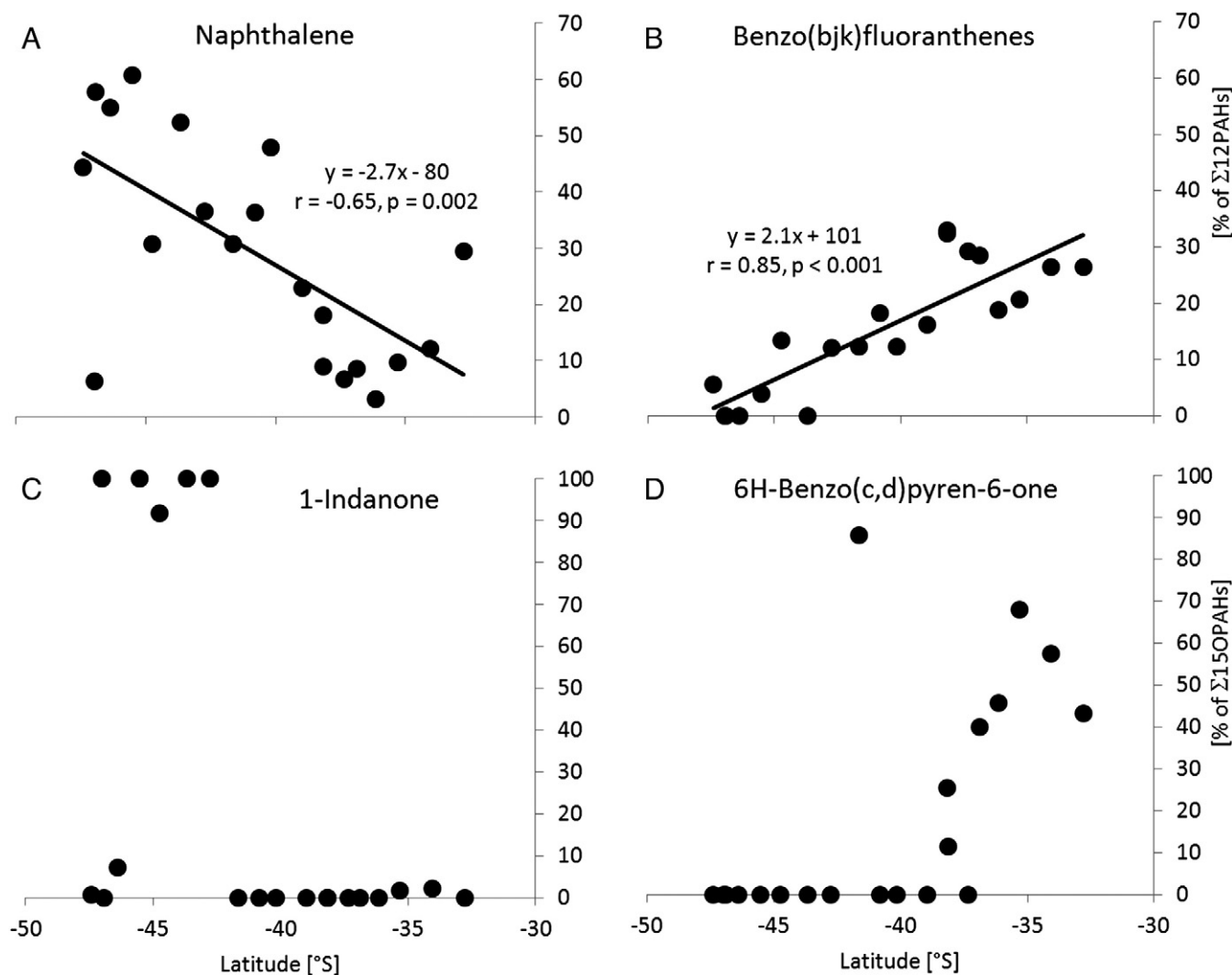


Fig. 5. Relationships between latitude and (A) NAPH, (B) B(BJK), (C) 1-INDA and (D) BPYRone contributions to the respective sum of compound concentrations.

