



Anthropogenic and biogenic hydrocarbons in soils and vegetation from the South Shetland Islands (Antarctica)



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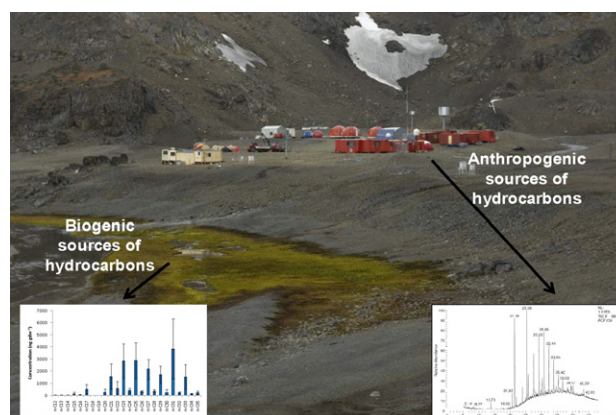
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HIGHLIGHTS

- Lipid content and soil organic carbon control the load of n-alkanes in Antarctic vegetation and soils
- Even a small settlement can affect the loading of aliphatic and aromatic hydrocarbons in nearby soils
- Biogenic derived sources of aliphatic and aromatic hydrocarbons are not negligible in Antarctica

GRAPHICAL ABSTRACT



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ABSTRACT

Two Antarctic expeditions (in 2009 and 2011) were carried out to assess the local and remote anthropogenic sources of aliphatic and aromatic hydrocarbons, as well as potential biogenic hydrocarbons. Polycyclic aromatic hydrocarbons (PAHs), n-alkanes, biomarkers such as phytane (Ph) and pristane (Pr), and the aliphatic unresolved complex mixture (UCM), were analysed in soil and vegetation samples collected at Deception, Livingston, Barrientos and Penguin Islands (South Shetland Islands, Antarctica). Overall, the patterns of n-alkanes in lichens, mosses and grass were dominated by odd-over-even carbon number alkanes. Mosses and vascular plants showed high abundances of n-C₂₁ to n-C₃₅, while lichens also showed high abundances of n-C₁₇ and n-C₁₉. The lipid content was an important factor controlling the concentrations of n-alkanes in Antarctic vegetation ($r^2 = 0.28\text{--}0.53$, $p\text{-level} < 0.05$). n-C₁₂ to n-C₃₅ n-alkanes were analysed in soils with a predominance of odd C number n-alkanes (n-C₂₅, n-C₂₇, n-C₂₉, and n-C₃₁), especially in the background soils not influenced by anthropogenic sources. The large values for the carbon predominance index (CPI) and the correlations between odd alkanes and some PAHs suggest the potential biogenic sources of these hydrocarbons in Antarctica. Unresolved complex mixture and CPI values ~1 detected at soils collected at intertidal areas and within the perimeter of Juan Carlos research station, further supported the evidence that even a small settlement (20 persons during the austral

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summer) can affect the loading of aliphatic and aromatic hydrocarbons in nearby soils. Nevertheless, the assessment of Pr/n-C₁₇ and Ph/n-C₁₈ ratios showed that hydrocarbon degradation is occurring in these soils.

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1. Introduction

Antarctica is one of the most pristine areas of the world due to its geographical location and distance to populated regions. The lack of large in-situ anthropogenic sources of pollution, and the existence of the Antarctic Treaty, protects the Antarctica against several human activities leading to the introduction of pollutants (Consultative Parties to the Antarctic Treaty, 1991). The low temperatures and abundant snow/rain events in some regions such as the Southern Shetlands and Antarctic Peninsula, favor the atmospheric deposition of organic pollutants and their persistence in soils and vegetation, which are only free of snow/ice cover in coastal areas and for few weeks/months during the austral summer. However, human activities in Antarctica, especially in accessible areas of the Antarctic Peninsula, such as growing tourism (Tin et al., 2008), fishery activities, and scientific operations, together with long range atmospheric transport (LRAT) and deposition, are the main input vectors of organic pollutants (Cabrerizo et al., 2012; Cabrerizo et al., 2014). A wide range of organic pollutants have been described in Antarctic biota, soils, sediments, ocean and atmosphere (Cabrerizo et al., 2012; Cabrerizo et al., 2014; Sanchís et al., 2015; Galbán-Malagón et al., 2013a, 2013b, Bengtson Nash, 2011; Montone et al., 2003; Bargagli et al., 1993; Kallenborn et al., 2007; Corsolini et al., 2006). Of significant importance and magnitude are those derived from the use of fossil fuels, such as aliphatic and aromatic hydrocarbons (UNEP, United Nations Environment Programme Chemicals, 2002; USEPA, United States Environmental Protection Agency, 1985). High concentrations of polycyclic aromatic hydrocarbons (PAHs) have been measured in soil and sediment samples collected close to research stations or where oil spills, fossil fuel combustion, or sewage discharge have occurred (Cabrerizo et al., 2012; Bicego et al., 2009; Aislabie et al., 1999; Cripps, 1992; Mazzera et al., 1999). Soil organic matter (SOM) in Antarctica is low in background Antarctic soils (Cabrerizo et al., 2012), but higher under the influence of anthropogenic activities, vegetation, biota feces (Cabrerizo et al., 2012), ancient glacial tills and lakes (Hopkins et al., 2006). The influence of SOM on alkane concentrations is still unknown. The low temperatures occurring in Antarctica delay the biological degradation of hydrocarbons in contaminated soils (Okere et al., 2012), but can potentially preserve information provided by soil/vegetation biomarkers to infer the source of the organic matter (biogenic hydrocarbons) from anthropogenic hydrocarbons originated from local sources or atmospheric deposition. Biomarkers, such as n-alkanes, have been assessed in soils and sediments close to scientific stations (Prus et al., 2015; Green and Nichols, 1995, Guerra et al., 2013; Woolfenden et al., 2011), showing higher concentrations (Prus et al., 2015; Green and Nichols, 1995, Guerra et al., 2013; Woolfenden et al., 2011) due to accidental releases of hydrocarbons. Conversely, input of terrigenous organic matter is indicated by a strong predominance of high molecular weight odd-numbered alkanes (n-C₂₇, n-C₂₉ and n-C₃₁), which are associated with vegetation waxes (Wakeham and Carpenter, 1976; Prah and Muehlhausen, 1989), while marine algae are known to produce lower molecular weight n-alkanes with maximum at n-C₁₇ (Dachs et al., 1999). The carbon predominance index (CPI) is often used to identify specific sources of n-alkanes and to estimate relative contributions from higher plant waxes (CPI > 1) or fossil fuel hydrocarbons (CPI = 1; Simoneit and Mazurek, 1982). However, despite the importance of hydrocarbons and n-alkanes to identify the source of pollutants and palaeoclimatological reconstructions (Izarta et al., 2012), the geochemical signature and extent of recent and past oil spills to Antarctic soil and

vegetation in comparison to long range atmospheric transport have not been comprehensively addressed.

Therefore, the main objectives of this study were: i) to contribute with a large data set of PAHs and n-alkanes concentrations in soils and vegetation from Deception, Livingston, Barrientos and Penguin Islands (all belonging to the South Shetland Islands). The sampling sites cover soils from intertidal areas affected by seawater inputs, background soils with and without vegetation, and lichens, mosses, grass and Antarctic pearlwort, ii) to assess the local and remote anthropogenic sources of aliphatic and aromatic hydrocarbons, as well potential biogenic hydrocarbon inputs. This is achieved by the determination of the concentrations of n-alkanes, biomarkers such as phytane (Ph) and pristane (Pr), the unresolved complex mixture (UCM) and PAHs.

