Source apportionment of polycyclic aromatic hydrocarbons in the terrestrial soils of King George Island, Antarctica

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ABSTRACT

This study employed chemical characterisation to determine the source of polycyclic aromatic hydrocarbons (PAHs) in the terrestrial soils of King George Island, Antarctica. The total concentrations of 12 PAHs in the samples of terrestrial soils collected at 44 sites ranged from 1.83 to 32.9 ng g^{-1} with an average value of 10.8 $\pm$ 8.22 ng g^{-1}. The concentrations of these PAHs were relatively lower compared with those found in other studies in other locations. The spatial distributions of PAHs showed the highest concentrations to be in areas adjacent to the Great Wall Station and the road network, and light molecular weight PAHs were predominant. Three- and four-ring PAHs were the most abundant, representing 48.3% and 27.1% of the total, respectively. Although the binary diagnostic ratios indicated petrogenic sources as the main PAH-emission sources, principal components analysis and hierarchical cluster analysis suggested that electricity generators (22.84%) and light-duty gasoline (18.94%) are the main sources in the soil of King George Island, Antarctica.

1. Introduction

Presently, several countries are experiencing rapid economic and industrial development. Unfortunately, this development has led to many environmental problems, such as air, water, noise, and waste pollution; further, various chemical substances used and produced have been emitted into the environment as pollutants, posing serious risks to human and environmental health. One crucial environmental issue of global concern is the so-called persistent organic pollutants (POPs), which are chemicals with the potential to persist in the environment, be transported over long distances, and bio-accumulate in an ecosystem (Breivik et al., 2004; Fuoco et al., 2012; Jones and de Voogt, 1999; Vallack et al., 1998). Moreover, polycyclic aromatic hydrocarbons (PAHs) are generally accepted as a type of POPs.

PAH compounds are a large group of complex organic chemicals composed of carbon and hydrogen atoms in the form of a fused-ring structure containing at least two benzene rings. Chemically, PAHs are white or pale yellow or almost colourless solids that are highly lipophilic

and are bonded in linear, cluster, or angular arrangements. The best known PAH is benzo[a] pyrene (B[a]P), which was the first chemical carcinogen to be discovered (Ravindra et al., 2008). PAHs can contaminate all parts of the environment, including the atmosphere, water, soil, sediments, and vegetation (Han et al., 2019; Wild and Jones, 1995; Zhang and Chen, 2017). PAHs can be generated from both natural and anthropogenic sources but mainly originate from anthropogenic activities including smoking, thermal power stations, traffic, domestic heating, and industrial emissions (Abdel-Shafy and Mansour, 2016). In addition, PAHs are regarded as priority pollutants as they demonstrate carcinogenic and mutagenic properties even at low levels and have been shown to affect organisms in various studies (Barakat, 2011; Boonya-tumanond et al., 2006; Davis et al., 2019; Duan et al., 2007; Fang et al., 2012; Karaca, 2015; Ouyang et al., 2016; Pongpiachan et al., 2013; Stout et al., 2015; Sun et al., 2009; Zhang et al., 2006). Further, several organisations such as the Safety and Health Administration (OSHA), National Institute for Occupational Safety and Health (NIOSH), and United States Environmental Protection Agency (US-EPA) have set exposure

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limits for PAHs (Abdel-Shafy and Mansour, 2016; NIOSH, 2010; U.S. EPA, 2000).

In recent decades, industrial development has caused a significant increase in PAH concentrations in the environment due to the incomplete combustion of carbonaceous materials during energy and industrial production processes (Han et al., 2012, 2017, 2019; Hsu et al., 2016; Qin et al., 2018; Zhu et al., 2019). PAHs can be transported over long distances when emitted into the atmosphere before they are deposited by atmospheric precipitation into the soil (a major source for deposited PAHs), vegetation, rivers, and oceans. However, the removal of PAHs from the atmosphere can be achieved through wet and dry deposition processes.

During the last few years, very few studies have examined PAH contents in Antarctica due to the difficulty of gaining access to the continent. Despite this challenge, several studies have attempted to assess contamination levels in Antarctic soils and the impact of the PAH-emission sources affecting them (Aislabie et al., 1999; Curtosi et al., 2007; Prus et al., 2015). Studies of PAH contents in snow samples collected from the Fildes Peninsula, southwest of King George Island (KGI) in Antarctica, detected three main PAHs in the samples: naphthalene, fluorine, and phenanthrene (Na et al., 2011). A similar pattern was found in sediment samples from Prydz Bay, East Antarctica, with the most abundant compounds detected being two- and three-ring PAHs. In 2014, the results of a PAH analysis of the terrestrial soils of KGI indicated that PAH contamination was considerably lower than in other terrestrial soils worldwide (Pongpiachan et al., 2017a, b; Pongpiachan et al., 2019). However, studies to identify the sources of PAHs in environmental samples are still crucial for the management and monitoring of PAH levels, including the estimation of their potential risk to humans and other organisms in ecosystems. While Antarctica was long considered to be a pristine environment, it has now been heavily affected by many anthropogenic operations, including research activities, military installations, and a rapidly growing tourism industry. All of these activities have led to increased vehicular, aircraft, and vessel traffic; fuel storage and usage; scientific drilling activities; and sewage discharge. (Aislabie et al., 2004; Green and Nichols, 1995; Martins et al., 2012; Prus et al., 2015). For all of the reasons, the study will focus on collecting terrestrial soils of KGI to cover areas that are expected to be affected by human activities, including areas near research stations, community sites, airports and transportation routes. However, soil sampling may be limited by geography and weather at that time.

In this study, the sources of 12 priority PAHs in terrestrial soil samples from KGI were investigated and subjected to both qualitative and quantitative analyses. Overall, the objectives of this study were to assess the concentrations of PAHs in the terrestrial soils of KGI and to distinguish and identify the potential sources of PAHs in the terrestrial soil through the application of diagnostic binary ratios coupled with principal component analysis (PCA) and hierarchical cluster analysis (HCA).

2. Materials and methods

2.1. Study area

Antarctica is considered a natural reserve because the continent has been devoted to peace and science under the Protocol on Environmental Protection to the Antarctic Treaty (PEPAT) of 1991 (PEPAT 1991, Article 2). Thus, Antarctica is the site of unparalleled international scientific collaboration (Verbitsky, 2018). Antarctica is located in the south polar area around latitude 90° 00′ S and longitude 0° 00′ E. It is the fifth-largest continent with a total landmass of 14 million km^2. This study collected soil samples at KGI, which is located in Antarctica and is the largest of the South Shetland Islands with an area of 1159 km^2. It has three main bays: Maxwell Bay, Admiralty Bay, and King George Bay. The majority of the samples were collected around the Base Presidente Eduardo Frei Montalva, Great Wall Station, King Sejong Station,

Bellingshausen Station, and Artigas Base.

2.2. Soil sampling and preparation

Terrestrial soil samples were collected from 44 sampling sites on King Gorge Island during January to February 2016 ($n = 33$) and June 2017 ($n = 11$). A map of the sampling sites is presented in Fig. 1. The terrestrial soil samples were collected from depths of 0–10 cm using hand-held coring equipment. The coordinates and information relating to individual samples are summarized in Table 1. After collection, the samples were wrapped with pre-cleaned aluminium foil, placed in glass bottles, and then kept at −20 °C. Before use, samples were freeze-dried, any wood debris or stones were removed, and then, samples were ground to homogenise them. Thereafter, each soil sample was wrapped in aluminium foil, packed in a plastic bag, and maintained at −4 °C until analysis (Pongpiachan et al., 2013, 2017a, b).

