

TEMPORAL TRENDS OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN A DATED SEDIMENT CORE OF A HIGH ALTITUDE MOUNTAIN LAKE: CHUNGARA LAKE- NORTHERN CHILE (18° S)

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ABSTRACT

In this study levels, fluxes and temporal trend of PAHs are reported in a sediment core from Chungará Lake (18° S) in Northern Chile. The sediments were obtained by Kayac corer and freeze dried. PAHs were extracted in SOXHLET system and measured by HPLC with diode array detector and fluorescence detection. Sedimentary record chronology was determined using ²¹⁰Pb isotopes and organic carbon (%) was also measured in sediments. Concentrations (ng g⁻¹ d.w.) of PAHs were low ranging from ~1 to 50. PAHs fingerprint was dominated by 3-ring (21%) and 4-ring. Organic carbon (%) ranged from ~17 to 24 (21±3) and no statistical significant correlation (p<0.05) was detected between OC (%) and PAHs along the sediment core. PAHs fluxes (µg m⁻²yr⁻¹) fluctuated from ~0.3 (cm 1) to 35 (cm 5) in 1978. LPAHs/HPAHs ratios (0.04 to 3) indicate petrogenic and pyrolytic origin of PAHs. This results contributes with new information of PAHs deposition at high altitudinal lake in Southern Hemisphere.

INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are widely distributed in different environmental compartments, they are derived from natural and anthropogenic processes, including forest and prairie fires, contamination by crude oils, consumption of fossil fuels (e.g. coal) and various refinery products (petrogenic origin)¹. It has been stated that after their emission part of them are prone to long range transport, and being detected at remote sites¹.

Previous studies reports that remote high mountain lakes could be acting as a natural trap for atmospherically transported pollutants. This phenomenon has been already described in the northern hemisphere for PAHs¹.

Sediment cores may provide insights into local and global time trends of past and present use of released chemicals²⁻³. For instance, investigations of contaminated sediment allow us to make useful comparisons of both global patterns and temporal trends⁴⁻⁶. In estimating human disturbance, the ¹³⁷Cs and ²¹⁰Pb isotopes are commonly used in sediment analysis to obtain temporal scales (geochronology) and sedimentation rates. In the last decade, this technique has considerably facilitated the interpretation of past time trends of PAHs¹ and PCBs sedimentary records⁶⁻⁷.

In Europe, Fernandez et al.¹ reported concentrations of PAHs in sediments of high altitudinal lakes, as higher as urban or industrial areas. In the Southern Hemisphere, particularly in Chile, there is little information on the contemporary levels of these pollutants at remote sites. For instance, few studies have been conducted to estimate temporal trends of some PCBs^{6,7}. In particular, Quiroz et al.⁸ have reported levels of PAHs at Laja Lake in central Chile. To increase our knowledge in other areas of Chile, in this study PAHs were determined at Chungará Lake, a high remote altitudinal lake in the northern Chile in order to determine PAHs fluxes and to establish depositional trend with the support of chronological studies using ²¹⁰Pb isotopes.

EXPERIMENTAL

Sampling sites

Chungará Lake is located in the Andean Mountain in the Lauca National Park of the 14th Region of Chile (18° 13' S; 69° 10' W) (Figure 1). Being one of the highest lakes, at 4320 meters above sea level (m a.s.l.), is the second in South America after Titicaca Lake. The lake has a surface of 13 km² and a watershed of about 260 km² with a maximum depth of 34 m⁶⁻⁷. Chungará Lake is considered a tropical highland lake, volcanic, polymictic with a high radiation and low temperatures and saline characteristics. The Lake has a variable annual and interannual pluvial regime depending on the "el ENSO" phenomenon¹⁰.

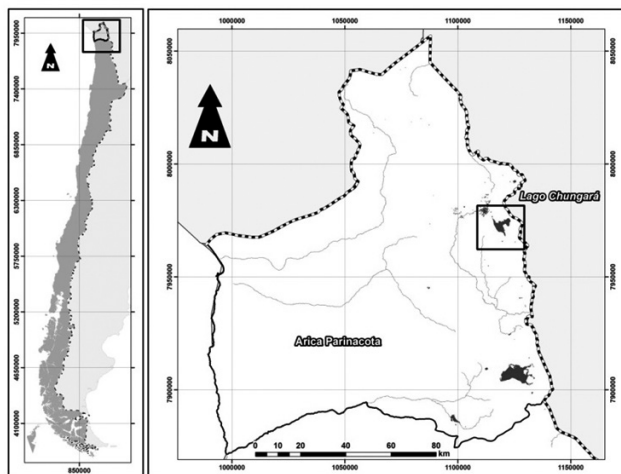


Figure 1. Location of study area and sampling site at Chungará Lake, northern Chile.

