

Evaluation of the contamination, distribution of POP in contaminated soils of Antarctica (King George Island)

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Persistent organic pollutants were analyzed in soil samples collected at King George Island, South Shetland Islands, in the Antarctica. The pollutants whose concentration were determined were PCB (CB 26, CB 52, CB 101, CB 118, CB 138 and CB 180) and PAH (acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, indene(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene). Total PAH concentration reached 936 ng/g and were found near the research stations. Total PCB concentration reached 178 ng/g. The single congener whose concentration was greatest was CB 118, presenting a concentration of 77,5 ng/g in one of the samples. The sites with higher PCB concentrations had a distribution of congeners similar to those obtained near the research facilities suggesting that these facilities could be the main source of these POPs.

Keywords: Antarctica, King George Island, PAH, PCB

1 – Introduction

Despite its remote location, Antarctica is affected by human activity, due to pollution and the introduction of exotic species in this sensitive ecosystem (Island et al. 2012). King George Island is part of South Shetland archipelago, being the most northern, more temperate, and the most densely populated (Martins et al. 2010). Over one hundred years of human presence in the Antarctic has inevitably led to anthropogenic contamination, particularly near scientific research stations, where fuel and waste spills are common. (Webster et al. 2003) Pollutants can result from local sources or from long range atmospheric transport – (LRAT). (Cabrerizo et al. 2016) According to LART, pollutants can be volatilize in more

temperate regions to later condense at areas with lowest temperature (Wania and Mackay 1995). The low temperature and high precipitation in the South Shetland islands cause the deposition of atmospheric pollutants (Cabrerizo et al. 2016). Pollutants such as polycyclic aromatic hydrocarbons – PAH – and Polychlorinated Biphenyls – PCB – have been detected all over the globe, including in Antarctic regions (Taniguchi et al. 2009). Studies near abandoned and functioning scientific basis have identified PAH and PCB contamination hotspots, indicating human contamination (Zhang et al. 2013). PCB have been detected in the Antarctic since the 60', (Montone, Taniguchi, and Weber 2003) up to the present day, despite PCB production prohibition in the

1970' (Wolschke et al. 2015). PAH are carbon and hydrogen molecules, composed by two or more aromatic rings, and can have anthropogenic or natural origin. (Alexander et al. 2008) Anthropogenic sources include combustion and oil and fuel spills. (Alexander et al. 2008) (Tobiszewski and Namieśnik 2012) (Dauner et al. 2015) PAH can be highly toxic to organisms due to their carcinogenic properties and mutagenic potential. (Martins et al. 2010)(Dauner et al. 2015) PAH molecules can travel large distances when associated with particles, (Lima et al. 2016), although PAH presence in remote locations such as the poles is usually an indicator of anthropogenic contamination. (Stortini et al. 2009) accidental fuel spills are the more common source of PAH in these locals. (Montone et al. 2016) (Martins et al. 2010).

2 – Sampling and methods

2.1 – Sampling

Soil samples were collected in Fildes Peninsula, King George Island, as described by Ana Padeiro, in February 2014. (Padeiro 2014). 82 soil samples were sampled in Fildes Bay, and 3 near Collins Glacier. The samples were collected at a maximum depth of 10 centimeters, using decontaminated material. Figure 1 represent the sampling locals, except the reference ones.

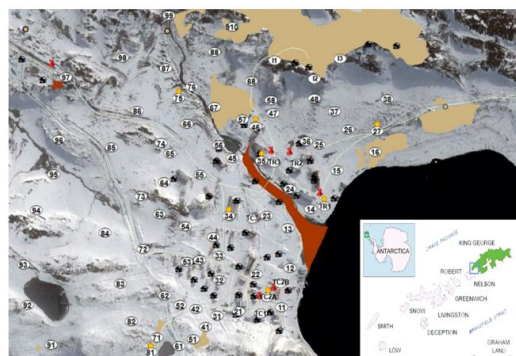


Figure 1 – Map whit 79 of the 82 sampling locations. Also representing an area contaminated whit oil spillage (dark orange) and residue deposition locals (brownish grey)

2.2 – Extraction of POPs

Prior to extraction, the soil samples, that had been frozen to -18°C were defrosted and dried at a temperature of 40°C for 48 hours, to eliminate humidity. After the drying stage, the soil samples were grounded and sifted to homogenize the granulometry (metal mesh sieve, 1mm, RETSCH).

