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Trans-nonachlor, octachlorostyrene, mirex and photomirex in Antarctic seabirds

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Abstract: Octachlorostyrene (OCS) and trans-nonachlor (TNC) were detected in cape petrels (*Daption capense*) of King George Island, which tallies with their presence in samples of gentoo penguins (*Pygoscelis papua*) of the Falkland Islands. The detection of TNC in a sample of the Antarctic southern fulmar (*Fulmarus glacialoides*) implies that the Antarctic region has been contaminated by this compound. Mirex and photomirex were also detected in samples of the cape petrels and southern fulmar, as well as in Adélie penguins (*Pygoscelis adeliae*) from Hop Island. The ratios of the mirex and photomirex concentrations in the truly Antarctic species from different locations are similar, which suggests that these compounds are diffusely distributed over the continent. The detection of organochlorine pollutants in Antarctic seabirds is an indication that these compounds have a global distribution. Screening of subcutaneous fat of Antarctic seabirds for organochlorines provides an excellent indication of the occurrence of organochlorine pollutants in Antarctica, and as such an 'early warning' for the global dispersion of these compounds.

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Introduction

Following the detection of DDT compounds in a crabeater seal (*Lobodon carcinophagus*) and Adélie penguins (*Pygoscelis adeliae*) by Sladen *et al.* (1966) there have been several reports on the occurrence of organochlorine pollutants in Antarctic samples (i.e. Hidaka *et al.* 1983, Tanabe *et al.* 1983, Focardi *et al.* 1992, Fuoco *et al.* 1994, Van den Brink 1997b). Data on organochlorine pollutants in Antarctic samples indicate contamination of this environment and as such can act as an 'early warning' for the global distribution of these man-made chemicals (Walton & Shears 1994).

Since concentrations of organochlorines in subcutaneous fat have been shown to correlate with concentrations in other tissues (Van den Brink 1997a), we initiated this study to assess the value of analysis of subcutaneous fat samples of Antarctic seabirds as indicators of the occurrence of unknown organochlorine pollutants at low levels in the Antarctic ecosystem.

Materials and methods

The eight Adélie penguins (*Pygoscelis adeliae*) used in this study were found dead in the summer of 1991–92 around their breeding colonies at Hop Island and Magnetic Island near Davis station (68°33'S 77°54'E). Three failed breeding pairs of cape petrels (*Daption capense*) were collected at Demay Point, near Arctowski station at King George Island (62º09'S 58º29'W) in January 1991. A southern fulmar (*Fulmarus glacialoides*) was found dead at Ardery Island near Casey station (66º17'S 110º32'E).

The birds were dissected under clean lab conditions and the subcutaneous fat analysed for organochlorines with GC-ECD (cf. Van den Brink 1997b) with confirmation and quantification using GC-MS. Compounds were identified on the GC-MS using their mass-spectrum and retention time. For quantification of the different compounds the masses of three ion fragments were summed. The ion fragments with following mass-to-charge ratios were used for the different compounds: OCS: m/z 341, 343, 345, TNC: m/z 407, 409, 411, mirex: m/z 270, 272, 274, photomirex: m/z 270, 272, 274. Standards of mirex, TNC and OCS were obtained from Ehrenstorfer. A standard of photomirex was quantified as the loss of mirex after photo-degradation (UV-light: 254 and 366 nm) for 16 hours.

Results and discussion

Identification of unknown peaks

In Fig. 1 a GC-ECD chromatogram is presented of a typical sample of a cape petrel. In this chromatogram some peaks are numbered for reference. In this sample three unknown peaks (number 2, 3 & 7) are of interest. Peak 7 also occurs in samples of Adélie penguins and peak 3 and 7 in the sample of the southern fulmar. In Figs 2–4 the mass spectra of the three unknown compounds in the subcutaneous fat of a cape petrel are presented.

The mass spectrum of peak 2 (Fig. 2) strongly resembles the mass spectrum of OCS and has an identical retention time. Hence, peak 2 is considered to be OCS.