Sampling procedure

Sediment cores were collected in the deepest part of the Chungará Lake in January 2003 with a Kayac corer. Sediments were sliced into 1 cm intervals "in situ" and transported to the laboratory in an ice cooler. Samples were weighed and sealed to avoid contamination.

Analytical procedure

Details about extraction and clean-up of samples have been described previously⁹. Briefly, sediments (5 - 10 g) were freeze dried at -50°C and at a pressure of 0.2 mbars. Samples were homogenised with anhydrous sodium sulphate, placed in cellulose thimbles, and Soxhlet extracted using dichloromethane (DCM) for 18 hrs. Extract were concentrated and percolated through activated copper to remove sulphur and exchanged into hexane solvent. Then, extract (0.5 ml) were cleaned up on a silica gel column activated at 130 °C over night. The final sample were eluted with 15 ml of hexane: DCM (1:1) for the PAHs fraction and concentrated until 0.5 ml, then exchanged into 0.5 ml of acetonitrile⁹.

PAHs identification and quantification were performed by HPLC on a Waters (Milford, MA, USA) liquid chromatographic system, with a Waters 474 Scanning Fluorescence Detector and Waters 996 Photodiode Array

Detector, using a Supelcosil-PAHs column (250×4.6-mm I.D., particle size 5 µm). Details about elution program, column temperature and fluorescence detection characteristics are reported elsewhere⁹. Each sample was quantified for 16 PAHs proposed by EPA as priority pollutants (see Table 1).

Quality Assurance and Control (QA/QC)

Procedural blanks and reference material purchase from National Research Council Canada were analysed for QA/QC purposes. Prior to sediment extraction six analytical blank was prepared using the same extraction and clean-up procedure. Analysis of the PAH reference material (HS-6) showed a mean recovery of 80% (only naphthalene) and 102 % for other PAHs. In addition, before to sediments extraction, samples were spiked with a recovery standard of anthracene (400 ng) ranging between 90 and 110%. Limits of detection (LODs) were defined as the average blank (n = 4) plus three standard deviations (SD). When target compounds were not detected in blanks, 2/3 of the instrumental detection limit was used as the method detection limit (IDL). All qualified data (i.e., exceeding the MDL) were blank corrected. MDLs was estimated in 0.05 ng g⁻¹ for PAHs.

Organic carbon determination

Organic carbon analysis was also conducted as reported by Gaudette et al.,¹¹. Briefly, 0.1- 0.5 g of dry sediment were thoroughly mixed with 10 ml of potassium dichromate (K₂CrO₇, 1 N). Concentrated sulphuric acid (20 ml) was successively added and the mixture was shook for 30 s and then left to rest for 30 min. The sample was diluted to 100 ml with distilled water, 10 ml of phosphoric acid (H₃PO₄) plus 0.2 g of sodium fluoride (NaF). Finally, samples were cooled and titled with ferrous ammonium sulphate Fe₈(NH₄)₂(SO₄)₂ 0.5 N¹¹.

Sediments dating

Two replicate core samples 50 cm long and 6 cm in diameter were analysed. The cores were X-rayed to check for biological or physical disturbance. Then, the cores were extruded vertically and cut into 1 cm slices for dating and for chemical analysis.

The ²¹⁰Pb (half-life 22.3 years) activity of each slice was calculated from

the measured activity of its first daughter isotope ²¹⁰Po (half-life 138.4) by means of α spectrometry¹². Supported ²¹⁰Pb (the amount in equilibrium with Ra in the sediment matrix) was estimated from the ²¹⁰Po activity of the three lowest slices; these slices showed nearly identical activities.

Ages and sedimentation rates were determined from ²¹⁰Pb activity by means of the constant rate of supply (CRS) model. In the model, the supply of ²¹⁰Pb from the atmosphere does not vary with time¹². In a simple case, where both ²¹⁰Pb fallout and sedimentation rate are constant through time, the ²¹⁰Pb activity in a core declines smoothly with depth from a maximum at the top to a constant value the supported ²¹⁰Pb activity in equilibrium with Ra in the sediments. Under these simple conditions, the downward decrease in unsupported ²¹⁰Pb activity is controlled solely by the age of the deposit, which controls progressive decay of the ²¹⁰Pb that had accumulated as fallout¹².

