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CHEMICAL SCIENCES

Polycyclic Aromatic Hydrocarbons in Antarctic Ice Core: Prior Study by Homogeneous Liquid-Liquid Extraction and High–Performance Liquid Chromatography

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Abstract: Organic contamination has been less investigated in Antarctic snow and ice than in other matrices due to analytical operational problems. In this study, the concentration of 14 Polycyclic Aromatic Hydrocarbons was determined in a shallow firn core by Homogeneous Liquid-Liquid Extraction and High–Performance Liquid Chromatography with a Fluorescence Detector. This investigation aimed to develop a simple analytical methodology for future application directly in fieldwork, taking advantage of the simplicity and small sample volumes. The analyte recoveries were 71–99% considering a 100 ng L^{-1} initial concentration of each compound, with a relative standard deviation of 1.1–9.9%. Analytical sensitivity/ detection limit/ quantification limits varied from 7.8/ 20.3/ 67.6 ng L^{-1} for fluoranthene to 0.6/ 1.5/ 5.1 ng L^{-1} for anthracene. These analytical parameters allow us to apply the method to real samples. We found visible differences at various firn core depths when considering the sum of total analytes under study. The highest total concentration was 741 ng L^{-1} and the lowest one 134.9 ng L^{-1}. The methodology can be applied without mixing samples with adequate analytical parameters, and it can preserve the firn core temporal resolution, which is an advantage for application in fieldwork.

Key words: Antarctica, HLLE-HPLC-FLD, ice core, PAH.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a family of over 400 organic compounds consisting of conjoined aromatic rings (having at least two fused aromatic rings) and are toxic and carcinogenic pollutants (Lammel et al. 2009, Zhao et al. 2009).

According to their origin or formation temperature, PAHs are classified into pyrogenic, petrogenic, and biogenic/natural. They are a geochemically relevant family of semi-volatile compounds and are associated with the incomplete combustion of organic material. They originate from accidental volcanic eruptions and forest fires, human activities such as burning gasoline and other petroleum-derived fuels, and a various combustion process, including industrial and local waste incineration. Due to their persistence and ability to revolatilize in the environment, they can travel long distances, with long-range atmospheric transport being a route of arrival to polar areas (Bengtson-Nash 2011, Cabrerizo et al. 2014).

The importance of extending the knowledge about organic pollutants in the Antarctic environment system is found in the process of bioaccumulation, as their lipophilic properties

can cause harmful effects in biota (Montone et al. 2016).

Due to PAHs' toxicity, persistence, and bioaccumulation, they are classified as part of the United States Environmental Protection Agency (US EPA) Priority Pollutants list. Establishing regulatory guidelines for the different matrices. For example, for benzo (a) pyrene, US EPA sets 200 ng L^{-1} like the maximum concentration in drinking water. (US EPA 2014).

Antarctica is a unique natural laboratory for researching global pollution and ideal for performing baseline studies on environmental contamination. Moreover, human impact on the Antarctic environment intensifies processes related to climate changes, even considering all the obligations for human activities and strict guidelines of the Protocol on Environmental Protection to the Treaty of Antarctica (Bargagli 2008, Szopinska et al. 2019).

Atmospheric emissions from human activities are transported to the Antarctic continent and are sources of PAHs. They include activities related to the research logistic, tourist vessels, and accidental fuel spills (Aislabie et al. 1999, Kim et al. 2019). Antarctic ecosystems have been subjected to increased human pressure for at least six decades (Bargagli 2008). The presence of PAHs in various matrices in Antarctica have been reported – soil, sediment, snow, seawater, and marine biota – at concentrations of parts per billion (Cincinelli et al. 2005, Curtosi et al. 2007, Minero et al. 2010).

Extraction and preconcentration steps are necessary before the analytical measurements at ultra-trace levels in aqueous matrices from remote areas. Different extraction methods have been used to extract analytes from liquid samples, ranging from the wide-spread conventional solid-phase extraction (SPE) and liquid-liquid extraction (LLE) to the more recently so-called microextraction techniques, in which the required sample volume, cost, and the solvent consumption are all reduced (Rezaee et al. 2006, Leong et al. 2010, Zheng et al. 2015, Benedé et al. 2018, Zeeb & Farahani 2018).

Studies of aqueous samples from Antarctica include, mostly, LLE and gas chromatography coupled to mass spectrometry (GC-MS) analysis in their extraction methods, reporting variable total PAH concentrations in different types of samples. For example, in seawater, concentrations from 1.21 to 3.96 ng L^{-1} have been reported by GC-MS (Cincinelli et al. 2008) and from 510 to 1200 ng L^{-1} by LLE-GC-MS (Bícego et al. 2009); in ice core samples from 0.7 to 9.1 ng L^{-1} by LLE-GC-MS (Fuoco et al. 2012) and freshwaters from 0.25 to 1365 ng L^{-1} by GC-MS (Szopinska et al. 2019).

The method recommended by the International Organization for Standardization (ISO) for determining PAHs in water, ISO 17993:2002, is based on LLE and HPLC (Wolska 2008), but LLE needs large sample volumes (liters) and is laborious. Therefore, the application of other extraction methods has also been implemented with different instrumental in aqueous antarctic samples, for example, for total PAHs concentrations in seawater, the application of SPE-GC-MS with reported values between 5.42 and 34.37 ng L^{-1} (Cao et al. 2018) and use of LLE coupled to High-Performance Liquid Chromatography with Fluorescence Detector (HPLC-FLD) reported values from 7.32 to 23.94 ng L^{-1} (Stortini et al. 2009).

