Persistent organic pollutants in soils and sediments from James Ross Island, Antarctica

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A survey of soil, sediment and air contamination in James Ross Island, Antarctica serves as a baseline study for evaluation of an anthropogenic impact of the new research facility.

Abstract

Soil and sediment samples from James Ross Island were analyzed for their PCB, OCP and PAH contents. Soil concentrations ranged between 0.51 and 1.82 ng g⁻¹ for seven indicator PCB congeners, between 0.49 and 1.34 ng g⁻¹ for HCH congeners, between 0.51 and 3.68 ng g⁻¹ for the sum of p,p'-DDT, DDE, and DDD, and between 34.9 and 171 ng g⁻¹ for the sum of 16 EPA PAHs. Sediment levels from 0.32 to 0.83 ng g⁻¹ were found for PCBs, from 0.14 to 0.76 ng g⁻¹ for HCHs, from 0.19 to 1.15 ng g⁻¹ for DDTs, and from 1.4 to 205 ng g⁻¹ for PAHs. A prevalence of low-mass PAHs, less chlorinated PCBs, and more volatile chemicals indicates that the long-range atmospheric transport from populated areas of Africa, South America, and Australia is the most probable contamination source for the solid matrices in James Ross Island.

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1. Introduction

Polar territories as the regions playing a very significant role in global environmental processes keep attracting an interest of environmental scientists. Increasing levels of persistent organic pollutants (POPs) in various environmental matrices in these pristine locations (Blais et al., 1998; Donald et al., 1999; Carrera et al., 2001) are the matter of a growing concern but they also enhance the understanding of atmospheric chemistry and transport (Legrand and Saigne, 1988). Organochlorine compounds (OCs) including polychlorinated biphenyls (PCBs) and organochlorinated pesticides (OCPs) continue to pervade global ecosystems despite of successful curtailing of most of their emissions (AMAP, 2003). Occurrences of POPs in such remote areas are the result of long-range transport in the atmosphere, precipitation and cold condensation (Wania and Mackay, 1993). Snow influences not only the deposition (Desideri et al., 1994), but also the fate of POPs in cold environments (Hoff et al., 1995). Sediment, soil, and snow/ice act as recorders of POP levels over the years, accumulating valuable information on past environmental and climatic events (Fuoco et al., 1996). However, due to their lipophilicity, these compounds also bioaccumulate through the food webs and reach the significant levels in the top predators (Kallenborn, 2006). Contamination of the samples of soil or sediment (Risebrough et al., 1990; Kennicutt et al., 1995; Fuoco et al., 1996; Aislabie et al., 1999; Negoița et al., 2003; Negri et al., 2006), biota, seawater (Cripps, 1992; Green et al., 1992; Cripps and Shears, 1997; Aislabie et al., 1999),...
and air (Larsson et al., 1992; Montone et al., 2003; Kallenborn, 2006) was documented in the last 15 years for many remote regions including Antarctica (Tanabe et al., 1983; Desideri et al., 1992, 1994, 1995, 1998).

Soil samples from the East Antarctic coast contained 0.20–157.45 ng g⁻¹ (d.w.) of PCBs, 0.86–43.06 ng g⁻¹ (d.w.) of HCHs, and 0.11–26.46 ng g⁻¹ (d.w.) of DDTs (Negoiita et al., 2003). PCB concentrations in the range of 0.13–0.24 ng g⁻¹ (d.w.) were also determined in the soil and sediment samples from the large area of Ross Sea and Victoria Land (Fuoco et al., 1996). PCB levels occurring in the sediments from highly polluted Winter Quarters Bay were within the range of 100–1400 ng g⁻¹ (d.w.) (Risebrough et al., 1990) and 250–4200 ng g⁻¹ (d.w.) (Rennicutt et al., 1995). First studies on PCB and DDT levels in snow from this region were carried out in the 1960s (Peterle, 1969). Organic compounds in the icepack, and in the surface and deep snow have been determined by Desideri et al. (1991, 1994, 1995, 1998). Persistent organic pollutants have also been detected in the air samples over the Antarctic region. Tanabe et al. (1983) have measured PCBs and OCPs in the Antarctic atmosphere and hydrosphere (Japanese Antarctic research stations) between 1980 and 1982. In 1994–1995, contaminant levels found in the atmosphere at the British Antarctic Survey research station in Signy Island ranged from 0.02 to 17 pg m⁻³ for single PCB congener, from 0.04 to 0.9 pg m⁻³ for chlordane, from 0.07 to 0.40 pg m⁻³ for DDT compounds, and up to 22 pg m⁻³ for γ-HCH (Kallenborn et al., 1998). PCB concentrations in the same order of magnitude were also found in the air samples from the Brazilian Antarctic Research Station at King George Island between December 1995 and February 1996 (Montone et al., 2003).