The PCB were extracted *via* soxhlet, for 17 hours, with hexane. In this method around ten grams of soil are consumed per extraction. The hexane later reacts with copper, in order to eliminate sulfur. After the copper (fine powder copper, by MERCK) treatment, the hexane is processed through 2,47 grams of 1% hydrated florisil (florisil by MERCK) column. After the chromatographic column, the hexane is treated with sulfuric acid (95-99% *pro analysis* sulfuric acid, by MERCK) to eliminate organic molecules. The hexane is transferred to an analysis vial and proceed to a chromatographic column (Agilent J&W Scientific, model Dura-Bond-5, internal diameter of 0,250 mm, film thickness or $0,25\ \mu\text{m}$ and length of 60 meters), followed by an ECD detector (Agilent Technologies, model 6890N).

The PAH were extracted with an accelerated solvent extractor (ASE model ASE 200, by DIONEX). In this method, around five grams of soil are accommodated in special cells. Prior to extraction, 2 mL of an internal standard are added (Semi-volatile Internal Standard Mix, by SUPLECO Analytical). The ASE equipment heats the cells up to 100°C and pressures the cell to 1500 PSI. The pressurized soil is extracted with a mixture of 50:50 hexane (n-Hexane SupraSolv by MERCK and n-Hexane ROTISOLV® by ROTH) and acetone (Acetone ROTISOLV® by ROTH) for 20 minutes. The mixture is treated with copper, like in the PCB extraction. The mixture proceeds to chromatography columns of eight grams of silica gel (Silicagel 100 by MERCK) topped with eight grams of aluminum oxide (Aluminum oxide 90 active neutron, by MERCK). After processing through the column, the mixture is treated with sulfuric acid, again, like in the PCB extraction. The hexane is transferred to an analysis vial and proceeds to a chromatographic column (Agilent J&W Scientific, model Dura-Bond-5, internal diameter of 0,250 mm, film thickness of 0,25 µm and length of 30 meters), followed by an MS detector (Trace CG Ultra, by Thermo Electron Corp).

2.3 – Quality control

To ensure quality control, one blank sample was analyzed for every nine PCB extractions and one for every eleven PAH extraction. The blanks presented concentration values within the values accepted by the laboratory.

The precision of the analysis varies from 10-20% for PCB. For PAH the precision is inferior, 40%.

3 – Results and discussion

3.1 – PCB

The sum of the different congeners analyzed (tPCB) ranged from below the detection limit to a maximum of 187,74 ng/g.

PCB concentrations determined by other authors were much smaller than those reported in this work. Klánová et al. (2008) determined a maximum concentration of 1,82 ng/g of PCB (sum of seven congeners) in soils from James Ross Island – a concentration 100 times smaller than the highest concentration of tPCB reported in this paper. (Klánová et al. 2008)

In six sampling sites reported tPCB higher than 10 ng/g of dried soil, being in two of them higher than 100 ng/g. Table 1 presents the different congener and tPCB concentrations in these samples, as well as in the reference site collected samples (C1, C2 and C3) These five samples presented different congener compositions, as showed in Figure 2, but most presented high concentrations of heavier PCB: in four of these samples, CB 153, CB138 and CB180 presented over 60% of their composition, being CB 153 and CB 138 hexa-chlorate compounds and CB 180 hepta-chlorate.

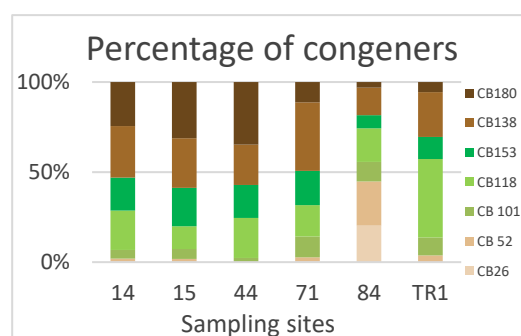


Figure 2 - Percentage of PCB congeners in the six most contaminated samples

Half of these locations (14, 15, 44 and TR1) are near the research stations, suggesting the anthropogenic origin for this contamination. The six more contaminated sites presented compositions similarly enrich in heavier congeners. PCB were commercialized as fluids whit many uses (Montone, Taniguchi, and Weber 2001). One of these fluids was Aroclor 1260 (Mayes et al. 1998) that is mostly composed by congeners detected in this work (CB 101, CB 153, CB 138 and CB 180) (Obaid M. Faroon et al. 2003). It has been proven that more chlorinated congeners can degrade and originate less chlorinated congeners. (Demirtepe et al. 2015) This Aroclor fluid may be, therefore, the source of the PCB detected from an old accidental spill.