2.3. Chemical analysis

PAH sample extraction, purification, analysis, and quality control were conducted according to the method described in previous studies (Pongpiachan et al., 2013, 2017a; b, 2018, 2019). The PAH analysis was conducted according to Norwegian standard PAH methods (NS 9815: S-4008-100-T). All organic solvents (i.e. DCM and hexane) were HPLC grade and purchased from Fisher Scientific (Hampton, NH, US). A cocktail of 15 Norwegian Standard PAHs (NS 9815: S-4008-100-T) (phenanthrene (Phe), anthracene (An), fluoranthene (Fluo), pyrene (Pyr), 11h-benzo[a]fluorene (11H-B[a]F), 11h-benzo[b]fluorene (11H-B[b]F), benz[a]anthracene (B[a]A), chrysene (Chry), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), benzo[e]pyrene (B[e]P), indeno[1,2,3-cd]pyrene (Ind), dibenz[a,h]anthracene (D[a,h]A), and benzo[g,h,i]perylene (B[g,h,i]P); each 100 μg mL^{-1} in toluene: unit: 1×1 mL) and a mix of recovery Internal Standard PAHs (d_{12}-perylene (d_{12}-Per), and d_{10}-fluorene (d_{10}-Fl); each 100 μg mL^{-1} in xylene: unit: 1×1 mL) were supplied by Chiron AS (Stiklestadveine 1, N-7041 Trondheim, Norway). For PAH analysis, 30 g of dried sample was placed in a prewashed cellulose container (dimensions: 30×100 mm) and inserted into a Soxhlet extractor. Before extraction, the dried samples were spiked with 50 μl of an internal reference standard (deuterated-fluorene and deuterated-perylene supplied by Chiron AS), added to 250 ml of organic solvents (DCM) containing 1 g of copper powder, and then extracted for 8 h. The fractionation, clean-up, and blowing-down processes were performed strictly following the method (a standard protocol applying the difference in solvent polarity) of Gogou et al. (1996, 1998). The solution was quantified using a gas chromatograph-mass spectrometer (GC-MS) (Shimadzu GC-MS-QP 2010 Ultra). The extractant was then transferred to the top of a silica gel column, and 15 ml toluene-n-hexane (5.6:9.4, v/v) was used as the eluent as the system was purged with nitrogen until almost dry. The final extraction was conducted using cyclohexane as the solvent while the system was again gently blown with nitrogen until a final volume of 100 ml was achieved. The solution was quantified using the same GC-MS, operated in the selective-ion-monitoring mode and equipped with a Restek RTX-VRX column. All the injections were performed using an injector in the splitless mode. The GC oven temperature was programmed as follows: 1 min at 40 °C, oven temperature at 40 °C, and injection temperature at 280 °C, and the total flow was 2.0 ml/min. The selected MS detector was operated at 70 eV electron energy with an ion-source temperature of 200 °C. The accuracy of the method was evaluated using the standard SRM 1941b. The mean recovery was in the range of 77–119% based on the extraction of matrix-matched certified reference materials. All statistical analysis in this study was conducted using Microsoft Excel (Microsoft Inc., USA) and SPSS software, version 18 (SPSS Inc., USA). The sampling site locations and the spatial distribution of the PAHs were mapped using ArcGIS version 10.5.
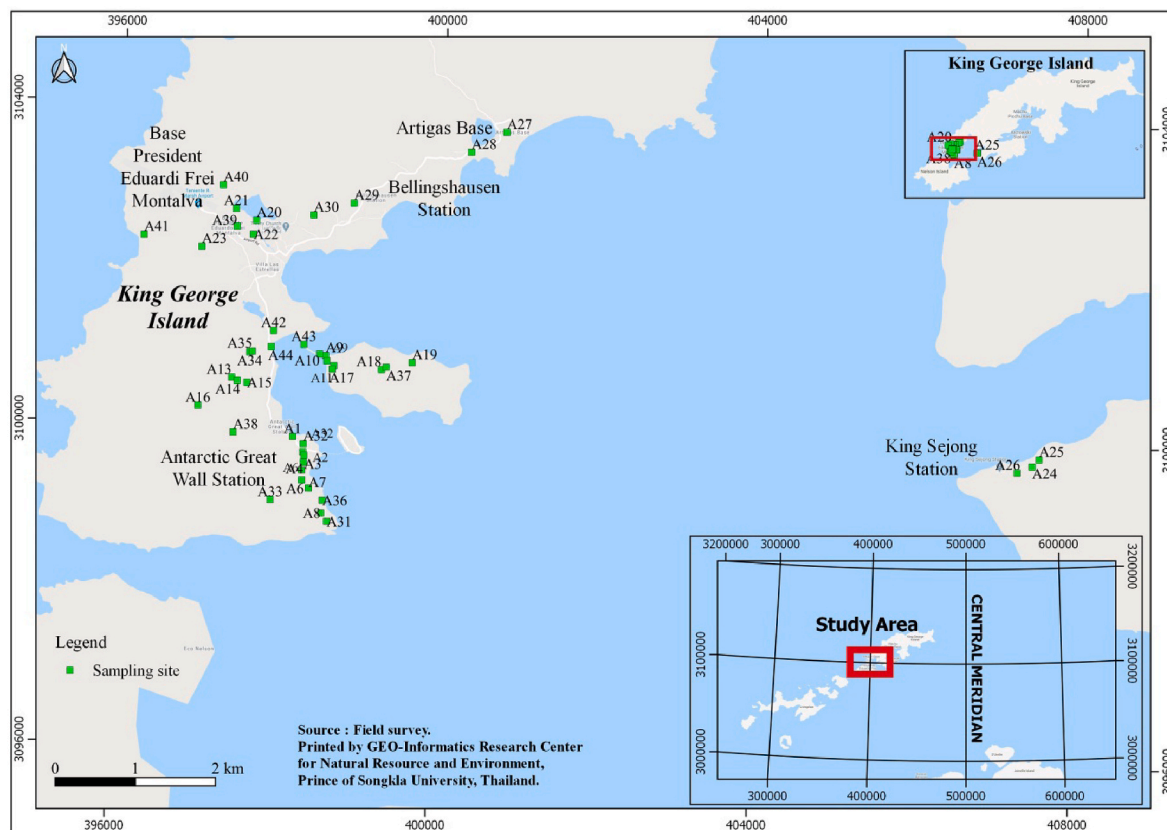
Fig. 1. Sampling site locations on King George Island, Antarctica.

2.4. Quality assurance/quality control (QA/QC)

As noted above, before extraction, all dried samples were spiked with deuterated-deuterated- fluorene and deuterated-perylene as internal standards to monitor the analytical recovery efficiencies, and Standard Reference Material (SRM 1941b) analysis was used in evaluating the accuracy of the analytical methods. The average concentrations of the SRM 1941b materials were 464 ± 16 (Ph), 721 ± 45 (Fluo), 538 ± 34 (Pyr), 289 ± 26 (B[a]A), 336 ± 25 (Chry), 480 ± 25 (B[b]F), 229 ± 19 (B [k]F), 321 ± 10 (B[e]P), 291 ± 14 (Ind), and 267 ± 17 (B[g,h,i]P), which are within acceptable values ranges according to SRM 1941b. The mean recoveries ($n = 8$) were in the range of 83–115%.

2.5. Source identification via PAH diagnostic ratios

This study used the binary ratio method for PAH-source identification, in which the PAH-emission profile from a source depends on the PAH production process (Manoli et al., 2004; Wang et al., 2017). Diagnostic binary ratios can be used to identify the sources of contamination by comparing the relative concentrations of each PAH, such as An, Phe, Fluo, Pyr, and B[a]A, and can identify the source as a pyrolytic or petrogenic process (Budzinski et al., 1997; Fang et al., 2004; Grimmer et al., 1983: Mandalakis et al., 2002; Pandey et al., 1999; Park et al., 2002; Pies et al., 2008; Ravindra et al., 2008; Rogge et al., 1993a,b; Tobiszewski and Namieśnik, 2012; Wang et al., 2017; Yunker et al., 2002; Zhang et al., 2008). A pyrolytic process is one involving the incomplete combustion of biomass or fossil fuels while a petrogenic process involves the slow maturation of organic substances which may cause pollution though the leakage of crude oil (Abdel-Shafy and Mansour, 2016; Manahan, 1994).

Six diagnostic binary ratios were applied to detect PAH sources in the terrestrial soil of KGI (i.e. An/(An + Phe), Fluo/(Fluo + Pyr), B[a]A/(B [a]A + Chry, B[b]F/B[k]F, and Ind/(Ind + B[g,h,i]P); see Table 2). A

$\sum$LMW/$\sum$HMW of less than 1 indicates a pyrogenic source, including the incomplete combustion of wood or fossil fuels, while a value greater than 1 indicates a petrogenic source. In the case of An/(An + Phe), a value > 0.1 signals a petrogenic source and a value < 0.1 indicates a pyrogenic source involving incomplete combustion. The upper bound of the Fluo/(Fluo + Pyr) ratio for petrogenic sources is taken to be 0.4, while values ranging from 0.4 to 0.5 indicate the combustion of mixed liquid fossils (vehicle fuel, gasoline and crude oil), and values > 0.5 are characteristic of the combustion of grass, wood, and coal. Ravindra et al. (2008) determined values which indicate sources related to diesel emissions. A B[a]A/(B[a]A + Chry) ratio < 0.2 indicates petrogenic sources, while values ranging from 0.2 to 0.35 indicate coal combustion, and values > 0.35 signal vehicular emissions and incomplete combustion. A B[b]F/B[k]F ratio > 0.5 is generally taken to indicate a diesel combustion source. For Ind/(Ind + B[g,h,i]P) ratios, a value < 0.2 signals a petroleum source, one between 0.2 and 0.5 implies petroleum combustion (vehicle fuel and crude oil), and a value > 0.5 implies coal combustion, while a value of 0.18 indicates cars as the source, a value of 0.37 indicates diesel emissions, and one of 0.62 implies wood burning.

