



A 150-year record of polycyclic aromatic compound (PAC) deposition from high Andean Cajas National Park, southern Ecuador

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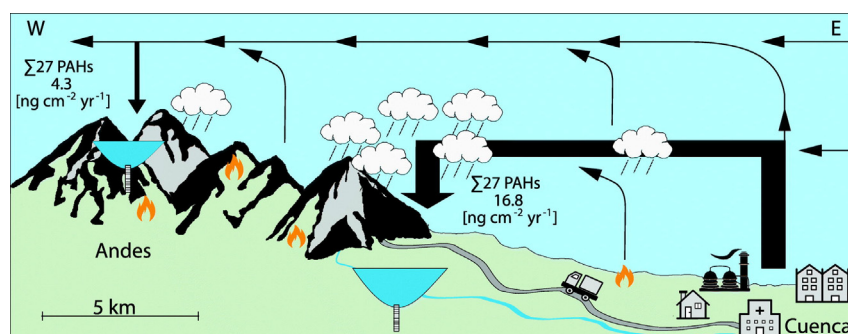
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HIGHLIGHTS

- Historical PAC depositional records are studied in lakes at low and high elevation.
- Increases in fluxes of PAC in Ecuador started later (1950s) than in the northern hemisphere.
- 2–3 ring PAHs (diagnostic of biomass burning) constitute 30% of the total PAHs.
- PAC depositions are 4–5 times higher at 3100 m than at 4100 m.
- High precipitation & proximity to city explains high fluxes of PACs at 3100 m.

GRAPHICAL ABSTRACT



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ABSTRACT

The temporal profiles of polycyclic aromatic compounds (PACs) in lake sediments reflect past changes in emissions, transport and deposition of these pollutants and, thus, record natural and anthropogenic processes. We document fluxes of PACs [(polycyclic aromatic hydrocarbons (PAHs), oxygenated PAHs (OPAHs) and azaarenes (AZAs)] deposited in two tropical high-altitude lakes in the Cajas National Park (Ecuadorian Andes, 2°50'S, 79°10' W). In remote and high elevation Laguna Fondococha (4130 m a.s.l.), the temporal fluxes of OPAHs and AZAs were similar to those of PAHs suggesting similar sources. A significant increase of PAC deposition after the 1950s reflects Ecuador's economic development. PAH fluxes were relatively low ($\sum 27\text{PAHs}$ (without retene and perylene): $0.86\text{--}11.21\text{ ng cm}^{-2}\text{ yr}^{-1}$) with a composition pattern typical for long-range atmospheric transport (high 9-fluorenone/fluorene ratios) and biomass burning (30% low molecular weight PAHs). PAHs diagnostic of high temperature combustion (industry, traffic) make up 20–25% of total PAHs. Perylene concentrations increase linearly with increasing sediment depth suggesting diagenetic in-situ production. At lower elevations (Laguna Llaviucu, 3140 m a.s.l.) and closer to urban areas, PAC fluxes in the past decades were 4–5 times higher than in the remote high-elevation lake. Laguna Llaviucu also showed higher concentrations of high molecular weight pyrogenic PAHs and a greater diversity of AZAs. Individual OPAHs and AZAs reflect mainly combustion

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activities. In Laguna Llaviucu, which is at a lower elevation (3140 m a.s.l.) and closer to the city, molecular ratios suggest short-range atmospheric transport and deposition of PACs. A very foggy climate (170 rainy days per year) with the precipitation maximum at 3500 m removes PACs very efficiently (by wet deposition) from the atmosphere at very short distances from emission sources. This partly explains why L. Llaviucu shows higher fluxes of PACs than the higher elevation L. Fondococha. This study presents the first historical record of organic pollutants from environmental archives in Ecuador.

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1. Introduction

Due to their carcinogenic and genotoxic potential, persistence in the environment, bioaccumulation in the food web and their ubiquitous nature, polycyclic aromatic compounds (PACs) have long been recognized as a major environmental threat (Bandowe and Wilcke, 2011; Bleeker et al., 2002; Canadian Council of Ministers of the Environment, 2010). PACs, including polycyclic aromatic hydrocarbons (PAHs), oxygenated PAHs (OPAHs) and nitrogen-heterocyclic polycyclic aromatic hydrocarbons (azaarenes, AZAs) are mainly produced from fossil fuel combustion and biomass burning related to anthropogenic and natural processes. Recent research has provided remarkably detailed insight into the sources, transport ways, sinks and the fate of PACs in the environment. OPAHs, for instance, are produced from their PAHs precursors by photolysis, photochemical and biological reactions; thus, molecular ratios between the PAH precursor [(e.g. fluorene (FLUO), all abbreviations in Table S1] and the respective OPAH (e.g. 9-fluorenone) may provide insight into the transport pathways (short- and long-range) through the atmosphere (Alam et al., 2014; Han et al., 2015; Keyte et al., 2013; Lundstedt et al., 2007; McKinney et al., 1999). The molecular weight distribution of PAHs has been related to combustion temperatures which is used to attribute the sources of PAHs to high-temperature [industry and engines; high molecular weight (HMW-PAHs)] and low-temperature burning [(forest and grassland fires, households; low molecular weight PAHs (LMW-PAHs)] (Denis et al., 2012; Lima et al., 2005; Tobiszewski and Namieśnik, 2012). The concentration ratios of specific PAHs can give indications of their sources (Tobiszewski and Namieśnik, 2012). Some of the PAHs are diagnostic for specific sources: retene, for instance, is an alkylated PAH produced from burning of conifers but also released by natural emissions of conifer stands (Fine et al., 2001; Wakeham et al., 1980). Other PAHs are less understood: perylene (PERY), often the dominant PAH in deeper lake and marine sediments, has been suggested to be produced diagenetically by in-situ biological processes. The conditions affecting their formation are, however, still poorly constrained: different precursors from the catchments or in the lakes, anoxia but also climatic conditions have been suggested (Bandowe et al., 2014b; Fan et al., 2011; Grice et al., 2009; Gschwend et al., 1983; Itoh and Hanari, 2010; Silliman et al., 2001, 1998; Venkatesan, 1988).

One of the challenges in environmental research and, ultimately, in science-based management is the lack of long-term observations of hazardous substances in the environment. Commonly, environmental monitoring begins only once concerns are raised and, as a result, little is known about natural pre-disturbance baseline levels or early appearances of the substances in the environment. Here, lake sediments are the most valuable natural archive documenting the history of many pollutants in detail (Smol, 2008). However, most of the studies with sedimentary archives were conducted in the Northern Hemisphere. Typically, PAC fluxes are low in pre-industrial times. A first increase is commonly observed around 1780 CE. Then, PAC fluxes rise with a substantial increase in the 20th century peaking in the 1960s. Afterward, gradual substitution of coal with oil, cleaner technologies and environmental legislation often reduced PAC deposition rates (Bandowe et al., 2014b; Elmquist et al., 2007; Fernández et al., 2000; Lima et al., 2003; Rose and Rippey, 2002; Sanders et al., 1993). Very few studies exist for the Southern Hemisphere, e.g. in South America (Barra et al., 2006;

Machado et al., 2014; Quiroz et al., 2005). It is unknown whether a common regional pattern exists and how that compares to areas in the Northern Hemisphere.

Particularly critical for the deposition of atmospheric pollutants are high altitude, remote 'pristine' mountain regions that are far away from direct human activities. In many cases, remote mountains are strongly contaminated with PACs because cold, humid environments trap pollutants very efficiently from the atmosphere (Fernández et al., 2000; Usenko et al., 2007; Van Drooge et al., 2011; Vilanova et al., 2001). The underlying physico-chemical scavenging mechanisms are still poorly understood and there are differences regarding the region, origin, type of compounds and enrichment factors with elevation (Daly and Wania, 2005; Tremolada et al., 2008; Wania and Westgate, 2008). In principle, wet deposition and cold condensation of organic pollutants is expected to be higher at higher elevations with cold ambient temperatures and frequent fog, clouds and precipitation (Blais et al., 1998; Daly and Wania, 2005; Wania and Westgate, 2008). On the other hand, microclimatic conditions in mountain topography are very complex and spatially heterogeneous; the vertical distribution of precipitation and, thus, the efficiency of scavenging depends on the climatic regime. Moreover, the distance to potential sources of PACs is typically larger in remote mountain areas. Detailed studies of PAC depositional rates along vertical gradients in different mountain settings may, therefore, provide insight into the net effects of such processes and help understand the complex and, sometimes, antagonistic processes of local PAC deposition.

Here, we present the 20th century history of PAC deposition in two lakes along an altitudinal gradient from 3140 to 4130 m a.s.l. in the Cajas National Park, southern Ecuador. This National Park forms part of the UNESCO Biosphere Reserve and the Ramsar convention, and is a hotspot of biodiversity and endemism. Guided by the scientific challenges mentioned above we asked the following questions:

- (i) What is the temporal pattern of PAC compositions and depositional rates in a high elevation tropical Andean setting over the past 150 years?
- (ii) Is there a difference in depositional rates between low elevation and high elevation and, if so, how large are enrichment factors for different compounds?
- (iii) Which are the major sources of the PACs? Are they local or transported from long distances?