In this context, Homogeneous Liquid-Liquid Extraction (HLLE) is an interesting method for determining organic compounds in aqueous matrices considering its accuracy and precision. HLLE is a microextraction based on the phase separation phenomenon in a ternary solvent (water/methanol/chloroform) system by salt addition. This method extracts the target compounds from a homogeneous solution into

a minimal sedimented phase. In HLLE, there are no interfaces between the water, consolute and the extracting solvent. In other words, the interface surface area is infinitely large. Accordingly, no vigorous mechanical shaking is necessary (Tavakoli et al. 2008, Rezaee et al. 2010, Shamsipur & Hassan 2010, Yazdanfar et al. 2014). In addition, the HPLC-FLD allows simultaneous PAHs analysis, detection and quantification at ultra-traces levels concentrations (Windal et al. 2008, Shamsipur & Hassan 2010).

The purpose of this research was to develop and evaluate an analytical methodology based on HLLE and adequated for measuring 14 PAHs in Antarctic snow and ice core samples, prioritizing the use of small sample volumes and a simple extraction technique to be eventually carried out in the fieldwork. This study was carried out at University of Chile Laboratories.

MATERIALS AND METHODS

Firn core samples

This work discusses PAHs analysis on seven sections from the 42.5 m firn core IC-5 (82°30.5'S, 79°28.0'W, 950 m above sea level) obtained in the austral summer 2004/2005 by the Chilean–Brazilian group on an ITASE (International Trans-Antarctic Scientific Expedition) traverse from Patriot Hills to the South Pole. Figure 1 shows the traverse path and the IC-5 location (Mello Marques et al. 2014). The IC-5 site is approximately 830 km from the South Geographic Pole (90ºS) and 270 km from the Parodi Chilean Meteorological station (80º10'S, 81º26'W) – in the Patriot Hills mountains.

These mountains are just south of the Ellsworth Mountains, where is found the highest Antarctic Peak (Vison Masif, 4,892 m above sea level), and it has a strong influence on the regional accumulation pattern, probably due to divergence in the flow of snow moved by the wind, which results in reduced accumulation. The rate of accumulation increases as you move far from the mountains, with ablation occurring over the blue ice field and accumulation in the glacier area (Casassa et al. 1998). At the firn core site, ice flows to the NE from Patriot Hills – towards the Ronne Ice Shelf.

The IC-5 firn core stratigraphy consists of snow and firn, and drilling did not reach the firn/ice transition. Some thin radiation-melting lenses were observed but with no apparent percolation. Using a calibrated platinum probe, the measured temperature at a depth of 10 m is -29 °C, virtually identical to the mean annual temperature in the Patriot Hills (-30 °C) (King & Turner 1997). The mean accumulation rate for the upper 10 m at the IC-5 site is 0.37 m year^{-1} (Hammes et al. 2009).

Drilling was performed using a Fast Electromechanical Lightweight Ice Coring System (FELICS) (Ginot et al. 2002) and was carried out during the expedition return trip. In the field, the IC-5 core was cut into sections of approximately 1 m in length, packed in polyethylene bags and then stored in high-density Styrofoam boxes and transported in solid state by air to New York (U.S.A.) and sent to the Climate Change Institute (CCI) at the University of Maine, USA, where it was subsampled by Osterberg's procedure (Osterberg et al. 2006) and stored at -20 °C in a cold room.

The samples used in this work correspond to the upper portion of the IC-5 core (from 3.7 to 6.0 m). These samples were divided into seven sections (see Table I). All samples were placed in deactivated amber glass vials and stored at -10 °C.

