DO PENGUIN CONCENTRATE PERSISTENT TOXIC SUBSTANCES IN THEIR BREEDING COLONIES?

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Introduction

The poles are remote areas, far from human settlements; however, many scientific studies identify the presence of persistent toxic substances (PTS) in those environments. The long range atmospheric transport (LRAT) is considered to be the most important dispersion form of these compounds and subsequent contamination of these regions[1].

Another important form of contamination to these environments occurs through biological transport. When large groups of migratory species gather in reproductive colonies or in spawning events, they eliminate PTS accumulated during their migration to lower latitudes. In some regions, contamination promoted by biological transportation might be much greater than contamination caused by LRAT. Studies indicate that reproductive colonies of marine birds in the Arctic region have soil that are 10 to 60 times more contaminated by HCB and DDT, respectively, than soil that is not inhabited by birds[2].

In the Arctic, concentrations of PTS show a higher order of magnitude than concentrations found in the Antarctic, and studies show that these values are stable or declining. However, at the South Pole, the contrary is being observed – increasing concentration values[3].

The great reproductive concentrations in the Antarctic region are formed by endemic species, such as penguins. In the summer months, they always return to the same nesting sites for about four months and form colonies with up to thousands of offspring. In spite of the fact that they do not spend the winter months in regions more contaminated outside the polar circle, these birds may bio-accumulate PTS that reach the Antarctic region by LRAT. Estimations predict that the quantity of guano deposits in the most populous penguin colonies might reach 10 kg/m^2 per year. This might promote the formation of pollution hot spots.

The present study analyzed the soil of penguin rookeries of the following species: *Pygoscelis papua* (Copacabana), *P. adeliae* (Arctowski), and *P. antarctica* (Chabrier Rocks). All of these species are restricted to the Antarctic region. Although the three species diet varies according to region, they mainly feed on krill (*Euphasia* sp.) and small fish (*Pleuragramma antarcticum*). Some of their characteristics may contribute to form different profiles of pollutants in the organism, and consequently in their penguin colonies. For example, *P. papua* begins the reproductive period earlier and spends more time upbringing its young ones (72 days), whereas *P. antarctica* is the species that begins reproduction later, and spends less time to up bring their young ones (52 days). Also, they have varying sizes - *P. papua* is the bigger and heavier (81 cm and 8.5 kg), while the *P. adeliae* species is smaller and weighs less (70 cm and 6.5 kg).

The aim of this study is to evaluate the influence that penguins have on the concentration of PTS in their rookeries, provide a variation of the contamination profile of the different species, and identify the influence of snow melting and summer rain showers on the PTS concentration and distribution on the rookeries.

Materials and methods

Samples were collected from penguin rookeries at the Admiralty Bay, King George Island, South Shetland Archipelago (62°05'0"S, 58°23'28"W). Due to its diverse character part of the bay, comprising the Arctowski and Copacabana rookeries, is considered an Antarctic Specially Protected Area (ASPA 128). This region has a humid climate with temperatures being 0 °C and higher during summer months. During this period, rains and cyclones also occur, which cause the air to be warm and humid.

Samples were collected in early summer (December) and late summer (February and March) of 2011, at three different locations in each species rookery: at the upper part, with very little penguin movements; at the rookery; and below the rookery where penguins pass on their way to and from the sea. Soils with no penguin influence (WPI) were also collected. Samples were freeze-dried, sieved through a 1000 mm sieve to remove stones and other large debris, and homogenized. Ten grams of each soil sample were extracted with dichloromethane and n-hexane in a soxhlet apparatus for 8 hours. Clean up was performed with a desulfurization column and a second column filled with sodium sulfate, acid silica, and activated alumina. Analyte detection and quantification was

performed with a gas chromatograph coupled to an electron capture detector. The temperature program and additional methodology details can be found elsewhere[4]. For statistics, the data normality Shapiro-Wilk's W test showed that data are non-parametric, so the Mann-Whitney U test and Spearman correlation test were used. The significance level used were $P < 0.05$. The following PTS were quantified: PCB 8, 18, 28, 44, 52, 66, 81, 101, 105, 114, 118, 123, 126, 128, 138, 153, 156, 157, 164, 167, 170, 180, 184, 187, 195, 206 and 209; α, β, γ and δ hexachlorocyclohexane (HCHs), α-endosulfan (Endo-I), β-endosulfan (Endo-II), hexachlorobenzene (HCB), p,p'-DDT, o,p'-DDT, p,p'-DDE, o,p'- DDE, p,p'-DDD, o,p'-DDD, trans-chlordane, cis-chlordane, oxychlordane, heptachlor, heptachlor-epoxide aldrin, dieldrin, endrin, isodrin, metoxichlor and mirex.