tPCB ranged from 1,00 to 1,19 ng/g on the tree reference samples from Collins Glacier. Values of this magnitude had already been reported by Klánová et al. (Klánová et al. 2008), while other values were lesser than the reported ones (Fuoco et al. 1996) (Vecchiato et al. 2015). These samples where not enrich in heavier PCB as some of the more contaminated samples, instead most presented less than 40% of hexa and hepta chlorinated congeners in their composition

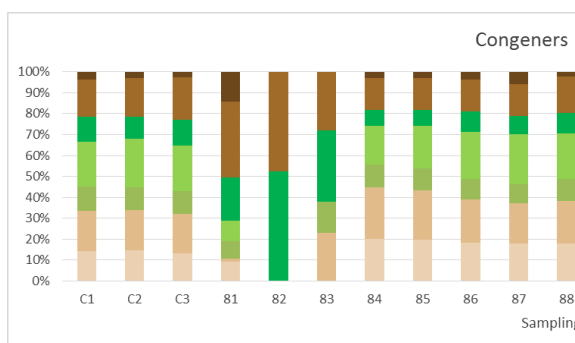


Figure 3). The composition from the reference samples is similar to most of the

periphery soil samples. (samples 81 to 88, 91 to 99 and 910) suggesting the same origin for the contamination on all these samples. Noticeably, sample 84, one of the most contaminated, presented a distribution of congeners compatible whit the ones from the reference sites. This could instead indicate that either site 84 could be the source of the pollution, or that there are two sources, whit similar PCB distribution. Some of the samples present a much different percentage of congeners (sample 82, 83 and 97), but that is due to very low concentration of PCB in the sample, and as such the concentration was below the detection limit.

Table 1 - PCB concentration in the control samples (C1, C2 and C3) and in the six most contaminated samples (#14, #15, #44, #71, #84 and TR1) (ng/g of dried soil)

Sample	Concentration of CB and tPCB (ng/g of dried soil)							
	26	52	101	118	153	138	180	Total
C1	0,15	0,20	0,12	0,23	0,13	0,19	0,04	1,06
C2	0,17	0,23	0,13	0,27	0,13	0,22	0,04	1,19
C3	0,13	0,19	0,11	0,22	0,13	0,20	0,03	1,00
14	0,06	0,21	0,69	3,10	2,57	4,07	3,46	14,17
15	0,09	0,77	2,52	5,83	9,84	12,77	14,40	46,22
44	0,06	0,00	4,38	41,67	34,23	42,23	65,18	187,74
71	0,05	0,34	1,67	2,51	2,73	5,49	1,62	14,41
84	2,88	3,49	1,52	2,66	1,04	2,17	0,43	14,19
TR1	0,13	6,70	17,69	77,55	21,92	44,20	10,11	178,30

The adsorption of PCB in sediments is favored by the presence of organic carbon (Larry W. Robertson 2001). The concentration of the different congeners and the tPCB were plotted, but there was no significant correlation found ($P > 0,01$). This result can be due to the low organic carbon content of the soil.

3.2 – PAH

The sum of the total PAH compounds (PAH_{total}) reached the top value of 936,51 ng/g. Due to technical problems, not all the

soil samples were analyzed. Thus, only 57 soil samples were analyzed. Yet, of these, only four locations presented PAH_{total} above 100 ng/g of dried soil (samples #21, #32, #34 and #44). The PAH_{total} levels were less than 10 ng/g in 33 of the soil samples. In all samples analyzed, the PAH with 2, 3 and 4

aromatic rings represent more than 60% of the composition of all samples, the remaining being compounds with 5 and 6 aromatic rings. In fact, these heaviest molecules, were not detected in some of the samples.