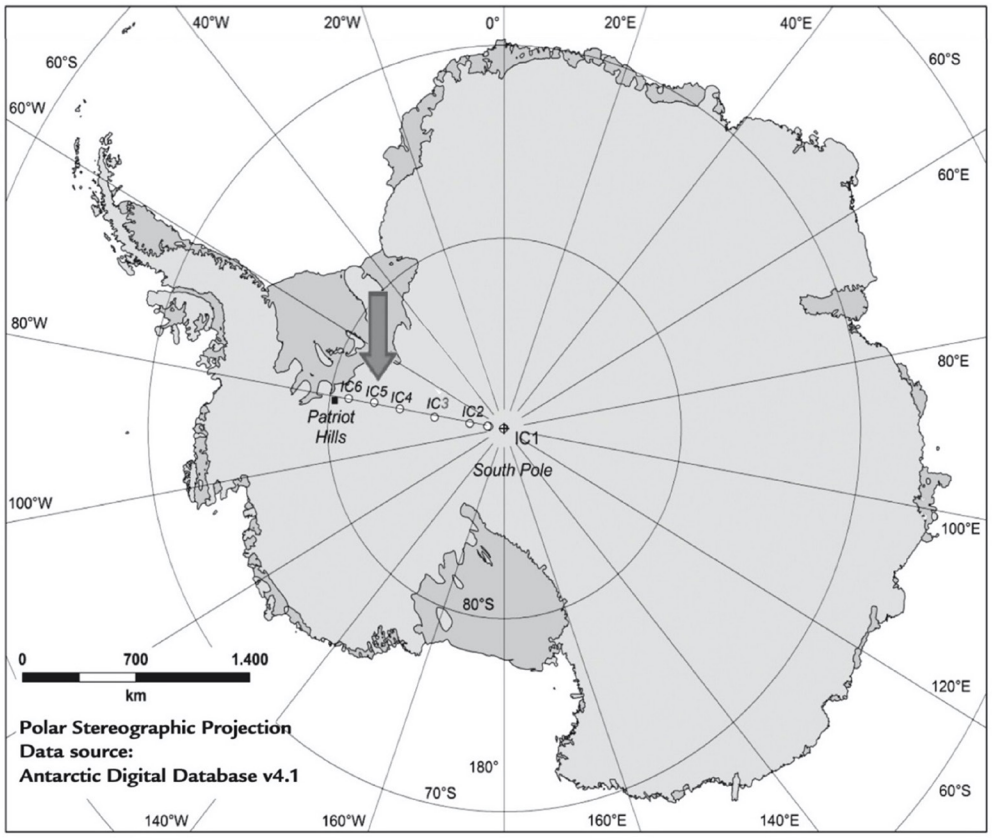

Figure 1. Ice core collection site (green spot). Geographical localization of IC-5 core in Antarctica (82°30.5'S, 79°28'W).

Chemicals

All working material and glass containers were deactivated with Sylon-CT solution (5% dimethyldichlorosilane in toluene, Sigma-Aldrich) and rinsed with methanol. Certified solid references of anthracene (Anth), fluoranthene (Flu), naphthalene (Naph), phenanthrene (Phen), benzo[k]fluoranthene (BkF), benzo[b] fluoranthene (BbF) and benzo[a]pyrene (BaP) from AccuStandard (New Haven, CT, USA); benzo[g,h,i]perylene (BghiP), chrysene (Chry), pyrene (Pyr) from Sigma-Aldrich (Darmstadt, Germany); benzo[a] anthracene (BaA), dibenzo[a,h]anthracene (DahA), indeno [1,2,3-c,d] pyrene (IP), and coronene (Cor) from Dr. Ehrenstorfer (Augsburg, Germany). All reagents were of high-purity grade and used as received. Acetonitrile, methanol, chloroform, and toluene were from Merck (Darmstadt, Germany). All of these reagents were of HPLC grade and used as received.

Sodium chloride was of analytical grade. Stock solutions of each PAH were made at a concentration of 200 μg mL^{-1}, and a standard mixture of all PAHs (5 μg mL^{-1}) was prepared in

Table I. Ice core IC-5 subsamples description.

Sample	Top [m]	Length [m]
IC-5.1	3.725	0.320
IC-5.2	4.045	0.350
IC-5.3	4.395	0.380
IC-5.4	4.130	0.355
IC-5.5	5.130	0.400
IC-5.6	5.600	0.180
IC-5.7	5.780	0.240

Acetonitrile: $CHCl_3$ (1:1) to achieve a response at the comparable level in HPLC-FLD. Working solutions were freshly prepared by diluting the mixed standard solution with nanograde water to the required concentrations. All standards and working solutions were stored at 4 ºC in darkness.

Instruments

HPLC with fluorescence detector analysis was performed on a liquid chromatograph equipped with a Waters 600 HPLC pump, a Waters 2475 fluorescence detector and a Waters 717 autosampler (Milford, MA, USA). The column was an Inertsil HPLC ODS-P (250 x 4.6 mm ID, 5 µm particle size, 35 ºC) from GL Sciences (Tokyo, Japan). The mobile phase was a mixture of acetonitrile (A) and water (B) at a flow rate of 1.4 mL min^{-1}. The following gradient sequence was used: 0–0.1 min 70% (A) isocratic; 0.1–10 min linear gradient 90% (A); 10–15 min 90% (A) isocratic; 15– 20 min linear gradient 100% (A); 20–32 min 100% (A) isocratic. Then, back to the initial condition: 32–35 min linear gradient 70% (A); 35–38 min 70% (A) isocratic. An injection volume of 20 µL was employed. Four channels were used to define the excitation and emission wavelengths (λexc/λem) in the fluorescence detector: channel A 220/330; channel B 292/410; channel C 292/426; and channel D 300/500. Waters Empower 2 (Milford, MA, USA) was the chromatograph software.

Homogeneous liquid-liquid extraction procedure

A glass system method was implemented by Cerón-Neculpan (Cerón-Neculpan 2012) based in the Tavakoli system (Tavakoli et al. 2008). The extraction from 3.5 mL of aqueous samples was performed by adding a mixture of 120 µL of chloroform ($CHCl_3$, extracting solvent) and 1.2 mL of methanol (CH_3OH, as consolute solvent) in a tronconic deactivated glass vial and manual shaking for 60 seconds. The phase separation was performed by adding 0.47 ± 0.10 g of NaCl into the solution and shaking until the complete dissolution of the salt at room temperature. A cloudy mixture was formed in the tube that was centrifuged (Function Line Centrifuge Heraeus Instruments, 4000 rpm maximum speed, 3939 g maximum force) for 10 minutes at 3500 rpm, and the extract (sedimented phase) was recovered with a glass syringe (Hamilton™ 1700 Series Gastight™ Syringes: TLL Termination; 100 µL). This extract was diluted with acetonitrile (HPLC grade, Merck) at a 1:1 rate and then analyzed by HPLC-FLD.

