PENGUIN COLONIES AS SECONDARY SOURCES OF CONTAMINATION WITH PERSISTENT ORGANIC POLLUTANTS

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Abstract

Levels of several organohalogenated pollutants, such as p,p'-DDE, HCB, CHLs and PCBs, were 10 to 100-fold higher in soil samples collected from penguin colonies than in soil from reference areas. This is likely related to local penguin activity, such as a higher abundance of guano and the presence of bird carcasse. While background contamination of the Antarctic region is mostly explained by the long-range atmospheric transport, this paper suggests that bird populations contribute also substantially to the local redistribution of contaminants.

Introduction

Long-range atmospheric transport (LRAT) from the production and application regions is the main supplier of anthropogenic organic pollutants, such as organochlorine pesticides (OCPs), polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs), to Antarctica[1-3]. Their persistence and ability to volatilise result in the transport of these contaminants to remote areas, far from places where they were used or emitted[4,5]. Deposition occurs mostly in colder regions, such as the polar regions[6]. However, other sources of contamination to remote polar regions, namely human activities[7,8], transport by migratory sea birds[9] or local bird activities[10], have recently been identified. Levels of organic pollutants in lakes with seabirds were 10-60 times higher than in lakes with no visiting bird populations[11].

The present study aims at investigating the hypothesis that Antarctic birds may be an efficient vector for transport and redistribution of contaminants, and that concentrations of POPs in Antarctic soil may be locally elevated due to bird activities. If so, this would indicated that in Antarctica biological activities may spatially redistribute contaminants and associated risks.

Materials and methods

Sample collection. Soil samples were collected at Hop Islands, in the Rauer Island group near the Australian base Davis (68˚50'S, 77˚42'E) in January 2004. Five soil samples were collected in each of three penguin colonies (identified as C1, C2, C3), and from three reference sites (R1, R2, and R3)s, away from any penguin activities. The upper 2 cm were collected with a large stainless steel spoon and kept in aluminum foil. The samples were stored in a snow-drift before they were transported to a freezer at -20 ˚C. Before analysis, the samples were thawed, dried at room temperature, sieved through a 1000 µm sieve to remove stones and other larger debris, and only the fine soil fraction was used for further analysis.

Analysis. The following PCB congeners (IUPAC no. 28, 52, 99, 101, 105, 110, 118, 128, 138, 153, 156, 170, 180, 183 and 187), hexachlorobenzene (HCB), α-, β-, γ-hexachlorocyclohexane isomers (the sum expressed as 'sum HCHs'), pp-DDE, op-DDT, pp-DDD, pp-DDT (the sum expressed as 'sum DDTs), oxychlordane (OXY), *trans*-nonachlor (TN), *trans*-chlordane (TC) and *cis*-chlordane (CC) (sum expressed as 'sum CHLs'), together with PBDE congeners (IUPAC no. 47, 49, 99, 100, 153, 154 and 183) were targeted for analysis. All OCPs and PCBs standards were bought from Dr. Ehrenstorfer Laboratories (Augsburg, Germany) and PBDE standards were from Wellington Labs (Guelph, Canada).

The analysis method was as described by Covaci et al.[12]. Approximately 20 g of R-samples (reference areas) and 4 g of C-samples (penguin colonies) were spiked with internal standards (PCB 46

and 143, BDE 77 and 128, and ε-HCH) and were extracted during 3 hours by hot Soxhlet with 100 ml hexane:acetone (3:1, *v/v*). The extracts were cleaned-up on 8 g acidified silica (44% H_2SO_4, *w/w*) and analytes were eluted with 15 ml *n*-hexane and 10 ml DCM. The cleaned extract was evaporated until dryness and resolubilized in 100 µl *iso*-octane. One µl cleaned extract was injected in cold pulsed splitless mode into an Agilent 6890 GC connected to an Agilent 5973 mass spectrometer (MS) operated in electron capture negative ionization (ECNI) mode, equipped with a 25 m x 0.22 mm x 0.25 µm HT-8 capillary column (SGE, Zulte, Belgium).

Validation and quality assurance. Multi-level calibration curves ($r^2 > 0.999$) in the linear response interval of the detector were created for the quantification. The identification of POPs was based on their relative retention times (RRTs) to the internal standard, ion chromatograms and intensity ratios of the monitored ions for quantification. The quality control was performed by regular analyses of procedural blanks, by random injection of standards and solvent blanks. A standard reference material CRM 481 (PCBs in industrial soil) was used to test the method accuracy. Obtained values were not deviating with more than 10% from the certified values. The quality control was also assessed through regular participation to interlaboratory comparison exercises for PCBs, OCPs and PBDEs. For each analyte, the mean procedural blank value was used for subtraction. After blank subtraction, the limit of quantification (LOQ) was set at 3 times the standard deviation of the procedural blank, which ensures > 99 % certainty that the reported value is originating from the sample. LOQs for the analysed compounds ranged between 5 and 100 pg/g soil (Table 1). Samples with concentrations below LOQ were calculated as f*LOQ with f being the fraction of samples above LOQ.

