

# **Persistent Organic Pollutants (POPs) in the Antarctic environment**

## ***A Review of Findings***

***by***

***The SCAR Action Group on  
Environmental Contamination in Antarctica***

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# **Persistent Organic Pollutants (POPs) in the Antarctic environment**

## ***A Review of Findings***

### **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  $\gamma$ -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,  $\alpha$ -hexachlorocyclohexane,  $\beta$ -hexachlorocyclohexane,  $\gamma$ -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).

## 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 2002) 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<sup>-3</sup> 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<sup>-3</sup>, 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<sup>-3</sup> (north) to 2.6 pg m<sup>-3</sup> (south); 4,4'-DDE from 0.34 to 0.05 pg m<sup>-3</sup> 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<sup>-3</sup>, 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<sup>-3</sup>) than in the Antarctic (19 pg m<sup>-3</sup>). 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<sup>-3</sup>. 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<sup>-1</sup> and 150–400 pg l<sup>-1</sup>, 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 PHE/ANT and low molecular weight PAHs/high molecular weight PAHs (LMW/HMW) 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  $\text{pg l}^{-1}$  and 2000–3000  $\text{pg l}^{-1}$ , respectively, whereas the mean contents in the sub-surface sea water samples were 48  $\text{pg l}^{-1}$  and 325  $\text{pg l}^{-1}$ , 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  $\mu\text{m}$  and we can assume that POPs are confined to a top layer about 0.01–0.001  $\mu\text{m}$  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  $\text{pg l}^{-1}$ . 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 ( $\text{pg g}^{-1}$ )/( $\text{m}^2\text{cm}^{-3}$ ).

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 three-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: 36–1,908 ng g<sup>-1</sup> during 2005, and 28–312 ng g<sup>-1</sup> 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<sup>-1</sup>. 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 (250–4,200 ng g<sup>-1</sup>). 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<sup>-1</sup>; the concentration of PAHs varied between 1.1 to 2.1 µg g<sup>-1</sup>, 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 polybrominated diphenyl 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<sup>-1</sup> dry wt for lake sediment samples and 0.06 (38%) ng g<sup>-1</sup> 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<sup>-1</sup> 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<sup>-1</sup> 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<sup>-1</sup> dry wt) and high (90–157 ng g<sup>-1</sup> 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<sup>-1</sup> dry wt, HCHs 0.49-1.34 ng g<sup>-1</sup> dry wt, DDTs 0.51-3.68 ng g<sup>-1</sup> dry wt. Among soil HCH, only the isomer  $\alpha$ -HCH was found above limit of detection between <0.01 and 0.026 ng g<sup>-1</sup> dry wt. HCB ranged between 0.034 and 0.17 ng g<sup>-1</sup> 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<sup>-1</sup> 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<sup>-1</sup>. PAHs were also measured in soil samples from James Ross Island and the concentration resulted in the range 35-170 ng g<sup>-1</sup>. 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<sup>-1</sup>; mean value 0.52 pg g<sup>-1</sup>). Moreover, samples from a 2.5-m deep pit at the Hercules N ev e collected in summer 1993–1994 and 1994–1995 showed slight higher total PCB concentration (1 pg g<sup>-1</sup>) in the deepest samples (presumably deposited around 1986-1988) than in surface snow (0.65 pg g<sup>-1</sup>). 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<sup>-1</sup> 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<sup>-1</sup> 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<sup>-1</sup> 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<sup>-1</sup> 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.  $\alpha$ -HCH and  $\gamma$ -HCH concentration ranges were 0.43–4.0 and 0.18–1.6 ng g<sup>-1</sup> dry wt., respectively. In almost all cases  $\alpha$ -HCH was found in higher concentration than the  $\gamma$ -isomer. The high proportion of the  $\alpha$ -isomer is consistent with previous observations in other remote sites, as these areas currently reflect past usage of  $\alpha$ -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 (OC) 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  $\gamma$ -HCH (<0.06-5.6 ng g<sup>-1</sup> lipid wt), heptachlor epoxide (<0.04-5.5 ng g<sup>-1</sup> lipid wt), p,p'-DDT (<0.04-16.4 ng g<sup>-1</sup> lipid wt), and p,p'-DDE (<0.03-5.2 ng g<sup>-1</sup> 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  $\alpha$ -HCH,  $\gamma$ -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  $\alpha$ - +  $\gamma$ -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<sup>-1</sup> 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  $10\text{-}100 \times 10^6$  tonnes, which 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 from 1988 to 2008:

