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Distribution and bioconcentration of semivolatile organic compounds (SVOCs) in soils and vascular plant *Colobanthus quitensis* from Sub-Antarctic and Antarctic regions

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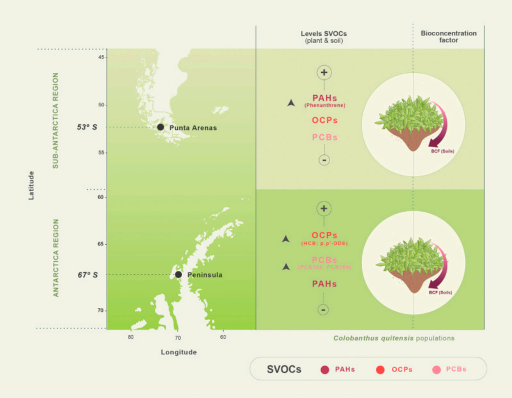
HIGLIGHTS

- Distinct contamination patterns observed between Punta Arenas and Peninsula in plants and soils.
- Most of the studied compounds showed BCF_{Soil} values close to 1.
- Bioconcentrations factors for estimated compounds showed negative correlation with $LogK_{OW}$.
- PAH sources show pyrogenic origin in Punta Arenas while petrogenic and pyrogenic are shown the Antarctic Peninsula.

GRAPHICAL ABSTRACT



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ABSTRACT

Semi-volatile organic compounds (SVOCs) are widely distributed across the globe, including polar regions. This study investigates the distribution and bioconcentration of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) in soils and *Colobanthus quitensis*, while also estimating potential emission sources. Results indicated high concentrations of PAHs in soils and plants from the

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Persistent organic pollutants (POPs) semi-volatile organic compounds (SVOCs)
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Bioconcentration

Sub-Antarctic region, while OCPs and PCBs were more prevalent in the Antarctic region, with higher contaminant concentrations found in soils than in plant tissues. Hexachlorobenzene (HCB) and dichlorodiphenyldichloroethylene (p,p′-DDE) were significantly higher in the Antarctic region, suggesting historical dichlorodiphenyltrichloroethane (DDT) use, while PCB 153 and 180 were the most representative PCBs in the Antarctic region. Phenanthrene (Phe) was the dominant PAH in both regions. The bioconcentration factor analysis from soils (BCF_{Soils}) revealed potential anthropogenic influences for certain contaminants, including γ-hexachlorocyclohexane (γ-HCH) and PCB 9 in the Sub-Antarctic region, and HCB, p,p′-DDE, PCB 9, and benzonaphtho-thiophene in the Antarctic region. However, compounds with higher hydrophobicity showed lower Bioconcentration factor (BCF_{Soils}) values, indicating a tendency to accumulate in soil rather than plant tissues. This was consistent with the inverse relationship found between BCF_{Soils} and the octanol-water partition coefficient (Log K_{OW}). Diagnostic ratios of PAHs revealed a predominantly pyrogenic source in the Sub-Antarctic region, while a mixture of sources was observed in the Antarctic region.

1. Introduction

Persistent Organic Pollutants (POPs) and polycyclic aromatic hydrocarbons (PAHs) are semi-volatile organic compounds (SVOCs) characterized by their high persistence and resistance to chemical, biological, and photolytic degradation (UNEP, 2019). These compounds tend to bioaccumulate and biomagnify through polar food webs and exhibit toxic effects on wildlife; furthermore, they are subject to long-range transport (Göktaş and MacLeod, 2016; Lohmann et al., 2007; Galbán-Malagón et al., 2023); with polar areas serving as their final sinks (Kallenborn et al., 2015; Wang et al., 2019; Mangano et al., 2017). Currently, chemical pollution is part of the current planetary crisis (UNEP, 2021); SVOCs in Antarctica are a significant research topic and concern for polar science and public policy programs (Bengtson-Nash et al., 2023) due to their persistence over years, the accumulation of new organic compounds in the region, and their bioaccumulation in the trophic chain (Luarte et al., 2023; Xiong et al., 2021; Hao et al., 2019).

The total SVOCs burden in polar and subpolar regions comes from (i) primary sources linked to regional emissions subject to long-range atmospheric transport (LRAT), (ii) local anthropogenic activities (such as research stations, scientific activities, and tourism) mainly during the summer season, and (iii) secondary sources, where "old" organic pollutants are re-emitted from soils and oceans (Cabrerizo et al., 2013, 2014; Luarte et al., 2024). In Antarctica, the presence of SVOCs is primarily attributed to LRAT from Southern Hemisphere continents (Pozo et al., 2017; Cabrerizo et al., 2013; Bengtson-Nash, 2011; Galbán-Malagón et al., 2013a, 2013b, 2023).

The transport of semi-volatile compounds to colder regions is primarily driven by a cold condensation effect, where low temperatures prolong their persistence (Gouin et al., 2004; Wania and Mackay, 1993, 1995). Due to their physical-chemical properties, these compounds tend to accumulate in surface environments of Antarctica, such as surface waters, soil, ice/snow, and surface tissues, which can act as sinks or even secondary sources (Cabrerizo et al., 2013; Galbán-Malagón et al., 2013a). Their lipophilic and hydrophobic nature further facilitates their incorporation into plant and animal tissues (Bhardwaj et al., 2018; Bates et al., 2017).

Furthermore, the physicochemical behavior of these pollutants is temperature-dependent, meaning that rising temperatures driven by climate change may enhance their remobilization in polar ecosystems. This, in turn, can alter the fate of these contaminants, influencing their environmental concentrations and trends (Hung et al., 2022; Ma et al., 2011, 2016).

Soils, particularly in cold regions, are significant sinks for POPs and SVOCs (Meijer et al., 2003). Historical analyses indicate a declining trend in soil concentrations over time, reflecting an aging burden (Na et al., 2020). In contrast to other areas, Antarctic soils are less influenced by atmospheric gas-phase concentrations and may act as sources of these compounds back into the environment (Cabrerizo et al., 2012, 2013, 2014). Notably, Na et al. (2020) reported that pollutant levels on King George Island in the Antarctic Peninsula are largely attributed to local sources rather than long-range atmospheric transport, potentially due to the effectiveness of international emission reduction agreements.

Soils form the foundation for vegetation development; therefore, understanding how plants are capable of accumulating compounds is crucial for gaining insights into the environmental fate of these substances. The ratio between the soil and plants has been demonstrated as an adequate tool to evaluate the extent of anthropogenic impact of contaminants in terrestrial Antarctica (Lu et al., 2012). In this context, using Plant Bioconcentration Factors from soils (BCF_{Soils}) can serve as an effective tool for studying the accumulation of hydrophobic organic compounds in plants. It also provides a valuable reference index for assessing accumulation levels. However, the rate of accumulation is influenced by several soil characteristics (such as texture, composition, water content, and organic matter content) and plant traits (including lipid content, water content, and species). Despite these variables, BCF_{Soils} remains a useful index (Li et al., 2019). The enrichment of these SVOCs can be explained based on their physical-chemical properties (e.g., partition coefficient), the organic matter content of the soil and plant characteristics (e.g., lipid content), which determines the degree of accumulation in the substrate and their absorption, diffusion, translocation, and uptake in plant tissue (Li et al., 2017). Additionally, possible sources in soils can be identified using PAH diagnostic ratios. Further, compounds that undergo LRAT are subject of photodegradation, but studies conducted in soils demonstrated that in soils the use of these ratios is a good approach to confirm the mechanism of transport and possible influence of particular emissions since some of them are quite stable to degradation compared to air compartment (Tobiszewski and Namieśnik, 2012). For instance, the sources of PAHs have been evaluated in soils from Punta Arenas at 53°S in the Sub-Antarctic region (Apiratikul et al., 2021; Deelaman et al., 2020) and on King George Island at 62°S in Maritime Antarctica (Deelaman et al., 2020; Pongpiachan et al., 2017). However, to date no study has addressed the characterization and potential sources of SVOCs in soils and plants in Antarctica. Identifying the sources of SVOCs emissions is essential to understand the distribution and fate of pollutants since they can have negative effects on local flora and fauna, altering food chains and the biodiversity of Antarctica.

