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Persistent Organic Pollutants in the Antarctic

Persistent Organic Pollutants in the Antarctic: An Update

Introduction

At CEP 8 (ATCM XXXI), the Committee noted that the Stockholm Convention on Persistent Organic Pollutants (2001) had requested a review of information on persistent organic pollutants (POPs) in the Antarctic Region.

During the discussion SCAR offered to provide this information to the Committee.

The newly formed SCAR Action Group on Environmental Contamination in Antarctica undertook this task under the leadership of Prof. Roger Fuoco, Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Pisa, Italy, and Prof. Gabriele Capodaglio, Dipartimento di Scienze Ambientali, Università Ca' Foscari – Venezia, Italy.

This review of information is an update of the material presented in the United Nations Environment Programme Report of 2002, entitled '*Regionally Based Assessment of Persistent Toxic Substances. Antarctica Regional Report*' (hereafter UNEP 2002).

Information format

Updated information has been provided by SCAR in two forms. The first, provided here as Appendix A, is a report of the major findings, compares its summary findings with those derived from UNEP 2002, and makes six recommendations. The summary findings of this report are presented in this Information Paper.

The second form of report provided (as Appendix B), is the fully referenced report including summary data tables and the sources of the data. This is a comprehensive technical document, but one which is essential for documenting the sources which underlie the main findings and recommendations of this paper and the concise report presented as Appendix A.

Main findings of the 2009 Review

Data on POPs do not cover all media and biota for the 12 compounds banned by the Stockholm Convention, but much data have been produced for hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs).

Long-range atmospheric transport has been confirmed as the primary mechanism transporting POPs into the region.

Sampling of local species breeding and wintering in the Antarctica has improved knowledge of POPs in the Antarctic food web and provides evidence of temporal trends in contaminant levels.

The use of ice cores as an archive of POP inputs to the region needs to be assessed. Evidence is accumulating that warming may remobilize POPs buried or immobilized in soils by permafrost, producing a potential effect on the biota.

Contaminants such as polybrominated diphenyl ethers (PBDEs), perfluorooctanesulfonic acid (PFOS) and endosulfan, which are not yet been listed by the Stockholm Convention, are being considered for listing and have been the subject of investigations in Antarctica.

Some organochlorine compounds (mirex, dieldrin, chlordane) included in the Stockholm Convention have been recently investigated, but data are sparse.

Data on the presence of POPs in terrestrial and limnetic environments is sparse.

Investigations of POPs have predominantly been restricted to the Antarctic Peninsula and the Ross Sea regions and broader coverage is needed.

Variable sampling and analytical methods, target analytes, and reporting often prevent comparison between studies and regions.

Although much data have been collected in recent years, a coordinated data collection strategy is not in place though the SCAR Action Group on Environmental Contamination in Antarctica is addressing this need. Key research areas that deserve further attention include temporal trends of contaminants in biotic and abiotic matrices, the processes controlling the distribution and transport of POPs in polar environments, and mass transfer at environmental interfaces such as air-water, air-snow, air-biota, and water-biota.

An internationally coordinated Antarctic Monitoring and Assessment Programme (AnMAP) would greatly improve knowledge of the distribution and sources of POPs in the region.

APPENDIX A

POPs IN THE ANTARCTIC ENVIRONMENT

A Review of Findings, by the SCAR Action Group on Environmental Contamination in Antarctica (ECA), February 2009

INTRODUCTION

1. The main objective of programs on environmental contamination is to determine the processes influencing global environment quality. Data and feedback from this can then be employed to improve models to predict the environmental evolution. Understanding the way the earth system answers to stimuli is a formidable scientific challenge, and it is also an urgent priority owing to the growing effects of human activities on the quality both of life and environment. The possibility to study records of atmosphere, snow and ice composition as a function of time together with the improvement in the knowledge of interactions between ice/atmosphere/water make this continent the ideal environment in which to monitor the global environmental quality, to study the processes controlling the transport and dispersion of micro-pollutants at a global level, and to assess their relationships with climate changes.
2. Antarctica and the adjacent islands and ocean (area delimited by the Antarctic Convergence) have a very small human population. There is no industrial activity and no agriculture. Human presence in the region is concerned largely with scientific investigations and the logistics operations in support of these. Locally the greatest impact can be expected where research is carried out at long-term stations. The number of people conducting and supporting scientific research and other work on the continent and its nearby islands varies from about 1,000 in winter to about 5,000 in the summer. Pelagic fisheries are an important operation in some parts of the region, and tourism is also an increasingly important activity. Both of these may account for slight increases in emissions of some POPs, but these will normally be highly dispersed (UNEP, 2002).
3. Although leading scientific organizations involved in polar studies are planning to carry out interdisciplinary research, monitoring and surveying activities designed to extract new knowledge from the Antarctic continent, the information is limited and often fragmented. Frequently data and information are collected in relation to projects with aims different from defining the environmental quality or to study mechanisms contributing to this, therefore data are not always correlated with all the accessory information necessary for a correct interpretation from this point of view.
4. The actual change in the climate may also affect biological and microbiological taxonomy, therefore any consideration of changes in environment quality should consider contamination also from this point of view. Actually data are available only for some micro-components and for limited areas, frequently studies are focussed on monitoring the contribution from local activity and not on describing contamination at the continental scale, therefore it is at the moment impossible to derive a general idea of

the environmental quality of the entire Antarctic continent or, at least, in sufficiently extended regions of Antarctica.

5. The Standing Scientific Group on Physical Sciences of SCAR, which is very much involved in the environmental contamination issue, accepted a proposal from the Polar Chemistry Project of the Italian Research Program in Antarctica (PNRA) and established the Action Group "Environmental Contamination in Antarctica (ECA)" at XXIX SCAR in Hobart (July 2006). The main aims of the ECA action group are as follows:

   - to understand the mechanisms and processes controlling distribution and transport of micro-components in polar environments, and their environmental effects;
   - to assess the effects of global climatic changes on processes controlling the dispersion and transport of micro-components and to estimate the contribution of micro-components on climate and environmental changes in polar regions;
   - to monitor the environmental characteristics in Antarctica and set up a data base of environmental parameters to follow the environmental evolution in polar regions.

   ECA held its first workshop in Venice, Italy (June 2007) and the second one at XXX SCAR in St Petersburg (July 2008).

6. A request was submitted by Chile via an Information paper (IP 97) with reference to the Stockholm Convention for information on persistent organic pollutants (POPs) in the Antarctic Treaty Area.

7. The POP issue was raised at the Antarctic Treaty Consulting Meeting held in Kiev (Ukraine) on 2-13 June 2008. SCAR had prepared for that discussion with a briefing paper from the ECA Action Group. Following discussion, SCAR agreed to provide a review of such information for submission to CEP XII (April 2009).

8. Persistent Organic Pollutants (POPs) are defined as "organic substances that possess toxic properties, resist degradation, bio-accumulate and are transported, through air, water and migratory species, across international boundaries and deposited far from their place of release, where they accumulate in terrestrial and aquatic ecosystems". Where the term "Substance" means "a single chemical species, or a number of chemical species which form a specific group by virtue of (a) having similar properties and being emitted together into the environment; or (b) forming a mixture normally marketed as a single article". Starting from 1990, several international initiatives were started aimed at reducing and/or eliminating emissions and discharges of POPs, recognizing the need for global actions to better protect and safeguard Human Health and the Environment. At present, POPs have been considered in several internationally accepted protocols and conventions. Among them, the following can be cited:

   - the United Nations Economic Commission for Europe (UNECE) protocol on POPs which was signed in Aarhus (Denmark) on 24 June 1998 and entered into force on 23 October 2003. The protocol includes the following 16 POPs: aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins, dibenzofurans, chlordecone, hexachlorocyclohexane (including lindane γ-HCH), hexabromobiphenyl and polycyclic aromatic hydrocarbons (PAHs).
   - the Stockholm Convention on POPs signed on 21 May 2001 and entered into force on 17 May 2004. The Convention includes the following 12 POPs: aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and dibenzofurans.