RESULTS AND DISCUSSION

In Table 1 are reported ²¹⁰Pb activities, concentrations as ΣPAH (ng g⁻¹ d.w.), fluxes and organic carbon content (%). As seen in Figure 2a the core radiography shows that Chungará Lake is suitable for stratigraphic analysis. The core lacks obvious signs of perturbations that have redistributed ²¹⁰Pb or PAHs after their deposition. Sediments from Chungará Lake are mainly composed by medium silt texture with a characteristic particle size ranging between 10.1 and 10.2 µm with the absence of coarse particles. However, the values obtained for ²¹⁰Pb activities from surface to 4 centimeter, suggest a little disturbance in the superficial section of the sediments (Figure 2a). Below this layer the activities decreased exponentially with depth showing a typical decay activity profile, reaching a background value at 11 cm. Sedimentation (0.3±0.03 cm yr⁻¹) and mass accumulation rates (0.05±0.006 g cm⁻² yr⁻¹) were estimated below the surface layer (Figure 2b). The CMR model obtained also describes the decay activity and, suggesting that mixing does not prevail over the sedimentation process. The dating of the core accounts for surface activities, however the calculated ages do not show higher discrepancies compared to the ages obtained from the model-predicted values, which do not include the surface layer (Figure 2c). The total inventory accounts for 36.5±3.3 dpm cm⁻², supported by a flux of 1.1±0.1 dpm cm⁻² yr⁻¹ (Table 1).

Table 1. ²¹⁰Pb chronology, ΣPAH (ng g⁻¹ d.w.), fluxes (µg m⁻² yr⁻¹) and organic carbon (OC) (%) in sediments of Chungará Lake, northern Chile.

Depth (cm)	²¹⁰ Pb _{ss} ^a (dpm g ⁻¹)	Inventory ^b (dpm cm ⁻²)	Age Years	Date	ΣPAH (ng g ⁻¹ d.w.)	PAHs Flux (µg m ⁻² yr ⁻¹)	Ratio ^d Low/High PAHs	OC (%)
1	20.0±0.9	3.4±0.3	0	1999	2	0.3	0.8	17±0.3
2	21.7±0.8	3.7±0.3	3.16	1996	6	1.1	1.1	20±0.8
3	15.5±0.7	4.1±0.3	3.79	1992	46	24	0.2	18±0.1
4	17.6±0.8	6.5±0.4	4.83	1987	17	14	3	22±0.2
5	11.0±0.6	4.6±0.4	9.47	1978	40	35	0.04	21±0.2
6	7.6±0.5	3.6±0.3	9.04	1969	1.1	0.8	2.5	24±0.2
7	6.7±0.6	3.3±0.3	9.42	1959	0.8	0.5	1.8	22±0.5
8	5.6±0.5	2.8±0.8	11.83	1947	0.9	1	3	24±0.04
13	4.3±0.5	2.0±0.2	15.19	1930	c	c	c	c
17	3.3±0.4	1.5±0.2	18.79	1913	c	c	c	c
21	2.5±0.4	1.1±0.2	27.48	1886	c	c	c	c

^a ²¹⁰Pb_{ss} ± σ (counting error), Inventory ± σ (propagated error); ^b Inventory is the accumulated activity beneath the surface, corrected for background activity; ^c not detected; ^d Low molecular weight PAHs/ High molecular weight PAHs.

ΣPAH concentrations (ng g⁻¹ d.w.) presented a minimum of ~1 (7 cm) and a maximum of 50 (5 cm). The profile showed two clear picks along the sediment core, one detected in the upper section, however downward the core PAHs were not detectable (from 8 cm to 20 cm depth). These levels are lower than those detected in other areas of central Chile i.e., Laja Lake (~230 ng g⁻¹ d.w.), in Galletue Lake (~290 ng g⁻¹ d.w.) and at Icalma Lake (~3180 ng g⁻¹ d.w.)⁵.

PAHs with 3-ring (21%) and 4-ring were dominant along the sediment

core of Chungará lake (Figure 3). Table 2 present concentrations of individual PAHs in the first 20 cm of the sediment core of Chungará Lake. The most dominant individual PAH was pyrene accounting for 62% followed by phenanthrene (13%) and fluoranthene (12%) of the total ΣPAH composition (Figure 3). The predominance of pyrene in highland lakes has been previously reported in European lakes with a percentage fluctuating between 50-70%¹.

However, low concentrations of HMW PAHs (B[b]F, B[k]F, B[a]P, D[ah]A, B[ghi]P) were also detected in the surface sediments of the lake (cm 1-4).