Antarctic plants, *Deschampsia antarctica* and *Colobanthus quitensis*, are the only two native Antarctic vascular plant species adapted to adverse climatic conditions, exposed to different levels of SVOCs in their tissues (Cipro et al., 2011; Cabrerizo et al., 2012). However, there is no related information on SVOCs in soils or populations of vascular plants that would allow for a spatial comparison of the accumulation of SVOCs and their potential emission sources. There is a lack of information about accumulation of SVOCs in soils and associated vegetation from the Antarctic and Subantarctic areas. Thus, the objectives of the present study are: i) determine the levels of SVOCs present in soils and plant tissues of *C. quitensis* populations in two sites with contrasting latitudes; ii) evaluate bioconcentration of SVOCs in *C. quitensis* populations through enrichment factor estimation, and iii) identify potential sources of SVOCs emissions in soils and *C. quitensis* plants, to evaluate the potential impacts of contaminants.

2. Materials and methods

2.1. Sample collection and sample preparation

Samples were collected during the summer Antarctic Scientific Expedition (January to March 2022) of the Instituto Antártico Chileno, as part of the POLARIX project (ACT192057). Soils and individuals of *C. quitensis* (Kunth) Barttl. (Caryophyllaceae) were collected from two different sites distanced by 1500 km: Punta Arenas in Sub-Antarctic region (53°S 70°W) and Lagotellerie Island in the Antarctic Peninsula (67°S 67°W). These *C. quitensis* populations will be referred hereinafter to as Punta Arenas and Peninsula, respectively. Sampling of *C. quitensis* plants was carried out ($n = 5$) for each individual cushion with complete leaf structure (in the development stage) during the growing season from December to February. Along with the sampling of plant tissue, soil samples (n = 5) were collected between 1 and 5 cm deep from the plant surface. Soil and plant samples were stored in zip-sealed plastic bags in the freezer (−20 °C) and transported to the laboratory (GEMA, Universidad Mayor) until their analysis. Prior to the extraction, plant samples were gently washed to remove adhered soil, lyophilized and dry frozen with liquid nitrogen, while soil samples were lyophilized and sieved to remove coarse elements. For both samples, the dry weight of the pulverized material was recorded. The plant tissues and soil samples were mixed with 5 g of anhydrous sodium sulfate (previously washed with acetone:hexane by Soxlet extraction) in accordance with Cabrerizo et al. (2012). Samples ($n = 20$) were stored in glass vials at −20 °C for chemical extraction at the RECETOX Laboratory (Masaryk University).

2.2. Chemical extraction of SVOCs

A subsample of 5 g of soil or plant tissue samples were weighed into Whatman cellulose extraction thimbles, previously cleaned twice in dichloromethane (DCM). Before extraction, samples were spiked with isotopically labeled surrogate PCB (13C12: PCB28, PCB52, PCB101, PCB138, PCB153 and PCB180) and OCP standards (13C6: γ-HCH, PeCB, HCB, 13C12: p,p′-DDT, p,p′-DDD, p,p′-DDE, Cambridge Isotope Laboratories, MA, USA), as well as PAHs (phenanthrene-D10, perylene-D12, Sigma-Aldrich, MA, USA). Subsequently, soil and plant tissue samples were soxhlet-extracted in 150 mL of DCM in a Büchi system (B-811 automatic extractor, Switzerland) with the program set to hot solvent extraction for 40 min and washing with solvent condensate for 20 min. Extracts were concentrated under a stream of nitrogen to around 10 mL using a LabEva concentrator and then divided into fractions (10 % for PAHs analysis and 90 % for PCBs and OCPs analysis) by weighing.

PCB and OCP fractions (90 %) were cleaned using a destructive acidic-silica gel glass column, containing 1 g of activated silicagel, 8 g of 44 % H_2SO_4 silicagel, 1 g of deactivated silicagel, and 1 cm of anhydrous Na_2SO_4, eluted with 40 mL of hexane/dichloromethane 1:1. Samples were concentrated to 1 mL using SuperVap (FMS, MA, USA) and transferred to 1,5 mL minivials, 50 μL of nonane were added as keeper solvent and samples were concentrated in LabEva to final volume of 50 μL. Before instrumental analysis, samples were spiked with 13C12-PCB95 syringe standard (CIL, MA, USA) for determination of % recoveries of surrogate standards (see Table S1). PAHs fraction (10 %) was cleaned using non-destructive silica gel glass column, containing 5 g of activated silica gel and 1 cm of anhydrous Na_2SO_4, eluted with 10 mL of hexane and 20 mL of dichloromethane. Samples were concentrated to 1 mL using SuperVap (FMS, MA, USA) and transferred to 1,5 mL minivials, 50 μL of nonane was added as a keeper solvent and samples were concentrated under gentle stream of nitrogen in LabEva to final volume of 50 μL. Before instrumental analysis, samples were spiked with *p*-terphenyl (Wellington, MA, USA) syringe standard.

2.3. OCPs, PCBs, and PAHs identification and quantification

The target compounds for identification and quantification included Polychlorinated Biphenyl (PCB) congeners — specifically PCB 9, PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, and PCB 180. Organochlorine Pesticides (OCPs) were also analyzed, such as Hexachlorobenzene (HCB), Pentachlorobenzene (PeCB), and various isomers of Hexachlorocyclohexane: α-Hexachlorocyclohexane (α-HCH), β-Hexachlorocyclohexane (β-HCH), γ-Hexachlorocyclohexane (γ-HCH), δ-Hexachlorocyclohexane (δ-HCH), and ε-Hexachlorocyclohexane (ε-HCH). Additionally, dichlorodiphenyltrichloroethane (DDT) and its metabolites were included, such as o,p′-DDT, p,p′-DDT, o,p′-Dichlorodiphenyldichloroethylene (o,p′-DDE), p,p′-Dichlorodiphenyldichloroethylene (p,p′-DDE), o,p′-Dichlorodiphenyldichloroethane (o,p′-DDD), and p,p′-Dichlorodiphenyldichloroethane (p,p′-DDD). For Polycyclic Aromatic Hydrocarbons (PAHs), the target compounds included Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Fluo), and Pyrene (Pyr). Higher molecular weight PAHs included Benzo(*a*)anthracene (BaA), Chrysene (Chr), Benzo(*b*) fluoranthene (BbF), Benzo(*k*)fluoranthene (BkF), and Benzo(*a*)pyrene (BaP). Additional complex PAHs assessed were Indeno(1,2,3-c,d)pyrene (IcdP), Dibenzo(*a*,*h*)anthracene (DahA), and Benzo(*g*,*h*,*i*)perylene (BghiP). Other notable compounds included Biphenyl (Bip), Retene (Ret), Benzo(*b*)fluorene (BbFl), Benzo-naphtho-thiophene (BNT), and Benzo(*g*,*h*,*i*)fluoranthene (BghiFl). Furthermore, Cyclopenta(*c*,*d*)pyrene (CPcdP), Triphenylene (Tri), Benzo(*j*)fluoranthene (BjF), Benzo(*e*)pyrene (BeP), Perylene (Per), Dibenzo(*ac*)anthracene (DBacA), Anthanthrene (AntA), and Coronene (Cor) were included to provide a comprehensive assessment of PAH contamination.

