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Sources and composition of chemical pollution in Maritime Antarctica (King George Island), part 1: Sediment and water analysis for PAH sources evaluation in the vicinity of Arctowski station

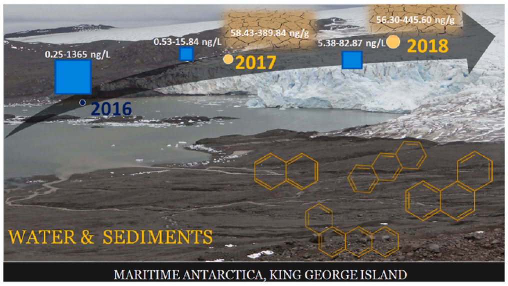
Joanna Potapowicz[a], Małgorzata Szopińska[b,**], Danuta Szumińska[c], Robert Józef Bialik[d], Żaneta Polkowska[a,*]

[a] *Gdansk University of Technology, Faculty of Chemistry, Department of Analytical Chemistry, 11/12 Narutowicza St., Gdansk, 80-233, Poland*
[b] *Gdansk University of Technology, Faculty of Civil and Environmental Engineering, Department of Water and Wastewater Technology, 11/12 Narutowicza St., Gdansk, 80-233, Poland*
[c] *Kazimierz Wielki University, Institute of Geography, Kościelecki Sq 8, 85-033, Bydgoszcz, Poland*
[d] *Institute of Biochemistry and Biophysics, Polish Academy of Science, Pawińskiego 5a, 02-106, Warsaw, Poland*

HIGHLIGHTS

- The concentration of PAHs in waters varies seasonally.
- The highest PAH concentrations in sediments were observed in 2018.
- Naphthalene, phenanthrene and anthracene are the dominant PAH congeners.
- Pyrogenic sources of PAHs dominate in the research area.

GRAPHICAL ABSTRACT



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ABSTRACT

The paper presents a study regarding the identification of polycyclic aromatic hydrocarbons (PAHs) in fresh waters and surface sediments on the western shore of Admiralty Bay over four sampling seasons from 2017 to 2018. The results were compared to literature data from 2016 to provide a more comprehensive image of the environmental fate of PAHs over the years. The highest value of Σ PAHs was 82.9 ng/L and 445 ng/g dw in water and sediment samples, respectively. The analysis of PAH indicator ratio values showed that pyrogenic or mixed sources contribute to the PAH pollution in Antarctic sediments and water more than does petroleum. The main source is the combustion of biomass (e.g. as a result of fires) and coal, and PAHs are mostly associated with the activity of stations or are transported to a lesser extent by long-range atmospheric transport (LRAT) from South America. The values of the ΣLMW/ΣHMW ratio in sediments indicate that petrogenic sources contribute to PAH contamination, but among the six PAH ratios tested, petrogenic sources were identified as dominant in approximately 17–19% of cases. Lack of coherence in the obtained results confirms the mixed origin of PAHs in the studied samples. Although the differentiation of PAHs sources is still ambiguous, caution is recommended in light of the Antarctic system's evident and rapid response to global and local PAH emissions, and the dependency

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* Corresponding author.
** Corresponding author.
E-mail address: zanpolko@pg.edu.pl (Ż. Polkowska).

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of accumulation and release cycle processes on weather conditions. A reduction in petrol usage in favour of renewable energy sources, and restriction of tourism are strongly recommended for better preservation of the pristine Antarctic environment.

1. Introduction

Human impact on the Antarctic environment has been increasing over recent decades (Curtosi et al., 2009; Szopińska et al., 2019). A number of chemical pollutants, including persistent organic pollutants (POPs), have been proven to exist in Antarctica in both animate and inanimate elements of nature (Cipro et al., 2012; Curtosi et al., 2009; Martins et al., 2004; Potapowicz et al., 2019). One challenge faced by scientists, however, is that of compounds that, apart from having anthropogenic sources, may also be of natural origin, like polycyclic aromatic hydrocarbons (PAHs) (Cai et al., 2016; Cao et al., 2018; Cincinelli et al., 2008; Fuoco et al., 2012). The primary sources of PAH emissions are: incomplete combustion of biomass, fossil fuels, oil spills and diagenesis of organic matter (Cincinelli et al., 2008; Fuoco et al., 2005; Szopińska et al., 2019). PAH pollution in Antarctica reflects total pollution emitted in the Southern Hemisphere, in spite of the continent's comparatively (to the Northern Hemisphere) small land mass, low human activity, and short history of industrial activity (Cao et al., 2018). As a result of atmospheric circulation, dust transport and cyclic volatilisation/deposition processes (Cabrerizo et al., 2011), PAHs are distributed in various elements of the Antarctic environment, e.g. atmosphere (Cao et al., 2018), seawater (Fuoco et al., 2005), freshwater (Szopińska et al., 2019), sediments (Curtosi et al., 2007, 2009; Rodríguez et al., 2018; Sutilli et al., 2019) and biota (Curtosi et al., 2009). The various activities of numerous scientific stations also contribute to PAH pollution (Aislabie et al., 1999; Ferguson et al., 2003). Moreover, as a result of the increase in global temperature (Bockheim et al., 2013; Turner et al., 2016; Vaughan et al., 2003), a number of processes are affecting the chemical composition of different elements of the Antarctic environment. Glacier retreat (Pętlicki et al., 2017; Pudełko et al., 2018) and intensive weathering processes (Navas et al., 2017; Oliva et al., 2016a, 2016b) may cause the release of pollutants previously stored in ice (Herbert et al., 2006; Szopińska et al., 2018), permafrost (Potapowicz et al., 2019; Szopińska et al., 2019) and sediments (Martins et al., 2010; Pongpiachan et al., 2017; Potapowicz et al., 2020). Due to the multitude of sources of PAHs in the Antarctic environment, it was decided to determine it on the basis of PAH index values that were used in many previous studies eg. (Ravindra et al., 2008; Stogiannidis and Laane, 2015; Yu et al., 2015).