2. Experimental section

2.1. Study sites and sampling methodology

The collection of soil and vegetation samples was performed at different sites of the South Shetland Islands during the austral summer campaigns in 2008/09 (ATOS-2, 10th January–14th February'09) and 2010/11 (24th January–10th February'11). Deception Island (62° 58' S, 60° 40'W), Livingston Island (62° 39'S, 60° 23'W), Barrientos Island (62° 24' S, 59° 44'W), Penguin Island (62° 06' S, 57° 56'W) and Byers Peninsula, (62° 34'S, 61° 13'W), an Antarctic Specially Protected Area located in the westernmost part of the Livingston Island, were selected as the study region (Fig. 1 and further details in Annex I of Supporting Information (SI)). Soil samples from surface top 1 cm and profile (top 5 cm) (n = 46) and vegetation samples (n = 16) were collected in the Islands coastal sites during the 2008–2009 campaign and at medium-high intertidal areas mainly during the 2010–2011 campaign (Annex I SI for information regarding sampling sites, sampling maps and sampling information). Many of these areas are not accessible by land and they were reached by sea. Some of these samples, especially those within the Islands (on-land soils) and further away from intertidal areas were collected at zones with penguin colonies, with vegetation cover, in ancient stations or proximate to the current main research buildings of Juan Carlos I research station. Vegetation types collected include lichens (*Usnea Antarctica*, n = 7), mosses (*Sanionia uncinata*, n = 6), and a couple of vascular plants, Antarctic hair grass, (*Deschampsia Antarctica*) (n = 2) and Antarctic pearlwort (*Colobanthus quitensis*) (n = 1) (Annex I for sampling sites, sampling map, vegetation types and sampling details). Samples of soil from intertidal areas were analysed for PAHs and n-alkanes, while vegetation and on-land soil samples were only analysed for n-alkanes, as PAHs were reported in a companion study (Cabrerizo et al., 2012). Both soil and vegetation samples were collected in pre-cleaned glass jars. Soil samples were collected using a stainless steel spoon, which was rinsed with acetone between samples to avoid cross contamination, while vegetation samples were collected with pre-cleaned stainless steel scissors and clean nitrile gloves for each sample. Samples were kept air-tight until their analysis. After sampling, soil and vegetation samples were stored in freezers at –20 °C until analysis.

2.1.1. Analytical methods

Prior to the extraction, soil samples (~20 g) were homogenized and dried by mixing with anhydrous sodium sulphate. Vegetation samples (~25 g) were frozen with liquid nitrogen and homogenized and dried by mixing with anhydrous sodium sulphate. The whole sample was

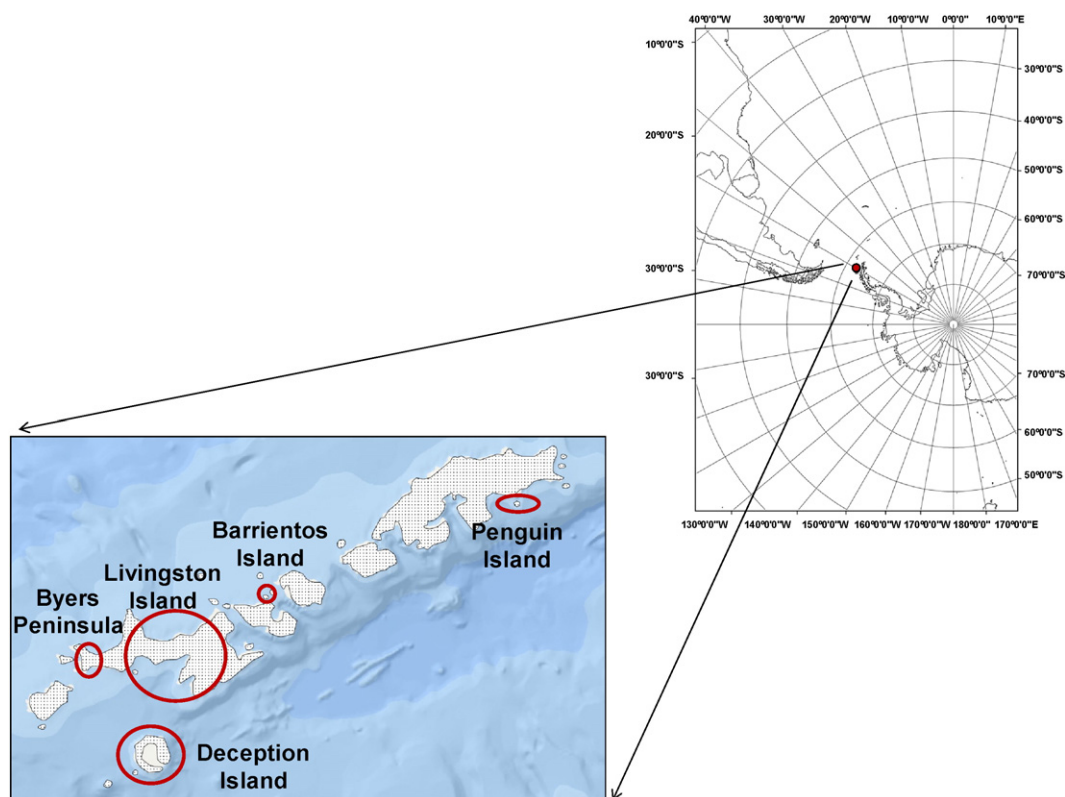


Fig. 1. Sampling regions in Livingston and Byers Peninsula, Deception, Barrientos and Penguin Islands (South Shetland Islands, Antarctica).

transferred into a pre-extracted cellulose thimble (Whatman) and extracted in Soxhlet for 24 h in dichloromethane:methanol (2:1), followed by a concentration using a rotary evaporator and solvent exchange to hexane until 1 ml. Prior to the extraction, samples were spiked with a solution containing the following deuterated compounds; phenanthrene- d_{10} , pyrene- d_{10} , perylene- d_{12} and tetracosane- d_{12} , which were used as surrogate standards to determine the potential losses during the analytical procedure. 1 ml extracts were cleaned and fractionated using glass columns filled with neutral alumina (Merck, 70–230 mesh, 3 g of 3% deactivated) and a top layer of anhydrous sodium sulphate (0.5 cm) to separate the aliphatic and aromatic fractions. The fraction containing the low polarity aliphatic hydrocarbons (n-alkanes) and the aliphatic UCM was eluted with 6 ml of hexane and the aromatic fraction (containing the PAHs) was eluted with 12 ml of dichloromethane/hexane 2:1. Samples were concentrated in a rotary evaporator until 1 ml, and then transferred to a vial and solvent-exchanged to isooctane under a gentle stream of nitrogen to a final volume of 150 μ l. Nonadecane- d_{40} , and a mix containing anthracene- d_{10} , fluoranthene- d_{10} and benzo(b)fluoranthene- d_{12} were used as internal standards.

All samples were analysed for n-alkanes (in the range from n- C_{12} to n- C_{35}), Ph, Pr, and the aliphatic UCM using an Agilent 6890 gas chromatography coupled to an Agilent 5973 mass spectrometry (GC/MS) with a EI + source operating in full SCAN mode with a HP-5 MS column (30 m length \times 0.25 mm i.d \times 0.25 thickness). 2 μ l of each sample were injected in splitless mode with the injector temperature at 280 °C. Helium was used as carrier gas at a flow rate of 1 ml min^{-1} . The oven temperature was programmed to increase from 90 °C to 180 °C (1 min hold) and from 180 °C to 300 °C (2 min hold) at a rate of 3 °C min^{-1} . The mass spectrometer was operated in the electron impact (EI) mode (70 eV) with a scanning range between m/z 50 and 500. Reference to the sum of n-alkanes (Σ n-alkanes) considers the aforementioned n- C_{12} to n- C_{35} .

The following parent and alkylated PAHs were analysed in the aromatic fraction: phenanthrene (Phe), anthracene (Ant), fluoranthrene

(Flu), pyrene (Pyr), benzo(a)anthracene (B(a)ant), chrysene (Cry), benzo(b&k)fluoranthene (B(b + k)f), benzo(e)pyrene (B(e)pyr), benzo(a)pyrene (B(a)pyr), perylene (Pery), dibenzo(a,h)anthracene (Dib(a,h)ant), benzo(g,h,i)perylene (B(g,h,i)pery), indeno(1,2,3-cd)pyrene (In(1,2,3-cd)pyr, dibenzothiophene (DBT), methyl dibenzothiophenes (Σ MDBT), methylphenanthrenes (Σ MP), dimethylphenanthrenes (Σ DMPD). PAHs were analysed by GC/MS using an Agilent 6890 operating in selected ion monitoring (SIM) mode. The GC system was equipped with a 30 m \times 0.25 mm \times 0.25 μ m i.d., Agilent, HP-5MS (5%-phenyl-95%-dimethylpolysiloxane) capillary column with a film thickness of 0.25 μ m. The oven temperature was increased to 90 °C and held for 1 min, then increased to 120 °C at 10 °C/min, and then increased from 120 to 315 °C at 5 °C/min and finally held at 315 °C for 5 min. Injector and transfer line temperatures were 280 and 300 °C, respectively, and 2 μ l of sample were injected. Further details of the extraction, fractionation, temperature programs and monitored ions are given elsewhere (Cabrerizo et al., 2009, 2011, 2013). Reference to the sum of PAHs (Σ PAHs) considers the aforementioned parent and methylated PAHs.