PCBs, OCPs, and PAHs were analyzed on 8890 GC (Agilent, USA) equipped with a 60 m × 0.25 mm × 0.25 μm Rxi-5Sil-MS column (Restek, FR) coupled to a triple quadrupole 7000D MS (Agilent, USA). In the case of OCPs and PCBs the instrumental conditions were following: The GC temperature program was 80 °C (1.5 min hold), then 40 °C min^{-1} to 200 °C (18 min hold), and finally 5 °C min^{-1} to 305 °C. Inlet temperature was 280 °C. Injection volume was 3 μl in pulsed-splitless mode. Temperature of the transfer line was 310 °C and 250 °C of the ion source. For PAHs the conditions were slightly different. The temperature program for GC oven started at 80 °C (2 min hold), then continued with 15 °C min^{-1} to 180 °C (no hold) and lastly 5 °C min^{-1} to 310 °C (20 min hold). The inlet temperature was 280 °C. Injection volume was 1 μl in pulsed-splitless mode. The carrier gas was helium with a flow rate of 1.5 mL min^{-1}. The temperature of the GC–MS transfer line was 310 °C. Ion source was heated to 320 °C. In both cases the carrier gas was helium with a flow rate of 1.5 mL min^{-1}. For OCPs and PCBs, mass spectrometer was operating in multiple reaction monitoring (MRM) mode with nitrogen as collision gas with flow rate of 1.5 mL min^{-1}. In the case of PAHs, mass spectrometer was operating in selected ion monitoring (SIM) mode. All the compounds were quantified with MassHunter Workstation 10.1 software.

2.4. Quality assurance/quality control (QA/QC) of analytical process

PCBs and OCPs were quantified using the isotopic dilution method, with an external eight-point linear calibration curve. The native compound concentrations ranged from 1 ng mL^{-1} to 1000 ng mL^{-1}, and isotopically labeled compounds were present at a concentration of 10 ng mL^{-1} across all calibration levels. Limits of detection (LOD) and limits of quantification (LOQ) were calculated from the lowest calibration point, defined as the amount producing a signal-to-noise ratio of 3 (LOD) and 10 (LOQ) (see Table S2). PCBs and OCPs concentrations in the samples were recovery-corrected using ^{13}C-labeled surrogate compounds. PAHs were quantified using an eight-point linear calibration curve, with native and deuterated compound concentrations ranging from 1 ng mL^{-1} to 1000 ng mL^{-1}, and *p*-terphenyl at a concentration of 200 ng mL^{-1} across all calibration levels. Limits of detection (LOD) and limits of quantification (LOQ) were calculated from the lowest calibration point, defined as the amount producing a signal-to-noise ratio of 3 (LOD) and 10 (LOQ) (see Table S2).

2.5. Bioconcentrations capacity of plants

We evaluated the bioconcentration capacity of *C. quitensis* by estimating the Bioconcentration factor from soils (hereinafter $\text{BCF}_{\text{Soils}}$) as follows:

$$BCF_{Soils} = \frac{C_{Plants}}{C_{Soils}}$$

where the C_{plants} is the concentration of each individual compound in *C. quitensis* (ng g^{-1} or pg g^{-1}) and C_{soils} is the concentration of each individual compound in soil (ng g^{-1} or pg g^{-1}) for both sites and different chemical species. The values were calculated using the concentration data described in Tables S5 and S6.

2.6. PAHs diagnostic ratio determination

To identify potential pollution sources of PAHs in soils and plants from Punta Arenas and the Peninsula, molecular diagnostic ratios were used. These ratios distinguish PAH pollution originating from petroleum products, petroleum combustion, and biomass or coal burning, such as $\sum$LMW/$\sum$HMW, $\sum$COMB/$\sum$PAHs, Ant/(Phe + Ant), Flu/(Pyr + Flu), and BaA/(BaA + Chr) (see Table S9). Where, LMW: Compounds with molecular weight < 178 g mol^{-1}; HMW: compounds with molecular weight > 178 g mol^{-1}; COMB: Combustion characteristic PAHs; Ant, Phe, Flu, Pyr, BaA, and Chr. Diagnostic ratios were calculated using the concentration data described in Tables S5 and S6, and the reference values reported in Tables S8 and S9.

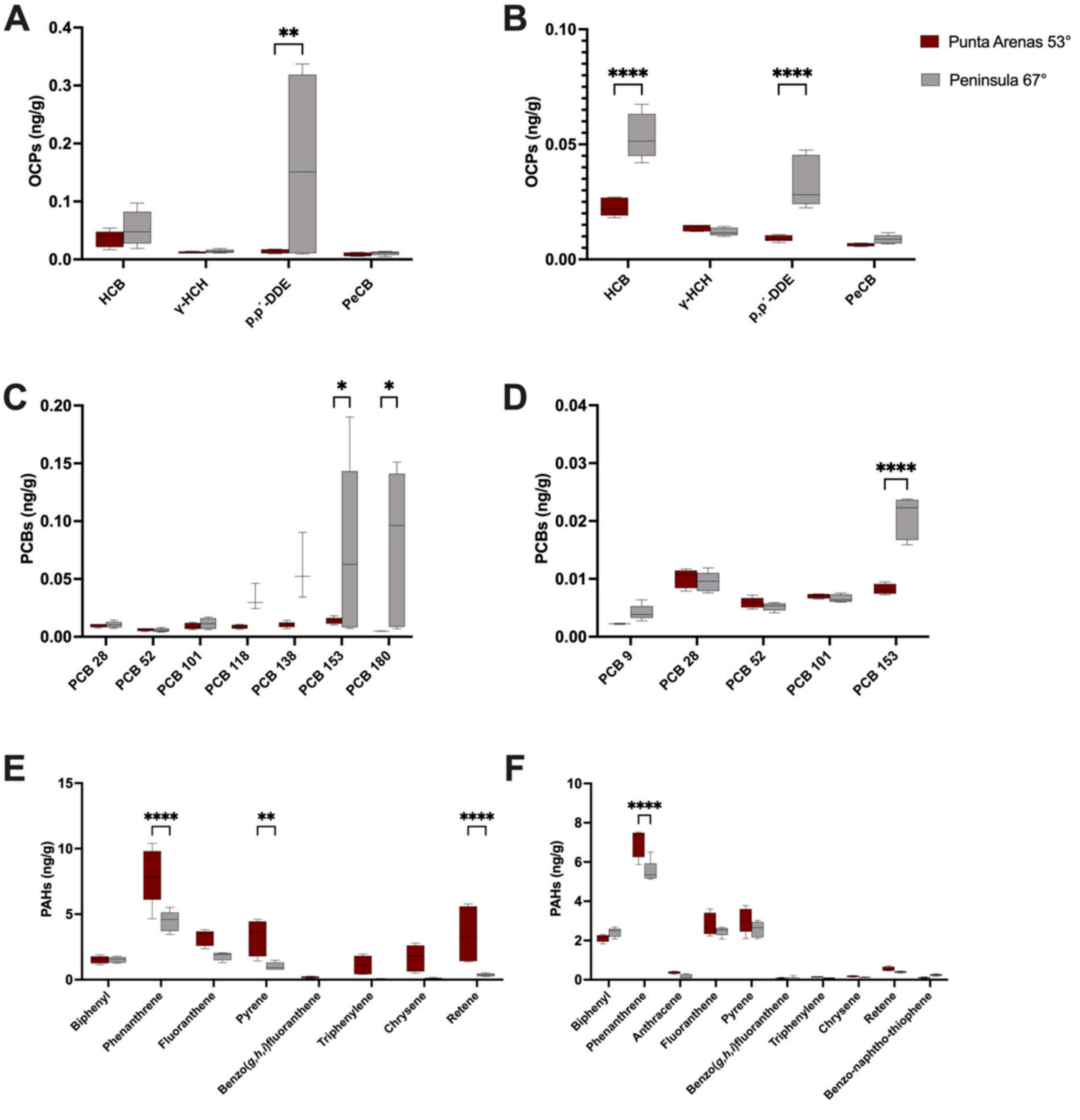

Fig. 1. Box-Plot comparing SVOCs concentration (ng g^{-1}) of soils (A, C & E) and *C. quitensis* plants (B, D & F): A & B: organochlorine pesticides (OCPs); C & D: polychlorinated biphenyls (PCBs), and E & F: polycyclic aromatic hydrocarbons (PAHs) of Punta Arenas (red) and Peninsula (gray). Statistical significance of the data was evaluated by Kruskal-Wallis test. Asterisks indicate significant differences between populations (Šídák's multiple comparisons test): $*p < 0.05$; $**p < 0.01$; $***p < 0.001$; $****p < 0.0001$.