3. Results and discussion

3.1. PAH concentrations

PAHs were measured in terrestrial soil samples sourced across KGI in 2016 and 2017, and the concentrations of the 15 individual PAHs ($\sum_{15}$PAHs: the sum of Phe, An, Fluo, Pyr, 11H-B[a]F, 11H-B[b]F, B[a]A, Chry, B[b]F, B[k]F, B[e]P, B[a]P, Ind, D[a,h]A, B[g,h,i]P) are presented in Table 3. The average concentrations of $\sum_{15}$PAHs were 12.06 ± 9.26 ng g^{-1} (dry weight) and 11.16 ± 9.73 ng g^{-1} (dry weight) for 2016 and 2017, respectively.

Individual PAH concentrations were measured in 44 terrestrial soil samples collected over two years. At all the sampling sites, the total

Table 1
Sampling locations of terrestrial soil samples collected in King George Island, Antarctica (UTM system).

Sample Name	Date of Collection	Location (UTM)		UTM Zone	Central Meridian	Site Name
		X	Y			
A1	Jan. 2016	398211	3099868	21S	−57°W	Close to Great Wall Station
A2	Jan. 2016	398343	3099680	21S	−57°W	Close to Great Wall Station
A3	Jan. 2016	398358	3099638	21S	−57°W	Close to Great Wall Station
A4	Jan. 2016	398354	3099551	21S	−57°W	Close to Great Wall Station
A5	Jan. 2016	398336	3099454	21S	−57°W	Close to Great Wall Station
A6	Jan. 2016	398340	3099330	21S	−57°W	Close to Great Wall Station
A7	Jan. 2016	398427	3099231	21S	−57°W	Close to Great Wall Station
A8	Jan. 2016	398588	3098926	21S	−57°W	Close to Great Wall Station
A9	Jan. 2016	398592	3100889	21S	−57°W	Around Penguin Island
A10	Jan. 2016	398518	3100906	21S	−57°W	Around Penguin Island
A11	Jan. 2016	398610	3100825	21S	−57°W	Around Penguin Island
A12	Jan. 2016	398699	3100766	21S	−57°W	Around Penguin Island
A13	Jan. 2016	397428	3100585	21S	−57°W	Close to Great Wall Station
A14	Jan. 2016	397498	3100547	21S	−57°W	Close to Great Wall Station
A15	Jan. 2016	397620	3100526	21S	−57°W	Close to Great Wall Station
A16	Jan. 2016	397017	3100222	21S	−57°W	Close to Great Wall Station
A17	Jan. 2016	398680	3100722	21S	−57°W	Around Penguin Island
A18	Jan. 2016	399295	3100735	21S	−57°W	Around Penguin Island
A19	Jan. 2016	399675	3100832	21S	−57°W	Around Penguin Island
A20	Jan. 2016	397679	3102549	21S	−57°W	Close to the Base Presidente Eduardo Frei Montalva
A21	Jan. 2016	397424	3102690	21S	−57°W	Close to the Base Presidente Eduardo Frei Montalva
A22	Jan. 2016	397646	3102375	21S	−57°W	Close to the Base Presidente Eduardo Frei Montalva
A23	Jan. 2016	397007	3102204	21S	−57°W	Close to the Base Presidente Eduardo Frei Montalva
A24	Jan. 2016	407446	3099751	21S	−57°W	Around King Sejong Station
A25	Jan. 2016	407530	3099843	21S	−57°W	Around King Sejong Station
A26	Jan. 2016	407261	3099672	21S	−57°W	Around King Sejong Station
A27	Jan. 2016	400774	3103738	21S	−57°W	Close to Uruguai Station
A28	Jan. 2016	400339	3103476	21S	−57°W	Close to Uruguai Station
A29	Jan. 2016	398892	3102800	21S	−57°W	Close to Bellingshausen Station
A30	Jan. 2016	398392	3102636	21S	−57°W	Close to Bellingshausen Station
A31	Feb. 2016	398666	3098823	21S	−57°W	Close to Great Wall Station
A32	Feb. 2016	398345	3099780	21S	−57°W	Close to Great Wall Station
A33	Feb. 2016	397953	3099074	21S	−57°W	Close to Great Wall Station
A34	Jun. 2017	397643	3100907	21S	−57°W	Close to Great Wall Station
A35	Jun. 2017	397676	3100917	21S	−57°W	Close to Great Wall Station
A36	Jun. 2017	398603	3099084	21S	−57°W	Close to Great Wall Station
A37	Jun. 2017	399352	3100767	21S	−57°W	Close to Penguin Island
A38	Jun. 2017	397466	3099902	21S	−57°W	Close to Great Wall Station
A39	Jun. 2017	397440	3102468	21S	−57°W	Close to the Base Presidente Eduardo Frei Montalva
A40	Jun. 2017	397253	3102979	21S	−57°W	Close to the Base Presidente Eduardo Frei Montalva
A41	Jun. 2017	396281	3102333	21S	−57°W	Close to the Base Presidente Eduardo Frei Montalva
A42	Jun. 2017	397934	3101182	21S	−57°W	Around the Villa Las Estrellas
A43	Jun. 2017	398317	3101020	21S	−57°W	Around the Villa Las Estrellas
A44	Jun-2017	397910	3100980	21S	−57°W	Around the Villa Las Estrellas

concentrations of the 15 PAHs were between 1.88 and 34.94 ng g^{-1} (dry weight) with an average of 11.83 ± 9.27 ng g^{-1} (dry weight). In this study, $\sum_{12}$PAHs (the sum of Phe, An, Fluo, Pyr, B[a]A, Chry, B[b]F, B[k]F, B[a]P, Ind, D[a, h]A and B[g, h, i]P) represents the total concentration of 12 likely carcinogenic PAHs in the terrestrial soil of KGI, which ranged from 1.83 to 32.9 ng g^{-1} (dry weight) with an arithmetic mean of 10.8 ± 8.22 ng g^{-1} (dry weight).

Pongpiachan et al. (2017a, b) found that the $\sum_{12}$PAH concentration in the terrestrial soil of KGI in 2014 was 3.21 ± 1.62 ng g^{-1}, which was comparable to the values of 10.8 ± 9.26 ng g^{-1} and 12.8 ± 9.73 ng g^{-1} (all values dry weight) for 2016 and 2017, respectively (Table 3 and Fig. 2). The comparison of the individual PHA concentrations found in the present study with those reported by Pongpiachan et al. (2017a, b) shows that overall, the concentrations of the individual PAHs had increased from the values measured in 2014, as shown in Fig. 2. In addition, the concentration of each type of PAH did not follow a consistent trend over the three-year period. However, the three-ring PAHs (Phe and An) were consistently most prominent in the soil samples.

The individual PAH concentrations in each of the three years were subjected to an independent *F*-test to determine if there was evidence of significant alterations in individual PAH concentrations among the three groups, as presented in Table 3. The results indicated a significant

increase in An, Chry and B[a]P concentrations (p < 0.05). The concentrations of An in the studied soil samples were relatively high in the winter of 2017, indicating that three-ring PAH levels increased as a consequence of relatively high electric consumption for heating systems. Chry and B[a]P concentrations increased significantly (p < 0.005) during 2016–2017 compared to those in 2014. This can be explained by an increasing number of international polar researchers and thus the higher use of light-duty and diesel vehicles in 2016–2017. However, the concentrations of both Chry and B[a]P detected in 2016 were significantly higher than those of 2017, because the 2016 soil samples were collected in summer while the 2017 samples were collected in winter. In 2016, terrestrial soil samples were collected from January to February, the warmest months on the Antarctic continent and the period of the most human activity on KGI. Generally, the Antarctic summer season lasts for three–four months from November to February (Tothill and Martin, 2012).

It is well known that PAHs can be removed from the environment by various processes, including biological and photochemical degradation (Abdel-Shafy and Mansour, 2016; Perera et al., 2011). Most low molecular-weight PAHs (LMW PAHs) mainly exist in the vapor phase and more readily experience photo-decomposition and homogeneous/heterogeneous reactions than do high molecular-weight PAHs (HMW PAHs). Therefore, it appears reasonable that in 2016, LMW-PAH

Table 2
Characteristic values of PAH diagnostic ratios for source identification.