Both natural and anthropogenic polycyclic aromatic hydrocarbons (PAHs) can be found in the environmental samples (MacDonald et al., 2000). PAHs most often accumulate in Antarctic soils and sediments where the fuel oil spills have occurred in the past. PAH levels ranging from 41 to 8105 ng g⁻¹ (d.w.) were measured in the soil near the Scott Base Research Station and at two former research facilities at Marble Point and Wright Valley (Aislabie et al., 1999). Sediment samples from Winter Quarters Bay analyzed by Kennicutt contained 20000 ng g⁻¹ (d.w.) of PAHs (Cleveland et al., 1997). Significantly lower PAH concentrations were determined in the marine sediments from Scott Base, Turtle Rock, Cape Evans or Cape Armitage. The marine surface sediments collected near the Brazilian station in Admiralty Bay contained 9.5–270.5 ng g⁻¹ (d.w.) of PAHs (Martins et al., 2004), and those sampled near Davis-Station in Princess Elizabeth Land stayed generally below 1 ng g⁻¹ (d.w.) for the individual compounds (Green and Nichols, 1995). Up to 12 ng L⁻¹ of single PAH was found in the Terra Nova Bay icepack sampled between 1988 and 1989 (Desideri et al., 1991), and the PAH concentrations in the snow from eight other Antarctic sampling sites varied around 50 ng L⁻¹ in the surface, and 20 ng L⁻¹ in the deep snow sampled in 1987–1988, 1988–1989, and 1990–1991 (Desideri et al., 1994).

Results of various studies indicate that highest POP concentrations have been measured near some polar research facilities. When a Czech Antarctic station was established in James Ross Island, a soil, sediment, and air contamination survey was proposed as a part of the multidisciplinary scientific program, with the purpose of estimating whether the activities and dump sites of previous exploration bases caused the contamination of solid matrices. Twenty composite soil and sediment samples from various sites were collected during the terrain reconnaissance in January 2005. Their POP content was determined as a contamination baseline at the time of the station construction.

2. Materials and methods

2.1. Sampling sites

James Ross Island is a large island (2500 km²) off the southeast coast of the Antarctic Peninsula (64°10′S, 57°45′W) close to its north-eastern protrusion (Trinity Peninsula), from which it is separated by 12–20 km wide and 120 km long Prince Gustav Channel. A climate of the James Ross Island is characteristic with the short summer (December–March) when the air temperatures fluctuate between −5 °C and +5 °C. The glacier winds flowing down from the ice cap of Trinity Peninsula across the Prince Gustav Channel represent a local high-speed circulation system when the wind speed reaches its maxima. As the west winds prevail, the island lies in the rain shadow of the Antarctic Peninsula which forms an effective barrier to precipitation and partly buffers the wind circulation. Systematic investigation of the island started with British expeditions in the 1960s, continued with Argentine investigations in the 1970s and Swedish expeditions in the 1990s. A Czech Antarctic station focused on the function of deglaciated area in the northern part of the island was established in 2005.

Soil and sediment samples were collected from the north coast between Bibly Point and Lachman Cape (10 samples), Brandy Bay area (Abernethy Flats — one sample, Phormidium Lake — one sample), Whisky Bay (four samples), Solorina Valley (three samples), and Begtson Cliffs (one sample) (Table 1, Fig. 1). The river, lake and marine sediments as well as the soil were sampled in the high ablation season where the deglaciated area was almost entirely without snow except of the localized permanent snowfields, and the temperature fluctuated between −3 °C and +5 °C.