   Both international agreements include provisions for adding further substances that exhibit the characteristics of POPs to the technical Annexes. Actions will be promoted and supported to identify further POP candidates and initiate international action on their control. In fact, the Conference of the Parties (COP) of the Stockholm Convention which will be held in Geneva (CH) on 4-8 May 2009 will consider a recommendation from the POP-Review Committee to add the following nine chemicals in Annexes A, B and/or C of the Convention: chlordecone, hexabromobiphenyl, tetra- and penta-bromodiphenyl ether, hexa- and hepta-bromodiphenyl ether, α-hexachlorocyclohexane, β-hexachlorocyclohexane, γ-hexachlorocyclohexane (lindane), pentachlorobenzene, perfluorooctane sulfonic acid (its salts and perfluorooctane sulfonyl fluoride).

9. SCAR here presents a review of the scientific research findings describing the most significant results on the presence of POPs in the Antarctic atmosphere, marine and terrestrial environmental and food web (detailed findings are presented in Appendix I).

RESEARCH FINDINGS

The Stockholm Convention has stimulated international research projects on POPs aimed at evaluating sources, transport over a range of distances, levels in the environment, biological effects, existing alternatives to their use, and possible remedial action. To achieve these results, the Earth was divided into 12 regions, and Antarctica was designated by UNEP as a region for the global assessment of persistent toxic substances. Antarctic Regional Assessment was delegated to the SCAR, and the recently published report (UNEP 2002a) constitutes the first overview of sources, transport and impact of 26 persistent toxic substances (PTCs) in Antarctica (including the 12 POPs of the Stockholm Convention) that covered the period from about 1979 to 1998. Apart from this report on specific contaminants, another important source of data and references is the summary of environmental monitoring activities, produced by a group of environmental officers (AEON) under the aegis of the Council of Managers of National Antarctic Programmes (COMNAP) (COMNAP-AEON 2001). The New Zealand Antarctic Institute published a report (Waterhouse et al. 2001) on the state of the environment in the Ross Sea region, and other reviews and a book on POPs and trace metal contamination and bio-monitoring in Antarctica have been recently published (Bargagli 2000, 2001, 2005). However, most available publications refer to specific groups of chemicals or specific regions, and much data on persistent contaminants in the Antarctic environment is still scattered across a wide range of journals. Antarctic research and logistic organisations have established committees for the development of internationally coordinated monitoring networks; however, unlike the Arctic, where a coordinated assessment of environmental pollution is in progress (e.g. AMAP 1997, 1998), an Antarctic Monitoring and Assessment Programme (AnMAP) does not yet exist. Finally, there is the lack of an internationally accepted agreement on the meaning of "total PCBs" and "total PAHs", in terms of the compounds whose individual concentration should be included in the calculation of the total content.

Atmosphere

Literature data on persistent atmospheric contaminants in Antarctica and the Southern Hemisphere are scarce in comparison to those on the Northern Hemisphere, and refer to a rather long period of time. Studies emphasize that polar regions are interesting because of the presence of POPs, transported by a complex mechanism involving successive volatilization and deposition steps from warmer areas towards cooler regions. This process requires a continuous exchange of pollutants at the atmosphere-sea water interface, therefore it is essential to define the level of POP concentration in the aerosol, and to know what processes occur at the seawater surface.

Studies to determine POPs in the aerosols during the last decade were carried out to define mechanisms and processes contributing to their presence in Antarctica and also to differentiate between local sources and long-range transport. Indeed there is evidence that aerosols are the main medium contributing to long-range transport in Antarctica. Comparable levels of PCBs content in seawater from north and south of the Antarctic Convergence were reported, indicating that the atmosphere, not the water, was the dominant pathway for the transport of PCB compounds to the Antarctic. Concentrations of individual PCB congeners in the air of King George Island ranged from not detected to 33.2 pg m^{-3} and were comparable to those detected by previous studies respectively in Ross Island and Signy Island.

Measurements of POPs in the atmosphere carried out along transects from north to south can be useful to estimate the contribution of long range atmospheric transport (LRAT) to the input of different classes of POPs in the southern hemisphere. One study was performed in remote areas of Chile: the results clearly showed a north-to-south gradient of the endosulfan I content ranging from 99 to 3.5 pg m^{-3}, while the content of PCBs and other OCPs was related to the distance from urban areas. The contents of PCBs, HCB, 4,4'-DDE, and PAHs were determined from the island of Texel (The Netherlands) to Walvis Bay (Namibia) and Cape Town (South Africa). HCB in air decreased from 7.6 pg m^{-3} (north) to 2.6 pg m^{-3} (south); 4,4'-DDE from 0.34 to 0.05 pg m^{-3} for the same sampling sites. The content of PCBs and other OCP (HCH, endosulfan I, chlordanes, heptachlor and DDTs) were determined in atmospheric samples collected at Arctic and Antarctic sites. The backward trajectories suggest that the two areas are affected by long-range transport from source regions in Northern Europe and Russia and the southern tip of South America, respectively. The results are consistent with the hypothesis of global fractionation and long-range transport. A relatively high

level of PCB-11, averaging 60 pg.m^{-3}, was observed in Antarctica, suggesting an unusual source of PCB-11 to the Southern Hemisphere. The difference of concentration in terms of ΣPCBs reflects the hemispheric distribution of global PCB emissions; the average level of ΣPCB (excluding three mono-CBs and PCB-11) was five times higher in the Arctic (95 pg.m^{-3}) than in the Antarctic (19 pg.m^{-3}). A concentration gradient was also observed with distance from the main buildings of scientific bases in the Antarctic, which strongly indicated the influence of local sources. OCP levels were influenced by long-range transport, but not by local sources.

A study of temporal trends of OCP was carried out by measuring the content of HCB, heptachlor, α- and γ-HCH, heptachlor epoxide in air, seawater, sea ice, and snow samples from the Western Antarctic Peninsula. The results showed that HCB and HCH levels declined over the past 20 years, with a half-life of 3 years for ΣHCH in Antarctic air. However, heptachlor epoxide levels have not declined in Antarctic air over the past decade, possibly due to continued use of heptachlor in the southern hemisphere. Peak heptachlor concentrations in air were measured in coincidence with air masses moving into the region from lower latitudes. The ratio of α/γ-HCH in Antarctic air, sea ice and snow was <1, illustrative of a predominance of influx of lindane versus technical HCH to the regional environment. Water/air fugacity ratios for HCHs demonstrate continued atmospheric influx of HCHs to coastal Antarctic seas, particularly during late summer.

A recent study carried out in the Terra Nova region increased the limited atmospheric database on PCBs in remote areas by reporting PCB concentrations during the austral summer and hypothesizing their possible sources. Gas-phase concentration of individual PCB congeners in the air of Terra Nova Bay ranged from below the LOD to 0.25 pg m^{-3}. In agreement with other studies, the results emphasized that the PCB profile was dominated by tri-CB and tetra-CB with relatively high contributions from mono-CB and di-CB.

Marine Environment

Few investigations have been carried out to determine the POP content of seawater. One recent investigation was carried out to study the vertical distribution of PCBs and PAHs in the coastal area of the Ross Sea during the Antarctic summer (from November to February). PCBs and PAHs showed a concentration range in the water column of 30–120 pg l^{-1} and 150–400 pg l^{-1}, respectively, and these values were strongly dependent on the suspended matter content. A nearly two-fold decrease in the pollutant concentration was also observed in the depth profile obtained in February, i.e. late summer, which might be correlated both with the increase of sedimentation due to the high content of suspended matter, and the reduction of the pollutant input. Moreover, isomer ratios of PAHs, such as LMW/HMW and PHE/ANT, highlight that the main PAH source might be petrogenic in nature, whereas the pyrolytic source seems to be less important.

In consideration of the mechanism of cold condensation, the surface waters play an important role in the global distribution and in the long-range transport to cooler regions. Therefore a relatively high number of studies was carried out to assess the exchange at the seawater/atmosphere interface and the role of seawater on the transport of POPs in polar regions. The surface water is normally described by a widely accepted conceptual model based on a multi-layer structure in which individual layers may have different properties and thickness.