Diagnosis ratio	Value range	Sources	References
$\sum$LMW/$\sum$HMW[a]	<1	Pyrogenic	Wang et al., 2017; Zhang et al., 2008
	>1	Petrogenic	
An/(An + Phe)	<0.1	Petrogenic	Budzinski et al., 1997; Pies et al., 2008; Tobiszewski and Namieśnik, 2012; Wang et al., 2017;
	>0.1	Pyrogenic	
Fluo/(Fluo + Pyr)	<0.4	Petrogenic	Fang et al., 2004; Mandalakis et al., 2002; Ravindra et al., 2008; Rogge et al., 1993a, b; Yunker et al., 2002
	0.4–0.5	Fossil-fuel combustion	
	>0.5	Grass, wood, coal combustion; diesel emissions	
B[a]A/(B[a]A + Chry)	<0.2	Petrogenic	Tobiszewski and Namieśnik, 2012; Yunker et al., 2002;
	0.2–0.35	Coal combustion	
	>0.35	Vehicular emissions/combustion	
B[b]F/B[k]F	>0.5	Diesel combustion	Pandey et al., 1999; Park et al., 2002; Ravindra et al., 2008
Ind/(Ind + B[g,h,i]P)	<0.2	Petroleum	Grimmer et al., 1983, Kavouras et al., 2001; Ravindra et al., 2008; Yunker et al., 2002
	0.2–0.5	Petroleum combustion	
	>0.5	Coal combustion	
	0.18	Cars	
	0.37	Diesel emissions	
	0.62	Wood burning	

[a] $\sum$LMW is the sum of the lower molecular-weight substances (two–three-ring PAHs); $\sum$HMW is the sum of the higher molecular-weight substances (four–six-ring PAHs).

contamination levels tended to be less than those of HMW PAHs due to the comparatively higher temperatures and UV intensity during the sampling period. It is also notable that many scientists returned to the research centre along with a growing number of tourists, which consequently led to the unintentional release of PAHs in the summer of 2016. Therefore, the PAHs mainly stemmed from the incomplete combustion of the fuel (diesel and gasoline) used for generators, vehicles, aircraft, and ships, which was the main source of HMW PAHs. On the contrary, 2017 terrestrial soil samples, which were collected during the winter, featured comparatively lower HMW PAH contents than those of the

2016 soil samples. These findings reflected the fact that the majority of researchers had already departed to avoid Antarctica's extremely cold winter weather.

Table 4 shows the range and mean of PAH concentrations in KGI terrestrial soils and in other countries. As can be seen in Table 4, the mean PAH levels on KGI (3.21 ng g^{-1}) were comparable to those in Dajiuhu, China (2.4 ng g^{-1}), which is far distant from Antarctica (Pongpiachan et al., 2017a, b; Xing et al., 2020). However, the concentrations of PAHs in KGI were lower than those found in soils collected in Beijing, China (1,228,000 ng g^{-1}; Peng et al., 2011); Victoria and South Australia (305,000 ng g^{-1}; Juhasz et al., 2016); Dhanbad, India (3488 ng g^{-1}; Suman et al., 2016); and Dilovasi, Turkey (1077 ng g^{-1}; Cetin, 2016), which were mainly from industrial areas. In this study, the highest $\sum_{15}$PAH values were recorded at station A33, followed by those at stations A1, A35, A29, and A34, with values of 34.94 ng g^{-1}, 34.11 ng g^{-1}, 33.30 ng g^{-1}, 26.54 ng g^{-1}, and 25.20 ng g^{-1}, respectively.

The spatial distributions of the PAHs were mapped using ArcGIS (v.10.5) as shown in Fig. 3. In general, it was found that areas close to the research stations, such as sampling points A33, A1, A35 and A29, had relatively high PAH concentrations, while in areas far from research stations, such as sampling sites A6, A7, and A8, the concentrations were quite low. High PAH concentrations were more densely distributed near research stations due to the influence of anthropogenic activities, such as the use of carbon-based fuels for power generation, transportation, and household activities.

This study classified the 12 likely carcinogenic PAHs into four groups according to their molecular structure: three-ring PAHs (i.e. Phe and An), four-ring PAHs (i.e. Fluo, Pyr, B[a]A, and Chry), five-ring PAHs (i.e. B[b]F, B[k]F, B[a]P, and D[a,h]A), and six-ring PAHs (i.e. Ind and B[g,h,i]P). Based on the average concentrations found, the three-ring group (1.91 ng g^{-1}) was identified as the most abundant in the terrestrial soil of KGI, accounting for 48.3% of the total PAHs, followed by four-ring PAHs (1.07 ng g^{-1}), five-ring PAHs (0.765 ng g^{-1}), and six-ring PAHs (0.203 ng g^{-1}), representing 27.1%, 19.3%, and 5.14% of the total PAHs, respectively. The highest levels of the three-ring group were found at sampling points A35, A43, A34, and A37, as shown in Fig. 4. The highest levels of the three-ring group were found at sampling points A35, A43, A34, and A37, as shown in Fig. 4. The highest total PAH concentrations (Σ12PAHs) were observed at sampling sites A35, A33, and A1, for A1 is located near the Antarctic Great Wall Station. The station, like most in the Antarctic, relies on fuel generators for lighting

Table 3
PAH concentrations (ng g^{-1}) in 44 terrestrial soil samples.

Compound	Year of Collection						F-test (<0.005)
	2014[a] (n = 23)		2016[b] (n = 33)		2017[b] (n = 11)		
	AVG	SD	AVG	SD	AVG	SD	
Phe	1.60	1.36	2.05	1.96	2.63	3.37	NS
An	0.0800	0.110	0.140	0.160	5.91	6.65	S
Fluo	0.490	0.580	0.770	0.890	1.15	1.17	NS
Pyr	0.570	0.530	0.800	0.890	1.25	1.15	NS
B[a]A	0.0800	0.170	0.180	0.460	0.280	0.490	NS
Chry	0.160	0.240	2.83	3.34	0.870	1.28	S
B[b]F	0.0600	0.180	0.850	1.02	0.0300	0.0100	NA
B[k]F	0.100	0.130	0.630	0.920	0.350	0.650	NA
B[a]P	0.0500	0.0700	1.93	2.02	0.290	0.480	S
Ind	0.000194	0.000891	0.170	0.280	N.D.	N.D.	NA
D[a,h]A	0.0100	0.0100	0.170	0.260	0.0800	0.00	NS
B[g,h,i]P	0.0200	0.0800	0.380	0.610	N.D.	N.D.	NA
Σ_{12}PAHs	3.21	1.62	10.8	9.26	12.8	9.73	
three-ring PAHs	1.68		1.09	1.00	4.37	3.00	
four-ring PAHs	1.30		1.14	1.11	0.861	0.903	
five-ring PAHs	0.212		0.994	0.842	0.0773	0.224	
six-ring PAHs	0.0181		0.271	0.392	N.D		

N.D. = not detected. AVE = average. SD = standard deviation.
[a] The 2014 data represents the average PAH concentrations in King George Island terrestrial soil as reported by Pongpiachan et al. (2017a, b).
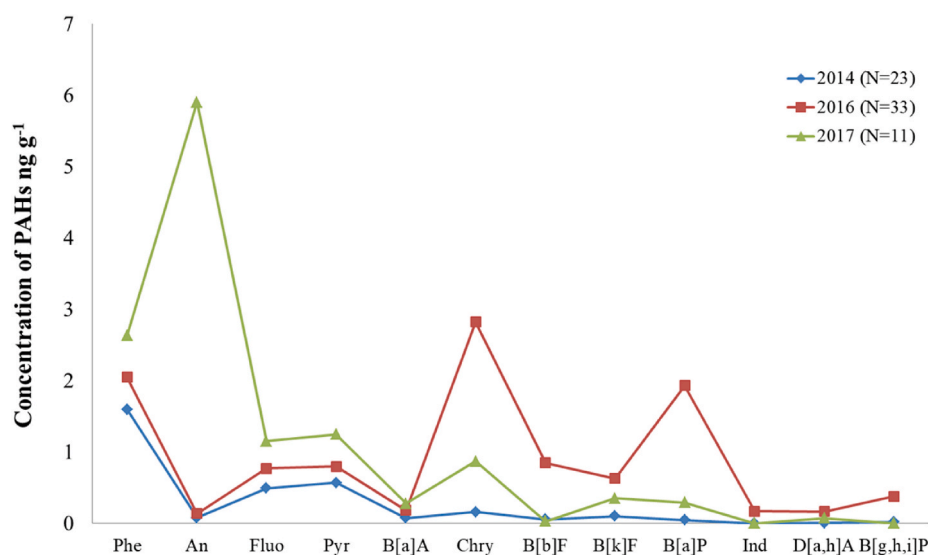[b] The average PAH concentrations in King George Island terrestrial soil KGI.