To further investigate the POP sources in the area, five passive air samplers (Shoib and Harner, 2002) have been employed for the period of four weeks along the northern coast where the western winds bring the air from the Antarctic Peninsula to the island.

2.2. Sample collection

Surface sediments (top 10 cm layer) were collected using a trowel from the sedimentation basis of the bed close to the bank. Representative samples were prepared by mixing five to eight sub-samples from the area of about 4 m². Wet samples (about 250 g) were wrapped in two polyethylene zip-lock bags and transported to the laboratory where they were homogenized, lyophilized, ground with a pestle and mortar, and sieved using a 2-mm sive.

Soils were sampled at 25 × 25 m sampling plots as five to ten sub-samples from the top 10 cm layer which were further homogenized. Wet soil samples (about 250 g) were transported to the laboratory in two polyethylene zip-lock bags, lyophilized, and sieved through a 2-mm mesh.

Passive air samplers consisting of the polyurethane foam disks (15 cm diameter, 1.5 cm thick, density 0.030 g cm⁻³, type N 3038; Gumotex Breclav, Czech Republic) housed in the protective chambers were employed in this study. Theory of the passive sampling using similar devices was described elsewhere (Shoib and Harner, 2002; Harner et al., 2004). Sampling chambers were prewashed and solvent-rinsed with acetone prior to installation. All filters were prewashed, cleaned (8 h extraction in acetone and 8 h in dichloromethane), wrapped in two layers of aluminum foil, and placed in the zip-lock
polyethylene bags. The exposed filters were wrapped in two layers of aluminum foil, labeled, placed into zip-lock polyethylene bags and transported to the laboratory.

2.3. Sample analysis

Soil and sediment samples as well as polyurethane foam filters from passive air samplers were extracted with dichloromethane in a Büchi System B-811 automatic extractor. Surrogate recovery standards (d₄-naphthalene, d₁₀-phenanthrene, and d₁₂-pyrene for PAHs analysis; PCB 30 and PCB 185 for PCBs analyses) were spiked on each sample prior to extraction. Terphenyl and PCB 121 were used as internal standards for PAHs and PCBs analyses, respectively. Volume was reduced after extraction under a gentle nitrogen stream at ambient temperature, and fractionation was achieved on silica gel column; sulfuric acid modified silica gel column was used for PCB/OCP samplings. Site to site variability was never greater than one order of magnitude for all chlorinated pollutants. Site to site variability was never greater than one order of magnitude for all chlorinated pollutants. Sixteen US EPA PAHs. Site to site variability was never greater than one order of magnitude for all chlorinated pollutants. Site to site variability was never greater than one order of magnitude for all chlorinated pollutants. Site to site variability was never greater than one order of magnitude for all chlorinated pollutants. Site to site variability was never greater than one order of magnitude for all chlorinated pollutants. Site to site variability was never greater than one order of magnitude for all chlorinated pollutants. Site to site variability was never greater than one order of magnitude for all chlorinated pollutants. Site to site variability was never greater than one order of magnitude for all chlorinated pollutants. Site to site variability was never greater than one order of magnitude for all chlorinated pollutants.

2.4. Quality assurance/quality control

Recoveries were determined for all samples by spiking with the surrogate standards prior to extraction. Amounts were similar to detected quantities of analytes in the samples. Recoveries were higher than 71 and 79% for all samples for PCBs and PAHs, respectively. Recovery factors were not applied to any of the data. Recovery of native analytes measured for the reference material varied from 88 to 99% for PCBs, from 75 to 98% for OCPs, and from 72 to 92% for PAHs. Laboratory blanks were always lower than 1% of the amount found in the samples. Field blanks consisted of pre-extracted PUF disks which were taken to the sampling site. They were extracted and analyzed in the same way as the samples; the levels in field blanks never exceeded 6% of quantities detected in samples.