The sea surface micro-layer (SML) (0.1-0.001 mm) is the geographically widest environmental interface that can be accessed by sufficiently reproducible sampling methods. It is the site where many important processes occur, including the accumulation of pollutants and other chemical substances, atmospheric particles, and microorganisms. Most of the studies on POPs in the sea-surface micro-layer have been undertaken in coastal environments. Very few data are available from the open ocean, and there is a lack of data on the sea-surface micro-layer in remote areas, in particular on the presence of POPs in the Southern Ocean.

A significant enrichment of PCBs and PAHs was observed in the sea surface micro-layer in respect to the subsurface water (SSW) samples gathered at Terra Nova Bay, Ross Sea. It was also evident that the same compounds identified in seawater samples were also present in “fresh” snow. Probably chemicals found in the SML were transferred to the “fresh” snow samples by marine aerosols and they were enriched particularly in the finest particles, which can be involved in the long range transport of pollutants. In this context, data on PAH concentrations were used to identify possible sources and to assess partitioning of pollutants between the dissolved and particulate fractions. The enrichment of PCBs and PAHs in the sea-surface micro-layer was investigated at Gerlache Inlet, Terra Nova Bay, Antarctica. Sea surface micro-layer (SML) and sub-surface seawater (SSW) samples were gathered simultaneously. Sea surface micro-layer

samples showed a total content of PCBs and PAHs in the range 400–450 pg l^{-1} and 2000–3000 pg l^{-1}, respectively, whereas the mean contents in the sub-surface sea water samples were 48 pg l^{-1} and 325 pg l^{-1}, respectively. The mean enrichment factors of PCBs and PAHs in the sea-surface micro-layer were about 10 and 7, respectively. A fairly good correlation was observed between the concentration of pollutants and water solubility. However if we consider that the thickness of the sampled sea-surface layer was about 100 _m and we can assume that POPs are confined to a top layer about 0.01–0.001 _m thick (sea surface nano-layer), an enrichment factor of 10^{5}–10^{6} for the sea-surface nano-layer can be estimated. Such a very high concentration increase was related to the two-fold increase of PAH concentration observed in the underlying 20 cm of the water column in late summer.

A series of surveys in a large area of the Ross Sea and Victoria Land was performed in the period 1988-1992. The results showed a low and quite homogeneous distribution in surface water of PCBs with a mean concentration of 130 pg l^{-1}. The concentration increased by 30-40% after the pack ice melted. This increment can be explained considering that ice acts as an accumulator that traps atmospheric particulates during its formation, and transfers them, and the pollutants adsorbed to them, to seawater during melting.

Very recently, the POP depth profile in the water column at Cape Adaire where the Modified Circumpolar Deep Water (MCDW) and the High Salinity Shelf Water (HSSW) converge and mix, has been reported, demonstrating for the first time the external input of pollutants from the open ocean circulation.

The concentration and the distribution of PCBs was also determined in marine sediments, and the mean content normalized for the relevant calculated specific surface area was 150 (pg g^{-1})/(m cm^{-3}). The same authors using the low to high molecular weight PAH ratio hypothesized a predominant petrogenic source of PAH contamination, although the use of PAH ratios for source identification could be questionable in remote areas such as Antarctica.

A relatively elevated number of studies were carried out to assess the local sources related to the scientific stations. Investigations were performed to estimate the influence of human activity on the content of PAHs near the Jubany Station. Two- and 3-ring PAHs (methylnaphthalene, fluorene, phenanthrene and anthracene) were the main compounds found in most sites, although total PAH concentrations showed relatively low levels compared with other human-impacted areas in Antarctica. Pattern distributions of PAHs observed in samples suggested that low-temperature combustion processes such as diesel motor combustion and open-field garbage burning are the main sources of these compounds. The PAH concentration drastically increased in surface sediment collected near the station during two sampling campaigns. The concentration range was: 36–1908 ng/g during 2005, and 28–312 ng/g during 2004. The analysis of soil and coastal sediment samples showed that the present PAH contamination level of Jubany Station is relatively low compared to other reported cases in Antarctica, but suggests that an increase in rain and in thawing processes caused by global warming could result in an important soil-associated PAH mobilization.

The PAH content was also determined in sediment samples collected around the Brazilian station in Admiralty Bay during different summer seasons, the total PAHs concentration varied from 9.45 to 270.5 ng/g. If we consider the concentration determined in areas not affected by scientific stations, the content was about 3 orders of magnitude higher. Therefore, in agreement with the authors, the area must be considered contaminated by local sources. Evidences of contamination by scientific bases were also highlighted by other studies. Sediment samples collected in McMurdo Sound and Arthur Harbor (close to the McMurdo Station and Palmer Station, respectively) presented high concentration of PCBs (250-4200 ng/g). One analogous study carried out at McMurdo station showed the PCB concentration at the Winter Quarters Bay to range between 220 to 375 ng/g; the concentration of PAHs varied between 1.1 to 2.1 _g/g, some orders of magnitude higher than in previous studies. Analysis of the PAH's composition emphasized that the area was contaminated by oil. The contamination of sediment was negatively correlated with the distance from the bases present in the area, which highlights the contribution from activities carried out at the stations.

More recently studies were carried out to determine emerging POPs, like polybominated dyphenil ethers (PBDEs), very commonly used as flame-retardants. Studies were carried out to assess the local sources of this class of POPs related to activity at bases. PBDE concentrations were determined in indoor dust and wastewater sludge from the U.S. McMurdo and New Zealand-operated Scott Antarctic research bases. Levels tracked those in sludge and dust from their respective host countries. The major constituent in the commercial deca-PBDE (BDE-209) was the dominant congener in sludge and dust, as well as in aquatic sediments collected near the McMurdo wastewater outfall. The pattern and level of BDE-209 sediment

concentrations, in conjunction with its limited environmental mobility, suggested to the authors inputs from local sources.

Terrestrial environment

Soil and lake sediment samples have been included in several studies on the environmental contamination of Antarctic regions. Total PCB mean concentration was 0.12 (87%) ng g^{-1} dry wt for lake sediment samples and 0.06 (38%) ng g^{-1} dry wt for soil samples collected in a large area of Victoria Land. These values were similar to those reported in lake sediments of Arctic regions (0.12–0.60 ng g^{-1} dry wt). The much higher PCB concentration in lake sediment is probably due to the nature of Antarctic lakes, which are formed during the deglacial season from ice melting waters that are rich in atmospheric particulate matter trapped into the ice matrix during its formation. The results of lake core sediments from King George Island support this conclusion. In fact, in the lake core sediments with glacier melt water input, the accumulation flux of DDT shows an abnormal peak around the 1980s in addition to the expected one in the 1960s, which is most likely caused by the discharge of the DDT stored in the Antarctic ice cap into the lakes. 4,4'-DDE and 4,4'-DDT were also measured in soil samples from Victoria Land. The concentration range was 0.053–0.086 and <0.005–0.020 ng g^{-1} dry wt, respectively. The higher abundance of 4,4'-DDE over 4,4'-DDT precludes that their occurrence may be due to recent spillages. Moderate (2–7 ng g^{-1} dry wt) and high (90–157 ng g^{-1} dry wt) PCB concentrations, along with high level of HCHs and DDTs, were observed in soil samples from the Eastern coast of Antarctica. This local contamination was attributed to biotic focussing of pollutants, due to bird activities (nesting and excrement). High concentrations were also observed in soil samples from James Ross Island: PCBs 0.51-1.82 ng g^{-1} dry wt, HCHs 0.49-1.34 ng g^{-1} dry wt, DDTs 0.51-3.68 ng g^{-1} dry wt. Among soil HCH, only the isomer _-HCH was found above limit of detection between <0.01 and 0.026 ng g^{-1} dry wt. HCB ranged between 0.034 and 0.17 ng g^{-1} dry wt. DDT and HCH were also measured in two lake cores from King George Island, West Antarctica. All concentration ranges are similar to those reported in Arctic lake sediments.