Fig. 2. Annual variations in the concentrations of 12 PAHs in the terrestrial soil of King Gorge Island in 2014, 2016 and 2017.

Table 4
Summed concentrations of PAHs in King George Island soil compared to those found in other locations (ng g^{-1}).

Sampling sites	Area	Number of PAHs	Concentration range (ng g^{-1})	Mean (ng g^{-1})	References
Dilovasi, north-western Turkey	industrial	Σ_{17}PAH	61–6726	1077	Cetin (2016)
Beijing, China	urban	Σ_{16}PAH	93,000–13,141,000	1,228,000	Peng et al. (2011)
Songhua River Basin, China	industrial	Σ_{15}PAH	30.1–870	209	Ma et al. (2013)
Hunpu, China	urban	Σ_{16}PAH	7.88–2231	275.04	Zhang et al. (2013)
Victoria and South Australia	urban	Σ_{16}PAH	18,400–871,000	305,000	Juhasz et al. (2016)
Ulsan, Korea	industrial	Σ_{16}PAH	65–12,000	960	Kwon and Choi (2014)
Gdańsk, northern Poland	near a landfill	Σ_{16}PAH	892–3514	1974	Melnyk et al. (2015)
Dhanbad, India	urban	Σ_{13}PAH	1019–10,856	3488	Suman et al. (2016)
Dilovasi, Turkey	industrial	Σ_{15}PAH	49–10,512	992	Yurdakul et al. (2019)
Beijing, China	urban	Σ_{16}PAH	0.066–6.867	0.46	Qu et al. (2020)
Dajiuhu, China	urban	Σ_{15}PAH	7.30–191.4	2.4	Xing et al. (2020)
Clay County, Florida, USA	urban	Σ_{16}PAH	797–7909	1821	Gao et al. (2019)
West Palm Beach, USA	urban	Σ_{16}PAH	1133–30,691	4055	Gao et al. (2019)
Ocala, Florida, USA	urban	Σ_{16}PAH	950–11,451	2748	Gao et al. (2019)
Pensacola, Florida, USA	urban	Σ_{16}PAH	922–17,698	3115	Gao et al. (2019)
Lesser Himalayan Region	urban	Σ_{15}PAH	62.79–1080	–	Riaz et al. (2019)
KGI, Antarctica	polar	Σ_{12}PAH	–	3.21	Pongpiachan et al. (2017a, b)
KGI, Antarctica	polar	$\Sigma15$PAH	1.88–34.94	11.8	**This study**
Chile	urban	Σ_{12}PAH	21.5–4376	618	Deelaman et al. (2020)

and warming the buildings from which fuel-oil spills may occur. Also, some of the sampling points such as A33, A34, and A35, which were a little far away from the Antarctic Great Wall Station, but were also close to the main road, and thus the PAH concentrations could have been influenced by human activities such as oil spills from transportation or even oil spills from vehicles themselves. However, most sampling sites that were far from the research station location have relatively low total PAH concentrations. These findings are consistent with those of Ravindra et al. (2008), who reported that PAH concentration may vary significantly in rural and urban areas.

The samples taken on KGI were dominated by LMW PAHs (Jiang et al., 2009; Yunker et al., 2002), followed by medium molecular-weight PAHs (MMW PAHs: four aromatic ring PAHs). Phe, Chry, and An were LMW–MMW PAHs with average concentrations of 2.17 ± 2.29 ng g^{-1}, 2.41 ± 3.11 ng g^{-1}, and 1.50 ± 3.95 ng g^{-1}, respectively. These LMW PAHs derived from petrogenic activity. However, three-ring PAHs can be released via wood combustion at low temperatures as well as from diesel engines (Navarro et al., 2017; Ravindra et al., 2008; Tao et al., 2006), and previous studies have shown that diesel trucks were the main source of LMW PAHs (Miguel et al., 1998). In contrast, pyrogenic PAHs are abundant within MMW PAHs and HMW PAHs (five–six aromatic ring PAHs) (Sanders et al., 2002). Such PAHs are largely associated with

the use of oil or gasoline which burns at high temperatures in light-duty gasoline vehicles (Miguel et al., 1998; Ravindra et al., 2008) as well as fossil-fuel combustion (industrial oil and domestic coal) (Tao et al., 2006). LMW PAHs and MMW PAHs were found to be the most abundant in the terrestrial soil of KGI, which indicates that the pollution in the soil samples mostly originated from mixed petrogenic and pyrogenic sources. This result was consistent with that of the previous study by Pongpiachan et al. (2017a, b), which reported that the most abundant PAH on KGI was Phe, followed by Pyr, Fluo, and Chry.

3.2. PAH sources

The potential emission sources (petrogenic processes or pyrolytic processes) of the PAHs presented in the highest concentrations in terrestrial soil samples can be identified using their binary diagnostic ratios, because the PAHs with the most stable properties are those originating in hydrocarbons (Budzinski et al., 1997; Chen et al., 2012; Tobiszewski and Namieśnik, 2012; Wang et al., 2017; Yunker et al., 2002; Zhang et al., 2008). Petrogenic processes are responsible for PAHs arising from the slow maturation of organic substances formed at low temperatures, and their presence may be indicative of crude oil spills (Abdel-Shafy and Mansour, 2016). Meanwhile, PAHs formed via
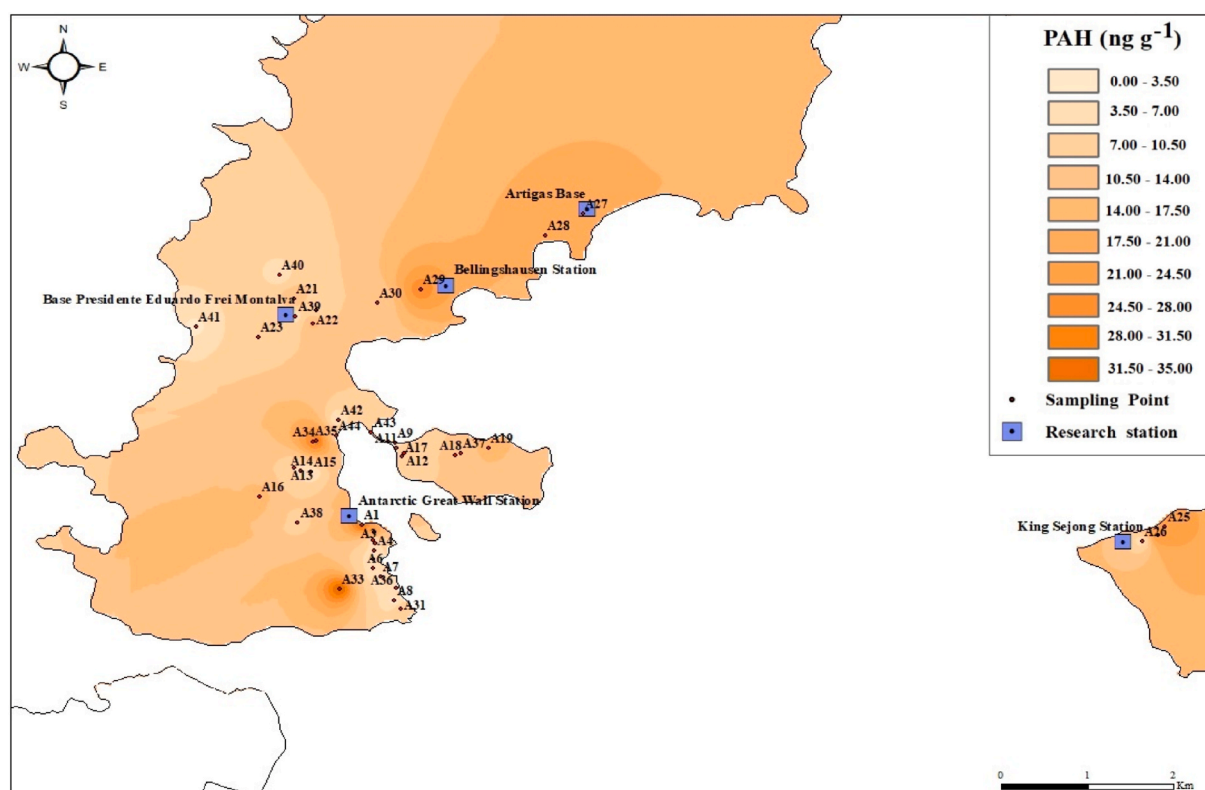
Fig. 3. Map of the study area on King George Island showing the sampling sites and spatial distribution of $\sum_{15}$PAHs.
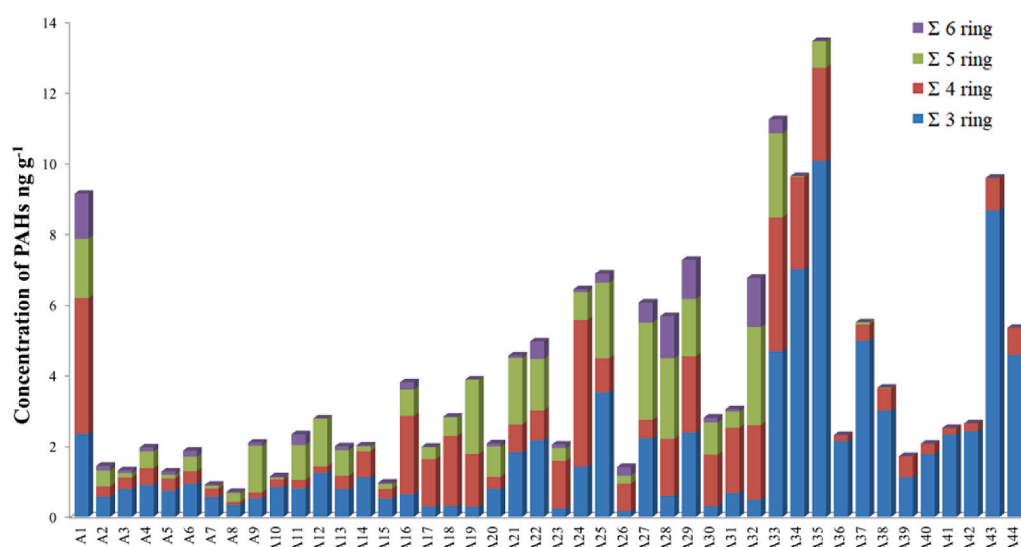