Considering the toxicity, mutagenicity and carcinogenicity of PAHs (Yang et al., 2014), and their tendency to bioaccumulate (Hale et al., 2008), exposure to PAHs in the Antarctic environment is a particular threat to the Antarctic fauna and flora (Lana et al., 2014; Mello et al., 2016). Most the study area belongs to Antarctic Specially Protected Area (ASPA) No. 128. This area is the place of breeding to three species of penguins (Adélie, Gentoo, Chinstrap), eight species of seabirds (e.g. southern giant petrel or south polar skua) and one representative of pinnipeds (i.e. southern elephant seal). PAHs have been observed to accumulate in mosses (Cabrerizo et al., 2012; Colabuono et al., 2015). The research may therefore be of key importance for the reduction of human activities potentially harmful to the Antarctic's pristine ecosystems. The primary objective of our research was (1) to present the chemical composition of PAH pollution in both sediments and water from the terrestrial environment of King George Island, and (2) to verify the accumulation and release cycle processes in sediment/aquatic environments over a three-year period (years: 2016–18). The novel research results obtained from different matrices over three years allowed us to estimate the mechanisms of PAH migration between various environmental media in the Maritime Antarctic. This study also includes a determination of spatial distribution and defines which sources (pyrogenic or petrogenic) contribute more to PAH pollution in Antarctic sediments and water. Considering the long-term character of the study, this paper may be a unique source of information on changes occurring in ASPA No. 128 and its surroundings. Furthermore, discussion of the results on the background of PAH levels in soils and waters at other sites may extend the knowledge about these contaminants and their accumulation in the Antarctic environment.

2. Materials and method

2.1. Site description and sample collection

The sampling area is located on King George Island (South Shetland Islands, Antarctic Peninsula). Water and sediment samples were collected from the largest ice-free areas on the western shore of Admiralty Bay (Fig. 1). Environmental factors potentially influencing the sampled water and soils were summarised (Table S1 [a–j]). Samples were collected twice during the austral summer of 2017 and 2018 (for details see Table S1). The first sample series (I) was collected in early summer, in January, when the snow cover was significantly reduced, while the second series (II) was collected in March or April, at the beginning of Antarctic autumn. Samples were taken from the forefield of the Ecology, Sphinx and Baranowski glaciers.

2.2. Analytical methods

Sixteen EPA PAHs in water and sediment samples were analysed. Samples preparation procedures are described in detail in the Supplementary Material. The PAHs were determined by gas chromatography tandem mass spectrometry using single ion monitoring mode. The system consists of an Agilent 7890B (Agilent Technologies, USA) equipped with a 7693A automatic sample feeder, and a 7000D GC/TQ triple quadrupole (Agilent Technologies, USA). The analyses were performed using Capillary GC Column Zebron™ ZB-PAH Capillary (30 m × 0.25 mm × 0.25 μm). The selected PAHs were determined based on the internal standard calibration method. The recovery (%) of individual elements and parameters was in a range 67–84% for water samples and 48–87% for sediment samples. Recoveries of surrogate standards were 81% and 83% for naphthalene-d8 and benzo(a)anthracene-d12, respectively. Blank sample analysis showed that the concentration of naphthalene in this sample was 0.11 ng/L, while the concentrations of the remaining PAHs were below the limit of detection. The limit of detection for each analyte was from 0.03 to 0.75 ng/L. Coefficient of variation (CV) was less than 5%. A detailed description of the monitored ions and detection limits can be found in Szopińska et al. (2019).

2.3. Statistical analysis

Concentrations of the target analytes that were below their limits of quantification (LOQs) were set to half the LOQ value for statistical purposes. A principal component analysis (PCA) was performed using MATLAB Version: R2020a with Statistics and Machine Learning Toolbox Version 11.7 manufactured by MathWorks, U.S.A.

2.4. PAHs diffusion between sediment: water phases

A useful source of information on the sediment–water diffusion of PAHs is the physicochemical partition coefficient for octanol–water (K_{OW}). It is typically assumed that PAHs adsorb to the organic fraction of samples, so total organic carbon (TOC) in water and in the sediment should be analysed for a full understanding of PAH partitioning. The dependence of organic carbon (K_{OC}) to octanol–water (K_{OW}) partition coefficients for PAHs, and to the organic carbon fraction (φ_{OC}) of the sediment, is characterised by a linear relationship as follows:

$$\log K_{OC} = A \log K_{OW} + B$$

where A and B are values characteristic for individual PAHs. Furthermore:

$$K_{OC} = K_{SW} / \varphi_{OC}$$

where K_{SW} = sediment–water partition coefficient.

$$K_{SW} = C_S \rho_S / C_W$$

C_S = concentration in sediment, ρ_S = the density of sediment solids, C_W = concentration in water (Wang et al., 2011).

3. Results

3.1. PAHs in sediment samples

The chemical analyses of PAH contents provided results for sediment samples (Table S2). The last column shows total PAHs in each of the sediment samples in both measurement series. Concentrations of individual PAHs and their totals were much higher in sediments than in water samples. In 2017, total PAHs ranged from 58.8 to 383 ng/g dw in January, and from 58.4 to 389 ng/g dw in March. For comparison, these concentrations were 46.1–445 ng/g dw in January 2018 (series I) and 59.4–221 ng/g dw in March/April (series II). Differences in PAH concentrations depending on the year and series in which the sediment samples were taken are shown in Fig. 2.

It is worth noting that the highest concentrations of the total PAH in 2017 and 2018 compared to other sediment samples were found in samples B (264 ng/g) and D (445 ng/g) in January 2018 and in samples: A (389 ng/g) in March/April 2017 and B (383 ng/g) in January 2017. The lowest concentrations were found in sediment samples A in both series (I: 56.3 ng/g; II: 59.4 ng/g), C in January (46.1 ng/g) and E in both series (I: 68.5 ng/g; II: 62.9 ng/g) from 2018, and in samples C in both series (I: 58.8 ng/g; II: 58.4 ng/g) and E in January (68.4 ng/g) in 2017.