PAHs are probably among the commonest contaminants near Antarctic research stations, because they are released as by-products of combustion and through hydrocarbon fuel spillage. Very high PAH concentration in surface soils at McMurdo Station during peak summer activity was measured for naphthalene, acenaphthalene, acenaphthylene and fluoranthene (27,000±2,600, 17,800±1,270, 15,700±6,300 and 13,300±430 ng g^{-1} dry wt, respectively), although around Davis Station very low PAH concentration were measured, and the content of individual PAHs around a fuel deposit only exceeded 1 ng g^{-1}. PAHs were also measured in soil samples from James Ross Island and the concentration resulted in the range 35-170 ng g^{-1}. As for HCHs and DDTs, also for PAHs, this local contamination was attributed to biotic focussing of pollutants, due to bird activities.

The area affected by hydrocarbons in Antarctica is not large, yet significant hydrocarbon contamination can be detected in soil around current and former scientific research stations more than 30 yr post-spill. Far from scientific stations, PAH concentrations are typically very low, and often close to limits of detection. However, when deposited on soils, PAHs may have a number of possible fates such as volatilisation, photo-oxidation, leaching or microbial degradation; it therefore seems likely that the risk of possible adverse effects on functional properties of Antarctic soils are negligible, except at sites directly affected by spillage of fuels.

PCBs were measured also in surface snow samples gathered in Victoria Land at several sampling sites located at different altitudes (from sea level to 3,000 m) and at varying distances from the sea. The total PCB concentration showed no significant spatial variations (range 0.28–0.73 pg g^{-1}; mean value 0.52 pg g^{-1}). Moreover, samples from a 2.5-m deep pit at the Hercules Névé collected in summer 1993–1994 and 1994–1995 showed slight higher total PCB concentration (1 pg g^{-1}) in the deepest samples (presumably deposited around 1986-1988) than in surface snow (0.65 pg g^{-1}). This result seems to corroborate previous findings and agrees with the general decreasing trend in POP concentration in the atmosphere of Antarctica and the sub-Antarctic islands during the 1980s and 1990s. These values were about 4 times lower than the average 4.1 pg g^{-1} reported for Canadian Arctic snow.

Lichens and mosses are the principal component of terrestrial flora in many ecosystems of Antarctica whose nutrient supply depends largely on atmospheric deposition. Thus, they can play a very important role as bio-monitors and long-term integrators of persistent contaminant deposition. POPs were measured in several samples collected in a large area of Victoria Land. Total PCB concentration in mosses ranges between <5 and 34 ng g^{-1} dry wt. These values are of the same order of magnitude as those reported for the moss *Hylocomium splendens* in Norway, e.g. 6.7–52 ng g^{-1} dry wt. The concentration ranges of HCB, 4,4'-DDE

and 4,4'-DDT were 0.85–1.9, 1.1–7.9 and 0.54–0.91 ng g g^{-1} dry wt., respectively. 4,4-DDE showed higher concentration than 4,4'-DDT in all samples, which is consistent with a long-range transport as responsible for the transformation of 4,4'-DDT to 4,4'-DDE after release into the environment. _-HCH and _-HCH concentration ranges were 0.43–4.0 and 0.18–1.6 ng g^{-1} dry wt., respectively. In almost all cases _-HCH was found in higher concentration than the _-isomer. The high proportion of the _-isomer is consistent with previous observations in other remote sites, as these areas currently reflect past usage of α-HCH enriched technical mixtures. These low values of the Antarctic mosses confirm the absence of local pollution sources and the lower use of organo-chlorine compounds in the southern hemisphere.

The overall tendency of lower molecular weight PAH compounds, less chlorinated PCB congeners as well as other more volatile POPs as HCB to be prevalent indicates that long-range atmospheric transport is the most important source of contamination in Antarctica, although high POP levels in proximity of scientific stations need to be continuously monitored.

Food web

The food web has been by far the most studied for environmental components in Antarctica. During the last three decades, a number of papers have been published on the concentration of persistent contaminants in Antarctic organisms, with the aim of using data from remote and uncontaminated areas as background values for more contaminated marine areas. Unfortunately, most data derive from one-off studies rather than repeated sampling; some results seem unreliable, and background levels in Antarctic organisms are not always clear. There is a lack of standard procedures for collecting, storing, preparing and analysing biological samples. It is often difficult to compare among values reported in different studies for the same Antarctic species, because results refer to the whole body or to particular organs or tissues, and different measurement units are often used (e.g. fresh or wet weight, dry weight, lipid weight). To perform reliable comparisons between bioaccumulation data on Antarctic organisms and that on related species from other areas, differences in age (i.e. exposure time), feeding behaviour, growth, reproductive cycle, and species-specific detoxification and excretion mechanisms should be considered.

Pelagic plankton

Algae and water column plankton samples were also collected in the Palmer Long-Term Ecological Research programme. PBDE concentration was 100-1000 times higher in ice algae and 2-10 times higher in phytoplankton than that of HCB, the most abundant organochlorine pesticide, reflecting the current production and use of PBDEs versus organochlorine pesticides. Moreover, concentration of HCB and PBDEs was significantly lower in summer plankton than in ice algae indicating lower atmospheric inputs, removal from the water column, and/or bio-dilution of POPs at the base of the food web during summer. The level of _-HCH (<0.06-5.6 ng g^{-1} lipid wt), heptachlor epoxide (<0.04-5.5 ng g^{-1} lipid wt), p,p'-DDT (<0.04-16.4 ng g^{-1} lipid wt), and p,p'-DDE (<0.03-5.2 ng g^{-1} lipid wt) was almost 2 orders of magnitude lower than the concentration previously reported for plankton samples taken in the Indian Ocean sector of the Antarctica. Similarly, lower concentration of _- HCH, _-HCH and DDTs was measured in phytoplankton than previously reported data for the Antarctic Peninsula region. The reduced frequency of occurrence and concentration of pesticides in Antarctic plankton can be attributed to decreases in use and to the subsequent decrease of atmospheric concentration over the past few decades. The decline in _- + _-HCH in Antarctic plankton over time yields an estimated environmental half-life of 2 yr for HCHs in coastal Antarctic surface waters. Phytoplankton (mainly diatoms) and mixed zooplankton (copepods, amphipods and krill) samples from Ross Sea showed a total PCB concentration of 1 and 4.2 ng g^{-1} wet wt. respectively.

Krill (*Euphausia superba*)

Krill has a central position in the Antarctic pelagic food chain The estimated annual consumption by predators (whales, seals, squid, birds and fish) is about 10-100 10^6 tonnes that gives an idea of annual krill production and of its role in transferring POPs to higher levels of the Antarctic pelagic food chain. The following POP concentrations were observed in krill samples from1988 to 2008:

- 1988 - samples from the sea area close to the Indian Maitri Base (70° S and 12° E): total DDTs 0.037 ng g^{-1} dry wt., p,p'-DDT and p,p'-DDE occurred in almost equal percentage, HCHs (_+_) 0.154 ng g^{-1} dry wt., total PCBs 0.152 ng g^{-1} dry wt.;