HLLE-HPLC-FLD method validation and analytical parameters

Before extracting, concentrating and measuring analytes in real samples, it was necessary to validate and determine analytical quality parameters. Analytical sensitivity (S), limits of detection (LODs), and quantification (LOQs) for 99% accuracy were calculated according to equations 1, 2, and 3. Five points in triplicate were measured for statistical determination of LODs, LOQs, S, and linear trend.

These samples were processed using the sample preparation procedure described above and spiked with different volumes (on the order of microliters) of dilute solutions of the selected 14 PAHs. The initials concentrations in the aqueous samples were between 30 and 110 ng L^{-1}. The analytical blank was nanopure water and was intercalated in the HLLE-HPLC-FLD process. Calibrations curves included the concentration of each PAH between 200 and 3000 ng L^{-1}. Linearity was established from the instrumental signal and concentration of every target compound.

$$S=\frac{S_{R/C}}{b} \quad (1)$$

$$LOD=3\left(\frac{S_{R/C}}{b}\right)\left[\frac{n-2}{n-1}\right]^{1/2} \quad (2)$$

$$LOQ=10\left(\frac{S_{R/C}}{b}\right)\left[\frac{n-2}{n-1}\right]^{1/2} \quad (3)$$

where $S_{R/C}$ is the standard deviation of the regression and b is the slope of the linear regression equation. The number of the data pair was n.

The recovery percentages (%R) and Enrichment Factors (EF) were calculated according to equations 4 and 5, respectively, considering an initial concentration equal to 100 ng L^{-1} for each PAH in an aqueous mix solution.

$$\%R=\frac{m_f}{m_i}\cdot 100 \quad (4)$$

$$EF=\frac{C_f}{C_i} \quad (5)$$

where m_i and m_f were initial mass in the sample and final mass in the extract of each PAH. C_i and C_f were the initial concentration and final concentration of each PAH in the sample and extract, respectively.

Real samples

The HLLE-HPLC-FLD method was applied, all samples were analyzed in triplicates and blanks were intercalated for analytical quality. The protocol previously defined was applied using 3.5 mL of sample volume. All blanks were analyzed in the same setup as the samples, using the same reagents and nanopure water. Acetonitrile was added to HLLE extract to avoid volatilization losses. The previous sample volume was named V_S, and extract volume before dilution was called V_E. Calibrations curves included the concentration of each PAH between 200 and 3000 ng L^{-1}.

Some environmental PAHs molecular ratios were studied: anthracene/(anthracene + phenanthrene), named I, and fluoranthene/(fluoranthene + pyrene), named II, can be calculated for some samples.

RESULTS AND DISCUSSION

HLLE-HPLC-FLD method

The obtained analytical parameters for the HLLE-HPLC-FLD method, considering a confidence interval of 99%, and the values are shown in Table II. The extraction method shows a linear behavior – with the correlation coefficients (R^2) between 0.9654 and 0.9998 for Flu and Anth respectively. The analytical sensitivity, LOD, and LOQ varied between 7.8/ 20.3/ 67.6 ng L^{-1} for Flu and 0.6/ 1.5/ 5.1 ng L^{-1} for Anth.

The PAHs enrichment factors were calculated as the ratio between the final concentration of analyte in the sedimented phase and its initial concentration in the sample solution, values obtained were 34 and 56 for BaP and BghiP, respectively. The mean recoveries were 71% (Cor) and 99% (BbF and Chry) with a relative standard deviation of 1.1 - 9.9% (see Table III). These EF and recovery values indicate that the pre-concentration method is highly efficient in all cases.

In another work, Leong et al. (2010) performed a 16 PAHs extraction through DLLE with different halo solvents from aqueous samples obtaining LODs in order of 100 ng L^{-1}. Considering that the DLLE method is based on the same extraction principle and that the determination of the analytes was by GC-MS, it can be said that our results obtained by HLLE-HPLC-FLD are better than the former method. Even when their EFs are higher than those obtained in the present

Table II. Analytical parameters for HLLE-HPLC-FLD method.

Analyte	R^2	S [ng L^{-1}]	LOD [ng L^{-1}]	LOQ [ng L^{-1}]
Naph	0.9854	6.8	17.7	59.1
Phen	0.9878	3.5	9.1	30.3
Anth	0.9998	0.6	1.5	5.1
Flu	0.9654	7.8	20.3	67.6
Pyr	0.9968	1.7	4.3	14.3
BaA	0.9977	1.4	3.7	12.3
Chry	0.9980	1.4	3.5	11.8
BkF	0.9818	4.9	12.7	42.3
BbF	0.9894	2.5	6.5	21.8
BaP	0.9970	1.6	4.3	14.3
DahA	0.9978	1.1	2.9	9.8
BghiP	0.9970	1.3	3.5	11.6
IP	0.9994	1.7	4.4	14.7
Cor	0.9995	1.0	2.5	8.3

Correlation coefficients (R^2), analytical sensitivity (S), limits of detection (LOD) and quantification (LOQ) for HLLE-HPLC-FLD method of PAHs (initial sample concentrations between 30.0 – 110.0 ng L^{-1} for each PAH).

study, it must be considered that our method was optimized to obtain a sufficient volume of extract to be measured by HPLC.

For other extractions techniques, like Stir Bar Sorptive Extraction (SBSE) with HPLC-FLD (Bourdat-Deschamps et al. 2007), the values about recoveries are similar with PAHs concentrations of 50 ng L^{-1}, but for lower concentrations, their recoveries are lower and more irregular (SD about 12.5%), in this case, HLLE had recoveries values at ultra-trace concentration levels better than SBSE, and the comparative advantage is LODs and extraction time (only a few minutes versus 2 hours).