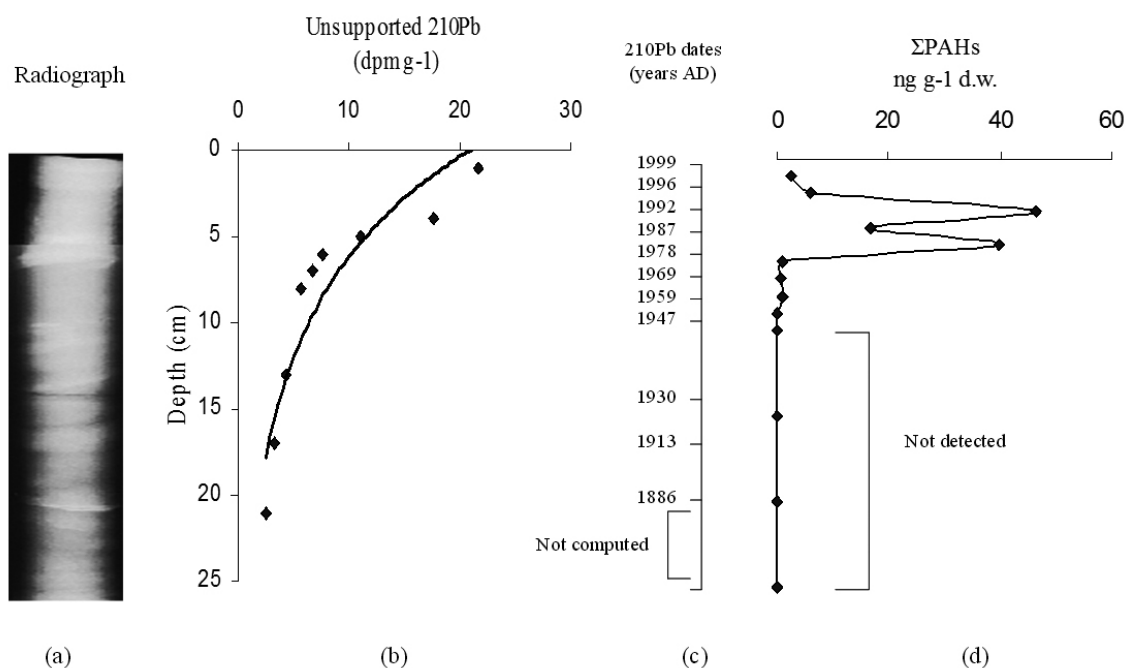


Figure 2. (a) X-ray radiograph, (b) unsupported ²¹⁰Pb activity, (c) chronological model and (d) PAHs ng g⁻¹ d.w. in a sediment core from Chungará Lake, northern Chile.

Table 2. PAH concentrations (ng g⁻¹ d.w.) in a sediment core from Chungará Lake, northern Chile.

Depth (cm)	1	2	3	4	5	6	7	8	9	10	15	20
Compound												
Ac	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Ace	<0.05	<0.05	<0.05	3	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Fl	<0.05	1	1	1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Phe	1	2	5	2	1	1	1	1	<0.05	<0.05	<0.05	<0.05
An	0.1	0.1	0.1	<0.05	<0.05	0.1	0.1	<0.05	<0.05	<0.05	<0.05	<0.05
Flo	<0.05	<0.05	11	1.44	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Py	<0.05	<0.05	26	<0.05	38	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
B[a]A	<0.05	<0.05	0.3	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Chry	<0.05	0.23	1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
B[b]F	0.2	0.3	1	0.3	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
B[k]F	0.1	0.2	0.4	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
B[a]P	<0.05	<0.05	1	0.1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
D[ah]A	<0.05	0.1	1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
B[ghi]P	1	2	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
I[cd]P	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Total PAHs	2	6	50	8	40	1	1	1	<0.05	<0.05	<0.05	<0.05

Abbreviations: Ac=Acenaphthylene, Ace=Acenaphthene, Fl=Fluorene, Phe=Phenanthrene, An=Anthracene, Flo=Fluoranthene, Py=Pyrene, B[a]A=Benzo[a]Anthracene, Chry=Chrysene, B[b]F=Benzo[b]fluoranthene, Benzo[k]F=Benzo[k]fluoranthene, B[a]P=Benzo[a]pyrene, D[ah]A=Dibenzo[ah]anthracene, B[ghi]P= Benzo[ghi]perylene, I[cd]P= Indeno[1,2,3-cd]pyrene; Method detection limit= MDL (0.05)