- 2001 - samples from Admiralty Bay (King George Island): total PCB concentrations in *Desmarestia sp*. samples ranged from 0.46 to 3.86 ng g^{-1} dry wt., and the predominance of low-molecular weight congeners indicated that there were no significant local sources of PCBs at Admiralty Bay;
- 2002 - samples from Ross Sea: p,p'-DDE 0.86 ng g^{-1} wet wt. and HCB 0.37 ng g^{-1} wet wt.. Total PCB concentration in these samples was 167 ng g^{-1} wet wt. (tetra-PCBs accounted for most of the residue). This value is much higher than previous data, although exact evaluation cannot be performed owing to different measurement units. The sum of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (DFs) in the same krill samples was 27 pg g^{-1} lipid wt, and that of non-ortho and mono-ortho-substituted PCBs (dioxin-like PCBs) was 0.9 ng g^{-1} lipid wt.;
- 2004 – samples from Palmer Long-Term Ecological Research (LTER) region west of the Antarctic Peninsula: HCB and PBDE concentrations were not significantly different from those of their primary food source (ice algae, phytoplankton), indicating no bio-magnification during transfer from plankton to krill. The high concentrations of BDEs and HCB in ice algae and associated juvenile krill illustrate the importance of sea ice as a vector for entry of POPs into the Antarctic marine ecosystem;
- 2006 - samples from Ross Sea: HCB 0.23 ng g^{-1}wet wt, HCHs 0.28 ng g^{-1}wet wt, DDTs 0.18 ng g^{-1} wet wt, PBDEs 0.20 ng g^{-1}fresh wt (krill whole body) and 5.60 ng g^{-1} lipid wt, PCBs 2 ng g^{-1} fresh wt levels (almost two order of magnitude lower than the values observed in 2002 in the same area), while chlordanes (CHLs) were below the detection limit (MDL< 0.02 ng g^{-1}wet wt);
- 2008 – samples from the eastern Antarctic sector: HCB was the single most abundant compound quantified: 4.37 ng g^{-1} lipid wt or 0.2 ng g^{-1} wet wt. HCB concentrations were comparable to those detected at this trophic level in both the Arctic and temperate northwest Atlantic, lending support for the hypothesis that HCB will approach global equilibrium at a faster rate than other chlorinated pesticides. p,p'-DDE was detected at notable concentrations: 2.6 ng g^{-1} lipid wt 0.13 ng g^{-1} wet wt.; PCB content was very low (1.2 ng g^{-1} lipid wt and 0.05 ng g^{-1} wet wt) in respect to the Arctic and also to previous data (about three orders of magnitude lower than values reported for Ross Sea). PBDE congeners -99 and -47 were quantified at low background levels (0.67 ng g^{-1} lipid wt, 0.03 ng g^{-1} wet wt, and 0.35 ng g^{-1} lipid wt, 0.007 ng g^{-1} wet wt respectively) with clear concentration spikes observed at around 70°E, in the vicinity of modern, active research stations. Finally, only PCDD/Fs quantifiable were trace levels of octachlorodibenzo-p-dioxin (OCDD) and 1,2,3,4,7,8/1,2,3,4,7,9-hexachlorodibenzofuran (HxCDF).

Coastal benthic organisms

The Antarctic shelf is dominated by a single suborder of fish (notothenioids), and most benthic and epibenthic species are notothenioids belonging to the genus *Trematomus* (e.g. *T. bernacchii*). *Trematomus bernacchii* is an ideal bioindicator of local contamination because it has restricted home ranges and is ubiquitous. Nototheniids also include a few pelagic species such as *Pleuragramma antarcticum* (Antarctic silverfish), which is the most important circum-Antarctic notothenioid species in terms of both number and biomass and is the only true pelagic species in the water column of most Southern Ocean shelf areas. *P. antarcticum* therefore, like krill, plays a prominent role as the main source of food for several species of predatory vertebrates, such as the Antarctic cod (*Dissostichus mawsoni*) and other fish, penguins (Gentoo, Adélie and Emperor), South Polar skuas, Antarctic petrels, Weddell seals, crabeater seals and whales.

- 2002 – samples of two species of Antarctic fishes (*Trematomus pennelli, Chionodrodraco hamatus*): PCDD/DFs total concentration 11–17 pg/g, dioxin-like PCBs (4 non-ortho and 8 mono-ortho PCBs) plus two di-ortho (congeners 170 and 180) concentration 6.2 ng/g.
- 2002 – samples of Antarctic silverfish (*Pleuragramma antarcticum*) from Ross Sea: total PCB, HCB, and p,p'-DDE concentrations in adults were 348, 4.85 and 2.01 ng g^{-1} wet wt. respectively. The higher PCB content in larvae than in adults was attributed to the affinity of PCBs for suspended particles and to the greater surface:volume ratio in larvae than in adult silverfish
- 2004 - a significantly increasing concentration within a decade (1987–1996) was noticed in two benthic fish species (*Gobionotothen gibberifrons, Chaenocephalus aceratus*) feeding on benthos invertebrates and fish, while a benthopelagic species (*Champsocephalus gunnari*) feeding on krill did not show this. In the pelagic food chain, lipid normalised concentrations of all compounds increased from Antarctic krill to fish proving that biomagnification of highly lipophilic pollutants (log octanol–water partition coefficient > 5) occurs in water-breathing animals;
- 2006 – samples of two species of Antarctic fish (*Chionodraco hamatus* and *Trematomus bernacchii*): accumulation of PBDEs, mono- and non-ortho PCBs, PCDDs and PCDFs was evidenced in various tissues. In general, POP levels were higher in the tissues of *T. bernacchii* than in *C. hamatus* and the highest concentrations were found in the liver of both species. The PBDE levels varied from 160.5 pg g^{-1}

wet wt in *C. hamatus* muscle to 789.9 pg g^{-1} wet wt in *T. bernacchii* liver. PCBs were the main organochlorine compounds detected and their concentrations ranged from 0.3 ng g^{-1} wet wt in *C. hamatus* muscle to 15.1 ng g^{-1} wet wt in *T. bernacchii* liver. Again the greater accumulation of POPs in the tissues of *T. bernacchii* may be attributable to the ecological differences between the two species. *T. bernacchii* is a benthic species mainly feeding on other benthic organisms, while *C. hamatus* mainly eats krill, fish larvae and other small fish;

- 2006 – samples of rock cod (*T. bernacchii*) from Terra Nova Bay (200 km from McMurdo): _PBDE6 concentrations 3.06 to 5.81 ng g^{-1} lipid wt. The dominance of the more volatile congeners was explained in terms of their preferential long-range transport;
- 2008 – samples of rock cod (*T. bernacchii*) from the vicinity of the McMurdo wastewater outfall: _PBDE6 1520 and 1840 ng g^{-1} lipid wt. Also cod collected at Cinder Cones contained _PBDE6 at 311 ng g^{-1} lipid wt. This is more than 10-fold greater than biota levels at other sites far from McMurdo. Cinder Cones cod may have previously resided near McMurdo. Its presence at Cinder Cones thus would represent biologically mediated export of pollutants from a contaminated zone to a more pristine area;
- 2008 – samples of a variety of marine biota (rock cod (*Trematomus bernacchii*), clams (*Laternula elliptica*), sea stars (*Odontaster validus*), sea urchins (*Sterechinus neumayeri*), sponges (*Haliclona sp* and *Homaxinella balfourensis*), proboscis worms (*Parborlasia corrugatus*)) collected at varying distances from the McMurdo wastewater outfall: PBDEs were not detected in biota or sediments at the most remote sites (100 km from McMurdo). In contrast, Penta constituents were quantifiable in all biota within 0.1 km of McMurdo and in invertebrates within 0.5 km of the outfall (mean concentration 356 ng g^{-1} wet wt).

Pelagic marine mammals

While commercial hunting was once the biggest threat to the survival of several species of marine mammals, a range of other human-induced threats is now affecting their populations. Among the most widespread are fishing activities and bycatch of cetaceans, environmental pollution, and ocean noise pollution from active sonar systems.

- 1997 - samples from northern and southern oceans: DDT and HCB concentrations in the blubber of northern minke whales decreased in the period 1984–1994, while they increased in that of southern whales. p,p'-DDE (the predominant DDT) tended to increase in Antarctic cetaceans, with a concomitant decrease in p, p'-DDT. This trend indicates that fresh inputs of p,p'-DDT were much lower than the degradation of this compound. Moreover, lindane was higher in the blubber of southern whales than that of northern whales. This suggests that lindane was being used to a greater extent in countries of the Southern Hemisphere than in those of the Northern Hemisphere;
- 2008 – samples of Antarctic Type C killer whales: PCBs, DDTs, CHLs, HCB and HCHs were determined in blubber samples and was found that Type C killer whales have the lowest levels of POPs (except HCB) of any killer whale population studied to date. HCB concentrations measured in Type C whales were comparable to others. Moreover, PCB pattern in the blubber of the Antarctic Type C killer whales was also very different from that of the other killer whale populations, primarily due to a high relative abundance of higher chlorinated congeners. In contrast POP concentrations in adult male Type C killer whales were found to be several times (c.5-90-fold) higher than those of male Antarctic minke whales sampled in western Antarctica (1992-1997) and to the single Antarctic minke whale biopsied in 2006. Most of the differences in concentrations in the two species were likely due to the low levels of contaminants in krill that dominate the minke whale diet, compared to higher levels of contaminants in fish or other higher trophic level species that comprise the Type C diet.