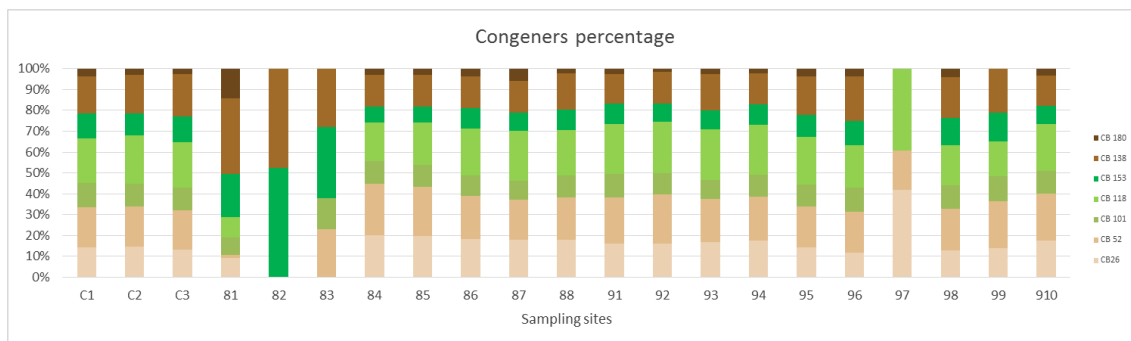


Figure 3 - Percentages of PCB congeners in the reference samples and in samples from the periphery of the local analyzed

Soils with concentrations of PAH similar (Webster et al. 2003) and higher (Curtosi et al. 2007) than those reported in this work had been detected in location in the Antarctic.

One way of determine the origin of PAH is the calculation some isomers ratios (Stortini et al. 2009)(Yunker et al. 2002)(Tobiszewski and Namieśnik 2012). Three ratios can be used are the ratio of isomers of molecular mass (MM) 202 of fluoranthene (FL) and pyrene (PY) ($FL/(FL+PY)$), MM 276 of indene(1,2,3-cd)pyrene (IN) and benzo(g,h,i)perylene (IN/(IN+BPE)) and MM 178 of anthracene (A) and phenanthrene (P) ($A/(A+P)$). PAH are always emitted as a complex mixture (Yunker et al. 2002), but relative concentrations can characterize different sources (Tobiszewski and Namieśnik 2012). By using isomers, the compounds have similar properties, and similar degradation processes, thus allowing for a larger time frame to evaluate the source or the contamination without losing

information. Yet the ratio of MM 178 is susceptible to information loss due to different degradation rates (Yunker et al. 2002). The ratio MM 276 is also prone to some information loss, since BPE photolically degrades faster than IN, leading to higher ratio values as the sample ages. The most viable ratio is MM 202. (Tobiszewski and Namieśnik 2012) the overlapping of different contributions to the PAH source can result in contradicting ratio conclusions. Hence diagnostic ratios should be used as a confirmation of a source rather as identifiers(Tobiszewski and Namieśnik 2012) (Yunker et al. 2002), as they will be used in this case.

MM 202

This ratio can identify three possible origins: petrogenic, combustion of liquid fossil fuel, or combustion of coal or wood. (Yunker et al. 2002) (Martins et al. 2010). The application of the ratio suggests that all these contributions are present. A outer crown of coal

combustion is present, along with scattered contributions of petrogenic origin and liquid fuel contributions.

MM 276

This ratio can identify the same sources than the MM 202 ratio, but the compounds needed to calculate this ratio were not detected in many of the samples. According to this ratio, almost all of the PAH have origin in the combustion of fossil liquid fuels. The locals are scattered and are not concordant to the conclusions of the MM 202 ratio.

MM 178

This ratio can only distinguish between petrogenic and pyrogenic contributions. Again not all samples presented the compounds needed for the calculation of the ratio. This ratio identifies one zone of petrogenic contribution near the research facilities and a zone of pyrogenic contribution in a periphery zone. Again not all results are concordant with the ones from the previous ratio.

There was a report of an accidental spill, but the ratios did not confirm petrogenic origin for the PAH detected in the locals around the spillage area.

The lack of consensus amongst the diagnostic ratios suggests a mixture of different PAH sources. Yet they seem to indicate a petrogenic source of PAH near the research facilities and buildings and a pyrogenic source of PAH in the periphery.

There have been reports of soils with similar concentrations of tPAH in Porter peninsula (12 to 1189 ng/g) (Curtosi et al. 2007)

4 – Conclusions

Although the tPAH concentrations are similar to those determined in other researches (Curtosi et al.), tPCB concentrations are higher than others determined in Antarctica (Klánová et al.).

The more polluted sites in terms of PCB contamination are probably due to small leaks in old equipment using Aroclor fluids, in particular Aroclor 1260. In these sites the heaviest congeners are predominant in the opposite of the periphery sites including the reference sites.

The higher values of tPAH were detected near research facilities, suggesting that a possible source would be accidental fuel spills and exhaust gas from motors and generators.

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