2.1.2. Quality assurance/quality control

All analytical procedures were monitored using strict quality assurance and control measures. Laboratory blanks were included at the rate of one blank every five samples processed. Phe, Ant, Flu and n-alkanes were detected in blanks at low concentrations, ranging from 4 to 12% of levels found in samples, indicating minimal contamination during processing. Therefore, samples were not blank corrected. PAHs and n-alkanes method quantification limits were derived from the lowest standard in the calibration curve; they were 2 pg gdw^{-1} for PAHs in soil and from 0.4 ng gdw^{-1} to 0.7 ng gdw^{-1} for n-alkanes in soil and vegetation respectively. Recoveries were routinely monitored using phen- d_{10} , chry- d_{12} , pery- d_{12} and tetracosane- d_{12} and they ranged from 70 to 86% for PAHs and from 68 to 110% for n-alkanes in soil and vegetation. Concentrations were not corrected for recoveries.

The following physico-chemical characteristics of samples were measured by standard methods described elsewhere (Cabrerizo et al., 2011; Cabrerizo et al., 2012): soil temperature (*Soil T*), lipid content and SOM. SOM in soils was assessed by the means of the total organic carbon (TOC) in % or the fraction of organic carbon (f_{OC}). The determination of TOC was performed by flash combustion at 1025 °C followed by thermic conductivity detection in a CHNS Elemental Analyser EA1108. The limit of detection for TOC was of 0.1%.

3. Results and discussion

3.1. Occurrence of n-alkanes in Antarctic vegetation

All the measured concentrations of individual n-alkanes are listed in Annex II SI. Extractable n-alkanes in Antarctic vegetation were dominated by odd-over-even carbon number, with high abundances of C₂₁ to C₃₅, especially for mosses and vascular plants (grass and Antarctic pearlwort), while the carbon chain length for lichens were in the range from C₁₇ to C₃₅ (Fig. 2). The short chain n-alkanes, such as C₁₇, in lichens may be derived from the photobiont (cyanobacteria or green algae) as reported in previous studies from temperate regions, where cyanobacteria extracts normally contained higher abundance of C₁₇ (Han and Calvin, 1969), while the long chain homologs may originate from the mycobionts (Torres et al., 2003). The distribution pattern is consistent with previous studies for other temperate/sub-arctic species (Bingham et al., 2010; Vonk and Gustafsson, 2009). The most abundant n-alkane was C₂₇ for lichens, C₂₉ for mosses and Antarctic pearlwort, and C₃₁ for grass. Carbon number predominance of n-alkanes are usually expressed using the CPI, which is defined as (Bray and Evans, 1961; Marzi et al., 1993),

$$CPI = \frac{(C_{23} + C_{25} + C_{27} + C_{29} + C_{31}) + (C_{25} + C_{27} + C_{29} + C_{31} + C_{33})}{2(C_{24} + C_{28} + C_{30} + C_{32})} \quad (1)$$

where C_m is the abundance of the n-alkane with m carbons. CPI values for vascular plants such as grass and Antarctic pearlwort were of 8.3 ± 0.2 (mean ± SD) and 3.6, respectively, which are typical for higher plants (Ficken et al., 2000; Bi et al., 2005). Lichens and mosses showed lower CPI values, in the range of 1.3 ± 0.6 and 2.9 ± 1.8 respectively. Previous non-Antarctic studies have shown that vegetation types

and environmental factors are the main controls of the higher plant n-alkane average chain length (ACL) defined as,

$$ACL = \frac{23C_{23} + 25C_{25} + 27C_{27} + 29C_{29} + 31C_{31} + 33C_{33}}{C_{23} + C_{25} + C_{27} + C_{29} + C_{31} + C_{33}} \quad (2)$$

where C_x is the abundance of the chain length with x carbons. (Bush and McInerney, 2013). The ACL values for our study were 28.2 ± 0.9 for lichens, 27.9 ± 0.7 for mosses, 27.7 ± 0.2 for grass and 27.3 for Antarctic pearlwort (Fig. S2.1). Although vascular plants showed the lower ACL, a Kruskal-Wallis test revealed that the ACL was not significant different ($p > 0.05$) between vegetation types. No significant correlations between ACL of the different vegetation species and latitude were found, consistent with results from non-polar lacustrine sediments (Sachse et al., 2004). Σn-alkanes' concentrations for lichens, mosses, grass and Antarctic pearlwort were 180–1180 ng gdw⁻¹, 441–3054 ng gdw⁻¹, 12023–27858 ng gdw⁻¹, and 3497 ng gdw⁻¹, respectively. The spatial distribution (Fig. S2.2) does not show a clear pattern accounting for the range of concentrations. The lipid content was in the range 1.4–14% for the different vegetation types, and its influence on n-alkanes concentration was assessed by regression analysis. Fig. 3 shows the significant dependence of low and high molecular weight n-alkanes concentrations ($r^2 = 0.28–0.53$, p -level < 0.05) on lipid content (as lipid fraction). This is the first time this dependence is described for n-alkanes, and it is consistent with the trends described for other hydrophobic compounds, such as polychlorinated biphenyls, in Antarctic vegetation (Cabrerizo et al., 2012).

3.2. Patterns and occurrence of PAHs at soils from intertidal areas

The spatial distribution of ΣPAHs concentrations at intertidal soils is shown in Fig. 4 (top panel) (complete data set and ancillary data in Tables S3.1 to S3.3, Annex III). Overall, the profile observed at the different islands (Fig. S3.1) were dominated by low to medium molecular weight PAHs (those having 4 and 3 rings), such as Flu, Pyr, ΣMP, ΣDMP and Phe, whose contribution accounted for ~60% of ΣPAHs. The ranges of soil concentrations of ΣPAHs at intertidal areas were 4–47 ng gdw⁻¹, 9–99 ng gdw⁻¹, 54 ng gdw⁻¹, and 66 ng gdw⁻¹ at Deception, Barrientos, Livingston and Penguin Islands, respectively. Previously reported PAHs concentration at soils from Deception and

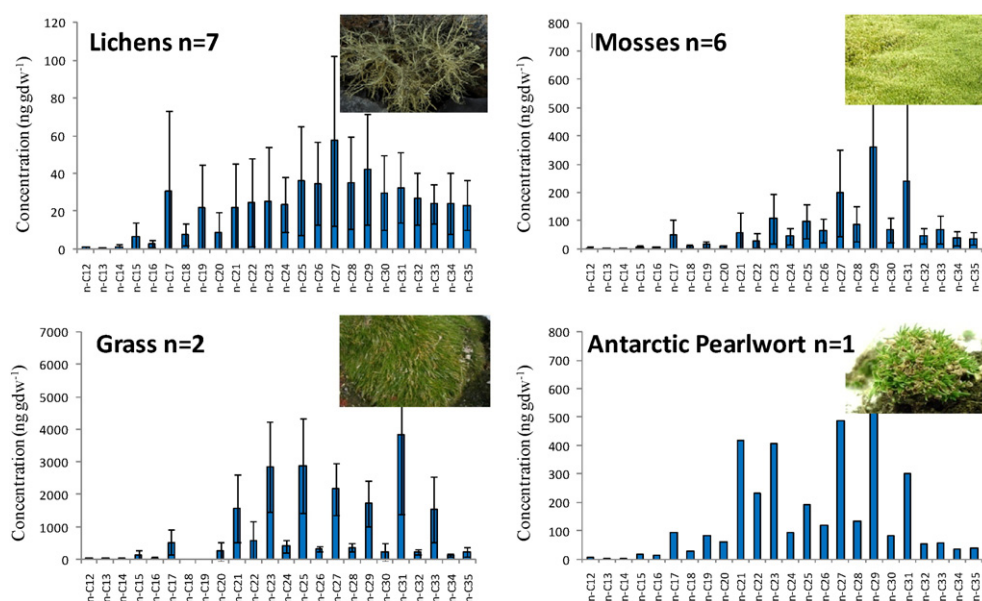


Fig. 2. n-Alkanes concentration (mean ± SD), in ng gdw⁻¹ in Antarctic vegetation.