Fig. 4. Three–six-ring PAH concentrations and distribution patterns in the terrestrial soil of King George Island, Antarctica.

combustion at high temperatures and under depleted oxygen conditions and similar processes are connected to pyrolytic processes (Abdel-Shafy and Mansour, 2016; Manahan, 1994).

Table 2 presents the values and ranges of the PAH ratios (An/(An + Phe), Fluo/(Fluo + Pyr), B[a]A/(B[a]A + Chry), B[b]F/B[k]F, and Ind/(Ind + B[g,h,i]P)) from which the emission sources were identified in this study. An/(An + Phe) ratio < 0.2 indicates a petrogenic source, while higher ratios indicate mixed sources. However, the ratios found in this study indicated that the predominant sources of PAHs in KGI were petrogenic, and the B[a]A/(B[a]A + Chry) ratio also tended to implicate petrogenic sources. However, the B[a]A/(B[a]A + Chry) ratio indicated

that contamination in the KGI terrestrial soil samples also stemmed from pyrogenic sources (e.g. petroleum combustion, coal combustion). The results from most sampling sites suggested PAHs from mostly petrogenic sources, with the exception of stations A16, A26, A34, A35, A39, A40, and A44, where pyrogenic sources appeared predominate.

Cross-plots between An/(An + Phe) and B[a]A/(B[a]A + Chry) are presented in Fig. 5. Previous studies have found that most of the oil delivered to Antarctica is used for electricity generation, heating, water production, and wastewater treatment in research stations around the continent, including those on KGI. The results of a previous study on contamination in Antarctica dating back to the last century indicated
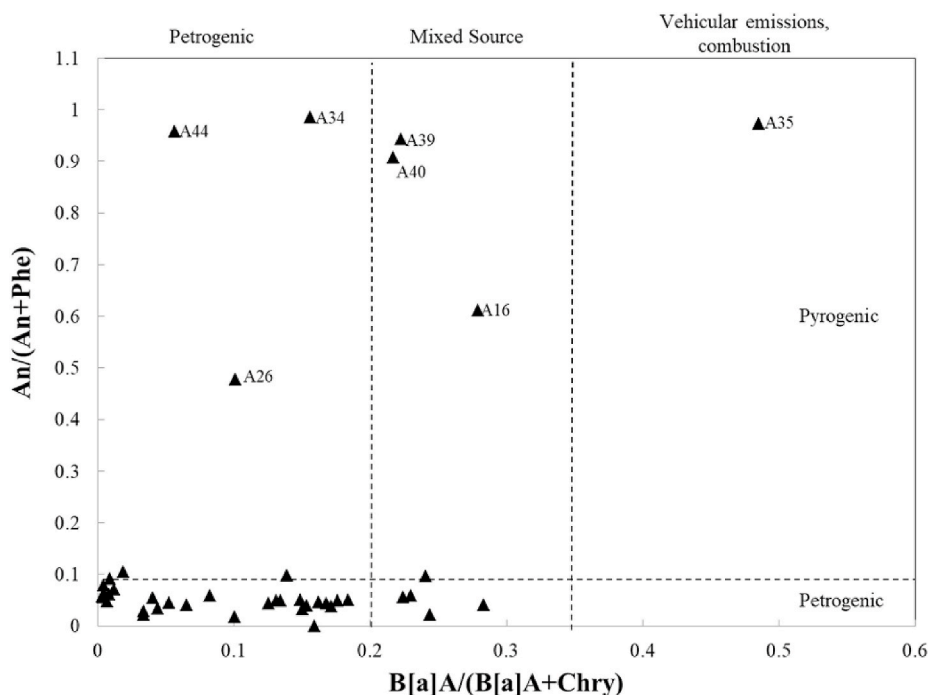
Fig. 5. Binary PAH diagnostic ratios between An/(An + Phe) and B[a]A/(B[a]A + Chry) in King George Island soil.

that between 1 and 10 million cubic meters of soil in Antarctica had been contaminated by oil (Snape et al., 2001; Raymond et al., 2017). Most fuel spills occur at stations in areas where fuel is stored and from motor vehicles and aircraft, as well as along road networks. Such occurrences happen repeatedly at the same locations, causing oil pollution to accumulate in the soil over time (Raymond et al., 2017).

The ratio of the diagnostic pairs Fluo/(Fluo + Pyr) and Ind/(Ind + B [g, h, i] P) (see Fig. 6A) can be used to identify the possible sources of PAHs in soil samples. This study's results indicated that the PAHs had originated from mixed sources, both petrogenic (fuel leaks and oil spills) and pyrogenic (incomplete combustion of petroleum vehicle fuels and crude oil, coal combustion, and diesel emissions). In addition, the $\sum$LMW/$\sum$HMW ratio (see Fig. 6B) > 1 indicated petrogenic sources, suggesting that the sources of PAHs in KGI soil were mixed. Meanwhile, the ratio of B[b]F/B[k]F (see Fig. 6C) indicated that the PAHs detected in the soil samples from some sites had originated from the incomplete combustion of diesel fuel.

The binary diagnostic ratio results showed that pyrogenic processes caused by the incomplete combustion of petroleum fuels were the main source of PAHs on KGI. Most sampling sites were located in areas around research stations and the road network, as 90% of the island's surface is covered by glaciers and is difficult to access (Rückamp et al., 2011). Therefore, it is logical to expect that the main PAH sources would be emissions from motor vehicles, aircraft, and ships as well as from electrical generators used for lighting, warmth, and the operation of scientific equipment. Thus, most PAHs can be attributed to the burning of petroleum products (gasoline, diesel, and jet fuel). This is consistent with the finding of Pongpiachan et al. (2017a, b) that Phe was the most abundant PAH observed in soil samples from KGI; they also found that the Comandante Ferraz Antarctic Station fire incident was the main cause of the high concentration of Phe, due to the combustion of diesel during the fire.

However, in this study, the binary diagnostic ratios of PAHs indicated that while Phe was the most common PAH in the soil samples, its presence mainly stemmed from petrogenic processes. This finding supports that of Mackie et al. (1978), who reported that legacy sources of oil pollution in Antarctica are the result of human activities such as oil spills, the abandonment of oil depots and stations, vehicle wrecks, and

waste disposal sites. Moreover, transporting fuel and oil to Antarctica is risky. Fuel spills have occurred due to the difficulty of pumping fuel ashore and the vulnerability of large fuel tanks and fittings to breakage under frigid temperatures (Tin et al., 2010).