Penguins

About 90% of the avian biomass in Antarctica consists of penguins. There are 18 species of penguins, of which seven breed south of the Antarctic Convergence and only four breed on the continent: Emperor (*Aptenodytes forsteri*), Adélie (*Pygoscelis adeliae*), Chinstrap (*Pygoscelis antarctica*) and Gentoo (*Pygoscelis papua*) penguins. Only Emperor and Adélie penguins are true continental birds, because the other two species are found exclusively in the northern Antarctic Peninsula. Thus, they are useful biomonitors of persistent contaminants in Antarctic marine ecosystems because of their distribution around the continent (exclusively within the seasonal pack-ice zone), their lifespan of more than ten years, and the occurrence year after year of many individuals in the same colony.

- 1986 – samples of Adélie penguins: the mother-to-egg transfer of PCBs and of p,p'-DDE was evaluated. Although the transfer rate was low (about 4% of the body burden of mothers), the pattern of individual PCB isomers and congeners in eggs was similar to that in mothers;
- 1996 – samples of penguin feathers from Dakshin Gangotri: t-HCH (_+_) 108 pg g^{-1} dry wt., total PCBs 109 pg g^{-1} dry wt. and total DDT 33 pg g^{-1} dry wt.;
- 1997 – 2002 - POP concentrations in penguins are generally lower than in birds from other seas and usually fall below recognised threshold levels for eliciting toxicological effects in birds. However, toxicity threshold levels for penguins are unknown, and there is evidence that the liver of Adélie penguins has a low capacity to detoxify PCBs and chlorinated pesticides;
- 2003 – samples from Edmonson Point (Northern Victoria Land): mean concentration of HCB, p,p'-DDE and PCBs in the stomach content of Adélie penguins were 1,412, 1,508 and 303 ng g^{-1} wet wt. respectively. The amount of POPs in the diet of penguins was rather high in comparison to concentrations usually measured in these birds. A significant amount of ingested xenobiotics is probably metabolised and does not build up in organs and tissues;
- 2004 – samples of Adelie penguins, which feed mainly on krill, and biomagnify most analysed compounds more than mackerel icefish. The higher biomagnification factors result from the fact that in air breathing animals clearance of xenobiotics by branchial and dermal diffusion is absent and elimination is mainly restricted to biotransformation and excretion;
- 2007 – samples of Adélie, Chinstrap and Gentoo penguins: measured POP concentrations were lower than those found in seabird species from other areas of the world. PCBs and p,p'-DDE together accounted for more than 70% of the total POP residue. The HCB made up 24% in Chinstrap penguins and 27% in the other two species. The PBDEs were approximately 1% POP concentrations. Different chemical accumulation patterns were observed in relation to species and sex; the Adélie penguin showed the highest POP levels. It feeds on krill (a fatty resource) more abundantly than the other two species during the rearing period;
- 2007 – samples of eggs of skuas, penguins and giant petrels: concentration accumulation of POPs were in the order of _PCB>_DDT>HCB>_HCH. The lower accumulation of HCHs in the seabird eggs might be due to the decreased use of HCHs in agriculture and easy degradation relative to that of PCBs, DDTs and HCBs.
  - Skua eggs: _PCB 91.9 - 515.5 ng/g, _DDT 56.6 - 304 ng/g, HCB 6.5 - 70.5 ng/g, and _HCH (_ + _ isomers) <0.5 t- 2.0 ng/g.
  - Penguin eggs: _PCB r 0.5 - 0.8 ng/g, _DDT 2.0 - 10.1 ng/g, HCB 6.0 - 10.2 ng/g, and _HCH 0.1 - 0.4 ng/g.
  - Giant petrel: _PCB 48.1 - 81.7 ng/g, _DDT 12.7 - 53.7 ng/g, _HCB 4.2 - 8.8 ng/g and _HCH 0.5 - 1.5 ng/g.

  The average concentration was brown skua > South Polar skua > giant petrel > penguin. By the prey-predator relationship it could be seen that the accumulation of PCBs and OCPs in the seabirds was the result of the increment of their position in the food chain;
- 2008 – samples of Brown skuas, Adelie, Chinstrap, and Gentoo penguins and opportunistic samples of Antarctic tern (*Sterna vittata*) Snowy sheathbill (*Chionis alba*) and Blue-eyed shag (*Phalacrocorax atriceps*): chlorinated pesticides, PCBs and PAHs were measured in subcutaneous fat samples. Results confirmed that the concentrations of most chlorinated pesticides were significantly higher in skuas than in the other species of birds, except for HCHs and HCB. On the other hand, comparable concentrations of HCB were found in skuas (573±278 ng g^{-1} lipid wt.), penguins (373±177 ng g^{-1} lipid wt.), terns (601±256 ng g^{-1} lipid wt.), shags (161 ng g^{-1} lipid wt.) and sheathbills (282 ng g^{-1} lipid wt.). HCB is a relatively volatile compound that can be transported to cold regions, incorporated into the food chain and accumulated by top species with concentrations comparable to those encountered in areas of application. Due to its high volatility and transport, HCB was even reported to be higher in species restricted to the Antarctica than in species that live in more temperate areas. PAH content (ng g^{-1} lipid wt.) was similar in all birds with a predominance of naphthalene and alkylnaphthalenes: the most frequently used petroleum derivative in the Antarctic is Diesel Fuel Arctic (DFA), which has a predominance of naphthalenes and alkylated naphthalenes. Therefore, the ingestion of these analytes either from food or during preening can be considered the primary source of PAHs for birds;
- 2008 – samples of Adelie penguin eggs and fat: p,p'-DDE levels have not declined in the Palmer population of Adelie penguins in more than 30 years. In contrast, _DDT decreased significantly from 1975 to 2003 in Arctic seabird eggs. ∑DDT in the fat of Adelie penguins from Cape Crozier measured in

2006 was significantly higher than that measured in 1964. p,p'-DDT/p,p'-DDE ratios <1.0 for several Antarctic organisms, including Adelie penguin eggs, suggest contamination by old DDT. But two independent measurements of _DDT indicate that 1-4 kg· y^{-1} _DDT is currently being released into the Antarctic marine environment due to glacier ablation

Skua and other birds breeding in Antarctica

Birds breeding along Antarctic coasts include the South Polar skua (*Catharacta maccormicki*), the brown skua (*Catharacta lonnbergi*) and some species of procellariforms such as the snow petrel (*Pagodroma nivea*), cape pigeon (*Daption capensis*), Antarctic petrel (*Thalassoica antarctica*) and Wilson's storm petrel (*Oceanites oceanicus*). As they mainly feed on zooplankton and fish larvae, food availability is limited to the summer after the break-up of pack ice. Seabirds have a short and intense breeding season in this period, after which they must migrate northwards.

Skuas are opportunistic top predators and, during the breeding season in Antarctica, they adopt a wide range of feeding tactics, which enable them to prey or scavenge on all profitable marine or terrestrial food resources. South Polar skuas have one of the longest migration flights of any bird, and they can range over huge areas of the ocean up to the north Atlantic and Greenland during the Antarctic winter. Their feeding behaviour in Antarctica and especially that in more polluted marine ecosystems of the Northern Hemisphere exposes South Polar skuas to enhanced uptake of persistent contaminants. Early bio-monitoring surveys of Antarctic wildlife identified the South Polar skua and brown skua as the species with the highest concentrations of persistent contaminants.