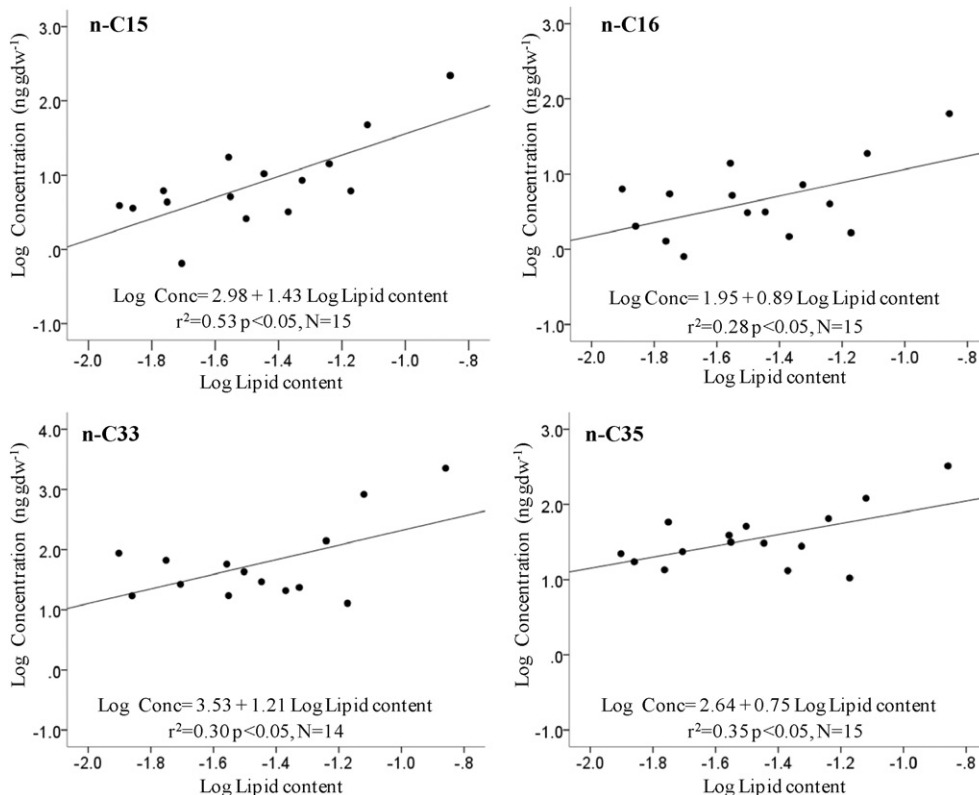


Fig. 3. Dependence of concentration (ng.gdw⁻¹) of n-C₁₅, n-C₁₆, n-C₃₃ and n-C₃₅ in vegetation versus lipid content.

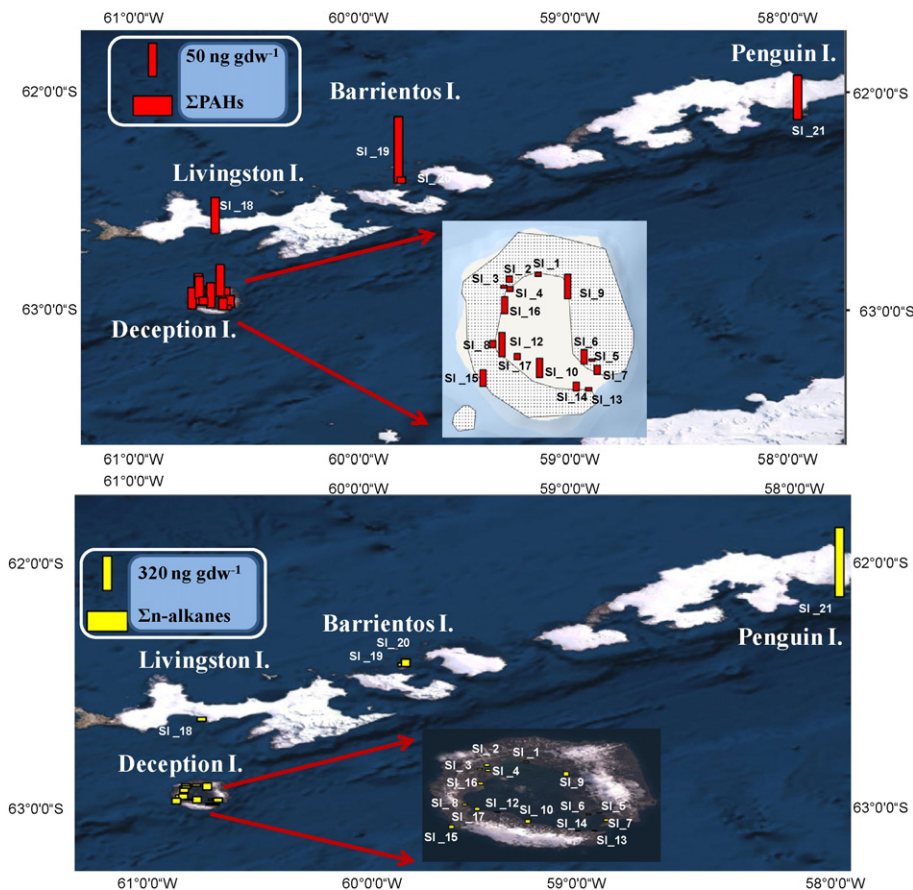


Fig. 4. Spatial distribution of soil ΣPAHs (top panel) and Σn-alkanes (bottom panel) at intertidal soils from Livingston, Deception, Barrientos and Penguin Islands.

Livingston Islands (Cabrerizo et al., 2012) were of the same range or slightly lower than those found at intertidal areas, probably related to the influence of seawater modifying the concentrations in soils. Highly contaminated areas where accidental spills have occurred, or close to research stations, have shown concentrations up to thousands of ng g dw^{-1} (Cripps, 1992; Kennicutt et al., 1992; Mazzer et al., 1999; Cabrerizo et al., 2012), while concentrations in background soils from Western Antarctica (soils and sediments) have been reported to be below detection limit (Aislabie et al., 1999). Antarctic soils are characterized by very low values of TOC (Meijer et al., 2003; Cabrerizo et al., 2012). At the intertidal areas, only 1 soil sample out of 20 showed TOC values above detection limit. The intertidal soil at Penguin Island had a TOC content of 0.33%, which is likely driven by penguin colonies feces, and where higher concentrations of PAHs were found. This is consistent with previous studies (Cabrerizo et al., 2012; Roosens et al., 2007) showing that penguin colonies enhance the soil organic carbon content and persistent organic pollutants (POPs) in Antarctic soils. Anthropogenic activities or tourism in Antarctica has apparently not contributed to increase TOC at the intertidal soils in the study area, and concentrations of Σ PAHs in the samples collected at intertidal areas close to Gabriel de Castilla and Deception research stations at Deception Island showed Σ PAHs in the range from 12 to 46 ng g dw^{-1} , which are not significantly different than the concentrations from the other intertidal soils.

3.3. Occurrence of n-alkanes in Antarctic soils

Fig. 5 shows the patterns of n-alkanes at the different islands, and the spatial distribution of Σ n-alkanes at intertidal soils and on-land soils within the Islands are shown in Fig. 4 (bottom panel) and Fig.

S3.2 respectively (data set in Tables S3.4 to S3.9). Generally, we observed a decrease of n-alkanes concentrations in soils ($p < 0.05$) at higher latitude (Fig. S3.3), while no longitudinal gradient ($p > 0.05$) was observed. Overall, C_{12} – C_{35} n-alkanes were occurring in most of the soils with a predominance of odd C number n-alkanes (n- C_{25} , n- C_{27} , n- C_{29} , and n- C_{31}), especially in the background soils not influenced by research stations. Concentrations of Σ n-alkanes ranged from 7 to 1769 ng g dw^{-1} in soils at Deception Island, 30–1300 ng g dw^{-1} at Livingston Island, 635 ng g dw^{-1} at Penguin Island, 30–746 ng g dw^{-1} at Barrientos Island, and 827 ng g dw^{-1} at Byers Peninsula. These concentrations are in the same range than those reported in soil samples (13–2200 ng g dw^{-1}) from McMurdo Dry Valleys of Southern Victoria Land (Matsumoto et al., 1990). Higher predominance of shorter n-alkanes (n- C_{15} to n- C_{25}) in comparison to high molecular weight n-alkanes were detected in soils collected within the perimeter of the Juan Carlos I research station (Fig. 5), which in fact showed the highest concentrations of Σ n-alkanes (334–3310 ng g dw^{-1}). Soils collected near the Juan Carlos I research station also showed one order of magnitude higher Σ PAHs concentrations in comparison to those collected at background areas of the Livingston Island (Cabrerizo et al., 2012). There are significant correlations (r^2 from 0.18 to 0.62, p -value < 0.05) between Σ PAHs and n-alkanes concentrations for both even (C_{18} , C_{20} , C_{24}), and odd numbered (C_{19} , C_{21}) n-alkanes for on-land soils (Fig. 6 and Fig. S3.4) and soils at intertidal areas (Fig. S3.5). These correlations explain a higher fraction of variability for even carbon n-alkanes, than for odd carbon n-alkanes. The fact that even n-alkanes are correlated with Σ PAHs, and individual PAHs (Fig. S3.6 and Fig. S3.7) suggests a common source of hydrocarbons in Antarctic soils and/or common partitioning processes.