Before statistical analysis, all data were log-transformed. An unpaired t-test was used to identify statistically compare differences between averages of the R- and C- groups, p was set at 0.05.

Results and discussion

According to the sampling locations, the 14 samples (one sample was lost during analysis) taken at penguin colonies (C-samples) were expected to contain higher amounts of contaminants (Table 1). The organic carbon percentage was 100 fold higher in C-samples compared to R-samples and was linked to the bird activity, such as droppings and penguin carcasses. This has also been seen in other studies where soil taken near penguin colonies contained up to 27% organic matter[13], with an average of 14%.

Concentrations of several organic pollutants, such as HCB, DDTs, CHLs and PCBs were significantly higher in C-samples compared to R-samples (Table 1). HCB concentrations were 10 times higher in C- than in R-samples. The concentration range in C-samples (116 - 296 pg/g dry weight) is in the same range as other studies (20 - 1070 pg/g soil), where the contamination was attributed also to other factors than atmospheric transport[8]. The C-samples had 70-fold higher concentrations of DDTs than R-samples. DDTs have already been indicated as the most predominant contaminants in Antarctic organisms[14]. The p,p'-DDT/p,p'-DDE, used to assess the time of exposure, was 0.02, 0.03 and 0.06 in the C-samples, suggesting an old DDT exposure. A 120-fold difference was present between CHL in C-samples compared to the R-samples. OXY, TC, TN and CC were present in similar concentrations. PCB concentrations were 120 times higher in C- than in R-samples. PCBs were below LOQ in the reference areas, whereas colony samples contained levels up to 163 pg/g dry weight. Only penta- to hepta-CBs were detectable (tri- and tetra-CBs were < LOQ). We mention that in comparison to other studies (200 - 157 000 pg/g sample) even the C-samples contain low levels of PCBs[8]. If penguin guano is responsible for the increased PCB levels, the contribution of the more persistent congeners due to the metabolism of the lower chlorinated PCBs by the penguins should be relatively high. It is however also possible that C-samples, with higher organic matter, are more effective in absorbing organic contaminants from the atmosphere. If so the PCB-profiles should be dominated by lower chlorinated PCBs, which are more volatile. However, this is not the case, since the persistent PCB congeners dominated the PCB profile (Figure 1) indicating penguins as the main contributors.

The profiles of contaminants in the C-samples closely matched the profiles of contaminants seen in penguin eggs[14,15] or penguin blood[3], with p,p'-DDE being by far the dominant contaminant. Both contamination profiles indicate DDTs as being the most important contributors (23 000 pg/g vs 504 pg/g) and HCHs the least (590 pg/g vs 16 pg/g). This is an additional indication that these contaminants originate from local bird activities. In general, values in penguin eggs are higher than values found in the

soil of the colonies, but it is remarkable that the ratios of these concentrations differ between the contaminants. For example DDTs contribute most in both profiles (penguin eggs and colony samples), but differ by a factor 50 from each other, while CHLs have a significant lower contribution but only differ only by a factor 4. CHLs thus contribute substantially more in the colony samples than in the penguin egg samples. This might be explained by differences in the metabolism and elimination through faeces of various organohalogenated contaminants.

HCHs show the least variation between both groups of samples. Sum HCHs were similar between the penguin colonies (average of 16 ± 11 pg/g sample) and the reference areas (average of 30 ± 18.1 pg/g sample). The dominance of the γ-HCH isomer has already been seen in several studies as it seems to be the most volatile isomer and thus more susceptible to LRAT[6]. The use of HCHs has been limited since 1970, but lindane, consisting of more than 90% γ-HCH, is still used in USA and in several European countries[16]. It appears that the input of HCHs in the soil via penguins is very limited and that this is mostly related to atmospheric deposition.

Table 1. Mean arithmetic concentrations and standard deviations of organic pollutants (pg/g dw) in soil samples collected in penguin colonies (n=14, C-samples) and in reference sites (n=15, R-samples).