Both low molecular weight (LMW) and high molecular weight (HMW) PAHs were identified in almost all samples from both years. LMW PAHs include naphthalene, acenaphthene, anthracene, fluorene and phenanthrene. High-molecular-weight (HMW) PAHs, i.e., those with four or five rings, include fluoranthene, benzo(a)anthracene and chrysene. Naphthalene had the largest contribution in total PAHs in all samples, with the exception of sample B from 2017 taken from Ornithologists Creek (area II) in January. In this sample, phenanthrene had the largest share in PAHs. Benzo(a)anthracene showed lower concentration levels compared to other PAHs. Traces of five or six PAH rings were found in sediment samples from the western shore of Admiralty Bay at negligible levels or below detection limits.

3.2. PAHs in surface water samples

PAH concentrations in the studied surface water samples are presented in Table S3. PAH concentrations in water samples collected at the beginning of austral summer ranged from 0.53 to 32.4 ng/L, and at the

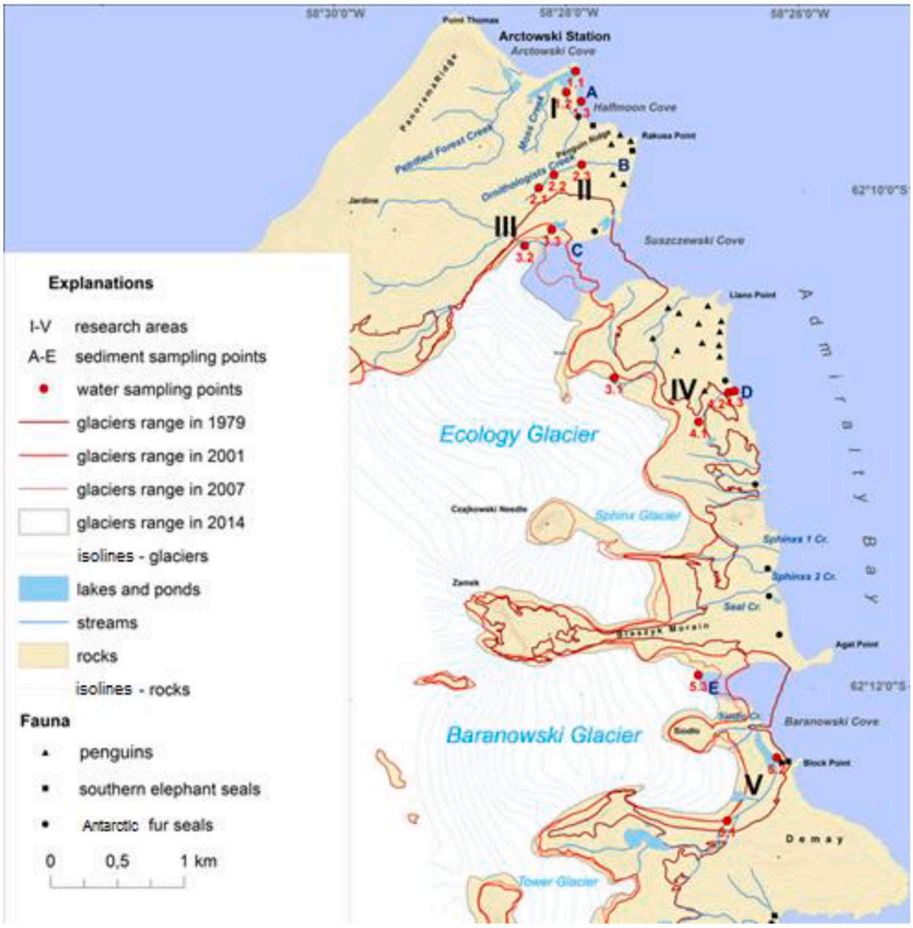

Fig. 1. Map of western shore of Admiralty Bay (Maritime Antarctica) showing glacier retreats between 1979 and 2014 and location of sampling points (prepared based on Pudełko, 2008; Landsat image LC82181032014016LGN00 obtained from www.usgs.gov; GoogleEarth application).