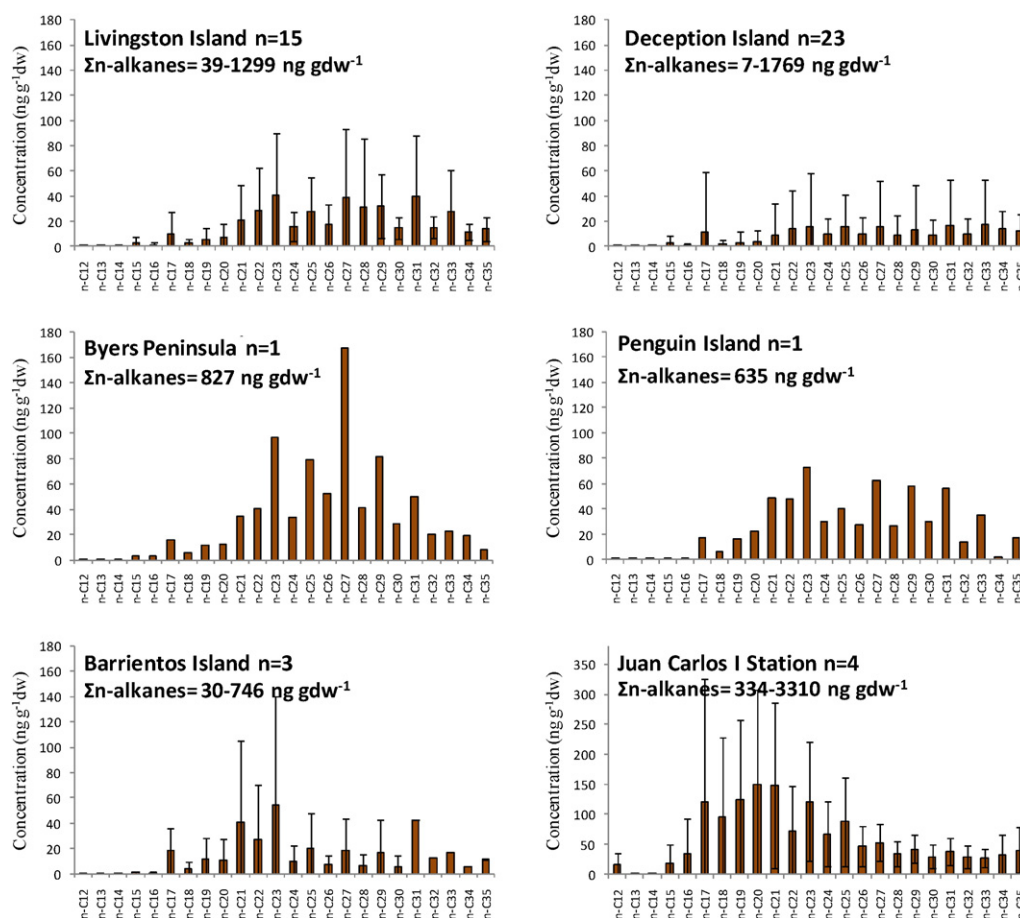


Fig. 5. n-Alkanes pattern and concentration (mean \pm SD) at soils from Livingston and Deception Islands, Byers Peninsula, Penguin and Barrientos Islands and at Juan Carlos I research station.

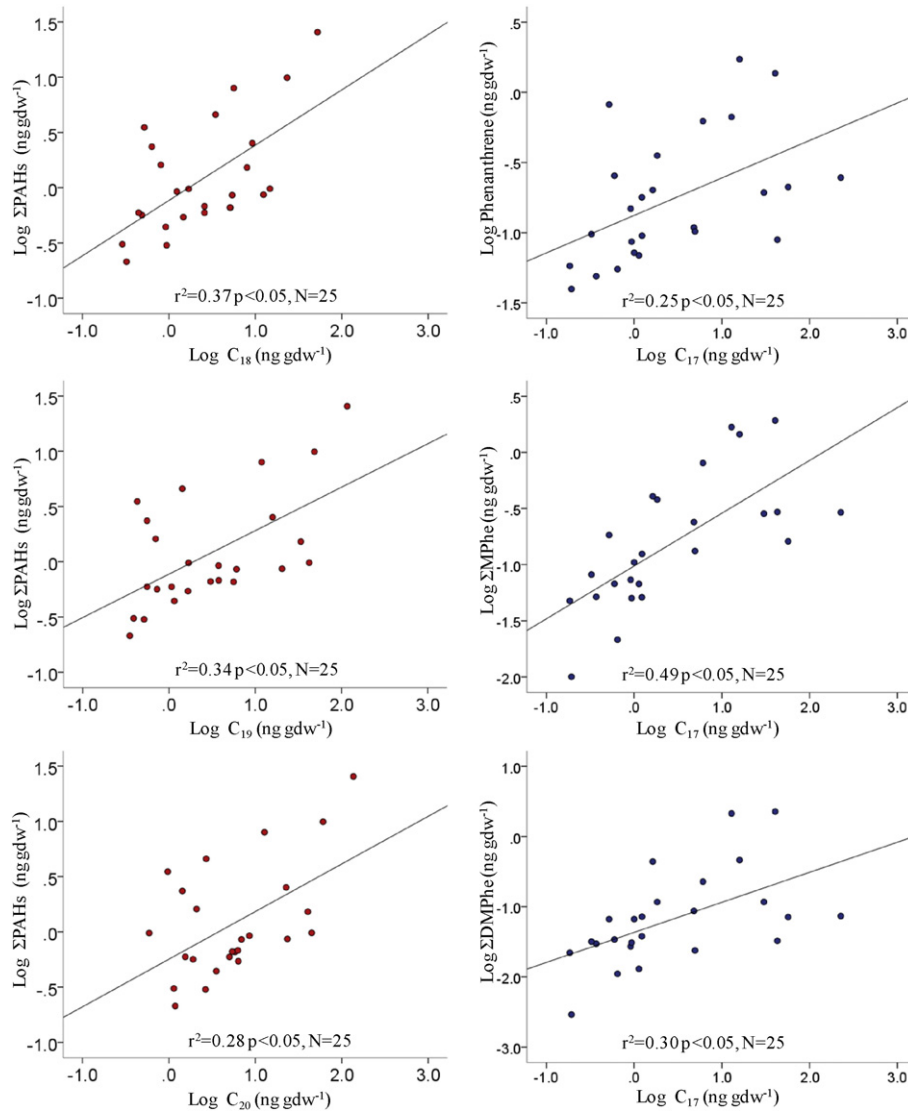


Fig. 6. Log Σ PAHs Concentration (ng gdw^{-1}) versus log even (C_{18} , C_{20}) and odd (C_{19}) n-alkanes concentrations (left panels) and Log Phen, Log Σ MPhen and Log Σ DMPhe versus log C_{17} n-alkane concentration at on-land soils.

TOC content was always below 0.1% for all soils collected at intertidal areas and on the islands, with the exception of samples with vegetation cover (0.12–0.43%), samples within the perimeter of Juan Carlos I research station (0.17%), and samples close to penguin colonies (0.33–2.6%). The influence of TOC on n-alkanes was studied by means of a least square regression. Overall, a stronger significant dependence of odd carbon n-alkanes (r^2 of 0.38–0.78, $p < 0.05$) than even carbon n-alkanes (r^2 of 0.40–0.46, $p < 0.05$) on f_{OC} was observed (Fig. 7) confirming the important role of soil organic carbon, even at low amounts, in the retention of biogenic derived n-alkanes. The larger percentage of variability that f_{OC} explains for odd carbon n-alkanes is due to the biogenic (vegetation) origin of most of these hydrocarbons. In addition, a close coupling correlation between biogenic derived n- C_{17} and phenanthrene, Σ MP and Σ DMP was found ($r^2 = 0.30$ –0.49) (Fig. 6) for soils collected within the Islands, which may evidence the potential biogenic generation of more volatile PAHs from degradation of SOM as suggested previously for temperate soils (Wilcke, 2007, Cabrerizo et al., 2011). Conversely, there were no significant correlations between n- C_{17} and Phe in soils from intertidal areas indicating a larger presence of anthropogenic sources of PAHs, in contrast with on-land soils. In order to distinguish the anthropogenic sources of PAHs, a diagnostic ratio such as Phe/Ant versus Flu/Pyr (Lima et al., 2005) was assessed

to identify petrogenic from combustion-derived sources of PAHs, but a combination of both signatures (with a potential contribution of biogenic PAHs) was observed in on-land soils and intertidal areas from the Southern Shetlands (Fig. S3.8).