2.7. Data analysis

To evaluate differences between Punta Arenas and the Peninsula (independent variable) for the SVOC concentration response variable (OCPs, PCBs, and PAHs) in soils (Tables S3 and S5) and plants (Tables S4 and S6), we used a non-parametric Kruskal-Wallis test followed by a post hoc Sidak multiple comparison test. A normality test (Shapiro-Wilk test) was performed beforehand, revealing that the data were not normally distributed. We tested the relationship between BCF_{Soil} and Log K_{OW} using simple linear regressions. A slope comparison test (or interaction test) was used to assess whether the slopes of the field obtained regressions were statistically different from the reported in the bibliography. This was conducted using an ANOVA test between regressions, indicating whether a significant interaction existed between $\log K_{OW}$ and the BCF_{Soil}. All statistical analyses were performed using GraphPad Prism 9.0 software.

3. Results and discussion

3.1. Levels of SVOCs in soil and C. quitenis from Sub-Antarctica and Antarctica regions

3.1.1. Organochlorine pesticides (OCPs)

In soils samples, the concentrations of OCPs for Punta Arenas ranged from 8.792 (PeCB) to 35.72 pg g^{-1} (HCB) and for Peninsula 10.77 (PeCB) to 161.988 pg g^{-1} (p,p′-DDE) (Fig. 1A). In the *C. quitensis* samples the OCPs displayed the following concentrations range 6.408 pg g^{-1} (PeCB) to 22.82 pg g^{-1} (HCB) for Punta Arenas and 8.724 (PeCB) to 53.58 pg g^{-1} (HCB) for Peninsula (Fig. 1B). Comparing the two locations, Punta Arenas and Peninsula present significant differences for p, p′-DDE in soils ($H_{(1,31)} = 5.4$, $p < 0.05$; see Fig. 1A). as well as for HCB and p,p′-DDE in plants ($H_{(1,32)} = 61.83$, $p < 0.0001$; see Fig. 1B). *C. quitensis* from Peninsula had higher concentrations of OCPs, in particular, HCB and p,p′-DDE were found in greater amounts than those in Punta Arenas. Notably, p,p′-DDE representing in average 63 % (162 ± 154.4 pg g^{-1}) and 31 % (33.4 ± 11.2 pg g^{-1}) of the total concentrations of OCPs in soils and plants, respectively, from the Peninsula, suggesting a significant presence of these pollutants in the region. These findings suggest a variation in OCPs distribution and possibly a differential exposure of plants between the two regions.

As for the OCPs, p,p′-DDE is a metabolite of the pesticide DDT, which was used extensively in the past. This is consistent with what was reported for HCB (67.9–108 pg g^{-1} dw) and p,p′-DDE (10.6–181 pg g^{-1} dw), where both were dominant contributors to the total OCP concentrations in soil samples (2009–2010) from King George Island at 62° S (Zhang et al., 2015). Additionally, the ratios of p,p′-DDE/p,p′-DDT have been applied to establish whether DDT emissions are recent or historical (Wang et al., 2009; Pozo et al., 2004). The ratio of p,p′-DDE/DDT >1 indicates old inputs of DDT, while p,p′-DDE/DDT <1 indicates fresh inputs (Cabrerizo et al., 2012). The values of p,p′-DDE/p,p′-DDT for soils from Punta Arenas (Table S5) were 1.789, and for the Peninsula it was 18.66 (>1), suggesting old DDT accumulations in the local area. It is well known that DDT can biodegrade to DDE under aerobic conditions (Hitch and Day, 1992). These results indicate old residual concentrations in soils due to historical usage. Recently, it was pointed out that atmospheric concentrations are decreasing, and exposure due to long-range atmospheric transport aligns with the occurrence of weathered DDT in the studied area (Luarte et al., 2023). This suggests that the direct transport of these compounds is decreasing, which is consistent with the prohibition of DDT use in recent decades in the surrounding South American countries (Galbán-Malagón et al., 2023; Luarte et al., 2024). Technical DDT was banned in Chile in 1984 (SAG, 1984) and in Argentina in 2005 (Law 26.011, 2005). But, for example, Dicofol has remained as a permitted alternative, though its use was prohibited in Argentina in 2018 (SENASA, 2018) it was still allowed in Chile until 2023 (SAG, 2023).

3.1.2. Polychlorinated biphenyls (PCBs)

In soil samples, concentrations of PCBs for Punta Arenas ranged from 4.92 pg g^{-1} (PCB 180) to 13.9 pg g^{-1} (PCB 153), and for Peninsula 5.79 pg g^{-1} (PCB 52) to 79.1 pg g^{-1} (PCB 180) (Fig. 1C). In *C. quitensis* samples, concentrations of PCBs for Punta Arenas ranged from 2.23 (PCB 9) to 10.1 pg g^{-1} (PCB 28) pg g^{-1}, and for Peninsula 4.188 (PCB 9) to 20.6 pg g^{-1} (PCB 153) (Fig. 1D). When comparing the two regions, there were significant differences for PCB 153 and PCB 180 in soils ($H_{(1,47)} = 13.84$, $p < 0.001$; see Fig. 1C) and PCB 153 in plants ($H_{(1,34)} = 24.46$, $p < 0.0001$; see Fig. 1D). For soils and *C. quitensis* from Antarctic Peninsula had higher concentrations of PCB 153 representing approximately 26 % of the total average PCBs concentration.

The results indicate no variability in PCB contamination (PCB 28, PCB 52, PCB 101, PCB 118, and PCB 138) between the two locations, which could reflect similar contamination sources and BCF_{Soils}. This could point to effective measures banning the use of PCBs due to international regulations. In fact, a recent study shows that atmospheric concentrations of PCBs are decreasing significatively (Luarte et al., 2023, 2024). The concentrations reported in this study indicate possibly a decrease when comparing our results with previous reports. For example, total PCB concentrations reported in James Ross Island (64°S 58°W) range from 0.51 to 1.82 ng g^{-1} (Klánová et al., 2008), i.e., higher values than our study with 0.063 ng g^{-1} at 53° and 0.272 ng g^{-1} at 67°. On the other hand, PCB 153 and PCB 180 concentrations between Peninsula and Punta Arenas suggest a variation in PCB distribution and possibly differential exposure. These compounds contain a higher number of chlorine groups associated with the biphenyl ring and molecular weight (360.88 g mol^{-1} and 395.32 g mol^{-1}, respectively), which may influence their longer permanence in the soil. There are no studies reporting values at 67° latitude, so greater monitoring covering these areas is necessary.

3.1.3. Polycyclic aromatic hydrocarbons (PAHs)

In soil samples, the observed PAHs from Punta Arenas displayed a range of concentrations, with Phe being the most abundant at an average of 7.93 ng g^{-1} and BghiF at 0.1925 ng g^{-1} being the one with the lowest concentration. In soil samples from the Antarctic Peninsula, Phe was again prominent, with an average concentration of 4.46 ng g^{-1}. The lowest detected average concentration was BghiF at 0.0559 ng g^{-1} (Fig. 1E). In *C. quitensis* the PAHs of Punta Arenas showed Phe at 6.98 ng g^{-1} as the most abundant compounds. The lowest detected average concentration was for BaA at 0.0844 ng g^{-1}. In the Antarctic Peninsula, similar patterns were observed. Phe was at 5.51 ng g^{-1}. The least abundant compound detected was Tri at an average of 0.0810 ng g^{-1} (Fig. 1F).