The main objective in the analytical field is to develop reliable, efficient, and practical procedures for performing qualitative and quantitative analysis. The method of extraction may vary according to the degree of selectivity, speed, and convenience. The sample pretreatment step has a crucial role in the analytical process due to intense handling before instrumental determination.

PAHs studies in an aqueous Antarctic matrix (snow/firn, and freshwater and seawater) have used samples volumes greater than 1 L (to 25 L), because they often used the classic Liquid-Liquid Extraction and Solid Phase Extraction (Fuoco et al. 2012, Giannarelli et al. 2017, Cao et al. 2018, Kim et al. 2019). Although these techniques achieved greater enrichment, they use large volumes of samples and are laborious, with extraction times exceeding 2 hours just for the extraction step. In this context, applying other techniques could be necessary, as ice core sections provide undisturbed stratigraphy, representing an archive of past chemical changes in the atmosphere. Thus, it's essential to have

Table III. Relative recovery of analytes, repeatability and enrichment factors by HLLE-HPLC-FLD method for PAHs*.

PAH	Recovery [%]	EF	Repeatability (n=5) RSD [%]
Naph	97	45	3.0
Phen	98	48	2.0
Anth	98	46	4.0
Flu	99	49	6.5
Pyr	84	39	2.7
BaA	89	38	3.2
Chry	99	46	2.4
BkF	89	39	6.3
BbF	99	38	1.1
BaP	72	34	2.4
DahA	95	46	5.3
BghiP	83	56	9.9
IP	78	36	2.0
Cor	71	35	7.0

***Initial concentration of each PAH 100.0 ng L^{-1}.**

enough sample volume for all analyses – a good temporal resolution depends on this – and it is important to expand the range of available extraction methodologies, which in addition to being quantitative in the extraction of analytes are also easy to apply *in situ*, requires less time (minutes) and require sample volumes of only a few mL.

Small sample volumes are required in microextraction systems and in recent years have been widely used for PAHs extractions from water samples in different extraction modalities (Reinert et al. 2018). The SBSE has recoveries close to 90% and LODs between 0.2 and 1.5 ng L^{-1} (Bourdat–Deschamps et al. 2007), although the processing time is 2 hours long. Similar LODs values have been obtained in a novel hybrid microextraction approach called stir bar sorptive-dispersive microextraction, with EFs close to 700 (Benedé et al. 2018), but recoveries have to be discussed, and the system requires some expertise. Dispersive liquid-liquid microextraction (DLLE) is also promising. It has EF between 296 and 462, LOD between 1000 and 10000 ng L^{-1} with little extract volumes (Leong et al. 2010, Rezaee et al. 2010). Comparatively, and taking into account that the DLLE method is based on the same extraction principle and that the determination of the analytes was by gas chromatography coupled to mass spectrometry, it can be said that the results obtained by HLLE-HPLC-FLD are far superior (Table II). Even with our EFs being lower than Leong et al. (2010), it must be considered that this method was optimized in terms of obtaining a sufficient volume of extract to be measured by HPLC.

The HLLE is an extraction methodology with interesting characteristics for environmental

water studies. The HLLE has advantages like the possibility of controlling extract volumes for HPLC injection, and it is inexpensive and straightforward at the same time. This technique allows the extraction and concentration of the target compounds, in one simple step, with short extraction times, low cost, and use of small volumes of solvent, and with LODs a at level of ng L^{-1}.

HLLE was selected according to its optimization in previous work (Cerón-Neculpan 2012) in which 15 PAHs were extracted from water samples using multivariate design (Doehlert and Complete Factorial designs) and high-performance liquid chromatography with diode array detection (HPLC-DAD) for the analytical studies. Table IV shows LODs, LOQs, and analytical sensitivity for the previously used HLLE-HPLC-DAD method (Cerón-Neculpan 2012), and for HLLE-HPLC-FLD discussed in this article, note the differences between the two techniques. The application of HLLE in the extraction/concentration with analysis by HPLC-FLD is considered more appropriate to detect and quantify concentrations of PAHs in the order of ng L^{-1} in firn and ice firn samples (Cincinelli et al. 2008, Fuoco et al. 2012, Giannarelli et al. 2017).

The HLLE-HPLC-DAD methodology was optimized by Cerón-Neculpan (2012), establishing the optimal extraction conditions according to the need to extract and concentrate 15 PAHs simultaneously in aqueous samples of the order of 8000 to 50000 ng L^{-1}, concentrations higher than those expected in the samples of interest of this study (expected in order of the ng L^{-1}), so the present study was started according to the response surface results of the multivariate experimental design used by Cerón-Neculpan (2012), analyzing the possibility of using their working conditions (NaCl concentration, $CHCl_3$ volume and CH_3OH volumes, stirring and extraction times), but at lower concentration levels according to the concentrations of the samples to be analyzed, finding a point of this could be optimized by exchanging the UV detector for a fluorescence detector and testing HLLE-HPLC.FLD for the determination of 14 PAHs, with initial concentrations in order a few ng L^{-1}. The differences between both methodologies are shown in Table IV, noting that LOQs, LODs, and S of the HLLE-HPLC-FLD method are more suitable for our purposes.