- 1988 - samples from the sea area close to the Indian Maitri Base ( $70^\circ$  S and  $12^\circ$  E): total DDTs  $0.037 \text{ ng g}^{-1}$  dry wt., p,p'-DDT and p,p'-DDE occurred in almost equal percentage, HCHs ( $\alpha+\gamma$ )  $0.154 \text{ ng g}^{-1}$  dry wt., total PCBs  $0.152 \text{ ng g}^{-1}$  dry wt.;
- 2001 - samples from Admiralty Bay (King George Island): total PCB concentrations in *Desmarestia sp.* samples ranged from  $0.46$  to  $3.86 \text{ ng g}^{-1}$  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  $0.86 \text{ ng g}^{-1}$  wet wt. and HCB  $0.37 \text{ ng g}^{-1}$  wet wt.. Total PCB concentration in these samples was  $167 \text{ ng g}^{-1}$  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  $27 \text{ pg g}^{-1}$  lipid wt, and that of non-ortho and mono-ortho-substituted PCBs (dioxin-like PCBs) was  $0.9 \text{ ng g}^{-1}$  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  $0.23 \text{ ng g}^{-1}$  wet wt, HCHs  $0.28 \text{ ng g}^{-1}$  wet wt, DDTs  $0.18 \text{ ng g}^{-1}$  wet wt, PBDEs  $0.20 \text{ ng g}^{-1}$  fresh wt (krill whole body) and  $5.60 \text{ ng g}^{-1}$  lipid wt, PCBs  $2 \text{ ng g}^{-1}$  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 ( $\text{MDL} < 0.02 \text{ ng g}^{-1}$  wet wt);
- 2008 – samples from the eastern Antarctic sector: HCB was the single most abundant compound quantified:  $4.37 \text{ ng g}^{-1}$  lipid wt or  $0.2 \text{ ng g}^{-1}$  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:  $2.6 \text{ ng g}^{-1}$  lipid wt  $0.13 \text{ ng g}^{-1}$  wet wt.; PCB content was very low ( $1.2 \text{ ng g}^{-1}$  lipid wt and  $0.05 \text{ ng g}^{-1}$  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 ( $0.67 \text{ ng g}^{-1}$  lipid wt,  $0.03 \text{ ng g}^{-1}$  wet wt, and  $0.35 \text{ ng g}^{-1}$  lipid wt,  $0.007 \text{ ng g}^{-1}$  wet wt respectively) with clear concentration spikes observed at around  $70^\circ\text{E}$ , 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).

## 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.

### 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<sup>-1</sup>, dioxin-like PCBs (4 non-ortho and 8 mono-ortho PCBs) plus two di-ortho (congeners 170 and 180) concentration 6.2 ng g<sup>-1</sup>.
- 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<sup>-1</sup> 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 (*Champscephalus 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<sup>-1</sup> wet wt in *C. hamatus* muscle to 789.9 pg g<sup>-1</sup> wet wt in *T. bernacchii* liver. PCBs were the main organochlorine compounds detected and their concentrations ranged from 0.3 ng g<sup>-1</sup> wet wt in *C. hamatus* muscle to 15.1 ng g<sup>-1</sup> 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): ΣPBDE6 concentrations 3.06 to 5.81 ng g<sup>-1</sup> 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: ΣPBDE6 1,520 and 1,840 ng g<sup>-1</sup> lipid wt. Also cod collected at Cinder Cones contained ΣPBDE6 at 311 ng g<sup>-1</sup> 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<sup>-1</sup> wet wt).