Soil samples from Punta Arenas and Peninsula present significant differences for Phe Pyr, and Ret ($H_{(1,62)} = 56.36$, $p < 0.0001$; see Fig. 1E). Plant samples from Punta Arenas and Peninsula present significant differences for Phe ($H_{(1,88)} = 14.54$, $p < 0.001$; see Fig. 1F). This could be attributed to several factors, including differences in local pollution sources, environmental conditions affecting PAH deposition and persistence, or variations in soil organic matter content, which can influence the concentration of hydrophobic organic contaminants like PAHs (Wei et al., 2024; Iriarte et al., 2023; Wu et al., 2023). For example, local pollution in Punta Arenas is exposed mainly to sources such as residential burning biomass or fossil fuels that contribute to a greater accumulation of PAHs, whereas Peninsula presents other sources such as burning fossil fuel, solid fuel, and biomass. This is complemented by the results in diagnostic ratios of PAHs that revealed a predominantly pyrogenic source in the sub-Antarctic region, while in the Antarctic region a mixture of sources was observed. In general, PAHs with 3-ring Phe were consistently prominent in soil samples from King George Island (Wei et al., 2024; Deelaman et al., 2021, 2020; Alekseev and Abakumov, 2020; Na et al., 2020; Pongpiachan et al., 2017). Furthermore, Phe has been one of the compounds studied in contaminated soils for the use of bioremediation mediated by Antarctic microorganisms and that has had interesting advances (Egas et al., 2023; Gran-Scheuch et al., 2017; Okere et al., 2012).

As a global view of the results, in Punta Arenas (53°) it was observed that the sum of PAHs in soils and plants (40.5 and 17.8 ng g^{-1}) is greater than in Peninsula (10.9 and 15.5 ng g^{-1}); while in Peninsula of continental Antarctica (67°) it was observed that in soils and plants the sum of OCPs (0.257 and 0.108 ng g^{-1}) and PCBs (0.272 and 0.067 ng g^{-1}) is greater than in Punta Arenas for OCPs (0.096 and 0.038 ng g^{-1}) and PCBs (0.063 and 0.037 ng g^{-1}), respectively (Tables S3 and S4). On the other hand, the obtained concentrations of SVOCs both in *C. quitensis* and its surrounding soil only have been reported by Cabrerizo et al. (2012) with samples from Livingstone Island (62°S). The concentrations of HCB, p,p′-DDE, PCBs (ICES) and PAHs are compared in Table S7. The concentration of HCB in *C. quitensis* by Cabrerizo et al. (2012) represents an intermediate value between the populations analyzed in the present study, which suggest a possible latitudinal gradient For PCBs, p,p′-DDE, and PAHs a higher concentration is observed in the soils of the present study for both sites. In the case of PAHs, the concentrations in soils and plants are considerably higher than those reported (Cabrerizo et al., 2012). To assess the local impact and emission sources linked to

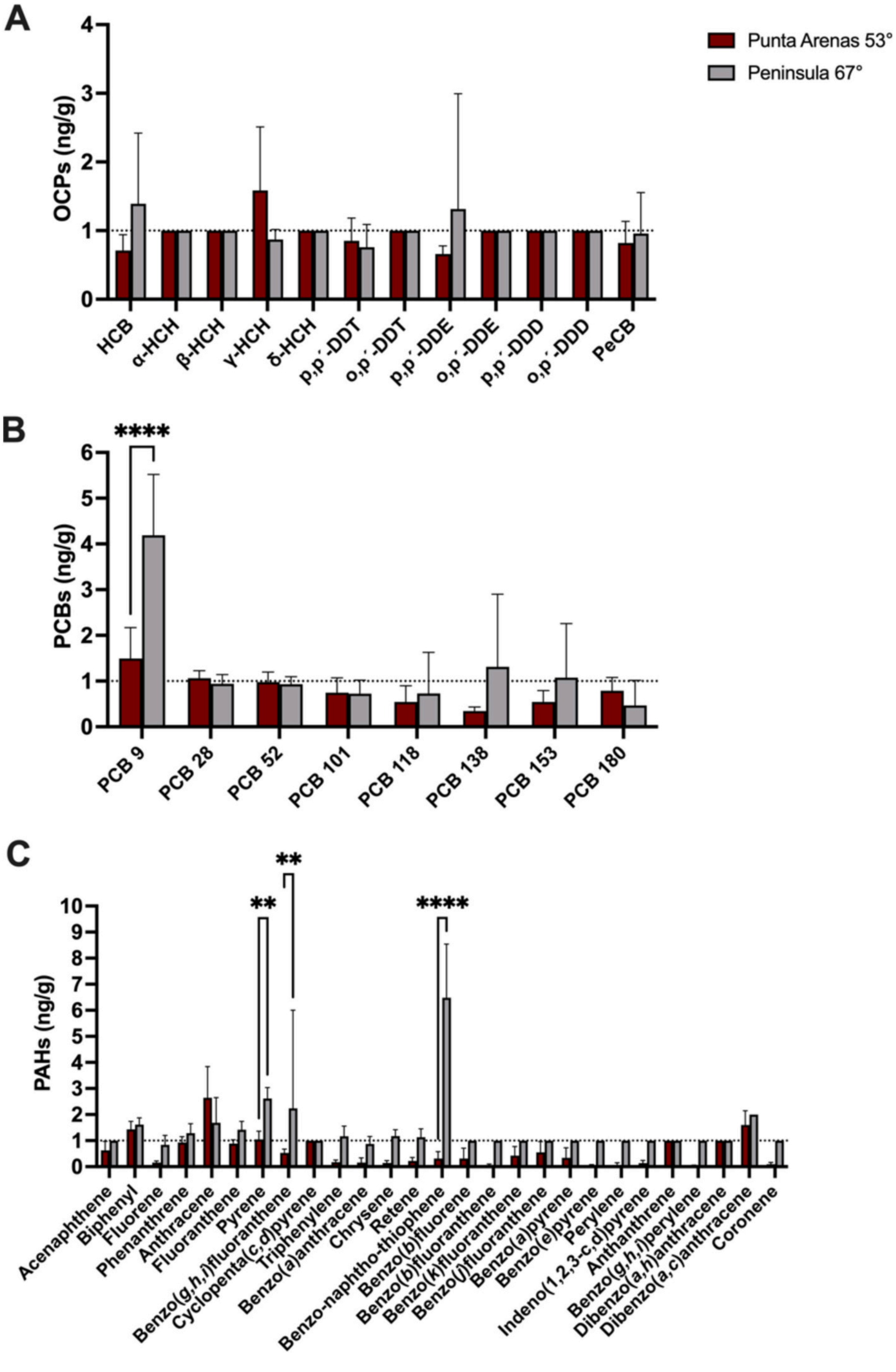

Fig. 2. Bioconcentration Factor from soils (BCF_{Soils}) of SVOCs in *C. quitensis* (ratio between concentration of each individual compound in *C. quitensis* and concentration of each individual compound in soil) from Punta Arenas (red) and Peninsula (gray): A: Organochlorine pesticides (OCPs); B: Polychlorinated Biphenyls (PCBs), and C: Polycyclic Aromatic Hydrocarbons (PAHs). Statistical significance of the data was evaluated by Kruskal-Wallis test. Asterisks indicate significant differences between populations (Šídák's multiple comparisons test): *$p < 0.05$; **$p < 0.01$; ***$p < 0.001$; ****$p < 0.0001$.

anthropogenic activities could help explain the highest concentrations observed. Nevertheless, it is undeniable that anthropogenic activities in the studied areas are steadily increasing (Bargagli and Rota, 2024).