- 1997 – samples of South Polar skua eggs at Cape Bird (Ross Island): DDTs (369 ng g^{-1} wet wt.) and PCBs (908 ng g^{-1} wet wt.) in its eggs; were 13 and 22 times higher respectively than those in eggs of Adélie penguins from the same coastal area. Concentrations of DDE, HCB and PCB in skua liver were 11, 3 and 4 times higher respectively than in the liver of penguins. Like in seals, levels of chlorinated hydrocarbons in the eggs and tissue of South Polar skuas were generally one to two orders of magnitude lower than those in the north Atlantic great skua (*Catharacta skua*);
- 2006 – blood samples of Antarctic and Arctic avian top predators: compared organochlorines (OCs) levels in blood samples of south polar skuas (142 skuas, 73 females and 69 males) breeding at Svarthamaren petrel colony in Dronning Maud Land (Antarctica). South polar skuas had 8% and 29% of the blood OCs concentrations (45 ng g^{-1} wet wt.) found in glaucous gulls and great black-backed gulls (158 ng g^{-1} wet wt.) living in northern hemisphere. PCBs, p,p'-DDE, and oxychlordane concentrations were much lower in the skuas. The HCB/PCBs ratio is usually higher at low trophic levels because of the lower persistence of HCB compared to heavy chlorinated PCB congeners. In skuas at Svarthamaren, the HCB/PCBs ratio was 0.8, whereas this ratio was less than 0.05 in the northern hemisphere, which could means that skuas at Svarthamaren are exposed to HCB locally. This probably results from high HCB levels in the prey. In 1991-1992, the mean HCB/PCBs ratio in juvenile Antarctic petrels at Svarthamaren was 10;
- 2006 – samples of Adelie penguin blood, unhatched Adelie penguin eggs and whole blood of South polar skua: the presence of perfluorinated chemicals (PFCs) was investigated. PFCs are surfactants used in industrial and commercial products for over 50 years: perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) are being considered for inclusion in the Stockholm Convention. PFOS was found in eggs (2.1-3.1 ng/g) and blood (<0.24-1.4 ng/ml) of polar skuas but was not detected in penguins from Antarctica, indicating that distribution of these compounds on a global scale even if at contamination levels in the Antarctic is still low.

Seals

Only three species of seals with very distinctive features are limited in distribution to the south of the Antarctic Convergence: the crabeater seal (*Lobodon carcinophagus)*, which comprises 30-40x10^6 individuals and constitutes more than half of total world pinnipeds), Ross seal (*Ommatophoca rossii*), and Weddell seal (*Leptonychotes weddellii*). The latter species breeds in areas adjacent to the Antarctic continent and has the most southerly distribution of any mammal. In spring Weddell seals form pupping colonies on fast ice (near broken ice, tide cracks and hummocking), and during the year they move only locally to exchange breathing holes (Siniff et al. 1977). In contrast, Ross and crabeater seals, along with leopard seals, inhabit unstable areas of shifting pack ice. The Weddell seal is therefore a more reliable biomonitor of environmental contaminants in coastal marine ecosystems around Antarctica.

- 2003 - samples of Weddell seals blubber from King George Island: DDT (11-19 ng/g) and PCB (1-2.5 ng/g) concentrations are the lowest value so far detected in comparable marine mammals from all over the world and one order of magnitude lower than in samples of the same species from other sites in the

Antarctica. This suggests a wide variability of organohalogen levels in the Antarctica, depending on the geographic site;

- 2004 – samples of Weddell seal and southern elephant seal (*Mirounga leonine*): they biomagnify most compounds by up to 2 orders of magnitude relative to krill. It is noteworthy that HCB levels in Weddell seals and in southern elephant seals were considerably lower than in their dominant prey (i.e., pelagic fishes and squids). The same result was found for ringed seals (*Phoca hispida*), and harbour seals (*Phoca vitulina*), in the northern hemisphere. Since the physical and chemical properties of HCB leave no doubt that pinnipeds absorb this compound from their food, an exceptional capacity to eliminate HCB by biotransformation must be postulated in these mammals
- 2006 – samples of elephant seal blood: perfluorooctanesulfonic acid (PFOS) was found in the blood of elephant seals from Antarctica at concentrations ranging from <0.08 to 3.52 ng/ml;
- 2007 - blubber samples of elephant seal from Elephant Island (Antarctica Peninsula): DDTs and PCBs resulted the most accumulated POPs in the blubber of elephant seals. Pups and juveniles of elephant seals had accumulated significant quantities of persistent contaminants as a result of contaminant transfer from mother seals through transplacental and lactational routes and therefore monitoring of marine mammals from Antarctica should continue to evaluate whether the concentrations of these compounds are increasing over time.

World regional comparison

- 1992 - pinniped milk samples from Arctic, Antarctic, California and Australia: p,p'-DDE and PCBs in the milk of Antarctic fur seals were about two orders of magnitude lower than those in pinniped milk samples from California. Although PCB levels were dramatically different in different geographical regions, a similar ratio pattern for PCB congeners 153, 138 and 180 in pinnipeds throughout the world was found. Average DDT, PCB, HCB and HCH concentrations in samples of Weddell seal blubber from various Antarctic locations are from one to three orders of magnitude lower than average values in the blubber of Arctic seals. Finally, the _HCB/_HCH ratio was >1 while in Arctic samples it was always <1;
- 2002 – samples of liver of polar bears from the Alaskan Arctic and of Weddell seals, eggs of Adélie penguins and South Polar skuas: skua eggs had the highest concentrations of total PCDD/DFs (181 pg g^{-1}), and an estimated concentrations of 2,3,7,8-tetrachlorodibenzo-p-dioxin equivalents (TEQs) (PCDDs, PCDFs and dioxin-like PCBs) in skua eggs of 344 pg g^{-1} higher than in the liver of polar bears (mean = 120 pg g^{-1}). These concentrations were close to values that may cause adverse health effects. The mean value in skua eggs, for instance, was only two-fold less than the toxicity threshold value reported for American kestrel eggs.

Conclusive remarks on food web

Pelagic plankton

1. Need to refer to concentration per dry weight basis due to the low phytoplankton density in the Antarctic.
2. Most of the studies reveal that higher concentration of PCB, PAH and PBDE are measured in the vicinity of research station and their sewage outfall. Therefore, despite the fact that Antarctica is protected by the Protocol on Environmental Protection, pollution can still occur and it is made worse by the fact that the degradation of deposited POPs is very slow in the polar regions. Moreover ice can be like a reservoir for POPs.

Krill

1. It seems that there is no bio-magnification from plankton to krill.
2. Between contaminants the organochlorine pesticides dominate with HCB being the most abundant.

Coastal benthic organisms

1. In *T. bernacchi*, considered an ideal bio-indicator of local contamination because it has restricted home ranges and is ubiquitous, DDTs, PCBs, PAHs and other POPs have generally been detected in concentrations similar to those reported for krill and significantly lower than those usually detected in fish from other seas.
2. Benthic fish species, feeding on benthic invertebrates and fish always have higher contaminant (PCB,

PBDE, PCDD PCDF) concentrations than benthopelagic species feeding on krill.

Pelagic marine mammals

1. POP concentration in whales from the Southern Ocean is much lower than in those from the Northern Pacific. However, DDT and HCB concentration increased in blubber of southern minke whales in the period 1984–1994 while decreasing in the blubber of northern whales.
2. Type C killer whales have the lowest POPs concentrations (except HCB) but still several times higher (up to 90 fold) than the Antarctic minke whale. This is likely due to diet type, which for the first one consists of fish and other higher trophic level species, while for the second one it consists mainly of krill

Seals

1. Samples of Weddell seal blubber from King George Island (the region with the mildest climate in the Antarctic) showed the lowest DDT (11÷19 ng/g) and PCB (1÷2.5 ng/g) concentrations so far detected in comparable marine mammals from all over the world, and one order of magnitude lower than in samples from other sites in the Antarctic, therefore suggesting a wide variability of organohalogen levels depending on the geographic site.
2. Weddell seals and southern elephant seals, feeding at higher levels in the food web on fish and cephalopods, bio-magnify most compounds by up to 2 orders of magnitude relative to krill. p,p'-DDE attained the highest concentrations (0.2 _g g^{-1}). However, HCB levels in Weddell seals and in southern elephant seals were considerably lower than in their dominant prey.

Also perfluorooctanesulfonic acid (PFOS) was found in the blood of elephant seals from Antarctica (up to 3.52 ng/mL) and in eggs (2.1-3.1 ng/g) and blood (<0.24-1.4 ng/mL) of polar skuas but was not detected in penguins from Antarctica indicating distribution of these compounds on a global scale even if contamination levels in the Antarctic is low.