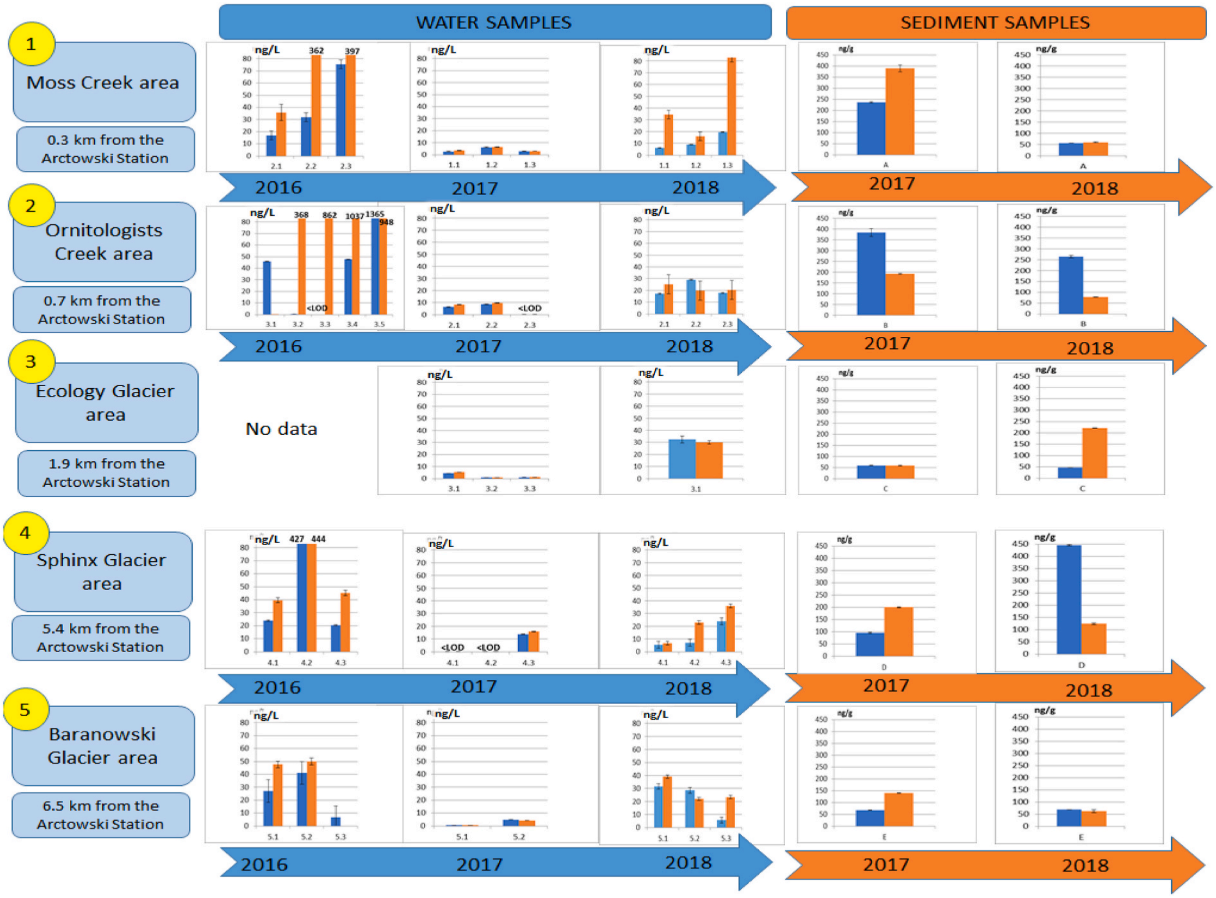

Fig. 2. Distribution of total PAHs in water and sediment samples during summer 2017 and 2018. Literature data for waters sampled in study area in 2016 taken from Szopińska et al. (2019). Values in blue and orange are derived from samples collected at the beginning and end of austral summer, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

end of austral summer from 0.58 to 82.9 ng/L, excluding samples: 2.3, 4.1, and 4.2 in which the concentrations of each PAH were below the limit of detection in 2017. In addition to the seasonal difference in concentration, variation was also apparent depending on the year in which the water samples were taken. The differences in PAH concentrations depending on year and sampling series are presented in Fig. 2. The ranges of ΣPAHs in 2017–18 were 0.53–15.8 ng/L and 5.38–82.9 ng/L for 2017 and 2018, respectively.

PAHs with two or three rings (LMW) have the highest contribution in total PAHs in both series. The presence of naphthalene was found in almost all water samples taken in both series, excluding samples: 2.3, 4.1, and 4.2 from 2017 (because of PAHs being below limit of detection at these points). Higher concentrations of acenaphthene, fluorene and phenanthrene were found in water samples from 2018. In 2017, the presence of these compounds was found in Moss Creek (area I), Ornithologists Creek (area II), and the forefield of Ecology Glacier (area III). In areas remote from the station (the forefields of Sphinx Glacier [area IV] and Baranowski Glacier [area V]), concentrations of these compounds were mostly below the limit of detection. In 2017, phenanthrene (0.40 ng/L in January and 0.42 ng/L in March) was found in sample 3.2, and fluorene (0.77 ng/L in January and 0.67 ng/L in March) and phenanthrene (0.98 ng/L in January and 0.65 ng/L in March) in sample 5.2. Anthracene was found in a small number of water samples. In the analysis of the sample from the middle section of Ornithologists Creek (2.2) from 2017, anthracene was found at a level of 1.10 ng/L in the first series (January), and 1.26 ng/L in the second series (March). In January 2018 (series I), significant anthracene concentrations were observed in the sample from the forefield of Ecology Glacier (3.1), and in March (series II) in the sample taken near Moss Creek (1.3).

Fluoranthene, one of the HMW PAHs was not identified in water samples from either of the years. Benzo(a)anthracene was only present in samples 4.3 (Sphinx Glacier area IV) from 2017 at 11.1 ng/L in January, and 13.1 ng/L in March, and in sample 1.3 (Moss Creek area I) from 2018 at 6.84 ng/L in March/April (series II). In sample 1.3 from 2018, in March/April (series II), the chrysene concentration was 5.53 ng/L, and in the remaining samples it was below the limit of detection. Five- and six-ring PAH concentrations were recorded as zero or negligible in water samples from the western shore of Admiralty Bay. It is not conclusive, however, that the compounds are absent in the studied area. The lack of HMW PAHs in water results from their low solubility in water and high affinity for organic matter.

3.3. *Multivariate data analysis result*

Principal Component Analysis was also conducted for all sediment and water samples. Some of the water datasets, however, were linearly dependent. Therefore, the results are not as expected and were omitted from further analyses. For sediment samples, two principal components were identified, representing 89% of the variance, and accounting for 58% and 31% of the variance, respectively (Fig. 3). The results showed a fairly strong positive correlation with naphthalene (0.60) and moderate positive correlation with anthracene (0.52) for PC1, and a fairly strong positive correlation with naphthalene (0.79) and moderate negative correlations with anthracene (−0.44) for PC2. The location of individual points representing the data provides an interesting image, and draws particular attention to data 1 (A form January 2017) and 16 (A from March 2018), which significantly affect the correlation with naphthalene. On the other hand, data 2 (B from January 2017), 3 (C from