3.2. Bioconcentration of organic pollutants

The analysis of the BCF_{Soils} for OCPs in samples from Punta Arenas shows majority BCF_{Soils} around 1 suggesting that their levels are within the typical range of natural occurrence (Fig. 2A) representing background concentrations; however, γ-HCH presented values reaching 3.22 suggesting a possible influence of human activities and accumulation of this compound in the plants from soils. On the Antarctic Peninsula, the BCF_{Soils} for most OCPs is consistently 1, which is in line with the results from Punta Arenas (Fig. 2A). p,p′-DDE stands out with a BCF_{Soils} value of 3.74 and HCB also shows significant variations with a maximum of 3.12, indicating a notable increase. This is consistent with the significantly high concentrations of both compounds observed in Peninsula plants compared to soils. Notably, γ-HCH tends to have EF values below 1, which indicates that there is low accumulation of this compound in plants contrary to what is happening in Punta Arenas.

In the case of PCBs in Punta Arenas and the Antarctic Peninsula, we observe a diverse range of values (Fig. 2B). In Punta Arenas, the BCF_{Soils} for PCBs are generally close to or below 1, indicating no significant deviation from typical environmental levels and low accumulation rates in plants compared to soils. PCB 9 exhibits higher BCF_{Soils} values reaching an EF of 2.34 in Punta Arenas, suggesting some level of enrichment above the expected natural levels. In contrast, the Antarctic Peninsula shows a greater variation in BCF_{Soils} values. PCB 138, and PCB 153 show notably high BCF_{Soils}, with values exceeding 2, which implies a significant enrichment compared to natural levels. PCB 9 also shows a remarkably high BCF_{Soils}, especially at 6.38, indicating a substantial increase from what would naturally be expected. This suggests that the Antarctic Peninsula may have specific sources of PCB contamination or environmental factors that contribute to these higher enrichment levels, e.g., remobilization influence on the fate of this compounds which were historically retained (Cabrerizo et al., 2013). In this sense, remobilization and ice, snow and soil melting during summer could increase the bioavailability of these compounds in soils from the Antarctic region as consequence of an amplification effect (Casal et al., 2019). For example, there is evidence that temperature affects remobilization of POPs in soils (Nadal et al., 2015; Casal et al., 2019). Besides, the influence of warming periods increases significantly the establishment and expansion of plant populations in terms of nutrients (Convey and Smith, 2005). On the other hand, increases in temperatures, for instance, have demonstrated and increase in the inventories of atmospheric PCBs of 30 % due to soil revolatilization (Cabrerizo et al., 2013), but also the increase in the organic matter in soils may retain PCBs in the soil-plant system limiting the exposure of plants to these compounds. However, some studies have shown the opposite effect. i.e., soils represented a source of PCBs to the atmosphere, especially with soils with low to moderate organic matter content (Cabrerizo et al., 2012). The increase of plant cover may increase the total amount of C in soils significantly (Roberts et al., 2009). However, results from field studies revealed that soils with vegetation could be lower in organic carbon than bare soils (Cabrerizo et al., 2013). In this sense, the increase of compounds in the soil may enhance the bioavailability of PCBs to plants through the root system (Cabrerizo et al., 2013). In fact, studies showed that highly hydrophobic compounds may accumulate significantly in plants after exposure experiments in real conditions (Terzaghi et al., 2022). However, the accumulation from soils could be discussed since the exposure to plant root system to soil PCBs is related to concentrations of these compounds in soil pore-water (Li et al., 2019).

The BCF_{Soils} analysis for PAHs in *C. quitensis* from Punta Arenas and the Antarctic Peninsula displays a general trend of values close to 1 for many PAHs, suggesting that their levels are within the typical range of natural occurrence, indicating no enrichment above the baseline (Fig. 2C). Particularly, Ant is more concentrated in plants compared to soils at both study sites: Punta Arenas (e.g., 4.85 and 4.07) and the Peninsula (e.g., 4.22 and 3.08). Similar trends are observed for Pyr and DahA in the Peninsula (e.g., 3.11 and 2.00). Notably, BNT shows a higher BCF_{Soils} value (e.g., 9.15) in the Peninsula; however, Phe does not show enrichment, although it did exhibit higher concentrations in Antarctic Peninsula plants. These differences may reflect localized environmental conditions or specific sources of PAHs, highlighting the complex nature of PAHs distribution in these ecologically sensitive areas.

We found statistically significant differences in the BCF_{Soils} for PCB-9 ($p < 0.00001$), Pyr ($p < 0.001$), BghiF ($p < 0.001$) and BNT ($p < 0.00001$) between Punta Arenas and Peninsula (PCB ($H_{(1,64)} = 9.53$, $p < 0.05$; Fig. 2B and PAHs ($H_{(1,216)} = 109.6$, $p < 0.001$; Fig. 2C). Moreover, when comparing the values of BCF_{Soils} obtained in the present work for all the studied compounds and sites in relation to what was found in previous works, we show an inverse relationship between the BCF_{Soil} ($p < 0.0001$) obtained for each compounds in comparison to Log K_{OW} conducted in laboratory experiments; which is in agreement with previous results conducted in laboratory and field experiments (Li et al., 2019) (See Fig. 3 and Fig. S2). Likewise, we tested the hypothesis that findings from Li et al., 2019 and our study are different, and the statistical analysis showed that the relationships found in Li et al., 2019 and the present study are not ($F = 1.3$; $df = 602$ and $p = 0.027$). There are enrichment values from 1 to 129 (especially for the more volatile ones i.e.: PCB-9) times at a given Log K_{OW}, and estimated enrichment values lower than 1 in most of the cases at a given Log K_{OW}. Note that the

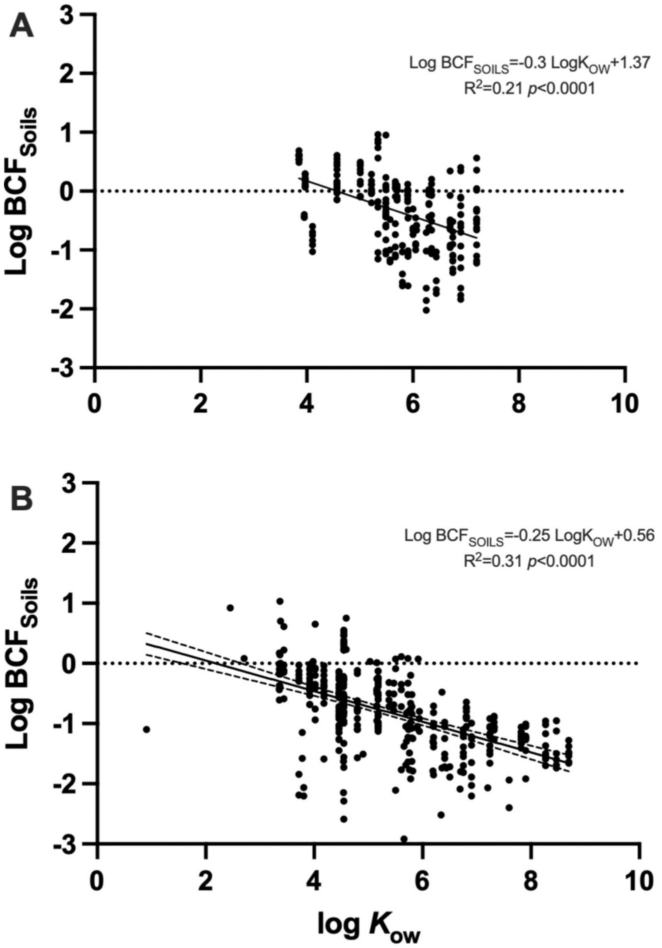

Fig. 3. Relationship among the estimated Log Bioconcentrations Factors from soils (BCF_{Soils}) and Log K_{ow} estimated in the present study (A) and those obtained from different studies as reported in Li et al., 2019 (B).

accumulation of semi-volatile organic pollutants from soils to plants has a better relationship with estimation of the Bioconcentration factor in plants but using the concentrations of semi-volatile organic pollutants in pore-water ($\text{BCF}_{\text{Porewater}}$), which has been established as a good predictor of the accumulation rates as stated in Li et al., 2019. However, we observed an inverse relationship, while the less hydrophobic ones have $\text{BCF}_{\text{Soils}}$ values >1, the most hydrophobic ones have $\text{BCF}_{\text{Soils}}$ <1. This would indicate that the more hydrophobic and less volatile compounds will tend to remain in the soil and accumulate to a lesser extent in the plants, which is consistent with previous studies, since no differences were found between the $\text{BCF}_{\text{Soils}}$ in Li et al., 2019 and our results.