load or by the “Global Distillation” hypothesis (Wania and Mackay, 1996). The “Preferential Removal” hypothesis (von Waldow et al., 2010) might be less supported by the data because PAH degradation and volatilization depend to a large degree on the available soil moisture which showed a minimum at Study Sites 11–14 and was higher N and S of these sites (Table S1, see also rainfall patterns in Fig. S1). Furthermore, it is, unlikely that increasing LMWPAHs concentrations from N to S can be related to volcanic activity because the plume of the recent volcanic exhalations mainly affected the central part of our transect (Watt et al., 2009). Among the OPAHs, 1-INDA was the only compound that was more frequently detected and contributed more to the $\Sigma 15\text{OPAHs}$ concentrations in the southern half of the transect (Study Sites 10–20) than in the northern half (Fig. 5C). All other OPAHs which were detected at more than two study sites occurred in contrast more frequently and contributed more to the $\Sigma 15\text{OPAHs}$ concentrations in the northern part of the study transect (Table S3, Fig. 5D). These results suggest that 1-INDA had in-situ natural sources which was also already suspected by Bandowe et al. (2011) for soils of Bratislava or alternatively was preferentially transported (because of its high volatility and presence in the gas phase of air) to the S while the other OPAHs originated from primary sources which were more abundant in the N.

Elevation only correlated significantly with a few individual compound concentrations including the lower molecular weight PAHs BP ($r = 0.69$, $p = 0.001$) and FLUO (0.68 , 0.001) and the high molecular weight PAHs RET (-0.46 , 0.040) and B(BJK) (-0.46 , 0.043).

Furthermore, elevation correlated with the contributions of FLUO (0.46 , 0.040), PHEN (0.47 , 0.037) and the LMWPAHs (0.46 , 0.043) to the $\Sigma 21\text{PAHs}$ positively and with those of most HMWPAHs (FLUA, PYR, B(A)A, B(BJK), B(E)P, B(A)P, B(GHI), and COR, $r = -0.46$ to -0.77 , $p < 0.040$) negatively. Thus, elevation influenced PAH concentrations and patterns in a similar way with the same reasons as latitude. Lower elevations (and higher temperatures) occurred in the northern half of the transect and the higher elevations (and lower temperatures) occurred in the southern half of the transect. Elevation did not have any significant influence on OPAHs and AZA concentrations and patterns.

The mean annual aridity index correlated negatively with the concentrations of BP (-0.64 , 0.002) and FLUO (-0.56 , 0.010) and positively with those of ACENY, 1-MPHEN, 3,6-DMPHEN, FLUA, PYR, RET, B(A)A, B(BJK), B(E)P, B(A)P, IND, DIBE, COR, QUI, 9,10-ANQ, B(A)FLUone, and BPYRone ($r = 0.48$ – 0.77 , $p < 0.031$). Thus, increasing aridity (i.e. decreasing mean annual aridity index) decreased concentrations of most PACs except for those of the most volatile parent-PAHs. The main reason for this finding is likely the reduction of microbial activity and thus biological turnover with increasing aridity allowing for a stronger conservation of the LMW compounds. This interpretation is further supported by our finding that increasing aridity (and decreasing aridity index) had a positive influence on the contributions of all LMWPAHs to the $\Sigma 21\text{PAHs}$ concentrations (-0.71 , <0.001 , Fig. S1A) and on the contribution of 1-INDA to the $\Sigma 15\text{OPAHs}$ concentrations (Fig. S1B). The reverse was true for the contributions of most HMW

alkyl-PAHs (3,6-DMPHEN, 0.49, 0.032) and parent-PAHs (FLUA, PYR, RET, CHRY, B(BJK), B(E)P, B(A)P and COR, 0.46–0.78, 0.048–<0.001) to the Σ 6Alkyl-PAHs and Σ 21PAHs concentrations, respectively. However, because most arid sites are located in the southern part of the study transect, the effect of aridity cannot be completely separated from that of latitude although aridity and latitude loaded different PCAs suggesting that they were not closely related (Table 2).

The Σ Alkyl-NAPH/NAPH (N: $0.64 \pm$ s.e. 0.13, S: $0.37 \pm$ 0.03), Σ Alkyl-PHEN/PHEN (N: $0.08 \pm$ 0.03, S: $0.05 \pm$ 0.02), and 9,10-ANQ/ANTH ratios (N: $16 \pm$ 2.8, S: 9,10-ANQ was only detected at one site where the 9,10-ANQ/ANTH ratio was 10) were on average higher in the northern than in the southern part of the transect (Fig. 6). This indicates that low temperature combustion processes occurred more frequently in the N (Masclat et al., 1987) and that there was a more pronounced emission and/or production of 9,10-ANQ relative to ANTH possibly because of the higher radiation intensity and more pronounced biological conversion of ANTH to 9,10-ANQ. Alternatively, 9,10-ANQ could originate from low-temperature combustion like the alkyl-NAPHs.