The CPI value for soil samples (Eq. (1), Tables S3.4–S3.9) varied between locations and soil types. Overall, CPI values were < 1.5 for most soils collected at intertidal areas (1.3 ± 0.4) and for those soils having $TOC < 0.1\%$ (1.2 ± 0.6). CPI values of 1 have been suggested in the literature as indication of anthropogenic origin from raw hydrocarbon deposits and during combustion of fossil fuels (Simoneit and Mazurek, 1982), but also direct input of long-chain n-alkanes derived from microorganisms into soil and sediment can result in the pronounced decrease of CPI ranging from 0.54 to 1.61 with a mean value of 1.1 (Pan et al., 2012). The low CPIs for the soils affected by the Juan Carlos I research station confirms a potential anthropogenic influence on the PAHs and n-alkanes occurrence discussed above. Conversely, higher CPI values were observed for those soils collected close to penguin colonies and soils covered by vegetation (2.6 ± 0.9). CPI values in the range from 4 to 10 have been suggested as markers of higher plant residues in soils (Wakeham and Carpenter, 1976; Prah and Muehlhausen, 1989) indicating an influence of vegetative detritus. Due to the lack of higher plants in the Antarctica and the

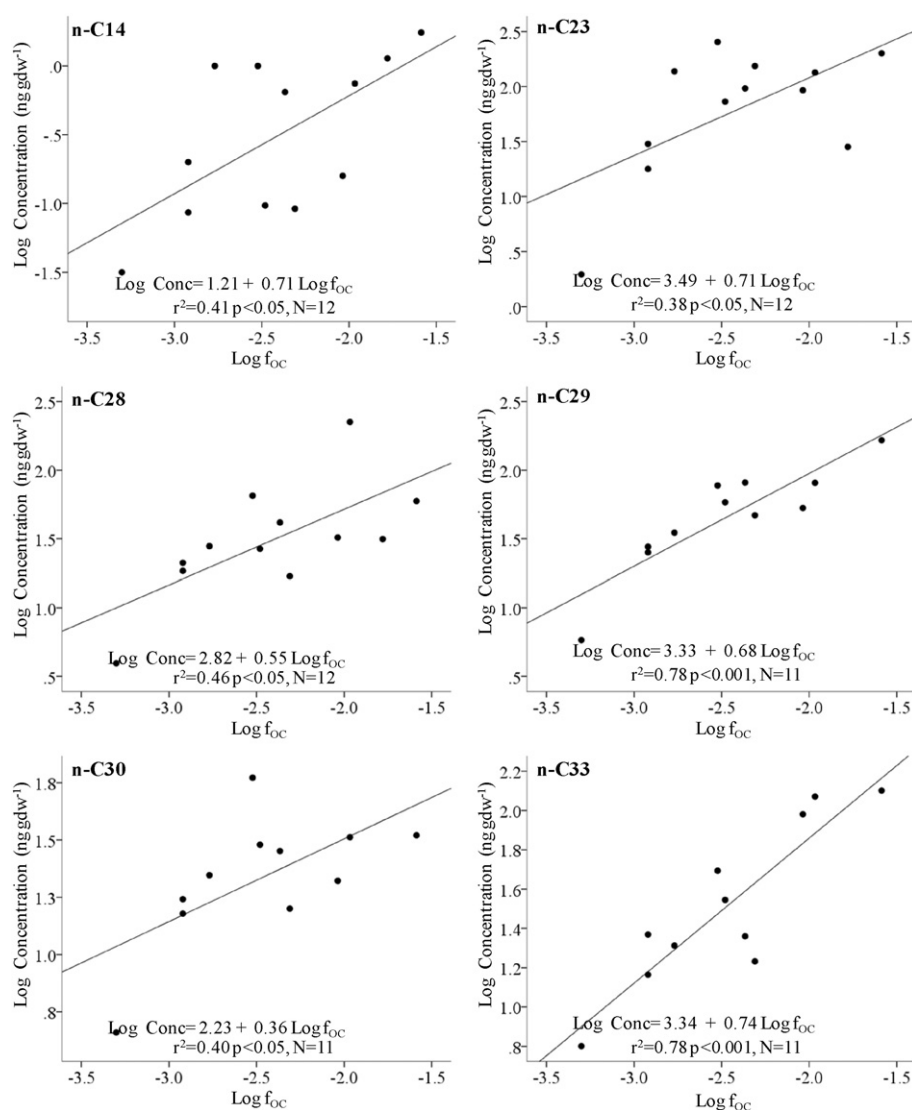


Fig. 7. Dependence of concentration (ng.gdw⁻¹) of odd (n-C₂₃, n-C₂₉, n-C₃₃) and even (n-C₁₄, n-C₂₈ and n-C₃₀) n-alkanes in soil versus the soil organic carbon fraction (f_{OC}).

fact that *CPI* values in Antarctic vegetation (see above) were always much lower than 4 for mosses, lichens and Antarctic pearlwort, with the exception of grass, it is unlikely to expect *CPI* values from 4 to 10 in Antarctic soils. However, the *CPI* > 1 observed here may reflect the influence of grass and moss derived n-alkanes on the soil *CPI* values. Atmospheric deposition could also be a source of n-alkanes with a *CPI* > 1. Indeed, *CPI* in the range from 1.4 to 3.4 were observed in aerosols in the Greenland atmosphere (Von Schneidmesser et al., 2009), showing largest values in the early summer and reaching a minimum in the early winter, corresponding to the seasonality of vegetation in the northern hemisphere and the increasing dominance of a fossil fuel alkanes during winter. However, aerosol deposition is unlikely an important source of n-alkanes for the South Shetland Islands due to the low amount of remote continental aerosols. Previous studies in the Antarctic McMurdo Dry Valleys reported *CPI* values of 1.98–2.59 in soils (Matsumoto et al., 2010), which were attributed to lichens and/or vascular debris, consistent with the results reported here. In order to study the influence of *TOC* on *CPI*, only those samples having *TOC* values above detection limit were considered for statistical analysis. Overall, a significant dependence of *CPI* on f_{OC} was observed with r² of 0.41, p < 0.05 (Fig. S3.9), which further confirms the influence of vegetation increasing the *SOM* content and *CPI* values (odd carbon n-alkanes).

The influence of environmental factors such as temperature (*T*) has been reported to influence the average chain length (Bush and McInerney, 2013). *ACL* values were 25 ± 0.8 for soils collected in intertidal areas and slightly larger, 27 ± 1 for the rest of the soils collected on the Islands. Although soil *T* was not measured in all soils due to logistical limitations, *T* was observed to influence *ACL* (r² = 0.32, p < 0.05) for the subset of samples for those *T* was measured (Fig. S3.10). This is in agreement with previous studies in warmer environments (Bush and McInerney, 2013), and can be attributed to an enhanced volatilization of the shorter chain n-alkanes (more volatile) during warm periods, and higher abundance of vegetation contributing with long chain n-alkanes at the warmer regions.

3.4. Local sources of organic pollutants from research stations and other human activities

The unresolved complex mixture of aliphatic hydrocarbons was detected as a hump (Annex IV, Fig. S4.1) in the chromatogram of the aliphatic hydrocarbon fraction from almost half of the samples collected at intertidal soil samples (8 out of 20). The *UCM* concentrations were in the range from 3.3 to 4.9 μg.gdw⁻¹. The fact that these samples showed higher concentration of *UCM* and PAHs in comparison to samples taken within Islands, and *CPI* values around unity, in the range of

0.5–1.2 for these samples, further supported the hypothesis of the presence of anthropogenic sources of hydrocarbons, such as petroleum contamination, at the soils collected at intertidal areas. Overall, a significant dependence of *UCM* on *CPI* was observed with r^2 of 0.54, $p < 0.05$ (Fig. S4.2). These hydrocarbons may have originated from anthropogenic activities occurring in coastal waters of the South Shetland Islands such as oil spill/leakage during ships operations (research vessels or tourist vessels).