Comparatively, our results are in accordance with the applications of miniaturized extraction techniques used in environmental analytical determinations. Although our EF values (Table III) are smaller than other microextraction studies for PAHs in aqueous samples (Leong et al. 2010, Rezaee et al. 2010, Benedé et al. 2018), EF values could be improved if the extract volume is reduced, but a sufficient extract volume was prioritized for its handling and injection in HPLC, avoiding dilution as much as possible. These factors are not difficult to modify in subsequent works according to the equipment available with multivariate models.

The LOD and LOQ values at ultra-traces levels were considered for the ice and firn samples. For this reason, this study considered the HPLC-FLD useful for detection and quantification. It requires

Table IV. HLLE-HPLC-DAD and HLLE-HPLC-FLD Compared methodologies.

Methodology	LODs range [ng L^{-1}]	LOQs range [ng L^{-1}]	S range [ng L^{-1}]
HLLE-HPLC-DAD*	7.81 – 4150.7	2604.5 – 13835.6	300 – 1600
HLLE-HPLC-FLD**	1.5 – 20.3	5.1 – 67.6	0.6 – 7.8

*** Minimum 15 PAHs initial concentration equal to 8000 ng L^{-1}.**
**** Minimum 14 PAHs initial concentration equal to 30 ng L^{-1}.**

small sample volumes, such as those attained from continuous ice core melting systems with discrete sampling for further chemical analysis, allowing a high temporal resolution for ice/firn study. In this case, the HLLE-HPLC-FLD was selected to achieve the appropriate LODs and LOQs according to possible concentration levels of the Antarctic ice core samples (Table II) and the possibility to use the HLLE in the fieldwork. In agreement with these results, we consider the pre-concentration method highly efficient in all cases to aqueous pristine samples.

Firn core samples

The presence of some PAHs was detected, and, in some cases, the HLLE-HPLC-FLD method allowed its quantification as well. The calibration curves show R^2 values from 0.9945 to 0.9984 (for Flu and Anth, respectively), describing a linear behavior in the range of working concentrations.

Table V includes the concentrations found for each PAH and the ratio between the sample volume (V_S) and the extract volume before dilution (V_E) with acetonitrile to avoid volatilization losses. This ratio demonstrates that it is possible to concentrate the analytes in a sedimentation phase volume much smaller than the initial one, with values between 47 and 56.

In addition to the high extraction values described in the previous section, it points out the possibility of applying the present method during the fieldwork in remote areas such as Antarctica, facilitating the transport of the extracted analytes for future analysis.

There are differences in the total 14 PAHs concentrations in IC-5, depending on their

Table V. PAHs determination in IC-5 samples by HLLE-HPLC-FLD.

PAH*	IC-5.1	IC-5.2	IC-5.3	IC-5.4	IC-5.5	IC-5.6	IC-5.7
Naph	D	65.3 ± 1.4	135.5 ± 8.2	70.2 ± 4.4	79.7 ± 3.6	D	231.4 ± 10.7
Phen	D	D	D	D	D	D	78.4 ± 6.9
Anth	D	ND	ND	ND	ND	6.4 ± 1.3	51.6 ± 1.0
Flu	ND	ND	ND	ND	ND	114.1 ± 6.1	96.0 ± 6.0
Pyr	15.7 ± 2.9	ND	ND	D	ND	63.9 ± 3.1	67.1 ± 1.9
BaA	ND	ND	ND	ND	ND	ND	ND
Chry	28.4 ± 1.8	26.3 ± 5.0	19.5 ± 3.3	24.1 ± 2.7	23.6 ± 0.4	45.4 ± 1.8	35.1 ± 0.7
BbF	D	D	D	D	D	44.3 ± 3.1	D
BkF	D	D	D	D	D	65.5 ± 10.2	67.2 ± 9.5
BaP	27.4 ± 4.7	D	D	D	D	D	23.5 ± 0.6
DahA	44.9 ± 5.3	22.9 ± 1.8	22.2 ± 6.9	18.5 ± 0.4	53.8 ± 1.1	52.4 ± 2.9	43.3 ± 8.9
BghiP	D	ND	D	ND	ND	D	D
IP	40.6 ± 5.7	20.4 ± 1.0	52.5 ± 1.2	26.7 ± 0.5	41.7 ± 1.3	146.8 ± 11.9	47.4 ± 5.8
Cor	ND	ND	ND	ND	ND	ND	ND
SPAH	**157.0 ± 9.7**	**134.9± 5.6**	**229.7 ± 11.3**	**139.5 ± 5.2**	**198.8 ± 4.0**	**538.8 ± 17.7**	**741.0 ± 20.1**
V_S/V_E	51	49	54	56	49	53	47

***Concentrations expressed in [ng L^{-1}] with its respective standard deviation (SD). ND means No Detected and D indicates values below LOQ.**

depth. Most of the analytes were detected and quantified in the order of ng L^{-1}, less coronene, and BaA. The use of analytical targets that do not show signals corresponding to the analytes and the absence of some compounds indicates no sample contamination due to the extracts used in the laboratory work and associated manipulation – highlighting in this context the non-detection of coronene and BaA in any sample, in contrast to Chry and IP which were detected and quantified in every sample.