Location	**Colonies (C)**			**Reference (R)**			**p[a]**
pg/g dry weight	**C1**	**C2**	**C3**	**R1**	**R2**	**R3**	
N	*5*	*5*	*4*	*5*	*5*	*5*	
% organic carbon	10.8	8.0	7.5	0.12	0.12	0.10	
HCB	**296 ± 57**	**170 ± 59**	**116 ± 55**	**< 20**	**< 20**	**< 20**	**< 0.001**
α-HCH	2	<5	<5	2	4	1	
β-HCH	5	2	6	4	7	1	
γ-HCH	21	6	6	26	36	9	
sum HCHs	**28 ± 24**	**8 ± 0**	**12 ± 9**	**32 ± 21**	**47 ± 33**	**11 ± 0**	**0.032**
pp-DDE	867	607	281	21	3	3	
op-DDT	<100	<100	<100	< 20	< 20	< 20	
pp-DDD	<100	<100	<100	< 20	< 20	< 20	
pp-DDT	21	21	17	< 10	< 10	< 10	
sum DDTs	**888 ± 45**	**629 ± 119**	**298 ± 69**	**21 ± 4**	**3 ± 0**	**3 ± 0**	**< 0.001**
OXY	80	62	40	<10	<10	<10	
TC	114	64	62	<10	<10	<10	
TN	215	121	111	5	3	4	
CC	126	70	69	<10	<10	<10	
sum CHLs	**535 ± 99**	**317 ± 17**	**599 ± 14**	**5 ± 3**	**3 ± 2**	**4 ± 3**	**< 0.001**
sum PBDEs	**< 200**	**< 200**	**< 200**	**< 70**	**< 70**	**< 70**	
Sum tri-CB (1cong)	< 100	< 100	< 100	< 20	< 20	< 20	
Sum tetra-CB (1cong)	< 100	< 100	< 100	< 20	< 20	< 20	
Sum penta-CB (5 cong)	163	91	63	< 35	< 35	< 35	
Sum hexa-CB (4 cong)	105	53	36	< 30	< 30	< 30	
Sum hepta-CB (4 cong)	57	17	15	< 25	< 25	< 25	
Sum PCBs	**328 ± 106**	**161 ± 44**	**114 ± 9**	**< 130**	**< 130**	**< 130**	**0.016**

[a]significance level for differences between C- and R-samples

Evenset et al.[11] compared concentrations of POPs in sediment samples from lakes often visited by migrating birds with corresponding levels in a nearby lake unaffected by seabird colonies and concluded that bird faeces are an important source of POPs in these remote environments. PCB and DDT concentrations were much lower in the uncontaminated sediment samples (14-fold), whereas CHL values varied to a lesser extent (1.5 to 5-fold). Our C-and R-samples showed a similar distribution, but larger concentration differences for PCBs, DDTs and CHLs were observed (200-, 50- and 100-fold, respectively). Concentrations of POPs in the R-samples should be related to LRAT. Concentrations of PCBs in the R-samples were to low to make a discrepancy between higher and lower chlorinated compounds. As previously seen[1], the application of lindane can be the reason for the higher γ- than α-HCH levels observed.

In conclusion, levels of several organohalogenated pollutants, such as p,p'-DDE, HCB, CHLs and PCBs, were considerably lower in soil from reference areas than soil collected from the penguin colonies. This is probably related to the penguin guano, but also to carcasses of dead animals. However, this is different for HCHs. It appears that levels in reference soils are similar to the soils in the colonies, and thus the input of these compounds through penguins is limited. While background contamination of most POPs in the Antarctic region is mostly explained by the long-range atmospheric transport, our results suggest that birds may locally redistribute contaminants on a more regional or local scale, resulting in elevated POP-levels in the soils of colonies.

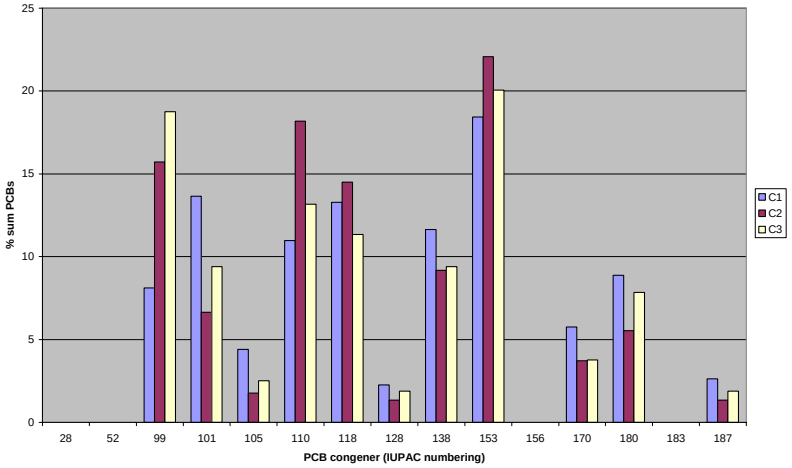

Figure 1. Persistent PCB congeners such as PCB 99, 110, 118 and 153 contribute more to the total PCB content in the colony samples

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