3.3. Source apportionment via principal component analysis

In this study, the sources of PAHs from pyrolytic and petroleum origins were identified by PCA, which was performed using the Varimax rotation method with the Kaiser standard adjustment. The factors identified by the PCA are summarized in Table 5. The data set comprised data relating to the concentrations of 13 PAHs in each of the 44 terrestrial soil samples. The scalable data were explained by five eigenvectors–principal components, which together accounted for 81.34% of the total variance. The first factor (PC1) explained 22.84% of the total variance, and this factor was predominantly loaded on An, Fluo and Pyr, which are three- or four-ring PAHs derived from numerous sources associated with the incomplete combustion of oil fuel (e.g. diesel engines, electricity generators) (Caricchia et al., 1999; Duval and Friedlander, 1981; Fang et al., 2004; Ho et al., 2002; Khalili et al., 1995). Therefore, PC1 was considered to represent a pyrogenic source, specifically emissions from diesel-powered machinery used to produce electricity as indicated by the B[b]F/B[k]F ratio; this thus indicated that more than 50% of the soil samples were contaminated by diesel fuel.

Meanwhile, the second factor (PC2) explained 18.94% of the total variance, and this factor was predominantly loaded on B[a]P and Ind, which are five- or six-ring PAHs derived from numerous sources associated with small-vehicle exhaust emissions. This is consistent with the research of Gambino et al. (2000), who reported that two-stroke and small engines were the sources of B[a]P and B[a]A, whereas light-duty gasoline vehicles were an important source of higher molecular-weight PAHs (Miguel et al., 1998). The third factor (PC3) explained 18.16% of the total variance and was mainly associated with D[a,h]A, which is a six-ring PAH. It is well known that D[a,h]A is a biomarker of the burning of biomass, including grass and wood (Freeman and Cattel, 1990). Therefore, long-range atmospheric transportation might have played a crucial role in this component, as there were no wildfires in Antarctica.
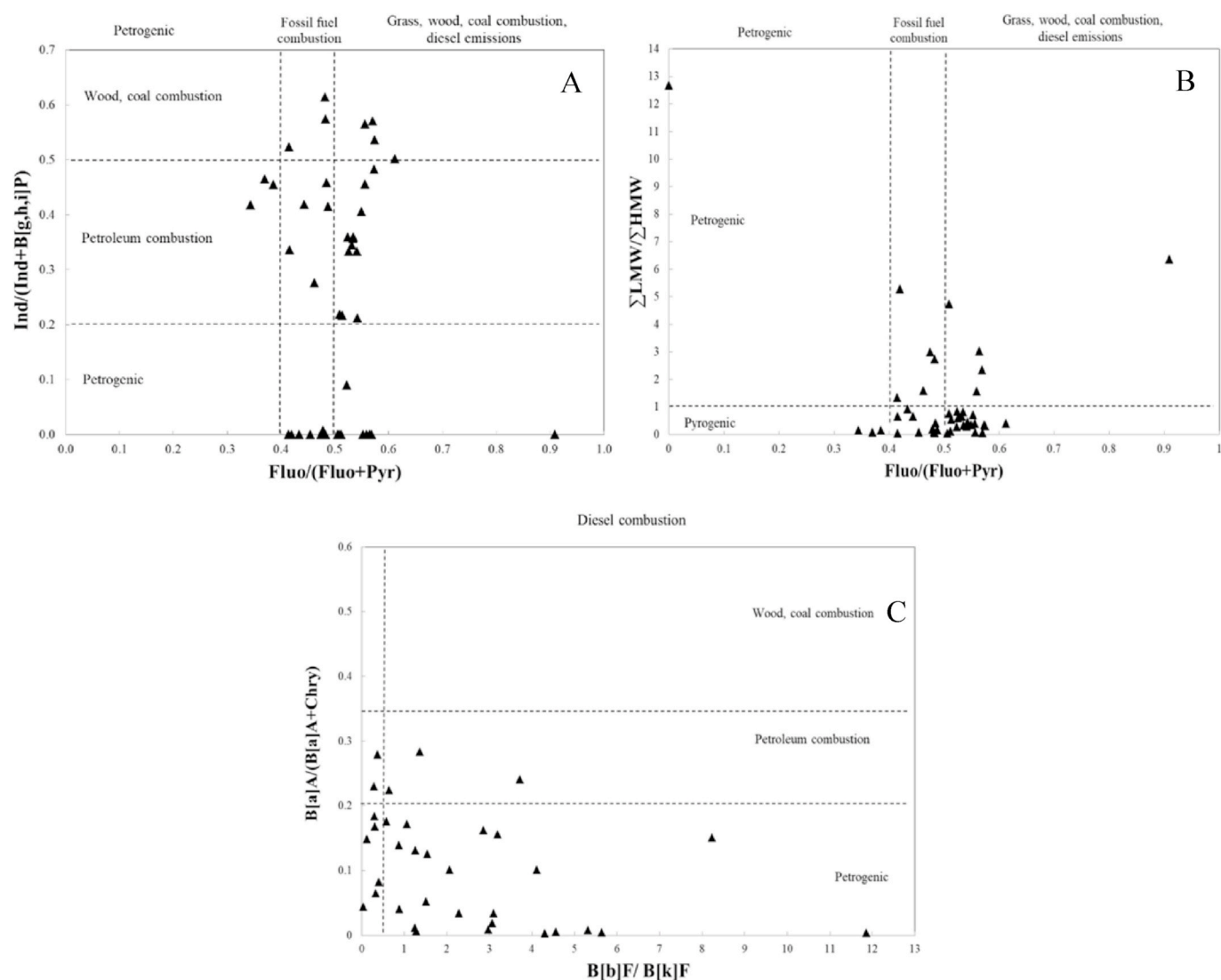
Fig. 6. Binary diagnostic ratios of PAHs: (a) Ind/(Ind + B [g, h, i] P) versus Fluo/(Fluo + Pyr), (b)∑LMW/∑HMW versus Fluo/(Fluo + Pyr), and (c) B[a]A/(B[a]A + Chry) versus B[b]F/B[k]F in King George Island soil.

It is also interesting to note that PC4, which was strongly connected with Phe, accounted for only 13.46% of the total variance four years after the Comandante Ferraz Antarctic Station burnt down on February 25, 2012. An explosion in the machine room, which housed the station's generators, was the main route of PAHs released into the atmosphere, including PAHs in the vapor or particle gas phases that were released from the oil (Pongpiachan et al., 2017a, b). Atmospheric PAHs can travel long distances and are continuously deposited to surface soil by wet or dry deposition processes. This factor represents petrogenic sources such as leakage from oil storage tanks, fuel-oil spills during transportation, and the waste treatment system on KGI. In addition to the fire at the Comandante Ferraz Antarctic Station, Raymond et al. (2017) also studied oil pollution in Antarctica and reported that most fuel spills occur at research stations, from aircraft, and in automotive areas. Contamination from oil spills have been found up to ten years after the spill occurred (Gore et al., 1999), and the concentrations of oil and PAHs can remain high even after many years (Blanchette et al., 2004), which is consistent with the PAHs' status as POPs.

Finally, factor PC5, which accounted for only 7.94% of the total variance, was predominantly loaded on five-ring PAHs (i.e. B[k]F). Most of the four-ring PAHs derived from incomplete combustion of diesel fuel used in diesel-powered vehicles, which is consistent with other studies

that suggest B[k]F originates from diesel vehicles (Duval and Friedlander, 1981; Khalili et al., 1995). Therefore, it appears reasonable to assume that factor PC5 was related to the incomplete combustion of fuel from diesel-powered vehicles.
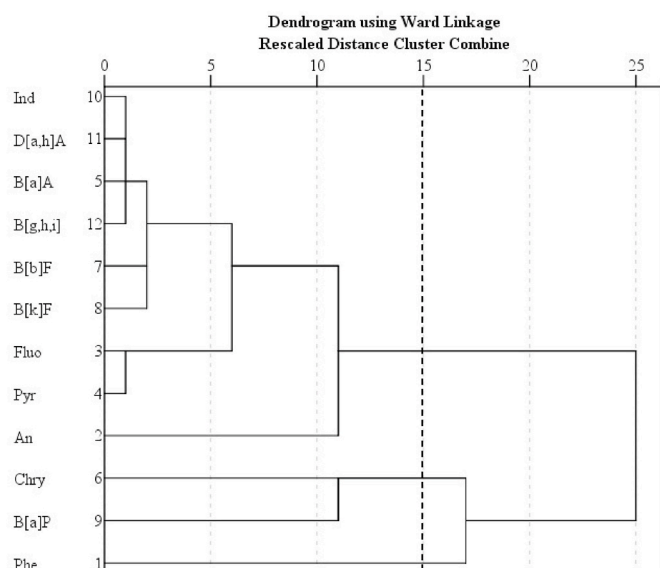
3.4. Hierarchical cluster analysis

The HCA results show that the PAHs can be divided into three main groups as shown in Fig. 7. The first group consists of An, Fluo, Pyr, B[a]A, B[b]F, B[k]F, Ind, D[a, h]A, and B[g, h,i]P. This group mostly originates from incomplete combustion, which is in line with the results of the PCA, which indicated that this group has a pyrogenic origin. Moreover, the results are consistent with those of Khalili et al. (1995) and Ravindra et al. (2008), who found that PAH molecules originating from pyrogenic sources (vehicles, diesel engines, petrol engines, and wood burning) mostly have two-to five-ring structures. The second group consisted of Chry and B[a]P, which are four-to five-ring PAHs. This group similarly have origins in incomplete combustion (light-duty gasoline, gasoline-powered vehicles). However, the last group includes only Phe, a three-ring PAH, and the binary diagnostic ratio results indicate that this group may stem from petrogenic activity.