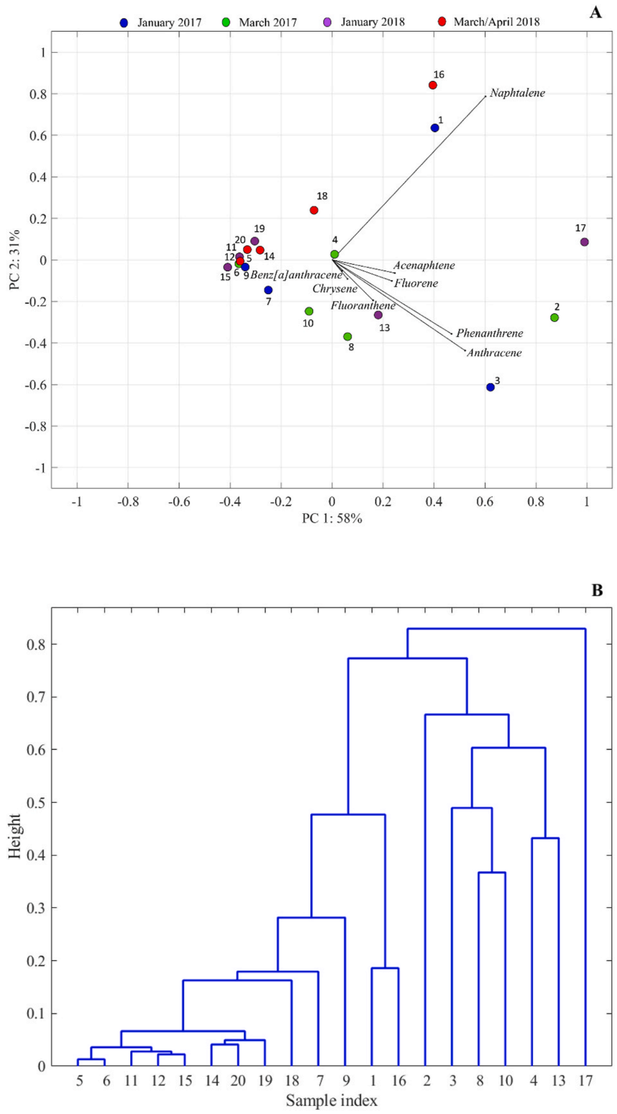

Fig. 3. PCA Biplots for various datasets (A) and dendrogram of sediments samples (B) taken in 2017 and 2018 from western shore of Admiralty Bay. Numbers 1–5 correspond to samples A–E from January 2017, respectively; 6–10 to A–E from March 2017; 11–15 to A–E of January 2018, and 16–20 to A–E of March 2018.

January 2017) and 17 (B from March 2018) generally result in a positive correlation of all variables.

3.4. *Relationships between individual PAH concentrations and their sources in study area*

PAH indicator ratios (Table 1) allow contamination sources to be identified. The six selected PAH ratios for individual environmental samples were determined based on descriptions included in other publications (Stogiannidis and Laane, 2015; Szopińska et al., 2019). The ratios allow results from 2017 to 2018 to be compared against results from 2016 (Szopińska et al., 2019). The identification of sources based on these results is ambiguous (in some cases different indices show different sources).

The PAH ratios: NP/PHE, BaA/CHr, PHE/ANT, ANT/(ANT + PHE) and BaA/(BaA + CHr) show a predominance of pyrogenic sources. Based on the calculation of the proportion between individual sample ratios indicating pyrogenic or petrogenic sources, it was found that pyrogenic sources dominated in all areas, being identified as dominating in 81.3–83.3% of cases (Fig. S3A). Petrogenic sources accounted for 16.7–18.8% of cases in areas I–V. In almost all of areas I–V, the NP/PHE values for both water and sediments were >1. Exceptions were area II in January/February 2017, where the source of PAHs in surface waters was identified as pyrogenic, while PAHs in sediments were indicated as petrogenic; and the area IV in March 2017, where PAHs were of petrogenic origin, though this indicator could only be calculated for sediment. Moreover, the BaA/CHr analysis showed that the origin of PAHs is mainly pyrogenic, although the value of this indicator may only correspond to the state of sediments in the studied areas, because it was not possible to determine this value for waters (except for sample 1.3 in March/April 2018, indicating pyrogenic source). The ratio of (<1) ΣLMW to ΣHMW PAHs showed that, in surface waters in area IV, PAHs were also pyrogenic, while in sediments of the same area they were petrogenic. In other areas, both for water and sediments, the petrogenic source of PAHs predominated (based on ΣLMW/ΣHMW). All PHE/ANT values for sediment and water samples in 2017 and 2018 were <10, and ANT/(ANT + PHE) > 0.1, which indicates pyrogenic sources in all regions I–V. BaA/(BaA + CHr) values at all sampled points were >0.2, which also indicates pyrogenic sources of PAHs in the studied environment. The exception is point 4.3, where the ratio values in January/February and March 2017 were 0.01 (<0.2), indicating a petrogenic source.

The type of pyrogenic source of PAHs was also examined on the basis of BaA/(BaA + CHr) values for the sediments (Fig. S3B), with indicator values as listed in Guarino et al. (2019). This analysis showed biomass and coal combustion as the source of PAHs for almost all I–V areas in both measurement series of 2017 and 2018. An exception was area II in January/February 2017, with the pyrogenic source of PAHs identified as petroleum combustion.

Due to the different sources of PAHs in the Antarctic environment, the percentage contribution of 2, 3, 4 and more rings in PAHs was analysed (Fig. S3C). The share of 2-ring PAHs in sediments ranged from 29.8 to 83.3%, and in waters from 59.0 to 76.7%. The 3-ring PAH percentage was 14.8–59.0% for sediments, and 14.0–24.8% for waters. For areas I, II, IV and V, the percentage of 2-ring PAHs was higher in waters than in sediments. Similarly, the percentage of 4-and-more-ring PAHs in areas I, III, IV and V was also higher in waters. However, the share of 4-ring PAHs was generally similar in water and sediment, spanning 7.77–24.2% in water and 2.92–27.4% in sediment samples (for areas I–V). On the other hand, 3-ring PAHs were typically more abundant in sediment (at all locations except area III).