First, we describe the short sediment cores from the lakes. Then we establish a detailed sediment chronology with $^{210}\text{Pb}_{\text{ex}}$ activity profiles, which allows us to convert PAC concentrations as measured in the sediment into depositional rates (fluxes). Then we evaluate potential sources of PACs and put the depositional rates in perspective of the vertical climatic gradient of the two lakes.

2. Material and methods

2.1. Study area

Laguna Llaviucu LLA (3140 m a.s.l.) and Laguna Fondococha FON (4130 m a.s.l.) are two lakes in the Cajas National Park CNP (2°50'0"S,

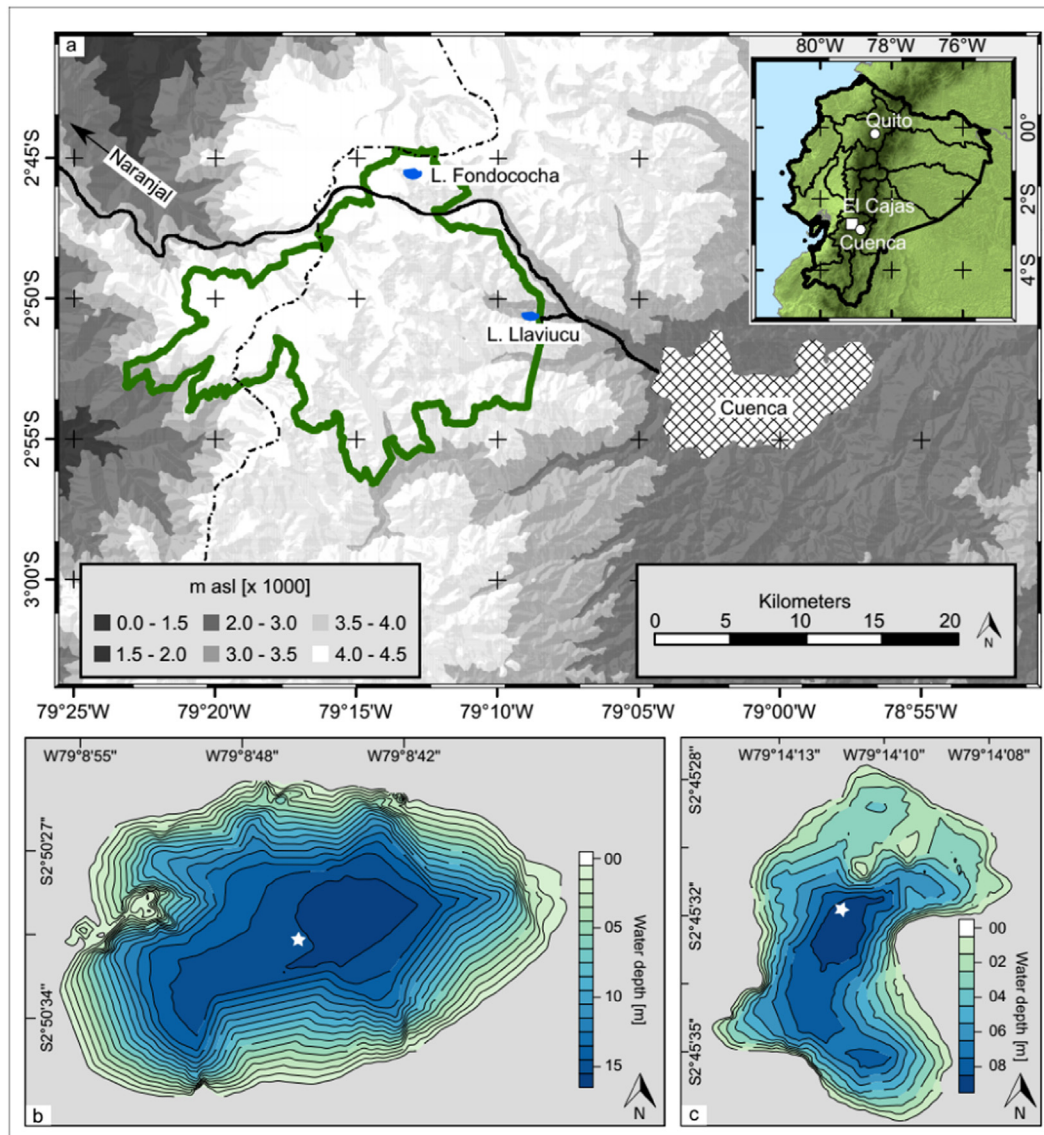


Fig. 1. Location of L. Llaviucu and L. Fondococha in Cajas National Park [a]. Location of Cajas National Park in southern Ecuador, the dashed line represents the water divide. Bathymetric maps for L. Llaviucu [b] and L. Fondococha [c] with the coring locations (asterisks).

79°10'0"W), southern Ecuadorian Andes (Fig. 1). This area was sculpted by glaciers and contains over 240 glacial lakes (Hansen et al., 2003). Typically, volcanic bedrock is covered by Pleistocene glacial moraines forming the substrate for Holocene Andosols and Histosols (Harden, 2006). L. Fondococha has a surface of 3.4 ha and a maximum water depth of 9.9 m. It is exorheic, polymictic and oligotrophic. Laguna Llaviucu is larger (18.9 ha), 16.5 m deep, mono- or dimictic and mesotrophic (Table 1).

On the eastern slope of the Andes, where both lakes are located and towards the city of Cuenca, mean annual precipitation rates increase from ca. 900 mm at 3100 m to a maximum of ca. 1400 mm at around 3400 m a.s.l. and decrease again to around 1000 mm further up. The climate is very foggy and wet; ca. 170 days per year receive rainfall (>1 mm, data from M. Cordova, unpublished data). On the western slope of the Andes towards the city of Guayaquil and the coastal plains on the Pacific coast with industrialized agriculture, an inversion layer with persistent fog efficiently traps moisture and aerosols from the Pacific below ca. 3000–3600 m (Vuille et al., 2000). Precipitation in the Cajas National Park is typically related to Easterly flow and moisture from the tropical continent (Amazon basin) (Kalnay et al., 1996). Temperatures show very little seasonal variation but strong diurnal

changes with average daytime values between 6 and 18 °C in the moist montane forest belt around 3100 m and between 3 and 6 °C in the Páramo at about 4000 m (ETAPA, 2016).

Páramo grasslands with patches of *Polylepis* sp. form the vegetation above 3500 m (Hansen et al., 2003). Naturally, moist montane forest covers the area below 3500 m. In many areas of the park, particularly in the valley floors, this forest has been replaced by grazing areas. In the catchment of Laguna Llaviucu, however, the forest cover is nearly

Table 1
Limnological parameters of the two lakes.

Parameters	L. Fondococha	L. Llaviucu
Location	2°45'36.6"S 79°14'11.1"W	2°50'33.84"S 79°8'43.15"W
Altitude (m a.s.l.)	4130	3140
Lake system	Exorheic	Exorheic
Max. depth (m)	9.9	16.5
Lake area (ha)	3.4	18.9
Vegetation	Páramo/sub-Páramo	Pasture grassland/montane Andean forest
Trophic state	Oligotrophic	Mesotrophic
Human impact	Low	Medium

complete. During the last few decades, large-scale reforestation with conifers is observed within and outside Cajas National Park (Buytaert et al., 2007; Hall et al., 2012).

Since the founding of the recreational area (1977) and the National Park (1996), human activities (mainly grazing) have decreased inside the park. At the same time, however, traffic has increased on the Cuenca-Molleturo-Naranjal highway which passes through the National Park (Fig. 1a). Since >200 years, traditional practices of forest and grassland burning were widely applied to stimulate growth of grass for cattle grazing (Hansen et al., 2003). While such practices have decreased in the park, they are still widely applied outside the protected area (Sarmiento, 2002), in particular in the downstream vicinity of L. Llaviucu near the suburbs of Cuenca.

2.2. Fieldwork and analytical methods

In 2014, multiple parallel sediment cores were retrieved from the deepest part of the lakes using a UWITEC gravity corer (Fig. 1b, c). The cores were kept unopened under dark and cool conditions (except for the transport by air) until processing in the lab. Then, the cores were split lengthwise, photographed and sediments were described according to Schnurrenberger et al. (2003). Elemental compositions of the half-cores were measured at 1 mm resolution (2 mm for L. Llaviucu) with a μ XRF ITRAX core scanner (Mo-tube, 10 s exposure time, 30 kV and 35 mA).