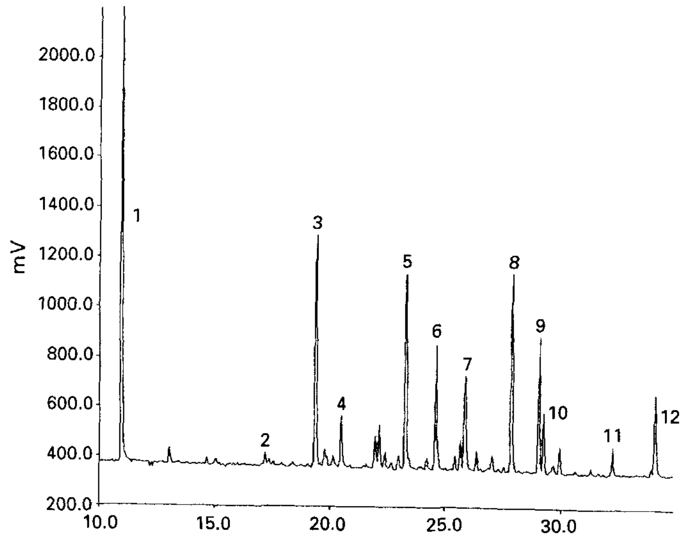

Fig. 1. ECD-chromatogram of subcutaneous fat of a cape petrel. Peaks with the following numbers are identified as: 1: hexachlorobenzene; 4: *p,p'*-DDE; 5: PCB153; 6: PCB138; 8: PCB180; 9: mirex; 10: PCB170; 11: PCB194; 12: octachloronaphtalene (internal standard). Peaks 2,3 and 7 are unidentified so far and discussed.

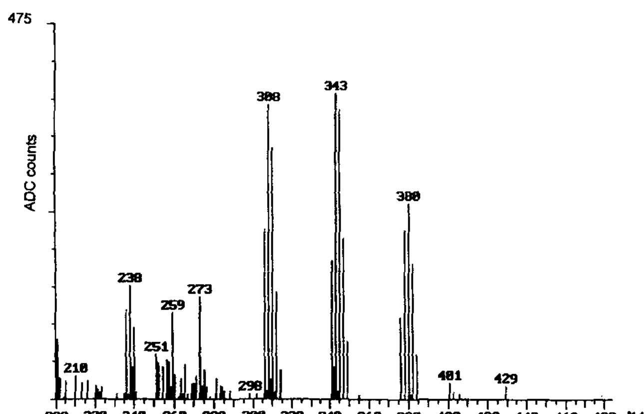

Fig. 2. Mass spectrum of peak 2 in subcutaneous of a cape petrel.

The mass spectrum for peak 3 (Fig. 3) corresponds with the mass spectrum of TNC. However, in the spectrum of this compound the ion fragments with the ratios of m/z 407, 409 and 411 are relatively low compared to the standard for TNC. This is probably due to contamination of the spectrum by the background signal because of the relatively low concentration of TNC. Nevertheless, the retention times of this peak in all samples are identical to the TNC standard. So, peak 3 has been provisionally identified as TNC, and results quantified on this basis.

The detection of OCS and TNC in samples of the cape petrels from King George Island is a confirmation of the detection of these compounds in brains, liver and muscles of

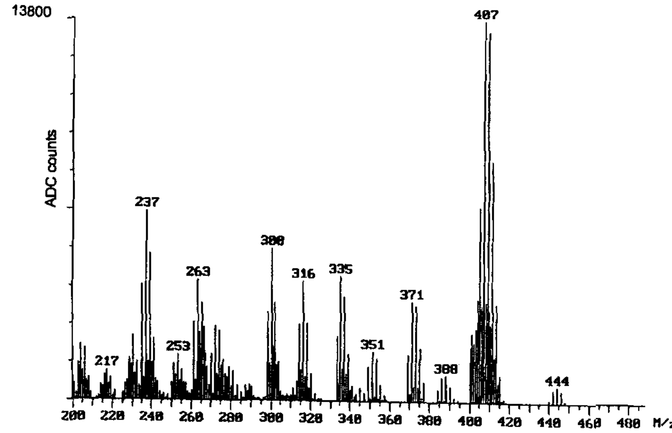

Fig. 3. Mass spectrum of peak 3 in subcutaneous of a cape petrel.

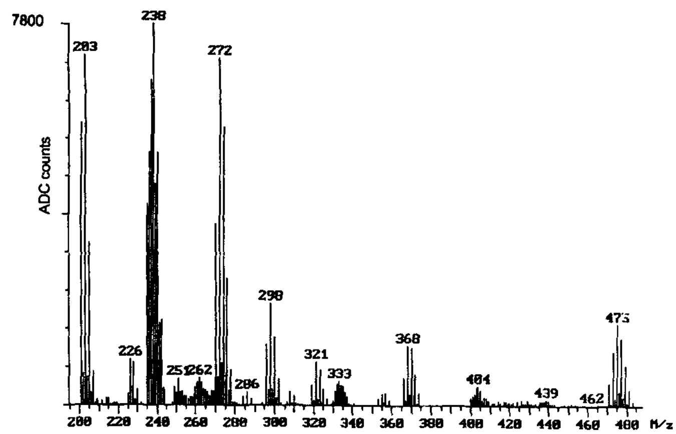

Fig. 4. Mass spectrum of peak 7 in subcutaneous of a cape petrel.

gentoo penguins (*Pygoscelis papua*) from the more northerly Falkland Islands (De Boer & Wester 1991).