3. Results

Levels of persistent organic pollutants were determined in the soils and sediments from James Ross Island in this study. Soil concentrations ranged between 0.51 and 1.82 ng g⁻¹ for the sum of seven indicator PCB congeners, between 0.49 and 1.34 ng g⁻¹ for HCHs congeners, between 0.51 and 3.68 ng g⁻¹ for the sum of p,p’-DDT, DDE, and DDD, between 2.41 and 7.75 ng g⁻¹ for HCB, from 0.59 to 2.24 ng g⁻¹ for PeCB, and between 34.9 and 171 ng g⁻¹ for the sum of 16 EPA PAHs. Site to site variability was never greater than one order of magnitude for all chlorinated pollutants and most of PAHs. Similarly, sediment levels from 0.32 to 0.83 ng g⁻¹ were found for PCBs, from 0.14 to 0.76 ng g⁻¹ for HCHs, from 0.19 to 1.15 ng g⁻¹ for DDTs, from 0.95 to 4 ng g⁻¹ for HCB, from 0.21 to 1.08 ng g⁻¹ for PeCB, and from 1.4 to 205 ng g⁻¹ for PAHs. Site to site variability of PCB and OCP levels was similar to those in the soils (within the same order of magnitude), while it was more than two orders
of magnitude higher for individual polyaromatic hydrocarbons as well as for their sum.

Organic carbon content was determined in all soil and sediment samples and the POP contamination of samples was plotted against the organic carbon fraction. There was, however, no significant correlation found between the organic carbon content and POP contamination in the soils or sediments. It can be partially explained by extremely low levels of organic carbon in the samples — it varied between 0.09 and 0.34% in the soil and between 0.04 and 1.71% in the sediment samples.

In general, PCB and OCP levels measured in this project were consistent with those obtained from the Ross Sea and Victoria Land (Fuoco et al., 1996) or less contaminated soil samples from the East Antarctic (Negoita et al., 2003), rather than from heavily contaminated sites in the Winter Quarters Bay where the PCB levels in sediments were as high as several mg/g (Risebrough et al., 1990) (Figs. 2–4). PCB congener patterns in the soils were dominated by the low-mass PCBs (28 and 52) while the concentrations of higher chlorinated congeners were very low with the exception of the Lachman Cape soil where the concentrations of all indicator PCB congeners were similar. The same congener distribution was observed in sediments. Levels of γ-HCH were about two times higher in all soil and sediment samples than those of α, while DDT concentrations reached only 2−5% of the DDE concentrations in the soils and were below the detection limits in sediments. HCB levels were the highest from all chlorinated compounds in both soils and sediments, and the concentrations of PeCB, as a degradation product, varied between 10 and 50% compared to those of HCB.

PAH levels ranging from 34 to 171 ng/g−1 in soils and from 1 to 205 ng/g−1 in sediments (Figs. 5 and 6) were similar to those in the marine surface sediments collected in Admiralty Bay (Martins et al., 2004) but smaller than the soil levels measured in the Scott Base Research Station, the Marble Point or the Wright Valley (Aislabie et al., 1999), or the sediment in Winter Quarters Bay (Cleveland et al., 1997) being as high as tens of μg/g−1. A concentration pattern of PAHs was dominated by phenanthrene followed by fluoranthene, fluorene, and pyrene.

For this survey, six soil samples, two lake sediments and two marine sediments were collected in northern coast between Bibby Point and Lachman Cape (Table 1, entries 5−14). Lakes are shallow basins with saline water. The surroundings of lakes are vegetated with dense moss cover, which is washed down to the lakes, forming thin peat deposits. Marine samples have been taken from tidal flats with seaweeds and sea animals’ occurrence. The whole area was repeatedly visited by British and Argentinean field parties. The Argentines camps were located close to the lakes in the area of Lachman Cape. This might be a reason why the soils from...
this area contained higher amounts of PCBs and OCPs (LC-S4–LC-S9) than other soil samples (Figs. 2 and 4). PCB and OCP contamination of both lake and marine sediments was on the level similar to other sampling sites (LC-L2, LC-L3, LC-M1, and LC-M3) with slightly higher levels in the lake sediments (Fig. 4). PAH contamination of the lake sediments, however, showed more variability because the PAH concentration in the southern lake (LC-L3) is about one order of magnitude lower than that in the northern lake (LC-L2).