Penguins, skuas and other birds

1. In Adelie penguins mother-to-egg transfer rates of PCB isomers and congeners and of p,p'-DDE seem to be low (about 4 % of the body burden of mothers)
2. POP concentrations in penguins are generally lower than recognised threshold levels for eliciting toxicological effects in birds. However, toxicity threshold levels for penguins are unknown, and the liver of Adélie penguins has a low capacity to detoxify PCBs and chlorinated pesticides.
3. Adelie penguins, feeding mainly on krill, have a high bio-magnification factor due to the fact that in air breathing animals clearance of xenobiotics by branchial and dermal diffusion is absent and elimination is mainly restricted to biotransformation and excretion.
4. p,p'-DDE concentration in Adelie penguin eggs has not declined in the Palmer population of Adelie penguins in more than 30 years. In contrast, _DDT decreased significantly from 1975 to 2003 in Arctic seabird eggs. p,p'-DDT/p,p'-DDE ratios <1.0 for several Antarctic organisms, including Adelie penguin eggs, suggest contamination by old DDT. Indeed, the ratio has significantly declined since 1964 indicating a predominance of old rather than new sources of _DDT in the Antarctic. But two independent measurements of _DDT indicate that 1-4 kg· y^{-1} _DDT is currently being released into the Antarctic marine environment due to glacier ablation.
5. Analysing eggs of skuas, penguins and giant petrels, it has been found that PCB and OCP concentrations increase with the increment of their position in the food chain: brown skua > South Polar skua > giant petrel > penguin.
6. Except for HCHs and HCB, the concentrations of most chlorinated pesticides were significantly higher in skuas than in the other species of birds.
7. PAH content was similar in all birds with a predominance of naphthalene and alkylnaphthalenes that are predominant in the Diesel Fuel Arctic (DFA), the most frequently used petroleum derivative in the Antarctic.

IN PROGRESS RESEARCH ACTIVITIES

In progress research activities and related topics on which research papers are expected to be published soon (list not exhaustive):

1. POP paleo-records in snow/firn cores from Talos Dome and sediment cores from Ross Sea. Temporal profiles should cover about five centuries (1600-2000).
2. POPs in the Antarctic atmosphere.
3. Long Range Atmospheric Transport (LRAT) of PBDEs.
4. Antarctica: A source or a sink for POPs?
5. Persistent Organohalogen Contaminant Burdens in Antarctic Krill (*Euphausia superba*) From the Eastern Antarctic Sector: A Baseline Study.
6. Mobilised Organic Contaminant Burdens in Migrating Antarctic Humpback Whales (*Megaptera novaeangliae*); Concentration Effects and Associated Toxicity Response.
7. TRENZ: The TRophic Ecology of the Antarctic Nearshore Zone: local and global constraints on patterns and processes (focus on biogeochemical cycling of POPs).
8. Ecology of marine birds and relationships between ecological variables and flow of contaminants in polar food webs.
9. Flows of POPs between PoLar Abiotic and Biotic Compartments (POP-LAB).

2009 ECA REPORT *vs.* 2002 UNEP REPORT

2002 UNEP Report

1.There is wide variation in the data coverage for different Persistent Toxic Substances (PTSs). For some, such as DDT and HCH, there is a good temporal and geographic spread of samples from different environmental media and biota. At the other extreme, there are compounds or groups of compounds for which there are little or no data.

2.Extra-regional sources dominate the input of PTSs to the region. Atmospheric transport appears to be the most important mechanism to bringing these PTSs into the region. It is noted that the current regimes for environmental protection will reduce the already very low releases of the few compounds with intra-regional sources.

3.Future development of a monitoring programme based on global requirements is possible. However, it will require a different approach from the majority of studies to date, which have been focused mainly on local impacts.

4. Further work on the dynamics of some local processes will be beneficial. Better understanding of these local processes will refine the modelling of transport and release; will enable better interpretation of some existing data, and will contribute to a better planning for future monitoring.

5.The use of snow cores as archive samples recording PTS input to the region needs to be assessed further. These data would greatly enhance a future monitoring programme by providing a historical record.

6.Interpretation of data from biota is often more equivocal, but it appears that in some cases where environmental levels have declined over the last one or two decades, this decrease may not be evident in biota. Some PTSs may be accumulating in the region.

2009 ECA report

1.Data on POPs are still non homogeneous and do not cover all media and biota for the 12 compounds banned by Stockholm Convention, but many data have been gathered also for HCB, PCBs and PAHs.

2.Long-range atmospheric transport has been confirmed to be the most important mechanism to bringing POPs into the region.

3.Although many more data have been collected in recent years a coordinated action is still lacking. An international coordinated project should be promoted on key targets in order to cover actual gaps (temporal trends of contaminants in biotic and abiotic environmental components; processes controlling distribution and transport of POPs in polar environments, including mass transfer at the environmental interfaces air-water, air-snow, air-biota, water-biota, etc.).

4.In compliance with the Madrid Protocol on Environmental Protection of Antarctica, sewage treatment plants have been implemented at many stations. Efforts should be done to better recognize and separate local sources (bases, aircrafts, ships, traverses) from global contaminant signatures by identifying proxies of the potential sources. In this activity, the national responsible for the application of the Madrid Protocol should be involved.

5.The use of snow cores as archive samples recording POP input to the region still needs to be assessed. The combination with data available for Antarctic air and snow, can give a significant contribution to learn more about the transport and cycling of contaminants in the Antarctic environment. Moreover, there are evidences that worming may remobilize POPs buried or immobilized in soils by the permafrost producing a potential effect on the biota. Ad hoc studies should be carried out to consider this input in models.

6.The sampling of local species, breeding and wintering in the Antarctica has brought to a better knowledge of the food web in Antarctica and indicated in some case a reliable temporal trend of the contaminant level in biota.

- Some contaminants like polybrominated dyphenil ethers (PBDEs), perfluorooctanesulfonic acid (PFOS) and endosulfan, not yet included in the POPs list but being considered for inclusion in the Stockholm Convention, have been already taken into consideration in a few studies carried out in Antarctica.

- There are still very few data on the presence of POPs in terrestrial environment (snow, soil, lakes).

- Some organochlorine compounds (mirex, dieldrin, chlordane) included in the Stockholm Convention have been recently investigated but data are still very limited.

- Studies have predominantly been restricted to the Antarctic Peninsula and the Ross Sea (circum-polar collaboration should be encouraged).

- Inconsistencies in sampling and analytical methods, target analytes and reporting information often prevents satisfactory comparison between studies and regions. Quality Control and Quality Assurance (QC/QA), including proficiency test and the development of Antarctic Environmental Reference Materials, should be implemented at an international level.

These limitations have further prevented progress in the comprehension of global diffusion process of POPs in the hydrosphere and in the atmosphere, as well as in the biosphere (parameterised transfer models, species specific toxicology and associated environmental risk assessment).

RECOMMENDATIONS FROM ECA REPORT 2009

1.An internationally coordinated Antarctic Monitoring and Assessment Programme (AnMAP) should be established.

2.All published data should be collected in a global database and archived in a way in which they can be used effectively for global assessment data. The possibility to point out gaps will make it possible to involve research units of various National research programmes in Antarctica in a coordinated network aimed at covering such knowledge gaps.

3.A database should be created, with limited access if required, containing all data collected within the national monitoring programmes on local environmental impact of research stations according to the Madrid protocol.

4.An inventory of all Antarctic Environmental Specimen Banks (AESBs) should be done, and a suitable information system should be implemented, including the availability of sample aliquots.

5.The integration of the ECA database in the SCAR Standing Committee on Antarctic Data Management (SCADM) should be supported by construction of one dedicated portal.

6.A faster process should be encouraged from sampling to analysis and data processing to ensure published data is up-to-date. Too often data refer to samples collected many years earlier (up to ten years).

NOTE THAT APPENDIX B (A 67-PAGE LONG REPORT) IS AVAILABLE ON REQUEST FROM SCAR