Subsequently, the uppermost 30 cm of each of the cores were sub-sampled at 0.5 cm contiguous intervals for radionuclide dating (cores FON14-1 and LLA14-1) and chemical analysis (cores FON14-2 and LLA14-2). Because of the sample mass required for dating and chemical analysis, the low sedimentation rates, low bulk density and high-resolution we used sample material from two parallel cores (1 and 2). Both cores were stratigraphically correlated using μ XRF data, cumulative dry mass accumulation, stratigraphic correlation of marker layers and linear interpolation. Correlation accuracy among the parallel cores is estimated ± 1 mm. Measurements of the water content and dry bulk density followed Håkanson and Jansson (2002). Carbon (C), Nitrogen (N) and Sulfur (S) in dry bulk sediments were determined with a vario EL cube Elemental Analyzer.

Radionuclide dating with ^{226}Ra , ^{210}Pb and ^{137}Cs followed Tylmann et al. (2016). All samples were stored for a minimum of three weeks in sealed containers to obtain secular equilibrium of radon and its short-lived daughter products with ^{226}Ra , ^{137}Cs and ^{226}Ra activities were determined with gamma-ray spectrometry. Because of the low sample masses available (priority was given to a high resolution of data), activity of total ^{210}Pb was determined indirectly with ^{210}Po using alpha spectrometry. Unsupported ^{210}Pb was calculated by subtraction of supported ^{210}Pb activity from the total ^{210}Pb activity on a level-by-level basis (Appleby and Oldfield, 1978). We used different variants of the Constant Initial Concentration (CIC) model and the Constant Rate of Supply (CRS) model (Appleby and Oldfield, 1978), with and without Missing Inventory corrections (Tylmann, 2014) to test the sensitivity of the age-depth relationships with regards to varying model assumptions (von Gunten et al., 2009).

Aliquots of freeze dried lake sediments (1–2 g), were mixed with inert bulk sorbent (isolute HM-N, Biotage Uppsala, Sweden) and transferred into 33 ml Accelerated Solvent Extractor (ASE) extraction cells. The samples were spiked with 50 μl of 7 deuterated PAHs mixture (10 $\mu\text{g}/\text{ml}$ each of naphthalene-D8, acenaphthene-D8, phenanthrene-D10, pyrene-D10, chrysene-D12, perylene-D12, benzo[ghi]perylene-D12), 40 μl of 2 deuterated OPAHs (10 $\mu\text{g}/\text{ml}$ each of benzophenone-D5 and 9,10-anthraquinone-D8) and 50 μl carbazole-D8 (10 $\mu\text{g}/\text{ml}$), serving as internal standard for the PAHs, OPAHs and AZAs respectively. Aliquots of the European Reference Material (ERM-CC013a: Polycyclic Aromatic Hydrocarbons in soil, $n = 3$) and blanks (100% Isolute HM-N, $n = 3$) were also prepared together with the samples as described above. Prepared sediments, blanks and ERM-CC013a were each extracted twice by

pressurized liquid extraction on an accelerated solvent extractor (Dionex, Sunnyvale, USA). The first extraction was done with dichloromethane (DCM), while the second extraction was with acetone: DCM: 1% trifluoroacetic acid (250:125:1 v/v). The two extracts from each sample were combined, spiked with 10 ml of hexane (Hex) and concentrated to <1 ml at 35 °C on a TurboVap II Concentrator (Biotage, Charlotte, NC, USA). The instrumental parameters of the ASE were the same as in previous studies (Bandowe and Wilcke, 2010).

The concentrated extract from each sample was transferred into a glass column filled with 3 g silica gel (10% deactivated) and sequentially eluted with [a] 15 ml Hex: DCM (5:1 v/v) followed by [b] 20 ml DCM. Eluates [a] and [b] from each sample were collected together, spiked with three drops of toluene and concentrated to a volume of <1 ml. PACs in each extract were measured with an Agilent 7890 Gas Chromatograph (GC) coupled to an Agilent 5975C Mass Spectrometer (MS). GC-MS instrumental parameters follow previous studies (Bandowe et al., 2011; Bandowe et al., 2014a; Bandowe and Wilcke, 2010; Lundstedt et al., 2014). The accuracy of the determination of PACs with our methods were checked by comparing the measured concentrations of PAHs in the ERM-CC013a ($n = 3$) with the certified values. The recovery of the sum of PAHs for which certified values were provided was $102.1 \pm 2.1\%$ (average \pm standard deviation). Since there are no reference materials (soils or sediments) with certified concentrations for of OPAHs and AZAs, we compared the measured values in the ERM-CC013a with the grand means of their concentration measured by several laboratories in a recent intercomparison campaign (Lundstedt et al., 2014). The mean of the sum of the concentrations of OPAHs and AZAs measured in the current study compared to same values in the intercomparison campaign was 101.1 ± 9.4 and 151.6 ± 62.9 (mean \pm standard deviation), respectively. Concentrations of the PAC compounds were converted into fluxes (depositional rates) using the Mass Accumulation Rate (MAR) of dry sediment as calculated from the Constant Rate of Supply model. The sums of the concentration/fluxes of all PAHs without retene and perylene is referred to as $\sum 27\text{PAHs}$. The sum of the concentrations of all non-alkylated PAHs and all non-alkylated PAHs without perylene are referred to as $\sum 21\text{PAHs}$ and $\sum 20\text{PAHs}$, respectively. The sums of the concentration/fluxes of non-alkylated PAHs with 2–3 benzene rings and 4–7 benzene rings are referred to as low molecular weight PAHs ($\sum \text{LMW-PAHs}$) and high molecular weight PAHs ($\sum \text{HMW-PAHs}$), respectively. The sum of the concentration of all OPAHs and all azaarenes are referred to as $\sum \text{OPAHs}$ and $\sum \text{AZAs}$ respectively. Differences in means fluxes between two age periods were tested by Welch two sample t -test. All statistical tests were conducted with (R Core Team, 2017). Tests were deemed to be significant at $p < 0.05$.

3. Results

3.1. Sediment description and chronology

The sediment of L. Fondocochoa (Fig. 2a) consists of brownish-black (HUE 10YR2/1) organic (7–12% C_{org}) diatomaceous fine silt with slightly darker and lighter bands. The organic matter was strongly decomposed. The mass fractions of carbon (C), nitrogen (N) and sulfur (S) averaged 96 mg g^{-1} (range: $71\text{--}123 \text{ mg g}^{-1}$), 7.2 mg g^{-1} (range: $5.4\text{--}8.7 \text{ mg g}^{-1}$) and 1.5 mg g^{-1} (range: $1.2\text{--}2.1 \text{ mg g}^{-1}$), respectively (Fig. S1). C, N, and S mass fractions and fluxes showed increasing trends towards recent times. The C/N ratio averaged at 13.3 (range: $12.7\text{--}14.7$). The water content was very high (around 80%, Fig. 2a) and the dry bulk density is low (0.2 g cm^{-3}). Scanning μ XRF data show that the elemental composition of the sediment was homogenous throughout the sediment section considered here (0–9 cm depth).

The sediment of L. Llaviucu (Fig. 2b) is very similar in colour and composition. The water content was slightly lower (ca. 70%), the dry bulk density is around 0.3 g cm^{-3} and the sediment was, with small variations, homogenous. The average mass fractions of C, N and S