Two sediment samples were collected in Abernethy Flats and Phormidium Lake near the Brandy Bay (Table 1, entries 15 and 16). Abernethy Flats relief consists of flat area with wide braided stream, intensively depositing sand and gravel sediments. A lake basin is filled with wash sediments of mudstones and sandstones which build adjacent slopes. Surrounding relief is flat, mostly without vegetation, locally with sparse lichen cover. The area of Brandy Bay was frequently visited by research expeditions, and rusty tanks and barrels deposited at the shore can be found there. Neither river nor lake sediment, however, showed elevated contamination when compared to the other sites in the island (BB-R2 and BB-L1, Fig. 3).

Whisky Bay is a remote area, less frequently visited by humans since the shoreline is often being blocked by icebergs from the glacier calving into the Whisky Bay. Sample WB-S1 was taken in the pass between the Sharp Valley system and the Whisky Bay coast, sample WB-S2 at the beach close to the shoreline; sample WB-S3 at the valley side (Table 1, entries 1–3). Surprisingly, while two samples had similar PAH levels as those of the other soil samples from the island, WB-S3 had the level ~threefold higher. The analysis also revealed a different profile with a higher amount of less volatile PAH compounds indicating potential local source of contamination (WB-S1–WB-S3). Similarly, the river sediment sample from Whisky Bay (Table 1, entry 4) showed PAH contamination one to two orders of magnitude higher than those in the other samples (WB-R1). On the other hand, there was no significant pollution with chlorinated compounds found.

Solorina Valley: samples SV-R3 and SV-L4 (Table 1, entries 17 and 18) were collected in poorly accessible, rugged terrain, which consists of the systems of moraines, rock glaciers, small ponds, and short streams. Sample SV-L5 (Table 1, entry 19) was taken from the lake near the shoreline. Melt water stream flows by the lake (sample SV-L5) into the drainage basin where an Argentinean annual summer camp is located. However, signs of the human presence are rather rare comparing to other parts of the James Ross Island. While the lake sediments (SV-L4 and SV-L5) had very low PAH contaminations, the river sediment contamination level was almost 1.5 orders of magnitude higher. PCB and OCP levels were similar to the other sampling sites (SV-R3, SV-L4, and SV-L5, Figs. 3 and 4).
Begtson Cliffs consists of a beach fringed with coastal cliffs abraded by a wave action. The sample BC-M2 (Table 1, entry 20) was taken below the line of a high tide. There is a biological material washed out by waves and tidal currents. Begtson Cliffs is an undisturbed area without human influence, however, the sediment sample showed similar PAH concentrations as well as very similar levels of PCBs and OCPs as the marine sediments from the northern shore (BC-M2).

4. Discussion

A prevalence of lower-mass PAH compounds (phenanthrene and fluoranthene), less chlorinated PCB congeners (the pattern dominated by tri- and tetrachlorinated congeners) as well as other more volatile chemicals as HCB in the soil and sediment samples indicates that the long-range atmospheric transport is the most probable source of contamination in the James Ross Island. However, the soil samples from the Whisky Bay area showed a different pattern with a higher amount of less volatile PAH compounds indicating a presence of local sources of pollution. Similarly, the river sediment sample from the same sampling area as well as one of the sediment samples from the Solorina Valley showed the same results. Contamination with the chlorinated compounds seems to be more uniform; only the northern regions (Lachman Cape) exhibited a higher concentration ratio of the more chlorinated PCBs than the rest of the island. Higher POP levels in the matrices collected from northern and western parts of the island also generally support the hypothesis of the long-range atmospheric transport of POPs to the Arctic.