Results and discussion:

All the samples contained PCBs and contamination that originated mainly by congeners with two to five chlorine atoms. The congeners with seven or more chlorine atoms practically were not present in the samples. They always appeared at low concentrations - no more than 180 $pg.g^{-1}$ (figure 1). The PCBs with up to five chlorine atoms responded for 94% and 87% of the contamination of WPI and rookery soils, respectively (figure 1). The WPI soils showed concentrations that were greater ($P = 0.0434$) than rookery soils (table 1). When the difference among the concentrations of all congeners was examined individually for these two groups, WPI and rookery, the difference ($P < 0.05$) only was seen for the congeners with five or less chlorine atoms. No significant difference was observed in the following comparisons: between the rookery soils for each species; between the soils collected from the different regions of the penguin colony; or between the soils collected in early or late summer period.

Table 1 – Samples grouped by collection site, WPI (without penguin influence) and rookery (AR - Arctowski, CO - Copacabana and CR – Chabrier Rock), and by collection period (E – early summer, L – late summer), with median values and standard deviation of concentration ($pg.g^{-1}$ d.w.) for the compounds measured. Sample number (n). Minimum, maximum and median values for all WPI and all rookery samples.

Samples	∑PCB	∑DDT	HCB
Without Penguin Influence			
WPI-E (2)	2,953.5 ± 2,681.7	694.4 ± 848.0	45.5 ± 64.2
WPI-L (4)	3,748.3 ± 843.5	400.6 ± 730.5	90.1 ± 9.8
min-max	1,057.2 - 5,237.5	94.7 - 1,834.5	0.0 - 103.8
median	3,868.9	400.6	88.1
Rookeries			
AR-E (11)	1,486.3 ± 1,735.0	481.3 ± 977.0	78.5 ± 45.4
AR-L (5)	1,037.4 ± 1,030.9	112.3 ± 265.6	65.3 ± 60.1
CO-E (10)	1,911.8 ± 981.1	360.6 ± 170.5	67.1 ± 40.6
CR-E (10)	1,860.3 ± 988.2	540.6 ± 232.9	54.1 ± 76.6
min-max	12.4 - 5,955.5	0.0 - 3,346.1	0.0 - 195.2
median	1,594.3	360.6	64.4

With the exception of one[4], the remaining studies determined that the concentrations of PCB in the Antarctic soils found a PCB profile, where congeners with up to five chlorine atoms [5, 6, 7, 8, 9, 10, 11] predominated. The atmospheric transport and deposition is considered to be the main source of PTS in the Antarctic region. This promotes a contamination profile according to compounds volatility, as is explained by the effect of global distillation that promotes a separation of compounds by evaporation, transportation over great distances and condensation at different temperatures[12]. The profiles of PCB found in this current and past studies confirm that atmospheric transportation is a major source for contamination of the Antarctic region.

All the samples were contaminated with organochloride insecticides (OC), with DDT, and HCB -contributing to the major part of contamination. When all of the OCs were compared, the WPI soils showed greater concentrations ($P = 0.0419$) compared to the soils of penguin rookeries. In the individual analysis, only heptachlor ($P = 0.0294$), heptachlor-epoxide a ($P = 0.0039$), heptachlor-epoxide b ($P = 0.0039$), o,p'-DDE ($P =$

0.0188), o,p'-DDD (P = 0.0283), β-endosulfan (P = 0.0024), cis-clordano (P <0.001) and dieldrin (P = 0.0373) presented higher concentrations in the WPI areas.

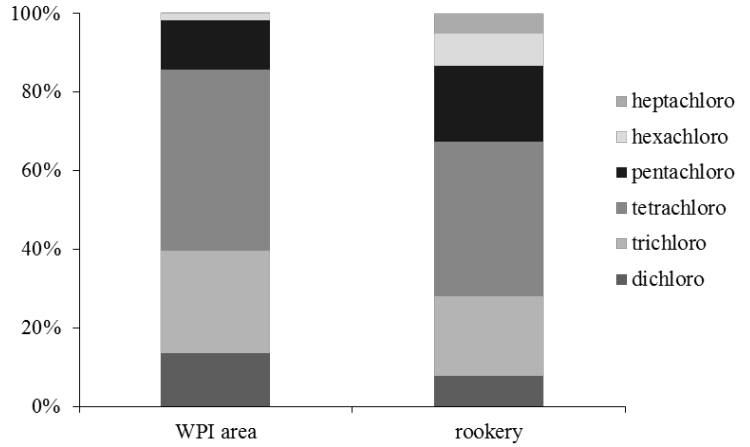

Figure 1 – Percentage of the contribution of the PCB congeners, according to their chlorination degree, to the WPI (without penguin influence) and rookery soil total contamination.