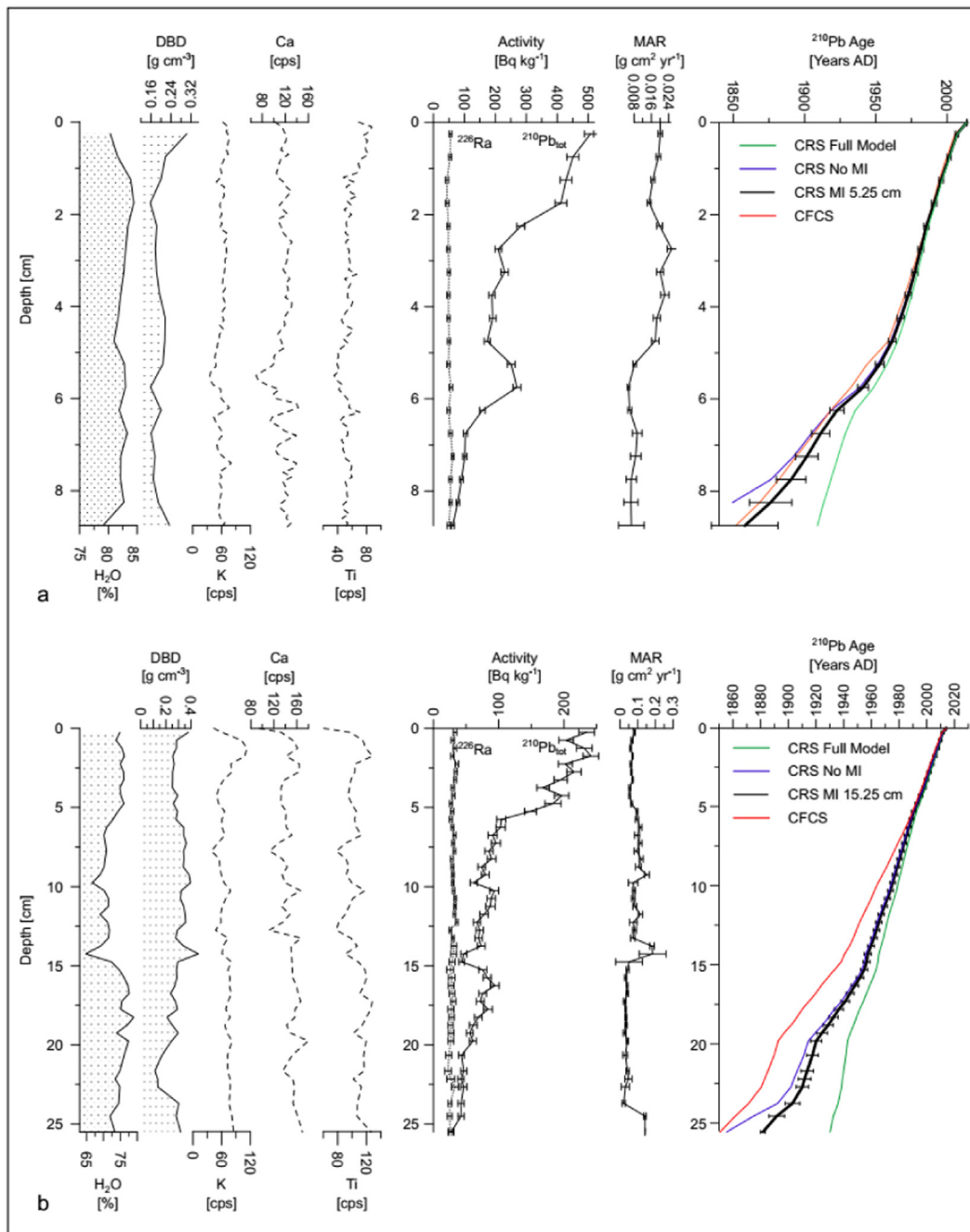


Fig. 2. Water content (H_2O %), dry bulk density (DBD, g cm^{-3}), XRF measurements (cps counts per second) for potassium (K), calcium (Ca) and titanium (Ti) in the sediment cores of L. Fondococho [a] and L. Llaviuco [b]. ^{226}Ra and total ^{210}Pb activities, and Mass Accumulation Rates (MAR) as calculated from the CRS model are shown in the middle. The age-depth models calculated with the CFCS and different variants of the CRS model (with and without missing inventory corrections) are shown on the right. The CRS model with missing inventory correction was used for all calculations (bold black line).

were 87.4 mg g^{-1} (range: $74.2\text{--}104 \text{ mg g}^{-1}$), 6.8 mg g^{-1} (range: $5.7\text{--}8.1 \text{ mg g}^{-1}$) and 1.8 mg g^{-1} (range: $1.4\text{--}2.2 \text{ mg g}^{-1}$), respectively (Fig. S1). The C/N ratio averaged at 12.9 (range: 12.2–13.7). The temporal trends indicate a decrease of the mass fractions and fluxes as well as the C/N towards recent times, which is in contrast to that observed for the L. Fondococho.

Fig. 2 a, b show the radionuclide activity profiles. In both lakes, ^{226}Ra activity profiles are very constant averaging around 50 Bq kg^{-1} (L. Fondococho) and 30 Bq kg^{-1} (L. Llaviuco), respectively. Despite extended counting times, ^{137}Cs activity rates were mostly below detection limits or measurable in traces with large uncertainties ($5.6 \pm 3.0 \text{ Bq kg}^{-1}$ L. Fondococho; $2.5 \pm 1.1 \text{ Bq kg}^{-1}$ L. Llaviuco; data not shown). The 1963 fallout peak could not be determined. Starting from

initial activities A_0 of 500 Bq kg^{-1} in L. Fondococho (A_0 of 250 Bq kg^{-1} in L. Llaviuco), total $^{210}\text{Pb}_{\text{tot}}$ (^{210}Po) follows broadly exponential decay with some anomalies. Unsupported $^{210}\text{Pb}_{\text{ex}}$ reaches background levels at 9 cm sediment depth in L. Fondococho (core FON14-1) and at 25 cm in L. Llaviuco (core LLA14-1), respectively. The CIC model shows several age inversions and is not pursued (data not shown). The CRS model variants show increasing ages with increasing depth and constant sedimentation rates. For our chronologies we selected the CRS model with Missing Inventory (MI) correction, which is an intermediate scenario that is most robust and plausible (homogeneous sedimentation). This model suggests ages around 1870 CE (L. Fondococho) and 1880 (L. Llaviuco) at the sediment depth where unsupported ^{210}Pb disappears. Mass accumulation rates (MAR) were

calculated from the CRS model (with MI) and show in both lakes constant values prior to ca. 1960 CE. Both lakes show an increase (factor 2) of MAR after around 1960 and, again, constant MARs afterward. Slightly decreasing MAR values, but still above pre-1960 levels, are observed in both lakes after ca. 1980.

3.2. Polycyclic aromatic compounds

3.2.1. PAC trends in Laguna Fondococha since 1860 CE

The temporal variations in the concentrations and fluxes of the $\Sigma 27$ PAHs, of individual groups of PACs, Σ OPAHs and Σ AZAs, and the molecular diagnostic ratios since 1860 CE are shown in Fig. 3 (abbreviations see Table S1). Flux values of $\Sigma 27$ PAHs (Fig. 3a) average at $3.48 \text{ ng cm}^{-2} \text{ yr}^{-1}$ (range: $0.82\text{--}10.99 \text{ ng cm}^{-2} \text{ yr}^{-1}$). Two local maxima are observed in the 1870s and around 1910 but the sustained increases in the $\Sigma 27$ PAHs fluxes to above-average values begin in the early 1950s. This increase is also mirrored in the fluxes of Σ HMW-PAHs, Σ OPAHs and Σ AZAs (Fig. 3b, f, g). The post-1950s fluxes of $\Sigma 27$ PAHs were significantly ($p < 0.01$) higher than their pre-1950 values (factor of 2.04). The highest flux of the $\Sigma 27$ PAHs was observed in the early 1980s.

The flux of Σ HMW-PAHs (Fig. 3b) remained low ($0.08\text{--}0.39 \text{ ng cm}^{-2} \text{ yr}^{-1}$) prior to ca. 1950, and increased by a factor of 7.2 ($p < 0.01$) compared to pre-1950s values. The average flux of the Σ LMW-PAHs (Fig. 3c) was $1.1 \text{ ng cm}^{-2} \text{ yr}^{-1}$. The post-1950 average flux of Σ LMW-PAHs was also higher than the pre-1950 average. The enrichment factor of 2.1 for Σ LMW-PAHs is, however, much lower than the enrichment of Σ HMW-PAHs (factor 7.2) for the same period of time. The fluxes of Σ LMW-PAHs show three peaks (occurring in the 1870s, the 1910s and the early 1980s). The ratio Σ HMW-PAHs/ Σ LMW-PAHs (Fig. 3h) can be used to diagnose the sources, combustion processes or transport origin of PAHs. A ratio < 1 suggests predominantly low temperature combustion (biomass burning, petrogenic sources) or long-range transport. In L. Fondococha, the ratio Σ HMW-PAHs/ Σ LMW-PAHs increases to > 1 after ca. 2000 suggesting predominant sources from high temperature combustion and, thus a substantial change in the PAHs mixture. Increases in vehicular and industrial

emissions, both of which contain higher levels of HMW-PAHs may explain this observation.

Flux values of retene (Fig. 3d) averaged at $0.09 \text{ ng cm}^{-2} \text{ yr}^{-1}$ and range from $0.03 \text{ ng cm}^{-2} \text{ yr}^{-1}$ in the lower part of the core to a maximum of $0.22 \text{ ng cm}^{-2} \text{ yr}^{-1}$ around 1980. From the 1950s onward, retene fluxes increased by a factor of 2.8 ($p < 0.01$) compared to pre-1950 values.

For the past 150 years, the PAH mixtures in L. Fondococha were dominated by perylene (Fig. 3e and Fig. S2) with an average contribution of 78% (range: 46–91%) of all the $\Sigma 29$ PAHs assessed. Other important PAHs are biphenyl (BP: 5%), naphthalene (NAPH: 4%), 1,3-dimethylnaphthalene (1,3-DMNAPH: 2%) and 1- and 2-methylnaphthlene (1-, 2-MNAPH) with contributions of 1.7 and 1.3%, respectively. Comparing the pre-1950 and the ca. 1950–2014 periods, we observe that the relative contributions of perylene (PERY) to the $\Sigma 29$ PAHs were significantly higher in the first period (88%, range 81–94%) than in the latter period (72%, range 48–88%; Fig. S2). Significant increases in the contributions of higher molecular weight PAHs such as benzo(b + j + k)fluoranthene (B(BJK)) and benzo(ghi)perylene (B(GHI)) to the $\Sigma 29$ PAHs can be observed in the post-1950 period (Fig. S2).