Latitude was negatively correlated with the CRs of several parent- and alkyl-PAHs including BP, 1,3-DMNAPH, ACENY, FLUO, and 1-MPHEN ($r = -0.50$ to -0.73 , $p = 0.001$ – 0.036) and elevation positively with even a larger number of compounds (1,2,3,4-THNAPH, NAPH, 1-MNAPH, BP, 1,3-DMNAPH, ACENY, FLUO, 1-MPHEN, $r = 0.46$ – 0.73 , $p = <0.001$ – 0.046). Because mean annual precipitation decreased from N to S (and with increasing elevation) this cannot be attributed to enhanced leaching. We suggest that in the N more of these compounds are deposited relative to their leaching than in the S. In multiple regression with OC concentrations and latitude as independent variables and compound concentrations as dependent ones, the models to explain B(BJK), B(E)P, COR and 9,10-ANQ concentrations had corrected R^2 values of 0.53–0.66 and showed significant partial correlation coefficients for

both considered explanatory variables. For all other compounds and all sums of compounds at most one of the drivers showed a significant partial correlation coefficient.

4. Conclusions

The concentrations of all studied compounds in the Argentinean soils were low; for parent-PAHs they were among the lowest ever reported. NAPH was the most abundant PAH which is typical for background concentration areas. The close correlation of OC concentrations in soil with many PAHs and HMWOPAHs concentrations illustrated that atmosphere–soil partitioning was the dominating process explaining the PAC concentrations in the study soils.

Latitude which was representative of all climate variables except for aridity strongly influenced PAHs concentrations and patterns. However, the latitudinal effect could not be separated from an elevational effect in our study design. The Σ 29PAHs and Σ 150PAHs concentrations decreased from N to S because of decreasing anthropogenic influence. The composition of the PAHs and OPAHs mixtures was increasingly dominated by the LMW compounds from N to S as a combined consequence of global distillation, preferential removal, and increasing natural contributions. The AZAs were only detected in some soils with QUI being the most ubiquitous compound. QUI occurred preferentially in the N suggesting combustion sources similar to most PAHs and OPAHs while CBZ occurred more in the S suggesting natural sources. Increasing aridity resulted in increasing LMW compound (and corresponding decreasing HMW compound) concentrations and contributions for parent-PAHs, alkyl-PAHs and OPAHs.

Our study demonstrates that OPAHs occur similarly frequently, show a similar affinity to soil organic matter, and are more mobile in soils than the parent-PAHs. Light OPAHs seemed to mainly originate from secondary and heavy OPAHs more from primary sources.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2013.12.037>.

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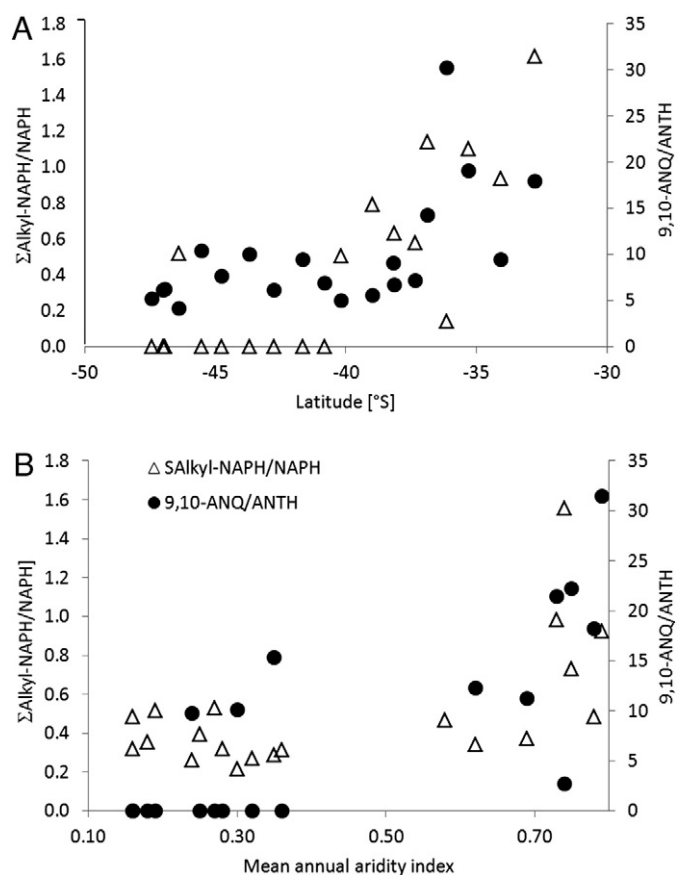


Fig. 6. Relationships between (A) latitude and (B) mean annual aridity index and alkyl-NAPH/NAPH and 9,10-ANQ/ANTH concentration ratios in topsoil.

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