When levels of p,p'-DDE and endrin concentrations were compared dependent on region of the rookeries, levels were found to be higher (P = 0.0341 and P = 0.0237) in the lower region of the rookeries than the region above them. Chabrier Rocks had the highest concentration of oxichlordane (P = 0.0138), p,p'-DDE (P = 0.0317) and p,p'-DDT (P = 0.0349), when compared to Copacabana, and of β-HCH (P = 0.0062) and endrin (P = 0.0075) when compared to Arctowski. When comparing the concentrations of the pesticides in the sampled soils in the middle (December) and at the end (March) of the reproductive period in Arctowski, a significant difference was found for p,p'-DDT (P = 0.0474) and oxichlordane (P= 0.0417). The concentrations of the pesticides were higher at the end of the season. The comparison between soils collected above, in and below the rookery showed significant differences for HCB in Copacabana (P = 0.0500). They were more contaminated in the rookery than below it. Similar results were observed in Chabrier rocks. There was more contamination of p,p'-DDE and endrin (P = 0.0357) below the rookeries than in the rookies (P = 0.0179).

The rate of 0.52 for p,p'-DDE/p,p'-DDT indicates a recent contamination of the Antarctic environment by DDT. Similar rate (0.32) was found by another study[5], in soils free from the influence of birds and humans. However, other reports[6, 10] found rates of 3.3 and 55.2 indicating that the majority of the DDT was degraded into p,p'-DDE, and a former contamination.

It is estimated that 28,200 tons of dicofol were produced and used between 2000 and 2012[13]. From this amount, approximately 2.2 tons reached Antarctica, which could explain the low p,p'-DDE/p,p'-DDT rate observed in the present study.

The median ∑DDT concentrations found in this study are intermediate when compared to concentrations found in other sites that have no penguin influence (9, 136, 702, 905 and 2,095 pg.g^{-1})[4, 6, 10, 5, 9]. Levels are also low when compared to values found in other rookeries (605, 625 and 7,185 pg.g^{-1})[4, 6, 5]. The determination of the contamination level of environmental samples is subjected to many different variables (collection site and period, analytical method, and congeners or isomers chosen for analysis), which makes the comparison of data from different studies difficult to make and at times inappropriate.

HCB concentrations found in the WPI soils and in the rookeries soils are small (88 and 64 pg.g^{-1}). They are in accordance with concentration levels found by other studies[4, 5, 7, 10]. These results show that the contamination level in Antarctica soils is low, have no difference in the concentration of these pollutants between the WPI and rookery soils. However, HCB showed higher levels of contamination than PCBs at the fatty tissue of penguins[14, 15], indicating that these compounds reach Antarctica at bigger proportions than those observed in the soils. Because of its elevated volatility, HCB enters the atmosphere shortly after it is released to the environment. Even at high latitudes or altitudes, after condensation and deposition, it does not stay in the soil for a long period, which leads to it volatilizing and returning to the atmosphere[7]. The low levels of contamination found in the analyzed soils corroborate this behavior.

The results of this study were contrary of what was expected and of what has been reported by prior studies about the contamination caused by guano accumulation[2,4,5,6,7]. Our expectation and what has been previous reported is higher PTS concentrations in the soil of rookeries.

Although not promoting an increase in the concentration levels of PTS in its reproductive sites in relations to the levels found in WPI soils, it is possible to detect some influence of the penguins in the rookery soil concentration and profile of contamination. The *Pygoscelis antarctica* rookery (Chabrier Rocks) had higher concentration of some OC when compared to the other two species. This result is corroborated by studies that detected higher DDT and HCB levels in the eggs of *P. antarctica*[17]. The higher contamination level of the *P. Antarctica* might be explained by the fact that this species is the last one to start the breeding season. This means that it stays longer in the water swimming and feeding while the ice and snow is melting and releasing once trapped contaminants to the water. At the same time the other two species are already building their nests and in their fasting period[16].

Despite the ∑DDT concentration been higher at the WPI sites, the rate of p,p'-DDE/p,p'-DDT was higher at the rookeries. In addition, only 6% of the ∑chlordane was composed of oxichlordane at the WPI soils with comparison to 19% at the rookeries soils. The difference indicates that these compounds are being degraded by these birds

At Chabrier Rocks, p,p'-DDE and endrin were more concentrated below the rookery. At Copacabana, HCB had higher concentration levels below the rookery. This distribution pattern suggests adduction of the pollutants by the snow melting and/or summer rains. It can also suggest action of penguins moving around, which leads to loosening of the soil and favoring adduction to lower regions and/or into the sea.

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