By analyzing each compound's presence separately, it was possible to individualize the variation of them in the IC-5 profile. BbF and BkF were detected but not quantified in most samples; despite the measured concentrations being close to the respective LOQ. Naph was found in all the samples, in IC-5.3 and IC-5.7, it reached the highest values, only 135.5 and 231.4 ng L^{-1}, respectively, well above the corresponding LOQ value (59.1 ng L^{-1}). The IP concentrations vary from 20.4 to 146.8 ng L^{-1} (the highest PAH concentration) in samples IC-5.2 and IC-5.6, indicating difference in PAH quantities from the analyzed fraction. The IC-5.6 has the highest concentration of Flu. In most cases, high molecular weight PAHs (4–6 aromatic rings) are mainly associated with combustion processes and are also found in sewage, small fuel spills, and by biogenic transformation. The predominance of these PAHs was observed in all measured samples.

Figure 2 shows the total PAHs differences in samples corresponding to the sum of quantified PAHs. The deeper samples concentrations, IC-5.6 and IC-5.7 (538.8 and 741.0 ng L^{-1} respectively), are more than three times the concentrations of the most superficial ones (e.g., IC-5.1 was 157.0 ng L^{-1}). The highest total PAHs concentration was 741.0 ng L^{-1} (IC-5.7) and the lowest 134.9 ng L^{-1} (IC-5.2). These values may indicate different strata, so an association with other kinds of chemical analysis can be helpful to the interpretation of these results.

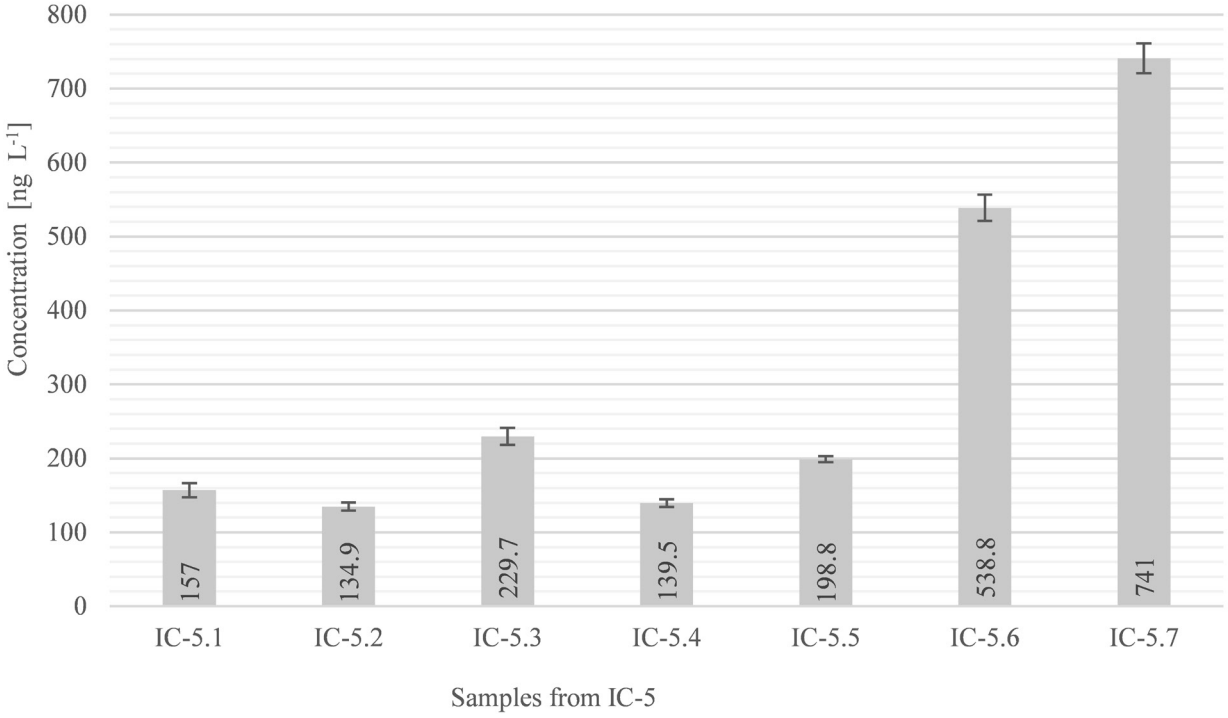

Figure 2. Total PAHs sum (concentrations) for each ice firn sample.

Working with the sum of PAHs is functional in a geochemical investigation. Antarctic researchers correlate total PAHs from ice cores with non-marine sulfate allowing volcanic activity determinations. Fuoco et al. (2012) applied the correlation of the non-marine sulfate with the sum of 14 PAHs concentrations reporting values between 0.7 to 3.4 ng L^{-1} by LLE with Gas Chromatography coupled to Mass Spectrometry (GC-MS) (recoveries 75–84%), corresponding to years from 1605 to 2003. Although there is a clear correlation of total PAHs peaks and major eruptions, the temporal resolution (from 3 to 14 years) could be improved with smaller volumes extraction techniques like HLLE.

Similar time resolution loss had been observed in ice core studies from Victoria Land (East Antarctica). The total PAHs concentration peaks were related to the most historically significant volcanic eruptions in the Southern Hemisphere in the period covered by the studied ice cores. Giannarelli et al. (2017) found total PAHs concentrations from 4.3 to 9.1 ng L^{-1} measured by LLE-GC-MS/MS (recoveries between 45 and 73%); the dating of each ice-core segment is reported from 1893 to 2011. They are some discrepancies between the total PAHs peaks and years of eruption, which are explained by the low time resolution of each ice-core segment, considering the great sample volume required in LLE (each melted sample resulted from three consecutive 60 cm long sections). This last observation shows the relevance of using a small sample volume for this kind of study. In the present work, we only use 3.5 mL for HLLE analysis.