Peak 7 (Fig. 4) shows a mass spectrum characterized by the ion fragments with the mass-to-charge ratios of m/z 272 and 475. The former fragment is typical of the spectrum of mirex, but the fragment of m/z 475 is not. The mass spectrum of photomirex strongly resembles that of peak 7 in the sample of the cape petrel. The retention time of photomirex is equal to peak 7, so this compound is considered to be photomirex.

Quantification

The results show the possibility of detection of unknown organochlorines in subcutaneous fat of Antarctic seabirds. In cape petrels the concentrations of TNC are highest of the three species (Table I). In the Adélie penguin no TNC could be detected and the southern fulmar only contained low concentrations of TNC. The latter is remarkable because the sample amount collected from the southern fulmar is small. The concentrations of TNC found in livers of gentoo penguins

Table I. The geometric means (range in between brackets) of concentrations of trans-nonachlor, octachlorostyrene, mirex and photomirex.

	TNC ng g^{-1} fat	OCS ng g^{-1} fat	mirex ng g^{-1} fat	photomirex ng g^{-1} fat
cape petrel (n = 6)	1.7*10^{2} (47–1.9*10^{3})	42 (22–1.0*10^{2})	2.3*10^{3} (1.4*10^{3}–5.2*10^{3})	5.1*10^{2} (2.8*10^{2}-1.4*10^{3})
Adélie penguin (n = 8)	< 0.5	< 0.5	82 (27-1.5·10^{2})	12 (7-21)
southern fulmar (n = 1)	51	< 40	3.0*10^{4}	4.7*10^{3}

caught near the Falkland Islands (De Boer & Wester 1991) are within the range detected in subcutaneous fat of cape petrels in the current study.

OCS was detected in the cape petrels but not in the truly Antarctic species. The OCS concentrations in livers of gentoo penguins are considerable lower than those in the cape petrels (De Boer & Wester 1991). The different tissues that were analysed in the two studies, or the different feeding ecologies of the species investigated may account for the differences in OCS concentrations.

In contrast to the absolute concentrations of mirex and photomirex, the ratio between the concentrations of mirex and photomirex are similar between the southern fulmar and the Adélie penguin. These species are both restricted to Antarctica, but the samples were collected at different locations. Although only one sample of the southern fulmar was analysed, the similar ratios of mirex and photomirex concentrations suggest a correlated distribution of mirex and photomirex in Antarctica.

The ratio of the concentrations of mirex and photomirex found in the cape petrel is lower than in the Antarctic species. This may be explained by the different geographic distribution of the species (Van den Brink 1997b). Ratios found in birds of the Great Lakes in Canada are lower (Sergeant *et al.* 1993) than in the cape petrels. The distribution ranges of the species of the current study are well away from the potential (Alley *et al.* 1973, Sergeant *et al.* 1993). The fact that the concentrations of the degradation product are lower further away from the source is in contrast for what is found for *p,p'*-DDT. It seems that photomirex disperses less easily through atmospheric transport than mirex. This may be related to physical and chemical properties of the compound (Van den Brink 1997b).

Conclusions

The detection of TNC and OCS in the cape petrels of the current study is in agreement with the reported occurrence of these compounds in gentoo penguins of the Falkland Islands (De Boer & Wester 1991). However, the OCS concentrations in the cape petrels in the current study are higher. OCS was not detectable in the species confined to the Antarctic region. TNC was detected in one sample of a southern fulmar which may suggest that this compound has reached the Antarctic region.

Mirex and photomirex, a degradation product of mirex, were detected in all species. The similar ratios between concentrations of mirex and photomirex in the southern fulmar and Adélie penguins from different locations suggest a diffuse distribution of the compounds within the Antarctic ecosystem. In the cape petrel the ratio is lower, which implies an higher relative concentration of photomirex. This may be related to the geographical distribution of the species.

Analysis of samples of subcutaneous fat of Antarctic seabirds indicates the occurrence of organochlorine pollutants in Antarctic seabirds and therefore the Antarctic environment. This information can be used as an 'early warning' for the global distribution of these compounds.

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