The temporal evolution of PERY (Fig. 3e; average $15 \text{ ng cm}^{-2} \text{ yr}^{-1}$) differs substantially from the combustion-derived PAHs. The concentrations of PERY increased linearly ($R^2 = 0.86$; $p < 0.01$) with increasing sediment age (depth), a trend which is contrary to the trend of combustion-derived PAHs of similar molecular weight (e.g. B(BJK), a 5-ring-PAH; $R^2 = 0.64$; $p < 0.01$) as PERY (Fig. S3). The contribution of PERY to the total concentration of the $\Sigma 21$ PAHs (unsubstituted PAHs) ranged from 67 to 97%, with the highest proportion in the older sections of the sediment cores. Even in the surface sediments the contribution of PERY to the $\Sigma 21$ PAHs was 71%. The concentration of PERY was significantly negatively correlated ($p < 0.05$) with organic matter properties such as C ($R = -0.70$), N ($R = -0.65$), S ($R = -0.89$) and C/N ratio ($R = -0.51$) (Fig. S4).

Variations in the fluxes of Σ OPAHs and Σ AZAs (Fig. 3f, g) follow the pattern of Σ HMW-PAHs. Both show relatively stable background fluxes from the beginning of our record (ca. 1860) to ca. 1950 followed

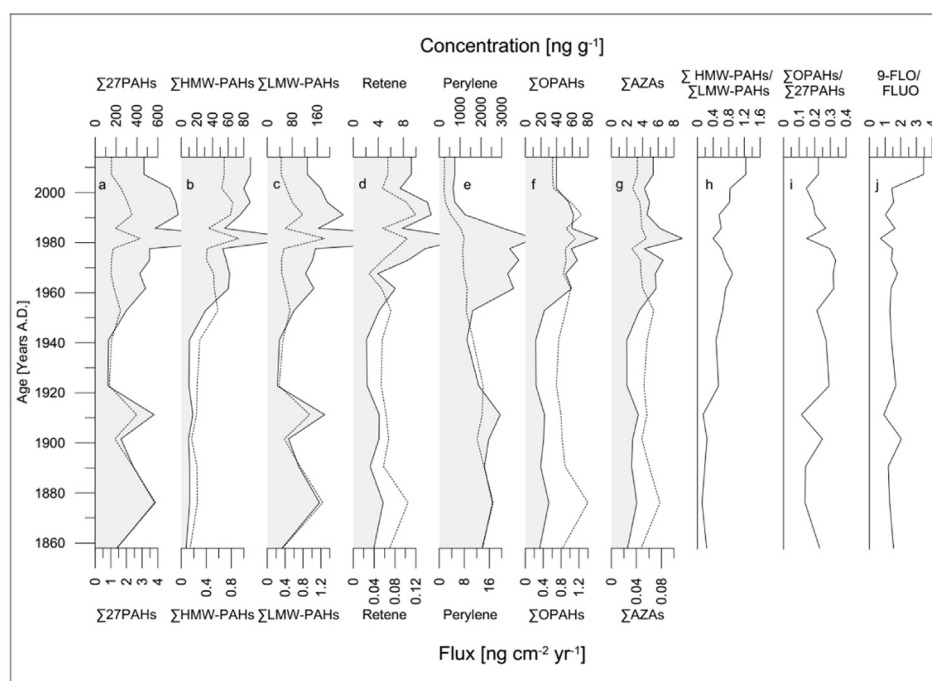


Fig. 3. Flux rates [$\text{ng cm}^{-2} \text{ yr}^{-1}$, dotted area] and concentrations [ng g^{-1} , dashed line] of the $\Sigma 27$ PAHs [a], Σ HMW-PAHs [b], Σ LMW-PAHs [c], Retene [d], Perylene [e], Σ OPAHs [f] and Σ AZAs [g] as well as molecular ratios of Σ HMW-PAH/ Σ LMW-PAH [h], Σ OPAHs/ $\Sigma 27$ PAH [i] and 9-FLO/FLUO [j] in L. Fondococha between 1860 and 2014. The abbreviations 9-FLO and FLUO refers to 9-fluorenone and fluorene, respectively.

by a significant ($p < 0.01$) increase of OPAHs (factor 2.6) and AZAs (factor 2.1). Average \sum OPAHs flux rates are $0.76 \text{ ng cm}^{-2} \text{ yr}^{-1}$, while average values for \sum AZAs are $0.05 \text{ ng cm}^{-2} \text{ yr}^{-1}$. Generally, the OPAH mixtures were dominated by 9,10-anthraquinone (9,10-ANQ), 9-fluorenone (9-FLO), 1-indanone (1-INDA) and benzo(a)anthracene-7,12-dione (7,12-B(A)Dione) with contributions of 35%, 25%, 15% and 9%, respectively to the \sum OPAHs. Similar compounds dominated in both the pre- and the post-1950 samples (Fig. S2). Carbazole was the only AZA detected.

Molecular ratios of 9-fluorenone/fluorene (9-FLO/FLUO, Fig. 3j) were calculated for L. Fondococha as possible proxies for long-range transport of PACs. Ratios were constantly (with only two exceptions) > 1 (average 1.6). This ratios significantly increased (> 3) after ca. 2000.

3.2.2. PAC trends in in L. Llaviucu since the 1950s

For comparison of the recent PAC flux rates with L. Fondococha, PACs were measured in L. Llaviucu in sediments covering the past 60 years (i.e. since in the increase around 1950). L. Llaviucu lies at a lower elevation (3140 m a.s.l.) and closer to the city of Cuenca. The temporal variations in the flux and concentration of PACs in L. Llaviucu are shown in Fig. 4a–g. Average fluxes for the \sum 27PAHs are $16.4 \text{ ng cm}^{-2} \text{ yr}^{-1}$ (range: 6.5 to $38.9 \text{ ng cm}^{-2} \text{ yr}^{-1}$). The \sum HMW-PAHs fluxes average $3.9 \text{ ng cm}^{-2} \text{ yr}^{-1}$ (range: 1.6 – $9.3 \text{ ng cm}^{-2} \text{ yr}^{-1}$) with overall increases towards recent times. The fluxes of \sum LMW-PAHs and retene showed similar temporal variations as the \sum 27PAHs, but differed slightly from those of \sum HMW-PAHs. Average flux values for retene (Fig. 4d) are $0.5 \text{ ng cm}^{-2} \text{ yr}^{-1}$, with a weak decreasing trend (but still at very high values) observed from the mid-1980s onward. A concomitant decreasing trend is observed for the \sum LMW-PAHs (Fig. 4c) with fluxes averaging at $5.9 \text{ ng cm}^{-2} \text{ yr}^{-1}$. In the entire period assessed in L. Llaviucu, the PAHs mixtures were mostly dominated by PERY (Fig. 4e). The average contribution of PERY to the \sum 29PAH mixture is 41% (ca. 1950–2014, Fig. S5), which is lower than in L. Fondococha. Lower molecular weight PAHs such as naphthalene and its alkylated derivatives, biphenyl, phenanthrene and their alkyl derivatives were the other main contributors to the PAHs in the entire record. The PERY record shows a negative upward trend which is generally opposite to the positive upward trends of the \sum 27PAHs and the \sum HMW-PAHs.

Both \sum OPAHs (average $4.1 \text{ ng cm}^{-2} \text{ yr}^{-1}$; Fig. 4f) and \sum AZAs (average $0.4 \text{ ng cm}^{-2} \text{ yr}^{-1}$; Fig. 4g) show a decrease after the 1980s, which follows the trend in L. Fondococha (Fig. 3f, g). The major OPAHs were 2-methyl-9,10-anthraquinone (2-MANQ), 9,10-anthraquinone, 9-fluorenone and 1-indanone (Fig. S5). L. Llaviucu revealed a greater diversity of AZAs (quinoline, acridine and carbazole).