For those soils collected further away from intertidal/coastal areas, at locations with penguin colonies, with vegetation cover, or proximate to the current main research buildings of Juan Carlos I research station, only 4 soils out of 25 showed the presence of a large *UCM* (25–1402 $\mu\text{g gdw}^{-1}$). These four soil samples belong to the areas sampled within the perimeter of Juan Carlos research station, which in fact showed the highest concentration of PAHs (Cabrerizo et al., 2012), and which further support the evidence that even a small settlement (20 persons during the austral summer) can affect the loading of aliphatic and aromatic hydrocarbons in nearby soils. Whether the input of anthropogenic hydrocarbons are fresh or weathered was assessed by the used of two isoprenoid alkanes; pristane and phytane. Soil samples were divided in samples collected: i) at penguin colonies, ii) at Byers Camp, iii) at abandoned old research stations visited by tourists (Deception Island), iv) samples contaminated by hydrocarbons as suggested from *UCM* and *CPI* values (samples taken at on-going research station Juan Carlos I and intertidal areas, v) at other background soils, and vi) below vegetation communities. Phytane is essentially absent in the uncontaminated recent soil/sediments. A high concentration of pristane can be derived from zooplankton and some other marine animals, which results in a higher Pr/Ph ratio (typically between 3 and 5) (Volkman et al., 1999). This is consistent with the Pr/Ph values (6–28) from the samples collected at penguin colonies (Fig. S4.3). The lowest values were detected in the soils collected at on-going Juan Carlos I research station and at soils collected at intertidal areas which showed the presence of the *UCM*, with values slightly below than 1. Pr/Ph ratios in soils influenced by the presence of lichens, grass and mosses were not significantly different from those found in bare soils from other background areas. As alicyclic Pr and Ph biodegrade more slowly when compared to the straight chain C_{17} and C_{18} , the Pr/ C_{17} and Ph/ C_{18} indices are widely used as indicators of hydrocarbon degradation (Kennicutt et al., 1987). As the easily degraded normal hydrocarbons (C_{17} and C_{18}) are lost, the more degradation resistant isoprenoids (pristane and phytane) are conserved. Fig. S4.4 showed higher values of Pr/ C_{17} and Ph/ C_{18} ratios (Pr/ $C_{17} > 1$ and Ph/ $C_{18} > 1$) at soils of Juan Carlos I and intertidal areas in comparison to soils having biogenic inputs of hydrocarbons from penguin colonies and/or vegetation, thus suggesting that despite the contamination of petroleum found in those samples, biodegradation processes are occurring in the contaminated soils of the South Shetland Islands.

4. Conclusions

The pristine and severe conditions of Antarctica, together with the lower content of organic matter in ice free areas where soil and vegetation have developed, make the study of biogenic and anthropogenic sources of hydrocarbons of great importance. The presence of biogenic over anthropogenic sources of hydrocarbons in Antarctic vegetation were shown by the predominance of odd-over-even carbon number alkanes and high abundances of $n\text{-}C_{27}$ to $n\text{-}C_{31}$ in mosses and grass, and also $n\text{-}C_{17}$ in lichens, being the lipid content an important factor controlling the load of n -alkanes in Antarctic vegetation. The presence of anthropogenic sources such as oil spills, fossil fuel combustion, etc., were mostly observed in soils within the perimeter of Juan Carlos I research station and at soils collected at intertidal areas, most likely due to research activities and ships operation (research or tourist vessels) in coastal areas close to the Islands. This was confirmed by the presence of an *UCM*, higher concentrations of PAHs, *CPI* values close to 1 and

higher ratios of Pr/ C_{17} and Ph/ C_{18} . The predominance of odd-to-even C number n -alkanes and the correlations between $n\text{-}C_{17}$ and most volatile PAHs such as Phe and Σ MP, especially in on-land soils, together with *CPI* values higher than 1, further support that biogenic derived sources of not only aliphatic, but also aromatic hydrocarbons, from vegetation waxes, *SOM* decomposition or marine algae, are not negligible in Antarctica and should be considered when assessing the overall inventory of hydrocarbons in Antarctica or elsewhere.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.06.240>.

References

- Aislabie, J., Balks, M., Astori, N., Stevenson, G., Symons, R., 1999. Polycyclic aromatic hydrocarbons in fuel-oil contaminated soils, Antarctica. *Chemosphere* 39 (13), 2201–2207.
- Bargagli, R., Battisti, E., Focardi, S., Formichi, P., 1993. Preliminary data on environmental distribution of mercury in northern Victoria Land, Antarctica. *Antarct. Sci.* 5 (01), 3–8.
- Bengtson Nash, S., 2011. Persistent organic pollutants in Antarctica: current and future research priorities. *J. Environ. Monit.* 13 (3), 497–504.
- Bi, X., Sheng, G., Liu, X., Li, C., Fu, J., 2005. Molecular and carbon and hydrogen isotopic composition of n -alkanes in plant leaf waxes. *Org. Geochem.* 36 (10), 1405–1417.
- Bicego, M.C., Zanardi-Lamardo, E., Taniguchi, S., Martins, C.C., da Silva, D.A.M., Sasaki, S.T., et al., 2009. Results from a 15-year study on hydrocarbon concentrations in water and sediment from Admiralty Bay, King George Island, Antarctica. *Antarct. Sci.* 21 (03), 209–220.
- Bingham, E.M., McClymont, E.L., Valiranta, M., Mauquoy, D., Roberts, Z., Chambers, F.M., et al., 2010. Conservative composition of n -alkane biomarkers in Sphagnum species: implications for palaeoclimate reconstruction in ombrotrophic peat bogs. *Org. Geochem.* 41, 214–220.
- Bray, E.E., Evans, E.D., 1961. Distribution of n -paraffins as a clue to recognition of source beds. *Geochim. Cosmochim. Acta* 22, 2–15.
- Bush, R.T., McInerney, F.A., 2013. Leaf wax n -alkane distributions in and across modern plants: implications for paleoecology and chemotaxonomy. *Geochim. Cosmochim. Acta* 117, 161–179.
- Cabrerizo, A., Dachs, J., Barceló, D., 2009. Development of a soil fugacity sampler for determination of air–soil partitioning of persistent organic pollutants under field controlled conditions. *Environ. Sci. Technol.* 43 (21), 8257–8263.
- Cabrerizo, A., Dachs, J., Moeckel, C., Ojeda, M.-J., Caballero, G., Barceló, D., Jones, K.C., 2011. Ubiquitous net volatilization of polycyclic aromatic hydrocarbons from soils and parameters influencing their soil–air partitioning. *Environ. Sci. Technol.* 45 (11), 4740–4747.
- Cabrerizo, A., Dachs, J., Barceló, D., Jones, K.C., 2012. Influence of organic matter content and human activities on the occurrence of organic pollutants in antarctic soils, lichens, grass, and mosses. *Environ. Sci. Technol.* 46 (3), 1396–1405.
- Cabrerizo, A., Dachs, J., Barceló, D., Jones, K.C., 2013. Climatic and biogeochemical controls on the remobilization and reservoirs of persistent organic pollutants in Antarctica. *Environ. Sci. Technol.* 47 (9), 4299–4306.
- Cabrerizo, A., Galbán-Malagón, C., Del Vento, S., Dachs, J., 2014. Sources and fate of polycyclic aromatic hydrocarbons in the Antarctic and Southern Ocean atmosphere. *Glob. Biogeochem. Cycles* 28, 1424–1436.
- Consultative Parties to the Antarctic Treaty, 1991. *The Protocol on Environmental Protection to the Antarctic Treaty*.
- Corsolini, S., Covaci, A., Ademollo, N., Focardi, S., Schepens, P., 2006. Occurrence of organochlorine pesticides (OCPs) and their enantiomeric signatures, and concentrations of polychlorinated diphenyl ethers (PBDEs) in the Adélie penguin food web, Antarctica. *Environ. Pollut.* 140 (2), 371–382.
- Cripps, G.C., 1992. The extent of hydrocarbon contamination in the marine environment from a research station in the Antarctic. *Mar. Pollut. Bull.* 25, 288–292.
- Dachs, J., Bayona, J.M., Fillaux, J., Saliot, A., Albaigés, J., 1999. Evaluation of anthropogenic and biogenic inputs into the western Mediterranean using molecular markers. *Mar. Chem.* 65, 195–210.