Other PAHs measurements in Antarctica from seawater samples show concentrations in the range 5.42–34.37 ng L^{-1} (Cao et al. 2018), 1.21–3.96 ng L^{-1} (Cincinelli et al. 2008), 7.32–23.94 ng L^{-1} (Stortini et al. 2009), and 510–1200 ng L^{-1} (Bícego et al. 2009). In freshwater and snow samples from the western shore of Admiralty Bay (King George Island, Maritime Antarctica), Szopinska et al. (2019) found total PAHs concentrations in the range of 0.25–1365 and 0.28–1037 ng L^{-1} for January and March 2016 (16 PAHs sum) respectively, the method included analysis by GC-MS (recoveries were 70–85%). Our study reported PAHs' total concentrations in the range 134.9–741.0 ng L^{-1}.

In environmental studies, molecular ratios are frequently used in the identification of possible sources of impurities. Having defined a range of values for each one, Stogiannidis & Laane (2015), including anthracene/(anthracene + phenanthrene), fluoranthene/(fluoranthene + pyrene), BaA/(BaA + chrysene) and IP/(IP + BghiP). Antarctic researchers have used PAH molecular indices successfully identifying sources relations for aqueous samples (Fuoco et al. 2009, Stortini et al. 2009). In our work, an exploratory study, it was possible to calculate two of the relationships mentioned above.

According to the information in Table V, anthracene/(anthracene + phenanthrene), named I, and fluoranthene / (fluoranthene + pyrene), named II, were calculated for some samples. Sample IC-5.6 has a value of 0.64 for II, while sample IC-5.7 has values of 0.40 and 0.59 for I and II, respectively. IC-5.6 and IC-5.7 could be related to the combustion of wood, coal, and/or grass – IC-5.7 would be related to pyrogenic sources according to the value of I (Wang et al. 1999, Yunker et al. 2002, Martins et al. 2010, Dvorská et al. 2011). But we need additional analyses (*e.g.,* Principal Component Analysis and other chemical analysis like spheroidal carbonaceous particles, n-alkanes or non-marine sulfate) for assigned PAH sources.

By the US EPA, the maximum concentration of BaP should not exceed 200 ng L^{-1} in drinking water (US EPA 2014); comparatively, all our results are below this value. In contrast, the European Union – in Directive 2008/105/EC – establishes maximum values for contaminant

levels in superficial waters, set at 10 ng L^{-1} for the highly toxic BaP and 100 ng L^{-1} for the sum of Flu, BbF, BkF, BghiP and IP (European Union 2008). Regarding our results (Table V), in most cases, the values obtained are below these established limits; only the IC-5.1 and IC-5.7 exceed the limit for BaP. While the sum of other PAHs is also above these regulation limits, IC-5.6 and IC-5.7 samples have 370.7 and 210.6 ng L^{-1}, respectively. It is necessary to compare with other chemical indicators to identify the cause of this excess since, according to the molecular ratios, it could be due to some particular event corresponding to the date of deposit of the compounds in the natural environment.

The characteristics of the IC-5 (vertical profile, temperature, and origin) allow us to infer that there is no percolation or mobilization of the compounds between layers. Hence, the observed differences correspond to concentrations differences at the moment of deposition in the snow. However, post-depositional processes can occur after snow crystal settling (e.g., fresh snow being gradually transformed into dense glacial ice and a substantial reduction in the surface area of snow characterizes the first stages of this process). This can lead to the release of adsorbed semi-volatile compounds, back into the gas phase. Then they are involved in advective/diffusive transport processes either towards deeper snowpack layers or out into the atmosphere, depending on vapor pressure, concentration and temperature gradients, and other factors.

Diffusion profiles are predominant with light winds (lower than 3 m s^{-1}), whereas ventilation occurs with strong winds. Temperature gradients modulate snow and firn metamorphism and may cause grain growth, especially in the top several meters, increasing firn permeability for several years after deposition. Hence, concentration levels of each individual PAH layer may vary unpredictably, which in turn may cause a discrepancy in the distribution pattern of low and high molecular weight compounds in other environmental records (Masclet et al. 2000, Fuoco et al. 2012, Giannarelli et al. 2017).

Data associated with time periods can help in the search for historical information, explaining variations in analyte concentrations and their relationship with specific events. The IC-5 samples represent only four years of precipitation, from the summer of 2000/2001 to the summer of 2003/2004, but the assignment of stations and years is unknown to specific samples.

CONCLUSIONS

The analysis of results obtained allows the following to be concluded:

The application of HLLE-HPLC-FLD to pristine aqueous samples from Antarctic ice core sections allowed the detection of 14 PAHs and quantified in the order of ng L^{-1}. The HLLE method shows advantages for its possible application in the fieldwork, and it requires a relatively simple procedure, small extract volumes (a few mL), adequate enrichment and recovery factors (EF = 71–99% for 100 ng L^{-1} initial PAHs concentrations, with a relative standard deviation of 1.1–9.9%), and short extraction times (minutes).

Further, the HLLE-HPLC-FLD method can be applied without mixing samples, preserving the temporal resolution that allows the melting of the sample, obtaining greater detail of the distribution of the compounds in the ice profile.

Although the shallow depth of the samples, it could be said that some natural or anthropogenic events had an effect on the presence of PAHs in the firn core studied sections. However, additional information is

required to make a statement about the origin of these compounds.

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