4. Discussion

4.1. PAC deposition record of L. Fondococha for the past 150 years

Fluxes of PAHs in lake sediments from the northern hemisphere are generally low and invariant until their first substantial increases at the onset of the (western) Industrial Revolution in the late 1800s. Subsequent temporal variations mirror changes in magnitude and type of fossil fuel usage (from coal to oil and gas), and reductions in PAH emissions resulting from emission control measures (Table 2, Bandowe et al., 2014b; Elmquist et al., 2007; Fernández et al., 2000; Lima et al., 2003). As a general tendency, these studies show an initial increase of PAHs in the late 1800s, followed by a maximum in the 1950s/60s, with decreasing trends thereafter. In contrast, the first major increases in PACs fluxes in the presented sediment records occurred much later than reported for sites in the northern hemisphere. The initial increase in the flux of PAHs that we see in the 1950s in L. Fondococha (Fig. 3) is similarly documented in the Chilean lakes Galletué (1963) and Laja (ca. 1960) (Barra et al., 2006; Quiroz et al., 2005). Given the dating uncertainties, the synchronous onset of the initial PAH increases in all three lakes from South America is remarkable. The peak in \sum 27PAHs that we see in L. Fondococha at the beginning of the 1980s was similarly found by Quiroz et al., 2005 in L. Laja (Table 2). All three South American lakes see peaks in the \sum PAHs fluxes in the late 1980s/90s, and a decrease in the levels of PAHs starting in the last 1–2 decades. Reconstructions of PAHs from river sediments in Brazil place the highest PAHs concentrations in the 1970s, which corresponds to a period of rapid economic growth (Machado et al., 2014). That study also demonstrated a direct and strong correlation between variations in the concentrations of \sum 16PAHs and indices such as energy consumption, population growth and the number of highways in that region (Machado et al., 2014).

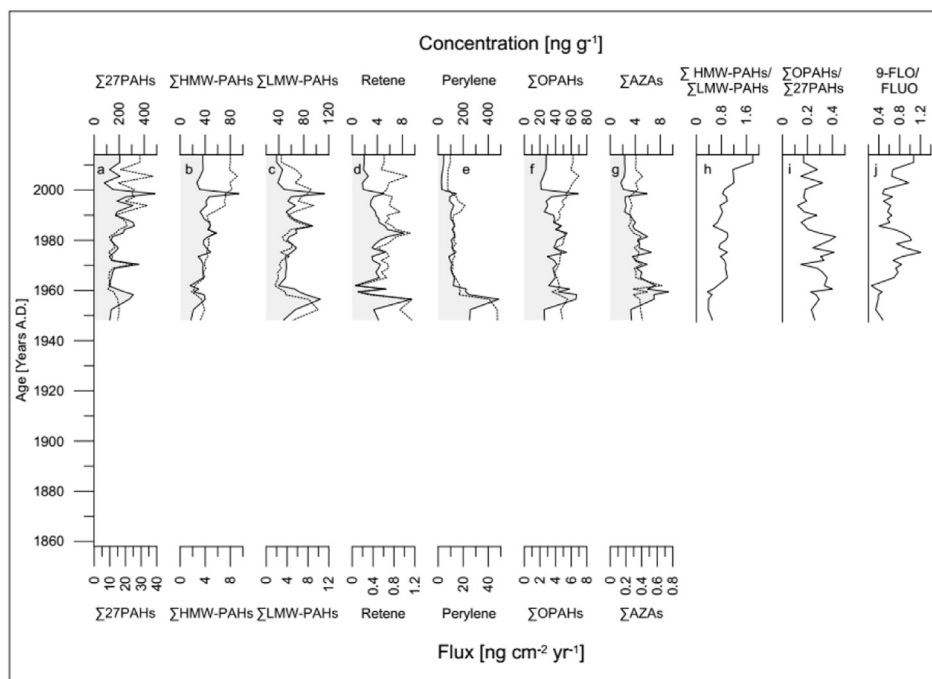


Fig. 4. Flux rates [$\text{ng cm}^{-2} \text{ yr}^{-1}$, dotted area] and concentrations [ng g^{-1} , dashed line] of the \sum 27PAHs [a], \sum HMW-PAHs [b], \sum LMW-PAHs [c], Retene [d], Perylene [e], \sum OPAHs [f] and \sum AZAs [g] as well as molecular ratios of \sum HMW-PAH/ \sum LMW-PAH [h], \sum OPAHs/ \sum 27PAH [i] and 9-FLO/FLUO [j] in L. Llaviucu between 1950 and 2014.

Table 2

Comparison of \sum PAH depositional fluxes ($\text{ng cm}^{-2} \text{yr}^{-1}$) to lake sediments from different regions worldwide (a selection). Note: the number of PAHs included in the \sum PAHs differs for each study, but do not include perylene. The table is meant to provide an overview of profile trends, not absolute PAH levels.

Region	Site	Elevation (m)	\sum PAH Flux ($\text{ng cm}^{-2} \text{yr}^{-1}$)	PAH Maximum (year)	PAH initial increase	PAH initial decrease	Reference	
South America	Remote	Laguna Fondococha, Ecuador	4130	0.86–11.21	Beginning of 1980s	Mid-1950s	Mid-1990s	This study
		Laguna Llaviuco, Ecuador	3140	7.4–53.9	Mid-1950s	–	No decrease yet	This study
		Lake Laja, Chile	1360	2.9–19.6	1989	~1960s	~Late 1990s	Quiroz et al., 2005; Barra et al., 2006
Europe	Remote	Lake Galletue, Chile	1150	0.8–11.5	1999	1963	~Late 1980s	Barra et al., 2006
		Lake Jezero na Planini pri Jezeru, Slovenia	1430	3–290	~1950s	~1900s	~Late 1950s	Muri et al., 2006
		Loch Coire nan Arr, Scotland	125	No flux values	1920–1934	1860–1874	1920–1934	Rose and Rippey, 2002
Asia	Industrial	Lake Huguangyan Maar, China	–	4.7–35.0	Increasing to present day	~1950s	Still increasing	Han et al., 2016
		Lake Chaohu, China	–	9.7–179.3	Late 1990s	~1900s	~2000s	Han et al., 2016
North America	Remote	Lone Pine Lake, USA	3024	0.48 (1870)–3.66	1949	1949	1967	Usenko et al., 2007
		Mills Lake, USA	3030	0.69 (1905)–5.8	1963	1938	Still increasing	Usenko et al., 2007

The increase in PACs in the sediment of L. Fondococha beginning after ca. 1950 can be attributed to Ecuador's industrialization which began at the same time (Flores and Merrill, 1991). Prior to the 1950s, Ecuador's economy was mainly based on agriculture. Between 1950 and 1970, there was a slow and steady expansion of non-agricultural activities, and the 1960s saw rapid growth and diversification of the manufacturing sector (Flores and Merrill, 1991). We attribute the initial increase of PAHs in the 1950s to the growth in industrial manufacturing in Ecuador. The discovery of petroleum fields in 1967 facilitated Ecuador's transformation to a world producer of oil. This process was further sustained by the discovery and exploitation of large natural gas deposits off the coast of Guayaquil. The increasing trend that we see in the \sum HMW-PAHs (combustion derived PAHs), \sum OPAHs and \sum AZAs since the 1950s is in line with Ecuador's expanding oil and gas industry and increase in vehicular usage (Cevallos Sierra, 2016). This interpretation is supported by steady increase in \sum HMW-PAHs/ \sum LMW-PAHs ratios from the 1980s onward and the very steep rise after ca. 2000, which suggests an increasing contribution of high temperature combustion sources (industries, vehicles) to the total PAHs in the sediments (Lima et al., 2005). The ratio of \sum HMW-PAHs/ \sum LMW-PAHs increases to >1 after ca. 2000 which corresponds to the improvement and opening of the new highway between Cuenca and Guayaquil in 1999. This highway crosses the National Park near both lakes.

The trends of \sum LMW-PAHs (Fig. 3d) reflect activities related to low temperature combustion from households, agriculture, forest and grassland fires, biogenic sources and long-range transport (Denis et al., 2012; Lima et al., 2005). PAHs in air and soils from rural regions in the tropics are dominated by LMW-PAHs, which contrasts with industrialized areas in the temperate northern hemisphere (Bandowe et al., 2009; Daly et al., 2007; Krauss et al., 2005). The peak fluxes of \sum LMW-PAHs that were observed since ca. 1860 in L. Fondococha can be attributed to local wildfires but also to local burning of the Páramo grasslands, which is common practice in this region (Hansen et al., 2003). Some restrictions were imposed in Cajas when the area became recreational in 1977; the National Park was established in 1996. Accordingly, LMW-PAHs fluxes show a decreasing trend from ca. 1980 onward, which is likely the result of restrictions in Páramo burning. The large peak at the beginning of the 1980s suggests a period with massive local grassland burning. Regional precipitation records show a short-lived negative anomaly in 1982 (Buytaert et al., 2007) which could be related to the 1982/83 El Niño event. El Niño events are typically dry years in the Ecuadorian Andes (Vicente-Serrano et al., 2017).