4. Discussion

4.1. *Differences in PAH concentrations (sediments and fresh water)*

Values of total PAHs in the sediments and water obtained in this study were approximate to those reported by past determinations of PAH concentrations for Antarctic sites (Table S4). For example, Cripps (1992) reported values ranging between 14 and 280 ng/g dw for the Signy Island, and Dauner et al. (2015) found 12.05–210.02 ng/g dw of PAHs in sediments from the vicinity of Carlini Station. Moreover, the sediments included more polluted ones, e.g. in a range of 36.5–1908.4 ng/g in the vicinity of Carlini Station (Curtosi et al., 2009), or 21.5–751 ng/g near Artigas Station (Rodríguez et al., 2018).

Σ_{16}PAH concentrations in the sediments in 2017 and 2018 examined in this study ranged from 56.3 to 445 ng/g. The exceptions are single measurement points near the research station, although constant pollution cannot be confirmed, because high values did not persist in more than one series of measurements for a given point.

PAH concentrations in water obtained in this study were lower than those obtained in sediments, and ranged from 0.53 to 82.9 ng/L. These values are approximate to those obtained by research conducted in Maritime Antarctica (Bícego et al., 1996; Cao et al., 2018). Compared to water samples taken in this area in 2016 (Szopińska et al., 2019), the

Table 1
Values of PAH indicator ratios for analysed sediment and water samples taken from western shore of Admiralty Bay during austral summer 2017 and 2018, and potential sources of emission of these compounds.

Year	2017						2018					
PAH indicator ratio[a]	NP/PHE	BaA/CHr	ΣLMW/ΣHMW	PHE/ANT	ANT/(ANT + PHE)	BaA/(BaA + CHr)	NP/PHE	BaA/CHr	ΣLMW/ΣHMW	PHE/ANT	ANT/(ANT + PHE)	BaA/(BaA + CHr)
Sampling area												
1.1	–	–	–	0.78	0.56	0.36	41.14	–	–	0.78–1.00	0.50–0.56	0.36
1.2	7.45–10.21	–	–	0.98–0.99	0.50–0.51	0.36	24.92	–	–	0.78–1.11	0.47–0.56	0.36
1.3	2.07–2.26	–	–	0.99–1.01	0.50	0.36	33.27–33.4	1.24	5.7	0.94–0.96	0.51–0.52	0.36–0.45
A	1.2–8.97	1.36–1.42	10.8–18.04	0.98	0.50	0.58–0.59	17.14–30.61	0.75–1.13	27–133.05	0.98–0.99	0.50–0.51	0.43–0.53
Area I/source	Pyrogenic	Pyrogenic	Petrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Petrogenic	Pyrogenic	Pyrogenic	Pyrogenic
2.1	3.59–4.35	–	–	0.98–0.99	0.50–0.51	0.36	32.86–41.93	–	–	0.95–0.98	0.51	0.36
2.2	1.33–1.34	–	–	0.99–1.01	0.50	0.36	12.84–27.16	–	–	0.99–1.04	0.49–0.50	0.36
2.3	–	–	–	0.78	0.56	0.36	25.47–41.96	–	–	0.98–1.00	0.50–0.51	0.36
B	0.88*-4.25	0.52–0.96	2.13–3.06	0.71–0.99	0.50–0.59	0.34–0.49	1.46–11.88	0.94–1.41	1.85–28.21	0.98–1.09	0.48–0.50	0.48–0.58
Area II/source	Pyrogenic/ *petrogenic	Pyrogenic	Petrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Petrogenic	Pyrogenic	Pyrogenic	Pyrogenic
3.1	2.85–3.26	–	–	0.98–1.01	0.50	0.36	12.86–16.46	–	–	1.03	0.49	0.36
3.2	1.18–1.18	–	–	0.59–0.63	0.61–0.63	0.36	–	–	–	–	–	–
3.3	–	–	–	0.78	0.56	0.36	–	–	–	–	–	–
C	16.81–17.11	0.71–0.83	77.45–82.41	0.95	0.51	0.42–0.46	20.93–34.18	0.63	35.56–327.93	0.99–1.01	0.50	0.38–0.41
Area III/source	Pyrogenic	Pyrogenic	Petrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Petrogenic	Pyrogenic	Pyrogenic	Pyrogenic
4.1	–	–	–	0.78	0.56	0.36	7.1	–	–	0.78–0.98	0.50–0.56	0.36
4.2	–	–	–	0.78	0.56	0.36	6.97	–	–	0.78–1.03	0.49–0.56	0.36
4.3	–	–	0.21–0.24	0.78	0.56	0.01**	28.88–33.79	–	–	0.90–0.92	0.52–0.53	0.36
D	0.95*-2.62	0.63	8.73*-43.42*	0.98–1.00	0.50	0.36–0.39	2.1–9.96	0.64–1.39	26.89–36.08	0.96–0.98	0.50–0.51	0.39–0.58
Area IV/source	Pyrogenic/ *petrogenic	Pyrogenic	Pyrogenic/ *petrogenic	Pyrogenic	Pyrogenic	Pyrogenic/ **petrogenic	Pyrogenic	Pyrogenic	Petrogenic	Pyrogenic	Pyrogenic	Pyrogenic
5.1	–	–	–	0.78	0.56	0.36	16.71–36.9	–	–	0.98–1.02	0.50	0.36
5.2	3.29–4.57	–	–	0.98–1.26	0.44–0.50	0.36	12.94–62	–	157.89	0.52–1.02	0.50–0.66	0.36–0.46
5.3	–	–	–	–	–	–	10.24–25	–	–	0.98	0.51	0.36
E	1.35–9.03	0.62–0.83	14.79–25.08	0.98–1.03	0.49–0.50	0.38–0.45	31.48–34.22	0.65	78.67–232.07	0.95–0.98	0.50–0.51	0.39–0.56
Area V/source	Pyrogenic	Pyrogenic	Petrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Pyrogenic	Petrogenic	Pyrogenic	Pyrogenic	Pyrogenic
Source												
Pyrogenic (combustion)	>1[b]	>0.5–1[c]	<1[d]	<10[e]	>0.1[f]	>0.2[g]	>1[b]	>0.5–1[c]	<1[d]	<10[e]	>0.1[f]	>0.2[g]
Petrogenic	<1[b]	<0.25–0.5[c]	>1[d]	>10[e]	<0.1[f]	<0.2[g]	<1[b]	<0.25–0.5[c]	>1[d]	>10[e]	<0.1[f]	<0.2[g]