The organic matter content in soil and the low lipid content of *Colobanthus quitensis* significantly influence the final fate of contaminants (Cabrerizo et al., 2012, 2013, 2014, 2018; Doucette et al., 2018). However, previous studies in Antarctica reported no significant differences in organic matter content between bare soils and plant-covered soils, which ranged from 0.12 % to 0.98 % (Cabrerizo et al., 2012). Similarly, findings from Subantarctic regions showed that bare soils (21 %) had a higher organic matter percentage compared to plant-covered soils (14 %) (Hervé-Fernández et al., 2023). These differences in organic matter, however, do not explain the variations in the BCF_{Soil} observed in this study.

Organic matter plays a key role in explaining differences associated with human activity and biota contributions to soil organic matter and persistent organic pollutants (POPs). For example, this has been demonstrated in penguin colonies and human settlements (Cabrerizo et al., 2012, 2018). Our findings likely reflect the BCFSoil of contaminants in plants growing in soils with environmentally relevant contaminant levels, similar to earlier studies conducted in remote regions, including other Antarctic areas (Cabrerizo et al., 2012). Additionally, laboratory and field experiments worldwide have consistently shown that bioaccumulation patterns remain stable across various plant species under different environmental conditions (see Fig. 3b). Specifically, a positive correlation between LogK_{OW} (octanol-water partition coefficient) and plant $\text{BCF}_{\text{Porewater}}$ has been widely reported, supporting the conclusion that non-ionizable chemicals tend to accumulate in plant tissues under comparable conditions.

In Antarctic and Subantarctic environments, soils play a critical role in the accumulation of contaminants in plants. Most studies suggest that the uptake of non-ionizable chemicals by plants depends primarily on the equilibrium between soil and soil-porewater. However, in Antarctic environments, low soil temperatures restrict water bioavailability, limiting the transfer of contaminants from soil to plants. Organic matter in Antarctic soils also binds pollutants, particularly hydrophobic ones, reducing their mobility and limiting their uptake by plants (Cabrerizo et al., 2012, 2013). This phenomenon is particularly evident in areas with plant cover, such as those dominated by *Deschampsia antarctica* and *C. quitensis*, where organic matter may sequester contaminants and hinder their accumulation in plants (Cabrerizo et al., 2012).

The physiological and morpho-anatomical traits of *C. quitensis* also influence its ability to accumulate contaminants. This species has evolved highly conservative adaptations to survive extreme environments, such as high-altitude Andean mountains and high-latitude Antarctic and Subantarctic regions. These environments are characterized by high radiation, low nutrient bioavailability, strong winds, and low temperatures. The plant's lack of root lipids, small leaf area, and limited gas exchange through the leaf system constrain its ability to absorb and store lipophilic contaminants (Ramírez et al., 2024; Sáez et al., 2017). Furthermore, the harsh climatic conditions of the Antarctic summer limit *C. quitensis*'s growth, further restricting its capacity to accumulate contaminants (Clemente-Moreno et al., 2020).

3.3. Sources of PAHs in Antarctic plants and soils

The possible sources of PAHs in the study sites were assessed using diagnostic ratios, as shown in Table 1 (see Tables S9 and S10 for reference values). Pyrolytic processes involve the incomplete combustion of biomass or fossil fuels, while petrogenic processes involve the slow maturation of organic substances (due to crude oil leakage) (Abdel-Shafy and Mansour, 2016; Deelaman et al., 2020). For *C. quitensis* from Punta Arenas and the Antarctic Peninsula, and soils from the Peninsula, the mean ratio $\sum$LMW/$\sum$HMW was >1, suggesting a petrogenic source. In contrast, soil samples from Punta Arenas had a mean $\sum$LMW/$\sum$HMW ratio of 0.43 (<1), typically indicating a pyrogenic source.

We further evaluated the individual contribution of PAHs grouped by aromatic rings (Fig. S1). In Punta Arenas soils, compounds with two to seven rings were observed, while in soils and plants from both study sites, and soils from the Peninsula, mainly compounds with two, three, and four rings were dominant. Across all samples, three- and four-ring compounds were the most common. Pyrogenic PAHs are typically abundant within the five- to six-ring group (Sanders et al., 2002), as reflected in the diagnostic ratios for Punta Arenas soils (Table 1).

The Ant/(Ant + Phe) ratio was <0.1 across all samples, suggesting a petrogenic source. The Flu/(Flu + Pyr) ratios ranged between 0.4 and 0.5 for plants from both sites, indicating fossil fuel combustion, while soils from both sites had ratios above 0.5, which is typically associated with wood combustion. The BaA/(BaA + Chr) ratios ranged from 0.2 to 0.35, suggesting mixed petrogenic and pyrogenic sources for soils from

Table 1

Diagnostic molecular ratios for PAHs were obtained in soils and *Colobanthus quitensis* from Punta Arenas and Peninsula. $\sum$LMW: Sum of PAHs with molecular weight $<$ 178 g mol^{-1}; $\sum$HMW: Sum of PAHs with molecular weight $>$ 178 g mol^{-1}; $\sum$PAHs (16EPA): Sum of PAHs of US EPA; $\sum$COMB: Sum of PAHs that are characteristic of combustion sources (Fluoranthene, Pyrene, Anthracene, Phenanthrene, Benzo(*a*)pyrene, Benzo(*b*)Fluoranthene, Benzo(*a*)anthracene, Chrysene, Dibenz(*a*,*h*)anthracene, Benzo(*g*,*h*,*i*)perylene, and Indeno(1,2,3-*cd*)pyrene); Ant: Anthracene; Phe: Phenanthrene; Flu: Fluoranthene; Pyr: pyrene; BaA: Benzo(*a*)anthracene; Chr: Chrysene.

			$\sum$LMW/$\sum$HMW	Ant/(Ant + Phe)	Flu/(Flu + Pyr)	BaA/(BaA + Chr)	$\sum$COMB/$\sum$PAHs
C. quitensis	Punta Arenas	Mean	1.19	0.05	0.48	0.24	1.19
		SD	0.12	0.01	0.05	0.11	0.12
		Min	1.05	0.04	0.41	0.1	1.05
		Max	1.32	0.06	0.55	0.33	1.32
	Peninsula	Mean	1.16	0.03	0.49	0.16	1.16
		SD	0.15	0.01	0.04	0.02	0.15
		Min	1.03	0.02	0.44	0.14	1.03
		Max	1.4	0.05	0.54	0.19	1.4
Soils	Punta Arenas	Mean	0.43	0.02	0.52	0.28	0.96
		SD	0.18	0.01	0.08	0.04	0
		Min	0.27	0.01	0.43	0.22	0.96
		Max	0.64	0.03	0.62	0.31	0.97
	Peninsula	Mean	1.37	0.02	0.64	0.22	0.97
		SD	0.1	0	0.05	0.03	0.02
		Min	1.27	0.02	0.58	0.2	0.94
		Max	1.53	0.03	0.69	0.27	0.98

Punta Arenas and the Peninsula, and plants from Punta Arenas; however, plants from the Peninsula had a BaA/(BaA + Chr) ratio of <0.2, suggesting a predominantly petrogenic source. Lastly, the ∑COMB/∑PAHs ratio was >0.7 in all samples, indicating high-temperature combustion processes.