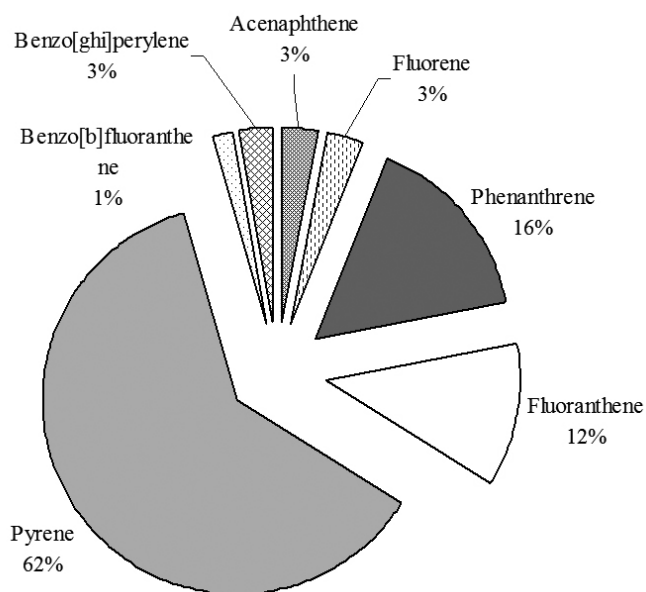


Figure 3. PAHs isomer composition (%) in a sediment core from Chungará Lake, northern Chile.

In order to discriminate between petrogenic and pyrolytic contamination low-molecular weight (LPAHs) and high-molecular-weight (HPAHs) compound abundances were assessed (Table 1).

Low values of LPAHs/HPAHs ratio (<1) suggest pyrolytic contamination, while petrogenic contamination is characterized by LPAHs/HPAHs ratio (>1)¹. LPAHs/HPAHs ratio showed a mixed origin at the first section of the sediment core (1-3 cm) ranging from 0.04 to 1 indicating a prevalence of pyrolytic origin. Therefore, the most likely source could include combustion processes (e.g., fossil, fuel combustion, forest fires, shrub and grass fires). Nevertheless, LPAHs/HPAHs ratio of ~2-3 was also detected at cm 4, 6, 7 and 8 suggesting a petrogenic origin whose origin is closely related to petroleum products (e.g., oil spills and road (tar coal)). This results might indicate two different sources of PAHs into this pristine environment: first the influence of atmospheric deposition (dry and wet) which are also supported by air masses passing over the Amazon basin¹³. This evidence has been demonstrated by analyzing the isotopic composition of rain in Northern Chile highland areas¹³. And, second, local sources related to anthropogenic activities mainly from vehicular traffic or road maintenance (road= Carretera Arica la Paz - Ruta 11) located closely to the lake ~100 m. Organic carbon (%) ranged from ~17 to 24 (21±3) in sediments of Chungará Lake (Pozo et al., 2007) and the Pearson correlation analysis indicates no significant ($p>0.05$, $r=0.6$) correlation between PAHs and OC (%) along the sediment core.

Fluxes ($\mu\text{g m}^{-2}\text{yr}^{-1}$) of ΣPAH in surface sediments were calculated using mass accumulation rates (Table 1). Estimated fluxes of total PAHs ranged between $0.3 \mu\text{g m}^{-2}\text{yr}^{-1}$ (1 cm) corresponding to year 1999 and $35 \mu\text{g m}^{-2}\text{yr}^{-1}$ (5 cm) in 1978 (Table 1). Fluxes and PAH concentrations were also detected in early 1947 in the 8 cm core section with $1.0 \mu\text{g m}^{-2}\text{yr}^{-1}$. These results were similar to fluxes reported in other remote lake i.e., Arresjøen—Artic [4], however, PAHs levels were lower than values detected in other remote lakes

in the west and central Europe ($44\text{--}150 \mu\text{g m}^{-2}\text{yr}^{-1}$), and than those reported by Barra et al.,⁵ and Quiroz et al.,⁸ in Central Chilean Lakes ($6\text{--}464 \mu\text{g m}^{-2}\text{yr}^{-1}$).

CONCLUSIONS

High altitude remote lakes provide useful information for studying environmental changes and the historical record of contamination events. Concentrations and fluxes of PAHs are lower than those reported in other Chilean and European Lakes and these data support the conclusion that the Chungará Lake is a relatively pristine area. LPAHs/HPAHs ratio analysis showed a mixed PAHs origin (petrogenic and pyrolytic) along the sediment core with two sources of PAHs corresponding to local source (for HPAHs) and atmospheric deposition (dry and wet) (for LPAHs). In particular, PAH deposition in this high altitude mountain lake has increased significantly in late '70 as a result of anthropogenic activities (i.e. construction of the road). Before 1970 the sum of PAH concentration (ΣPAH) was very low with total concentrations less than 2 ng g^{-1} d.w. Further research is needed to see the influences of national and international regulations on the global distribution of legacy and emerging compounds in pristine ecosystems.

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