The HCA results for the 44 sampling sites disclosed two main groups

Table 5

Principal component analysis results for PAHs in the terrestrial soil of King George Island, Antarctica[a].

PAH composition	Principle component (PC)				
	PC1	PC2	PC3	PC4	PC5
Phe	0.08	0.04	0.00	**0.91**[b]	0.17
An	**0.82**[b]	−0.16	−0.17	−0.41	0.10
Fluo	**0.89**[b]	0.04	0.24	0.33	0.07
Pyr	**0.89**[b]	0.07	0.26	0.28	−0.07
B[a]A	0.58	−0.06	0.67	−0.13	0.12
Chry	0.22	0.53	0.30	0.04	−0.42
B[b]F	0.21	0.58	0.24	0.54	−0.14
B[k]F	0.15	0.24	0.26	0.16	**0.78**[b]
B[a]P	−0.16	**0.81**[b]	0.11	0.08	0.06
Ind	−0.03	**0.84**[b]	−0.04	−0.01	0.27
D[a,h]A	0.06	0.07	**0.95**[b]	0.03	0.10
B[g,h,i]P	0.12	0.44	0.68	0.28	0.04
Total variance (%)	**22.84**	**18.94**	**18.16**	**13.46**	**7.94**
Cumulative (%)	22.84	41.78	59.95	73.40	81.34
Estimated source	Electricity generators	Light-duty gasoline	Biomass combustion	Explosion of Electric Generator at the Comandante Ferraz research base	Diesel-powered vehicles

Extraction Method: Principal component analysis.

[a] Rotation Method: Varimax with Kaiser normalisation.

[b] Bold number: Loading value greater than 0.7 (heavy loading).

Fig. 7. Hierarchical cluster analysis results for 12 PAHs in the soil of King George Island, Antarctica.

as shown in Fig. 8. The first group of sampling sites consisted of four stations: A34, A35, A43, and A44. These sites were identified as being contaminated by PAHs from pyrogenic processes by the binary diagnostic ratios of the PAHs (i.e. An/(An + Phe) and Fluo/(Fluo + Pyr)). In addition, at all of these stations, An, which results from the incomplete combustion of fuel, was identified as the most abundant PAH (Caricchia et al., 1999; Fang et al., 2004; Ho et al., 2002; Omar et al., 2002; Ravindra et al., 2008). All sampling stations in this group were located adjacent to each other and quite far from the Great Wall research station. Thus, it was unlikely that these soil samples would be contaminated by petrogenic sources, which mainly included oil spills at this research station. Therefore, these specimens would be expected to be influenced only by PAHs stemming from incomplete fuel combustion from research stations and vehicles. Such PAHs are released into the atmosphere and can move far from their source. Then, they are deposited to surface soil via wet or dry deposition processes. Thus, it seems reasonable to consider that the primary source of PAH contamination at these four stations are pyrolysis processes.

The second group consisted of all the remaining sampling sites. Most of these sampling sites are located near research stations (i.e. the Antarctic Great Wall Station, King Sejong Station, and Bellingshausen Station), and thus could be contaminated by PAHs from mixed sources (petrogenic and pyrogenic). Further, some sampling sites were adjacent to coastal areas, allowing those sites to be influenced by PAHs derived from stored-fuel spills and other activities at research stations. Additionally, PAHs may derive from contamination arising from engine oil from discarded motor vehicles. At the same time, an increased number of ships visiting the area either for research or tourism may result in more spillage of oil into the sea, which could be blown toward the coast and accumulate in the soil (Dos et al., 2018). Many previous studies have shown that the soil samples in study areas adjacent to the coast were highly likely to be contaminated with PAHs with crude oil from spill incidents involving oil pipelines and ships (Dos et al., 2018; Pongpiachan et al., 2018; Tipmanee et al., 2012). Thus, sampling sites in coastal areas may be highly contaminated with PAHs from petrogenic sources.

4. Conclusions

We analysed PAH components in the terrestrial soils of KGI using multivariate descriptive statistical techniques. The average $\sum_{12}$PAHs ranged from 1.83 to 32.9 ng g^{-1} (dry weight), which was lower than the values in many countries due to KGI's minimal population and scares human activities compared to other countries. The spatial distributions of PAHs could indicate that PAHs are highly dispersed in areas close to research stations and roads. The sources of the PAHs were determined based on the distribution of the individual compounds in combination with a PCA and HCA of the PAH binary diagnostic ratios. The results show that three-ring PAHs (48.3%) were the most abundant in KGI soil, indicating that diesel emission sources are the main contributors of PAHs. The results of the diagnostic PAH isomer ratios supported the finding that the PAHs in the KGI soil primarily stemmed from fuel contamination, and the B[b]F/B[k]F ratio showed that the main source of contamination was diesel oil. Meanwhile, PCA analysis showed that the fourth factor was solely the result of an electric generator explosion at the Comandante Ferraz research base. The results of the soil data analysis combined with the use of multivariate descriptive statistical techniques clearly showed that PAH contamination in the soil of KGI mainly derives from the leakage of fuel used for the activities of the research stations on the island. We expect that the results of this study
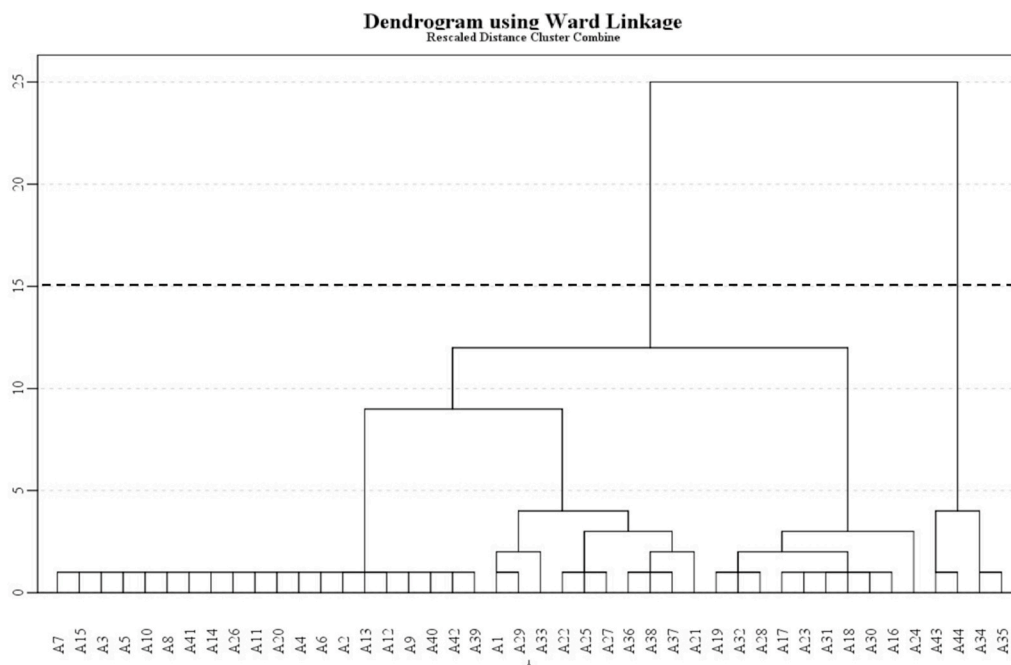
Fig. 8. Hierarchical cluster analysis (HCA) of 44 terrestrial soils from individual sampling sites on King George Island.

will be useful in managing soil pollution and in planning guidelines to reduce fuel consumption. Notably, Tin et al. (2010) showed that renewable energy (solar collectors, solar panels, and wind turbines) could be used more efficiently than fossil fuels in Antarctica, even though Antarctica is the darkest, coldest, and most remote continent on earth. However, studies on biological degradation and the frequency of occurrence of pollution are needed to our study in further work.

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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