Reviewed literature indicates that our results provide the first long-term OPAHs and AZAs depositional record in South America. Benchmark records for comparison are missing. The similarity of OPAHs and AZAs fluxes with those of the mainly combustion-derived PAHs (in particular HMW-PAHs) is plausible, because OPAHs and AZAs have similar pyrogenic sources as PAHs (Bandowe et al., 2011; Bleeker et al., 2002;

Han et al., 2016, 2015). The dominant OPAHs (9-fluorenone, 9, 10-anthraquinone, 1-indanone) and a 9-fluorenone/fluorene molecular ratio >1 have also been observed in soils from pristine tropical forest sites (*terra firme*, Amazonas region, Brazil), in smoke from combustion of amazon forest litter, in diesel particulate matter and in urban dust (Bandowe and Wilcke, 2010, 2011; Radzi bin Abas et al., 1995; Layshock et al., 2010). OPAHs such as 9-fluorenone can also be formed from PAHs by photochemical and biological transformation of PAHs in environmental compartments. Hence, in addition to the OPAHs being emitted directly from combustion sources, a fraction of them could also represent transformation products of PAHs. Such transformation processes (and higher OPAH/PAH ratios) with ageing of air masses have been observed in air and sediment samples (Alam et al., 2014; Han et al., 2015; McKinney et al., 1999).

Carbazole, the only AZA detected in L. Fondococha, has also been detected in lake sediments from the Great Lakes region in the USA (Guo et al., 2017). The sources and origin of carbazoles and their halogenated derivatives are controversially discussed with natural (non-combustion) and industrial (related to production and use of indigo-dyes) sources considered (Guo et al., 2017). The temporal profile of carbazole in L. Fondococha is very similar to that of the other combustion-derived PACs and, hence, suggests that combustion is the main source of carbazole in L. Fondococha.

Retene, a derivative of abietic acid (diterpenoid of conifer resin), can be used as a marker for the combustion of conifer fuel (Fine et al., 2004, 2001; Muri and Wakeham, 2009). In L. Fondococha, retene shows a large four-fold increasing trend (Fig. 3) in the past five decades (since ca. 1960). Over the past decades, Ecuador has seen a massive expansion of pine plantations in deforested areas and sub-Páramo belts. These plantations are part of carbon sequestration and highland management projects (Farley et al., 2004; Hofstede et al., 2002). For their case study area in the southern Ecuadorian Andes, Hall et al. (2012) report a four-fold increase in forest cover between 1991 and 2009, mainly grassland converted into pine plantations. Pine plantations are promoted throughout the Ecuadorian Andes although many adverse effects on hydrology and biodiversity are well established (Buytaert et al., 2007; Hall et al., 2012).

The predominance of PERY in older sediments is well documented in the literature (Bandowe et al., 2014b; Barra et al., 2006; Fernández et al., 2000; Han et al., 2015; Quiroz et al., 2005). This literature suggests that sedimentary PERY in deeper sediments does not primarily originate from combustion sources but, instead, might be mostly diagenetically produced (in-situ) under reducing conditions (Silliman et al., 2001, 1998; Venkatesan, 1988). In L. Fondococha, the linear positive trend of PERY concentrations with increasing sediment age (and depth) is opposite to the trend for combustion-derived PAHs (e.g. B(BJK)) which supports the interpretation of in-situ production. Similar observations have been made in other lakes from different geographic locations in Germany (L. Holzmaar), North America (L. Siskiwit, L.

Ontario), Japan (L. Biwa), China (Qinghai), Taiwan (Emerald Peak Lake) and Malaysia (L. Chini) (Bakhtiari et al., 2009; Bandowe et al., 2014b; Fan et al., 2011; Han et al., 2015; Itoh and Hanari, 2010; Silliman et al., 1998; Slater et al., 2013; Venkatesan, 1988). There is a considerable debate about whether the precursor of perylene comes from within the lake itself or the surrounding terrestrial ecosystems (Silliman et al., 1998). The C/N ratio in the sediment of L. Fondocochoa ranges from 12.7–14.7 with the highest values in the most recent sediments (Fig. S1). This suggests that sedimentary organic matter in this lake is admixtures of both terrestrial and aquatic sources (Meyers and Lallier-Vergès, 1999). The origins of organic matter are fairly constant with only slightly increasing proportions of land-derived organic matter in recent times. Considering that PERY concentrations show a significant but weak negative correlation with C/N ($R = -0.53$; Fig. S4), we suggest that, in L. Fondocochoa, the proportion of aquatic or terrestrial organic matter is not the main driver of the production of sedimentary PERY (Bakhtiari et al., 2009; Fan et al., 2011; Han et al., 2015). Specific precursors of aquatic or terrestrial origin which have been suggested to be important for the formation of PERY in certain lakes might not be applicable to L. Fondocochoa, but perhaps non-specific precursors and/or favorable depositional conditions are the main drivers (Itoh and Hanari, 2010; Silliman et al., 1998). S, C and N show significantly negative correlations with PERY (which is in contrast to the relationship between these organic matter properties and pyrogenic PAHs). Negative correlations between sedimentary PERY and C (also observed in other high mountain lakes, e.g. Han et al., 2015), N and S (as observed in this study) suggests the utilization of sedimentary organic matter for the formation of PERY (Han et al., 2015). PERY is also found to be one of the dominant PAHs in soils, plants and termite nests in background regions of tropical Brazil (Bandowe et al., 2009; Krauss et al., 2005). The high proportion of PERY in terrestrial samples from tropical regions is considered to be partly a result of their biological production (Bandowe et al., 2009). Hence PERY in sediments of L. Fondocochoa may partly have been deposited with terrestrial materials (PERY in soils, leaves). This may explain the much higher PERY proportion of total PAHs in L. Fondocochoa compared to lakes in temperate regions (where the proportion of PERY frequently reaches <10% of the total PAHs in the surficial sediment cores) (Fernández et al., 2000; Han et al., 2015; Wakeham et al., 1980).

PAH flux rates in L. Fondocochoa are comparable with other remote lakes in the southern hemisphere (L. Laja and L. Galletué in south central Chile (Barra et al., 2006; Quiroz et al., 2005; Table 2) with fluxes ranging from 0.8 to 19.6 ng cm⁻² yr⁻¹ (\sum PAHs without PERY). As shown in Table 2, PAH flux rates in L. Fondocochoa and other remote South American lakes are in a range comparable to remote mountain lakes in North America and Scotland, but lower than lakes in urban areas of China. With its low levels of PAHs (compared to values found in the literature for other remote and urban lakes) L. Fondocochoa can be considered relatively pristine.

4.2. Comparison of PACs of L. Llaviucu with L. Fondocochoa

In the period from the 1950s to 2014, the fluxes of all PACs groups in L. Llaviucu (lower elevation) are 3.6 to 5.1 times higher than those in high elevation and remote L. Fondocochoa (Fig. 5). This is particularly true for HMW-PAHs. This is most reasonable because of the proximity of L. Llaviucu to the city of Cuenca. On the other hand, it suggests that, in the foot zone of the Andes (below 3400 m a.s.l.), PACs are very efficiently and at very short distances (15 km distance from Cuenca) scavenged out of the atmosphere. They barely reach more remote areas (30 km distance from Cuenca, L. Fondocochoa) in the high Andes at 4100 m a.s.l. This contradicts earlier observations in other mountain areas (Daly and Wania, 2005; Tremolada et al., 2008; Wania and Westgate, 2008), where the largest depositions were observed in cool and moist high-elevation sites (cold condensation effect). However, the specific meteorological conditions in our study area on the eastern slope of the Ecuadorian Andes show that precipitation rates reach

their maximum at about 3400 m a.s.l. (just above L. Llaviucu) but decrease sharply at 3500 m a.s.l. and above (L. Fondocochoa at 4130 m a.s.l.). Throughout the vertical profile, the climate is excessively foggy and wet with ca. 170 rainy days annually. Such particular meteorological conditions favor wet deposition and efficient scavenging of PACs and other pollutants from the atmosphere at very short distance and at elevations below 3500 m. As a consequence, we would expect that remote high elevation L. Fondocochoa would rather carry the fingerprint of long-distance atmospheric transport.

Indeed, aside from the differences in the PAH profiles of both lakes, there are also differences in the relative fractions of OPAHs and AZAs. In L. Fondocochoa, the OPAHs mixtures are dominated by 9,10-ANQ, 9-FLO, 1-INDA and 7,12-B(A)Dione whereas in L. Llaviucu, 2-MANQ is most abundant (Fig. S5). The ratio of 9-FLUO/FLUO (OPAH/PAH precursor) is much larger (typically >1) in L. Fondocochoa as compared to L. Llaviucu (mostly between 0.4 and 0.8) suggesting a much higher contribution of long-distance transported PACs in remote high elevation L. Fondocochoa. Moreover, L. Fondocochoa shows a much smaller diversity of AZAs (only carbazole) as compared with L. Llaviucu (quinoline, acridine and carbazole). In addition to the meteorological conditions and efficient scavenging in the catchment of L. Llaviucu, further factors may explain why L. Llaviucu is generally more contaminated with PACs and shows a different PAC profile than L. Fondocochoa.