To confirm the atmospheric origin of the soil and sediment contamination, the samples of the ambient air were taken using five passive air samplers exposed along the northern coast of the island (Table 1). The prevailing wind directions at the station are SW, W and NW (total frequency of 68.7%), and E (frequency 16.4%) with the mean monthly wind velocity (January–February 2006) of 6.2 m s⁻¹ (the extreme value was 23.9 m s⁻¹). At the Bibby Point Mesa (sampling site 23), the corresponding values were 6.7 m s⁻¹ and 36.7 m s⁻¹. Passive air samplers of the same design were shown to have the sampling rates between 3 and 7 m³ per day. Meteorological conditions of the James Ross Island, especially the high wind velocities, suggest that the sampling rates can be significantly higher than at the sites of a milder climate.
Since it was not possible to perform the site-specific calibration experiment using co-employed high volume sampler, the results of the analyses are semi-quantitative, giving more information about the pattern of pollution than about the actual air concentrations. Providing the estimated sampling rate of passive air sampling devices was about 10 m$^3$ per day, the air concentrations varied between 1.8 and 4.7 (16.1) pg m$^{-3}$ for the sum of seven indicator PCBs (0.1–7 pg m$^{-3}$ for the individual congeners), 1.5–7.7 pg m$^{-3}$ for γ-HCH, 0.2–0.4 (1.2) pg m$^{-3}$ for $p,p'$-DDT, 0.3–0.9 (2.2) pg m$^{-3}$ for $p,p'$-DDE, 6.3–18.8 pg m$^{-3}$ for HCB, and 2–5 ng m$^{-3}$ of PAHs (16 EPAs). The atmospheric levels of POPs were similar at all sites except for Crame Col (sampling site 21) where the PCB levels several times higher were determined. A similar discrepancy, indicating some point sources, was also observed for DDTs (levels are reported in brackets). Considering the fact that the vicinity of Brandy Bay is the site most frequently visited by research expeditions and some disposal sites were found in this area, we cannot exclude some local contamination source. The passive air sampling campaign of the same design was repeated in January 2007 with similar results: 0.8–3.4 (26.1) pg m$^{-3}$ of seven indicator PCB congeners, 2.2–4.4 (11.5) pg m$^{-3}$ of γ-HCH, 0.05–0.5 (1.3) pg m$^{-3}$ of $p,p'$-DDT, 0.1–0.8 (3.2) pg m$^{-3}$ of $p,p'$-DDE, 12.6–24.3 pg m$^{-3}$ for HCB, and 0.2–2.4 ng m$^{-3}$ of PAHs. Higher atmospheric contamination of the Crame Col site (in brackets) was confirmed. Our estimation of the air concentrations is consistent with the previous atmospheric measurements (Larsson et al., 1992; Dickhut et al., 2005). Larsson et al. (1992) have been monitoring the POP concentrations in the lower atmosphere of the James Ross Island for two years and found the mean concentrations of 15.2 pg m$^{-3}$ for PCBs, 2.0 pg m$^{-3}$ for $p,p'$-DDT, 1.0 pg m$^{-3}$ for $p,p'$-DDE, and 25.8 pg m$^{-3}$ for lindane. Dickhut et al. (2005) reported the concentration between 0.02 and 2.98 pg m$^{-3}$ for lindane, and up to 32.1 pg m$^{-3}$ for HCB.

The atmospheric POP concentrations are, therefore, most probably responsible for contamination of the soils and sediments. Highly populated areas of Africa, South America, and Australia can be a source of POPs to the region. Southern Shetlands, with the high density of Antarctic stations, may be another potential source area. A seasonal application of lindane in the corresponding tropical regions, together with its higher vapor pressure, may account for its higher concentrations in the atmosphere as well as in the solid matrices. Similarly, DDT is still extensively used in the Southern Hemisphere. Prevailing western and north-western wind directions can explain elevated POP concentrations in the Whiskey Bay which is a most western part of the island.

5. Conclusions

Current levels of persistent organic pollutants in solid environmental matrices and the atmosphere of James Ross Island were determined in 2005. The influence of previous scientific expeditions operating in the island on its fragile environment was found negligible. Since a new polar station was completed in James Ross Island in February 2006, it also means that our results can serve as an initial point for the evaluation of an anthropogenic impact of new research station in following years. First scientific expedition arrived to the station in early 2007. Repeated atmospheric, soil and sediment contamination measurements as well as some moss, lichen and biota sample analyses will be performed in accord with the scientific program of the station, and they will provide additional information on the impact of various anthropogenic activities in the pristine Antarctic region.

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