Previous studies on PAHs in suburban soils from Punta Arenas (Apiratikul et al., 2021; Deelaman et al., 2020) suggest that the PAHs likely originated from pyrogenic sources, consistent with our findings (Fig. 4). The PAH diagnostic ratios in this study indicate mixed pyrogenic and petrogenic origins, as shown by the cross-plots of Flu/(Flu + Pyr) versus BaA/(BaA + Chr) and Flu/(Flu + Pyr) versus Ant/(Ant + Phe) in Fig. 4. The Flu/(Flu + Pyr) ratio of 0.4 suggests a mix of pyrogenic sources (e.g., wood burning) and fossil fuel combustion (e.g., diesel generators). Plants from the Peninsula could have both mixed and petrogenic sources (gray rhombuses), while soils from the Peninsula likely originate from mixed and combustion sources (gray triangles). The mixed sources revealed in the present work could reflect the impact of seasonal research bases, where diesel is the main source of energy (Tin et al., 2009), however the impact may be lower due to non-continuous use compared to permanent bases (Pineschi, 2001; Bargagli, 2005).

4. Conclusions and environmental implications

This study provides insights into patterns of contamination and bioconcentration of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) in soils and *Colobanthus quitensis* from the Sub-Antarctic (Punta Arenas, 53°S) and Antarctic regions (Antarctic Peninsula, 67°S). The results demonstrate regional differences in contamination sources and accumulation patterns, with PAHs being more prevalent in the Sub-Antarctic region and OCPs and PCBs being dominant in the Antarctic Peninsula. These findings indicate that contamination in Punta Arenas is likely influenced by both natural and anthropogenic sources, while the Antarctic Peninsula shows signs of historical contamination, particularly with HCB and p,p′-DDE, potentially linked to long-range atmospheric transport and previous DDT usage.

Bioconcentration factor (BCF) analysis revealed that, while most contaminants in plant tissues are within the natural range, there are notable exceptions suggesting anthropogenic influences, such as elevated levels of γ-HCH and PCB 9 in Punta Arenas, and HCB, p,p′-DDE, and PCB 9 in the Peninsula. Furthermore, hydrophobic contaminants like PAHs and certain PCBs tend to accumulate in soils rather than plant tissues, reflecting their affinity for soil organic matter and suggesting limited uptake by plants, supported by their inverse significant relationship with $\mathrm{LogK_{OW}}$.

Source analysis of PAHs indicates a mix of petrogenic and pyrogenic origins in both regions, with Punta Arenas showing a stronger tendency toward pyrogenic sources. In contrast, the Antarctic Peninsula shows a combination of mixed and petrogenic sources, highlighting the complexity of PAH pollution sources in these areas.

The vulnerability of polar regions to contamination from local and long-range sources is evident, with legacy pollutants like HCB and DDT derivatives persisting in Antarctic environments. A recently published study (Egas et al., 2025) demonstrates that even basal concentrations of POPs and SVOCs significantly affect plant physiology, including increased oxidative (Fig. S4A) stress and reduced photosynthesis (S4B) in *C. quitensis* populations from Punta Arenas (53°), Shetland Islands (62°), and the Antarctic Peninsula (67°). These impacts are exacerbated with slight increases above reported levels in antarctic soils (Egas et al., 2025). As plant populations expand and historically retained pollutants become more bioavailable. Further research is essential to inform conservation strategies for the Antarctic ecosystem (Bengtson-Nash et al., 2023).

CRediT authorship contribution statement

C. Egas: Writing – original draft, Software, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **T. Luarte:** Writing – original draft, Writing – review & editing, Methodology. **R. Vargas:** Writing – review & editing, Methodology. **E. Castro-Nallar:** Writing – review & editing, Project administration, Funding acquisition, Data curation. **K. Pozo:** Writing – review & editing, Methodology. **P. Přibylová:** Writing – review & editing, Supervision, Software, Methodology, Funding acquisition, Data curation. **J. Martiník:** Writing – review & editing, Methodology, Formal analysis, Data curation. **M. Molina-Montenegro:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition. **C. Galbán-Malagón:** Writing – original draft, Conceptualization, Methodology, Writing – review & editing, Supervision, Project administration, Funding acquisition.

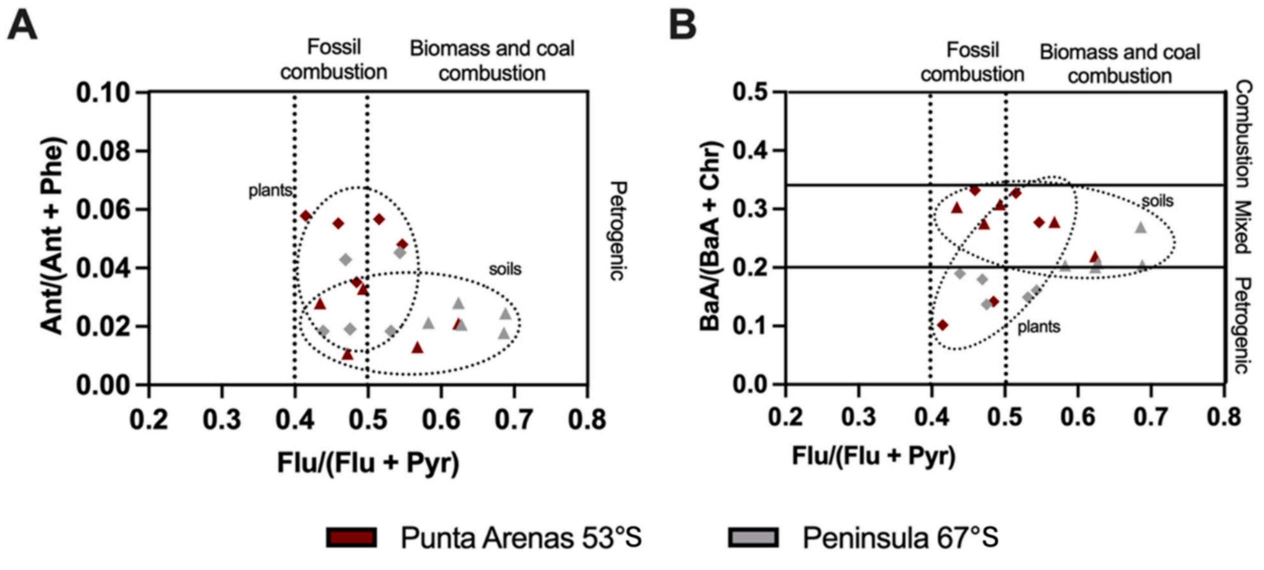

Fig. 4. Cross-plot for pollutant concentration ratios: (A) An/(An + Phe) versus Flu/(Flu + Pyr), and (B), BaA/(BaA + Chr) versus Flu/(Flu + Pyr) in the soils (triangle) and plants (rhomb) from Punta Arenas (red symbol) and Peninsula (gray symbol). Ant: Anthracene; Phe: Phenanthrene; Flu: Fluoranthene; Pyr: pyrene; BaA: Benzo(*a*)anthracene; Chr: Chrysene.

Declaration of competing interest

Cristobal Galban-Malagon reports financial support and administrative support were provided by Universidad Mayor. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2025.178494.

Data availability

All the used data are in the suplementary material

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