L. Llaviucu is situated adjacent (15 km) to the city of Cuenca (Figs. 1 and 5), Ecuador's third largest city, which has experienced a significant increase in population from 110,000 people in 1975 to >350,000 in 2013. Lake Llaviucu is particularly affected by the winds coming from Cuenca, due to the topographic features (valley/channeling) (Figs 1 and 5). This urban growth was concomitant with boosting domestic combustion, industrial and traffic activities. Since 1975, non-commercial vehicles have increased yearly by 12% (Sander et al., 2015). Residential combustion in stoves and fireplaces is commonly incomplete and at low-temperature burning conditions (Lima et al., 2005). Thus, situated east of Cajas National Park and given the persistent easterly wind flow, the city of Cuenca is thought to constitute the most significant source for PACs deposited in the lakes of that area, particularly in the lakes of the eastern foot zone of the Andes at elevations below the precipitation maximum (i.e. below 3500 m a.s.l.). This interpretation is supported by the higher relative proportions and fluxes of HMW-PAHs in L. Llaviucu which are diagnostic for high-temperature combustion related to urban, industrial and traffic activities. Benzo(a)anthracene-7,12-dione (7, 12-B(A)Dione) which is also less volatile and much more partitioned into particle phases and, thus, readily scavenged from the atmosphere in the vicinity of source areas. Furthermore, the AZAs profiles supports the urban sources of PACs in L. Llaviucu: quinoline and acridine, both indicative of higher impact of urban high-temperature combustion or petrogenic activities, present in L. Llaviucu but were not found in remote L. Fondocochoa. Carbazole, in contrast, is related to biomass burning or forest fires and was detected in both lakes. Last but not least, the lower average 9-FLO/FLUO ratios in L. Llaviucu suggest predominantly short-distance transport and local sources of PACs (city of Cuenca) whereas remote L. Fondocochoa carries more the 9-FLO/FLUO fingerprint of long-range transported PACs from remote and diffuse source areas (Alam et al., 2014; Han et al., 2015).

Land use practices and rural domestic activities, in particular biomass burning of grasslands, forests and fuel wood, are an important source of LMW-PAHs. L. Llaviucu is located at the border of the National Park, close to inhabited areas, whereas L. Fondocochoa is situated remotely in the Park, where fire control was enforced by park authorities after ca. 2000. Extensive biomass burning is a common practice in the grasslands of the Páramo and in the montane Andean forest belt, and has been documented in this area for the past 2000 plus years (Hansen et al., 2003). Slash and burn techniques are still practiced despite the restrictions (Sarmiento, 2002). Our data from L. Fondocochoa show that flux rates of LMW-PAHs were almost as high in the 19th century compared with the period after 1950 onward suggesting that

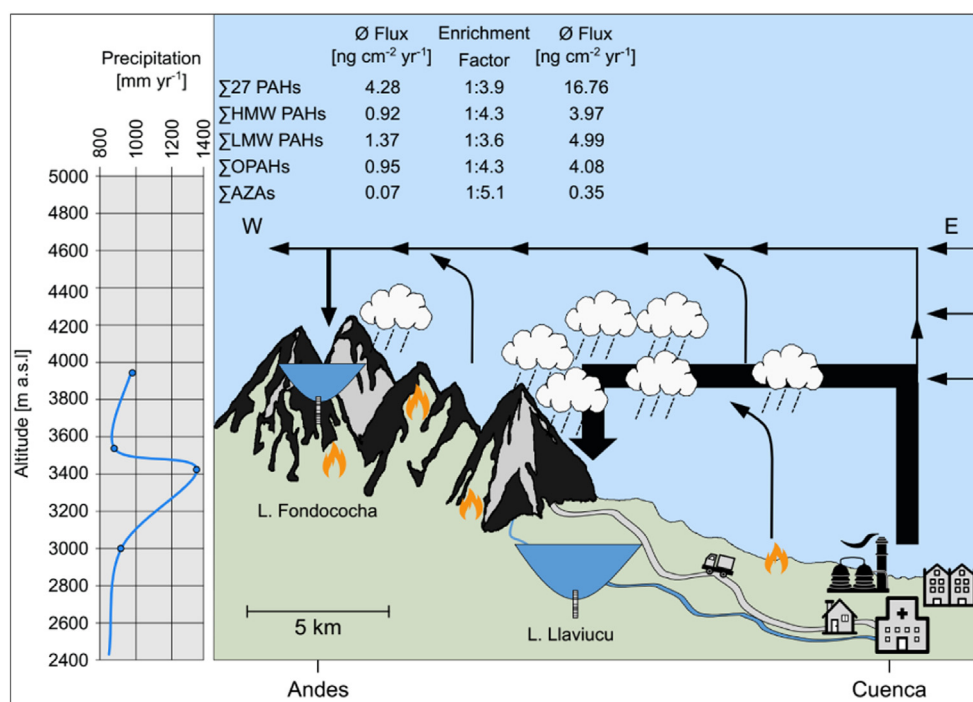


Fig. 5. Schematic diagram showing the geographic situation of both case-study lakes on the eastern slope of the south Ecuadorian Andes with the city of Cuenca. The climatic situation along the vertical gradient is shown with the elevation gradient of annual precipitation rates (station data and interpolation) and symbolized with the clouds. The arrows sketch qualitatively the pathways of PACs with the sources, the transport and the deposition.

biomass burning was as extensive in the past as it has been in the most recent decades. Again, L. Llaviucu shows about 4 times higher LMW-PAH flux rates than L. Fondococha, which can be attributed to the higher biomass of montane Andean forest compared to Páramo grasslands, and to the closer vicinity of L. Llaviucu to urban areas with generally more intense land use, rural and suburb activities at lower elevations. In both lakes, LMW-PAH fluxes show decreasing trends during the past 2–3 decades, which can be regarded as a response to better fire control by park authorities after ca. 2000. However, LMW-PAH emissions are still as high as they were during several decades in the past (19th century).

Moreover, ∑ HMW-PAHs fluxes are more than four times higher in L. Llaviucu than in L. Fondococha. However, whereas fluxes in L. Llaviucu increased until ca. 2000 and then levelled-off or even decreased, ∑ HMW-PAH fluxes in L. Fondococha show a strongly positive trend up to recent times. This suggests a source of HMW-PAHs in L. Fondococha which differs from emissions in L. Llaviucu. We attribute this source of additional HMW-PAHs to the Cuenca-Molleturo-Naranjal highway (Fig. 1) which experienced a strong infrastructure investment in the past 10 years, boosting traffic crossing the center of Cajas National Park close to L. Fondococha (ETAPA, 2016).

5. Conclusions

The sediments from high altitude mountain lakes in Cajas National Park, southern Ecuador, provide a record of historical depositional rates of PACs. These are the first PAC records for this part of the world.

The temporal fluxes of the PACs deposited in high elevation (4130 m a.s.l.) and remote L. Fondococha do not follow trends found in European or North American Lakes. Rather, the temporal trends show delayed increases and delayed peaks (compared to sites in the northern hemisphere). The PAC record in the Ecuadorian Andes (this study) is synchronous with the records from south-central Chile and follows the history of industrial and urbanization activities in Ecuador. In remote L. Fondococha, PAC depositional rates are generally low. The dominance

of more volatile PAHs (LMW-PAHs) and high 9-FLO/FLUO suggest mainly local biomass burning as the dominant PAH source, as well as PAHs that travel over long-distances in the atmosphere. The fluxes of PACs at lower elevation (3140 m a.s.l.) L. Llaviucu in the vicinity of the city of Cuenca are 4 to 5 times higher than those in L. Fondococha. The PAC profile in L. Llaviucu suggests local or regional fingerprints diagnostic for industrial and urban activities and road traffic, as well as for biomass burning related to agricultural activities and domestic low-temperature combustion in stoves and fireplaces.

The comparison of PAC profiles (depositional rates and speciation) in the two lakes at 3140 m and 4130 m highlights the very important role of microclimatic conditions along the altitudinal gradient on the eastern slope of the tropical Andes in Ecuador. From our data, we conclude that the very foggy and wet climate with a precipitation maximum at ca. 3500 m a.s.l. is very efficient in scavenging PACs from the atmosphere at short distances. This explains why the general principle of cold condensation (maximum deposition of pollutants in the remote highest areas of mountains) does not apply in the tropical Andes of Ecuador.

The depositional rates of PACs in remote L. Fondococha are broadly comparable with remote lakes in other parts of the world. L. Llaviucu at lower elevation and adjacent to the city of Cuenca reaches values that are reported for heavily industrialized and urbanized sites, e.g. in China.

Perylene was the most dominant PAH in the sediments of both lakes. Our data suggest in-situ formation of PERY from biogenic sources and non-combustion processes. The concentrations of sedimentary PERY were higher in remote L. Fondococha than in L. Llaviucu.

Our results provide further evidence that organic pollutants are transported through the atmosphere over short and long-distances and reach supposedly pristine and natural environments in high mountain areas such as Cajas National Park. Given the well-established, serious and multiple harmful effects of PACs in the environment, the protection of environments and safeguarding of ecosystem services must focus on the reduction of PACs emissions at their sources.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2017.10.060>.

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