[a] ΣLMW, sum of low molecular weight PAHs (two- and three-ring PAHs); ΣHMW, sum of high molecular weight PAHs (four- and five-ring PAHs); NP, naphthalene; PHE, phenanthrene; BaA, benzo(a)pyrene; CHr, chrysene.

[b] (Ravindra et al., 2008).

[c] (Stogiannidis and Laane, 2015).

[d] (Zhang et al., 2008).

[e] (Budzinski et al., 1997).

[f] (Tsapakis et al., 2003).

[g] (Yunker et al., 2002).

range of concentrations was clearly lower recorded in 2017 and 2018.

As presented in Fig. 3, the PCA performed for sediments in all series over two years showed that naphthalene represents the greatest contribution in chemical composition across the study area. Moreover, PC1 (58% of the variance) shows a strong positive correlation with naphthalene, phenanthrene and anthracene, and PC2 (31% of the variance) shows a strong positive correlation with naphthalene, and strong negative correlation with phenanthrene and anthracene. The dominance of NP, PHE and ANT in sediment samples may result from the fact they are characterised by relatively low molecular weight, high volatility and high solubility in water compared to other PAHs.

The analysis results suggest that the concentration of PAHs in various elements of the Antarctic environment depends on the nature and type of matrix. Based on Tables S2 and S3 (Supp. Mat.), it can be concluded that total PAH concentrations in sediments were multiple times higher than the concentrations of these chemical compounds in surface waters.

Fig. 2 shows total PAH concentrations in the studied years and seasons. In most cases, both in waters and sediments, total PAH concentration increased in March/April. Decreases have been observed in waters of Ornithologists Creek (point 2.2) in 2018, and similarly in soil sampled from the mouth section of this creek. The basin's surface at the middle section of Ornithologists Creek is characterised by patches of moss and lichens and initial humus level in the upper part of soil profiles. Moreover, the valley bottom is covered by muddy sediments accumulated in small, temporary reservoirs. This condition may support the accumulation of PAHs on sediment particles, but also the biodegradation of these chemicals by bacteria is possible (Curtosi et al., 2007; Kosek et al., 2018). In March/April, the other streams carry greater PAH loads than in January – through rainfall and washing out the fine particles (clay and mud) into streams.

The affinity of individual PAHs to sediments or water samples depends strongly on the logK_{OW} value (Table S4). Considering PAHs, the applied K_{OW} is approximately equal to K_{OC} because exponent A approaches a value of 1 (Wang et al., 2011). As a result, the concentrations of PAHs should be proportionally higher in the sediments than in the water samples. However, it should be noted that the parameter of organic carbon that applies to samples in the vicinity of the Polish Antarctic Station (samples 1.3, 4.4, A and D) was determined in water and in the aqueous extract for sediments. Based on the data in Table S4, it can be concluded that the sediments are a larger reservoir of PAHs than are water. The relationship of logK_{OW} to logK_{OC} (formula in section 2.4) shows that K_{OW} and K_{OC} are linked by an exponential relationship. Thus, at lower concentrations of organic carbon in Antarctic samples, the increase in PAH migration from sediment to water will be greater than for, for example, samples from China (Wang et al., 2011). The low and medium molecular weight PAHs may change their transfer tendency between sediment and water (Wang et al., 2011), but in our samples the sediment concentration was always higher than the equilibrium value.

Rapid drainage of porous soils related to rainfall and snow- and ice-melt during summer could be the cause of a considerable inter-annual change in PAH concentrations in soils (Curtosi et al., 2007). This is called the 'spring pulse' phenomenon, caused by the release of pollutants accumulated in snow and firn during spring thaws. It primarily occurred in the early summer of 2017 and 2018 in the Ornithologists Creek area. It was also observed in 2018 in the Sphinx Glacier area (for sediment). The presented data show that in the case of creeks with non-glaciated catchments (I and II), where flowing waters are fed by rain, snow-melt, buried-ice-melt, and shallow groundwater in the active layer, levels of PAHs in water and sediment samples were different than those for creeks with a glacier-melt source of water (areas III–V) (Fig. 3). Other differences between catchments I and II and catchments III–V include the occurrence of mosses and lichens that support accumulation of PAHs in the hummus soil horizons (Gabov and Beznosikov, 2014). This vegetation type and soil type occur in areas I and II.

4.2. Sources of PAHs in environmental samples from Maritime Antarctica

Pyrogenic and petrogenic sources were identified based on PAH ratios (Table 1). The results of PAH ratios we obtained clearly indicate the domination of pyrogenic sources (Table 1, Fig. S3A). Moreover, based on the BaA/(BaA + CHr) values in sediments (Fig. S3B), it was found that PAHs in the research area mainly come from the combustion of biomass and coal. Since the nearby research stations do not use such fuel, we interpret that the primary source of PAHs on the western shore of Admiralty Bay is long range atmospheric transport (LRAT), which involves both pyrogenic and petrogenic sources. Such an interpretation is also confirmed by previous studies (Lammel et al., 2015) discussing the relationship of PHE and NP concentrations with LRAT.