- Ficken, K.J., Li, B., Swain, D.L., Eglinton, G., 2000. An n-alkane proxy for the sedimentary input of submerged/floating freshwater aquatic macrophytes. *Org. Geochem.* 31, 745–749.
- Galbán-Malagón, C., Cabrerizo, A., Caballero, G., Dachs, J., 2013a. Atmospheric occurrence and deposition of hexachlorobenzene and hexachlorocyclohexanes in the Southern Ocean and Antarctic peninsula. *Atmos. Environ.* 80, 41–49.
- Galbán-Malagón, C., Del Vento, S., Cabrerizo, A., Dachs, J., 2013b. Factors affecting the atmospheric occurrence and deposition of polychlorinated biphenyls in the Southern Ocean. *Atmos. Chem. Phys.* 11, 12799–12811.
- Green, G., Nichols, P.D., 1995. Hydrocarbons and sterols in marine sediments and soils at Davis Station, Antarctica: a survey for human-derived contaminants. *Antarct. Sci.* 7, 137–144.
- Guerra, M.B.B., Neto, E.L., Prianti, M.T.A., Pereira-Filho, E.R., Schaefer, C.E.G.R., 2013. Post-fire study of the Brazilian Scientific Antarctic Station: toxic element contamination and potential mobility on the surrounding environment. *Microchem. J.* 110, 21–27.
- Han, J., Calvin, M., 1969. Hydrocarbon distribution of algae and bacteria, and microbiological activity in sediments. *Proc. Natl. Acad. Sci. U. S. A.* 64 (2), 436–443.
- Hopkins, D.W., Sparrow, A.D., Elberling, B., Gregorich, E.G., Novis, P.M., Greenfield, L.G., Tilston, E.L., 2006. Carbon, nitrogen and temperature controls on microbial activity in soils from an Antarctic dry valley. *Soil Biol. Biochem.* 38 (10), 3130–3140.
- Izarta, A., Palholb, F., Gleixner, G., Elied, M., Blaisea, T., Suarez-Ruize, I., Sachsenhofer, R.F., Privalov, V.A., Panova, E.A., 2012. Palaeoclimate reconstruction from biomarker geochemistry and stable isotopes of n-alkanes from carboniferous and early Permian humic coals and limnic sediments in western and eastern Europe. *Org. Geochem.* 43, 25–149.
- Kallenborn, R., Christensen, G., Evensen, A., Schlabach, M., Stohl, A., 2007. Atmospheric transport of persistent organic pollutants (POPs) to Bjornoya (Bear island). *J. Environ. Monit.* 9 (10), 1082–1091.
- Kennicutt II, M.C., Barker, C., Brooks, J.M., DeFreitas, D.A., Zhu, G.H., 1987. Selected organic matter source indicators in the Orinoco, Nile and Changjiang deltas. *Org. Geochem.* 11, 41–51.
- Kennicutt II, M.C., McDonald, T.J., Denoux, G.J., McDonald, S.J., 1992. Hydrocarbon contamination on the Antarctic Peninsula II. Arthur Harbor inter and subtidal limpets (*Nacella concinna*). *Mar. Pollut. Bull.* 24, 506–511.
- Lima, A.C., Farrington, J.W., Reddy, C.M., 2005. Combustion-derived polycyclic aromatic hydrocarbons in the environment—a review. *Environ. Foren.* 6:2, 109–131. <http://dx.doi.org/10.1080/15275920590952739>.
- Marzi, R., Torkelson, B.E., Olson, R.K., 1993. A revised carbon preference index. *Org. Geochem.* 20, 1303–1306. [http://dx.doi.org/10.1016/0146-6380\(93\)90016-5](http://dx.doi.org/10.1016/0146-6380(93)90016-5).
- Matsumoto, G.I., Akiyama, M., Watanuki, K., Torii, T., 1990. Unusual distributions of long-chain n-alkanes and n-alkenes in Antarctic soil. *Org. Geochem.* 15, 403–412.
- Matsumoto, G.I., Honda, E., Sonoda, K., Yamamoto, S., Takemura, T., 2010. Geochemical features and sources of hydrocarbons and fatty acids in soils from the McMurdo dry valleys in the Antarctic. *J. Polym. Sci.* 4, 187–196.
- Mazzera, D., Hayes, T., Lowenthal, D., Zielinska, B., 1999. Quantification of polycyclic hydrocarbons in soil at McMurdo Station, Antarctica. *Sci. Total Environ.* 229, 65–71.
- Meijer, S.N., Ockenden, W.A., Sweetman, A., Breivik, K., Grimalt, J.O., Jones, K.C., 2003. Global distribution and budget of PCBs and HCB in background surface soils: implications for sources and environmental processes. *Environ. Sci. Technol.* 37 (4), 667–672.
- Montone, R.C., Taniguchi, S., Weber, R.R., 2003. PCBs in the atmosphere of King George Island, Antarctica. *Sci. Total Environ.* 308 (1–3), 167–173.
- Okere, U., Cabrerizo, A., Dachs, J., Jones, K.C., Semple, K., 2012. Biodegradation of phenanthrene by indigenous microorganisms in soils from Livingston Island, Antarctica. *FEMS Microbiol. Lett.* 329 (1), 69–77.
- Pan, L., PingAn, P., HouYuan, L., Zhuo, Z., Xu, W., 2012. Latitudinal variations of CPI values of long-chain n-alkanes in surface soils: evidence for CPI as a proxy of aridity. *Sci. China Earth Sci.* 55, 1134–1146.
- Prahl, F.G., Muehlhausen, L.A., 1989. Lipid biomarkers as geochemical tools for paleogeographic study. In: Berger, W.H., Smetacek, V.S., Wefer, G. (Eds.), *Productivity of Oceans: Present and Past*. Wiley, New York, pp. 271–289.
- Prus, W., Fabiańska, M.J., Labno, R., 2015. Geochemical markers of soil anthropogenic contaminants in polar scientific stations nearby (Antarctica, King George Island). *Sci. Total Environ.* 518–519, 266–279.
- Roosens, L., Van Den Brink, N., Riddle, N.M., Blust, R., Neels, H., Covaci, A., 2007. Penguin colonies as secondary sources of contamination with persistent organic pollutants. *J. Environ. Monit.* 9, 822–825.
- Sachse, D., Radke, J., Gleixner, G., 2004. Hydrogen isotope ratios of recent lacustrine sedimentary n-alkanes record modern climate variability. *Geochim. Cosmochim. Acta* 68, 4877–4889.
- Sanchís, J., Cabrerizo, A., Galbán-Malagón, C., Barceló, D., Farre, M., Dachs, J., 2015. Unexpected occurrence of volatile dimethylsiloxanes in Antarctic soils, vegetation, phytoplankton and krill. *Environ. Sci. Technol.* 49, 4415–4424.
- Simoneit, B.R.T., Mazurek, M.A., 1982. Organic matter of troposphere-II. Natural background of biogenic lipid matter in aerosol over the rural western United States. *Atmos. Environ.* 16, 2139–2159.
- Tin, T., Fleming, Z.L., Hughes, K.A., Ainley, D.G., Convey, P., Moreno, C.A., et al., 2008. Impacts of local human activities on the Antarctic environment. *Antarct. Sci.* 21 (01), 3–33.
- Torres, A., Dor, I., Rotem, J., Srebnik, M., Dembitsky, V.M., 2003. Characterization of surface n-alkanes and fatty acids of the epiphytic lichen *Xanthoria parietina*, its photobiont a green alga *Trebouxia* sp., and its mycobiont, from the Jerusalem hills. *J. Biochem. Eur. J. Biochem.* 270 (10), 2120–2125.
- UNEP (United Nations Environment Programme Chemicals), 2002. Regionally Based Assessment of Persistent Toxic Substances. Antarctic Regional Report. Global Environment Facility, Geneva.
- USEPA (United States Environmental Protection Agency), 1985. Evaluation and estimation of potential carcinogenic risks of polynuclear aromatic hydrocarbons: carcinogen assessment group. Office of Health and Environmental Assessment, Washington DC.
- Volkman, J.K., Holdsworth, D.G., Neill, G.P., Bavor, H.J., 1999. Identification of natural, anthropogenic and petroleum hydrocarbons in aquatic sediments. *Sci. Total Environ.* 112, 203–219.
- Von Schneidemesser, E., Schauer, J.J., Hagler, G.S.W., Bergin, M.H., 2009. Concentrations and sources of carbonaceous aerosol in the atmosphere of Summit, Greenland. *Atmos. Environ.* 43, 4155–4162.
- Vonk, J.E., Gustafsson, O., 2009. Calibrating n-alkane sphagnum proxies in sub-arctic Scandinavia. *Org. Geochem.* 40 (10), 1085–1090.
- Wakeham, S.G., Carpenter, R., 1976. Aliphatic hydrocarbons in sediments of Lake Washington. *Limnol. Oceanogr.* 21, 711–723.
- Wilcke, W., 2007. Global patterns of polycyclic aromatic hydrocarbons in soils. *Geoderma* 141, 157–166.
- Woolfenden, E.N.M., Hince, G., Powell, S.M., Stark, S.C., Snape, I., Stark, J.S., George, S.C., 2011. The rate of removal and the compositional changes of diesel in Antarctic marine sediment. *Sci. Total Environ.* 410–411, 205–216.