The analysis of back trajectories incoming into the South Shetland Islands provided in previous research (Fernandoy et al., 2018; Szumińska et al., 2018) and in Szumińska et al. (2021) Part 2 (submitted) show the possibility that air masses incoming to the South Shetland Islands originated over inhabited regions (mostly South America). The frequency of air masses incoming from this area are in the range of 1–10% for the period of September 2016 to February 2017 and 5-day trajectories (Szumińska et al., 2021) (Part 2, submitted).

Additionally, our research confirmed the dominant share in the supply of PAHs from biomass and coal combustion (Fig. S3B). Due to LRAT, PAHs may also be transferred as a result of biomass combustion products, including those originating from fires, e.g., forest fires, bush fires and urban areas. Pollutants delivered to Antarctica this way are subject to dry and wet deposition in various elements of the environment (Curtosi et al., 2007; Fuoco et al., 2012; Szopińska et al., 2019). In 2018, compared to 2017, there was a clear increase in the total PAHs in waters (Fig. 2). As mentioned earlier, our results indicate that biomass combustion is the main source of these chemicals in the research area (Fig. S3B). In addition, the National Institute for Space Research (Inpe) reported, based on satellite imagery data, that there was an 84% increase in the number of fires in Brazil in 2018 (Andreoni and Hauser, 2019; BBC, 2019), which may plausibly explain the increased PAH concentrations from LRAT.

Despite human activity, South America also has numerous active volcanoes. The most active volcano in South America is Villarica in central Chile. It has been recorded to have been active for a total of 142 years between 1558 and 2017 (Szumińska et al., 2018). A total of six volcanoes were identified to be active in 2016 and 2017: Villarica, Láscar, Nevados de Chillán and Copahue in Chile, and Sabancaya and Ubinas in Peru (Fig. S1). In the next year – 2018 – most were still active (except Láscar and Ubinas) (www.volcano.si.edu).

Taking into consideration air masses frequency analysed by Szumińska et al. (2018), it is worth emphasising that the highest number of days with air masses incoming from South America together with high volcanic activity in the winter months of 2017 (May–Aug, Fig. S1C), and potential storage of PAHs in snow and ice may have contributed to its high levels in waters in the following spring–summer season (Fig. 2).

In areas I, II, III and V, in both water and sediment samples, the ΣLMW/ΣHMW ratio indicated the petrogenic source of PAHs as dominant. This demonstrates the potential contribution of direct petrogenic sources (such as diesel oil spills, particularly near station facilities). They are a minority compared to pyrogenic sources but should not be underestimated (Fig. S3A), as in this environment (the western shore of Admiralty Bay) they are closely related to the activity of scientists, as well as the maintenance and logistics of research stations. Considering that there are a total of 20 scientific stations (year-round and temporary) in South Shetland Islands (Bartolini et al., 2014), the load of chemical pollutants, including PAHs, they emit to Antarctic waters and sediments can be assumed to be significant. As our research has shown, in comparison with the percentage of pyrogenic sources, the activity of research stations located on Admiralty Bay does not have a major impact on the pollution of PAHs on the western shore of Admiralty Bay.

5. Conclusions

Research studies on the evaluation of PAHs are special important to protect the Antarctic environment against unforeseen anthropogenic activity. Based on our results, the main assumptions are as follows:

- It can be concluded that sediments can be a reservoir of PAHs in the Antarctic environment. The relationship of $\log K_{OW}$ to $\log K_{OC}$ can be concluded to be exponential, which proves that at lower concentrations of organic carbon in Antarctic samples, the increase in PAH migration from sediment to water will be more intense than in urbanised areas. The maximum value obtained for water was 82.9 ng/L, and for sediments 446 ng/g dw for ΣPAHs.
- The content of PAHs in water changes seasonally and between the two years, and in 2017–18 it was in the range 0.53–82.9 ng/L, which is the result of the 'spring pulse' phenomenon caused during spring thaws by the release of pollutants accumulated in snow and firn.
- Based on the analysis of PAH index values, it was determined that pyrogenic or mixed sources contribute more than petrogenic sources to pollution by PAHs in Antarctic sediments and water. In addition, the main source is the combustion of biomass (e.g., as a result of fires) and coal that can be assumed to be transported by LRAT from areas of South America. However, considering that the indicators of petroleum-derived PAH genesis are naphthalene and its homologues (which are less stable than pyrene, fluoroanthene and other PAHs formed during fuel combustion), the dominance of pyrogenic sources is probably associated with the activity of the stations itself.

In addition, the obtained results also confirm observations made in our previous studies:

- In contrast to Szopińska et al. (2019) a decrease in the value of ΣPAHs in water compared to 2016 was observed. In addition, comparing PAH concentrations in waters in 2018, their level increased compared to 2017, which may be due to the 85% increase in fires in Brazil.
- As part of the research presented in this article (samples taken in 2017 and 2018) and previous research by our team (Szopińska et al., 2019) (samples taken in 2016), a trend of higher levels of ΣPAH concentrations in the area surrounding the research station was observed. Therefore, incidental oil spills while using diesel fuel cannot be ruled out as a source of organic pollutants, including PAHs, in this environment.

Detailed PAH analyses in precipitation, snow cover, vegetation and animal tissues should be carried out in the future to provide a complete image of their environmental fate in Antarctica. Precipitation analyses in particular could help identify more precisely the sources of PAH pollution. Our results also call for petrol usage to be reduced in favour of renewable energy sources, and for tourism to be restricted for better preservation of the pristine Antarctic environment.

Credit author statement

Joanna Potapowicz: Conceptualization, MethodologySoftware, Validation, Formal analysis, Investigation, Resources, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization, Project administration. Danuta Szumińska: Conceptualization, Methodology, Validation, Investigation, Resources, Writing - Original Draft, Writing - Review & Editing, Project administration. Małgorzata Szopińska: Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Writing - Original Draft, Writing - Review & Editing, Visualization, Project administration. Robert Józef Bialik: Conceptualization, Software, Formal analysis, Investigation, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization. Żaneta Polkowska: Conceptualization, Methodology, Validation, Investigation, Resources, Writing - Review & Editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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