## 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 (α+γ) 108 pg g<sup>-1</sup> dry wt., total PCBs 109 pg g<sup>-1</sup> dry wt. and total DDT 33 pg g<sup>-1</sup> 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<sup>-1</sup> 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 Adélie 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  $\Sigma\text{PCB} > \Sigma\text{DDT} > \text{HCB} > \Sigma\text{HCH}$ . 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:  $\Sigma\text{PCB}$  91.9 - 515.5 ng g<sup>-1</sup>,  $\Sigma\text{DDT}$  56.6 - 304 ng g<sup>-1</sup>, HCB 6.5 - 70.5 ng g<sup>-1</sup>, and  $\Sigma\text{HCH}$  ( $\alpha + \gamma$  isomers) <0.5 - 2.0 ng g<sup>-1</sup>.
  - Penguin eggs:  $\Sigma\text{PCB}$  0.5 - 0.8 ng g<sup>-1</sup>,  $\Sigma\text{DDT}$  2.0 - 10.1 ng g<sup>-1</sup>, HCB 6.0 - 10.2 ng g<sup>-1</sup>, and  $\Sigma\text{HCH}$  0.1 - 0.4 ng g<sup>-1</sup>.
  - Giant petrel:  $\Sigma\text{PCB}$  48.1 - 81.7 ng g<sup>-1</sup>,  $\Sigma\text{DDT}$  12.7 - 53.7 ng g<sup>-1</sup>,  $\Sigma\text{HCB}$  4.2 - 8.8 ng g<sup>-1</sup> and  $\Sigma\text{HCH}$  0.5 - 1.5 ng g<sup>-1</sup>.

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, Adélie, 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<sup>-1</sup> lipid wt.), penguins (373±177 ng g<sup>-1</sup> lipid wt.), terns (601±256 ng g<sup>-1</sup> lipid wt.), shags (161 ng g<sup>-1</sup> lipid wt.) and sheathbills (282 ng g<sup>-1</sup> 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<sup>-1</sup> 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,  $\Sigma$ DDT decreased significantly from 1975 to 2003 in Arctic seabird eggs.  $\Sigma$ 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  $\Sigma$ DDT indicate that 1-4 kg y<sup>-1</sup>  $\Sigma$ 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 procellariiforms 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<sup>-1</sup> wet wt.) and PCBs (908 ng g<sup>-1</sup> 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<sup>-1</sup> wet wt.) found in glaucous gulls and great black-backed gulls (158 ng g<sup>-1</sup> wet wt.) living in northern hemisphere. PCBs, p,p'-DDE, and oxychlordan 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 mean 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<sup>-1</sup>) and blood (<0.24-1.4 ng ml<sup>-1</sup>) of polar skuas but was not detected in penguins from Antarctica, indicating that distribution of these compounds on a global scale even if contamination levels in the Antarctic are 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<sup>6</sup> 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<sup>-1</sup>) and PCB (1-2.5 ng g<sup>-1</sup>) 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<sup>-1</sup>;
- 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  $\gamma$ HCB/ $\alpha$ 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<sup>-1</sup>), 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<sup>-1</sup> higher than in the liver of polar bears (mean = 120 pg g<sup>-1</sup>). 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.

### **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

### **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.

### **Penguins, skuas and other birds**

1. In Adélie 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,  $\Sigma$ 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  $\Sigma$ DDT in the Antarctic. But two independent measurements of  $\Sigma$ DDT indicate that  $1-4 \text{ kg y}^{-1}$   $\Sigma$ 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.

## Seals

1. Samples of Weddell seal blubber from King George Island (the region with the mildest climate in the Antarctic) showed the lowest DDT ( $11-19 \text{ ng g}^{-1}$ ) and PCB ( $1-2.5 \text{ ng g}^{-1}$ ) 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 ( $0.2 \text{ } \mu\text{g g}^{-1}$ ). 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  $3.52 \text{ ng ml}^{-1}$ ) and in eggs ( $2.1-3.1 \text{ ng g}^{-1}$ ) and blood ( $<0.24-1.4 \text{ ng ml}^{-1}$ ) 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.

## 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 made 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 agency 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 make a significant contribution to learning more about the transport and cycling of contaminants in the Antarctic environment. Moreover, there is evidence that warming 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 improved knowledge of the food web in Antarctica and indicated in some case a reliable temporal trend of the contaminant level in the biota.
7. Some contaminants like polybrominated diphenyl ethers (PBDEs), perfluorooctanesulfonic acid (PFOS) and endosulfan, not yet included in the POPs list but being considered for inclusion in the Stockholm Convention, have already been taken into consideration in a few studies carried out in Antarctica.
8. There are still very few data on the presence of POPs in terrestrial environments (snow, soil, lakes).
9. Some organochlorine compounds (mirex, dieldrin, chlordane) included in the Stockholm Convention have been recently investigated, but data are still very limited.
10. Studies have predominantly been restricted to the Antarctic Peninsula and the Ross Sea (circum-polar collaboration should be encouraged).
11. 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 tests 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 processes 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 the local environmental impacts 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).

# **APPENDIX 1**

## **Review of recent research into the presence of Persistent Organic Pollutants (POPs) in the Antarctic Environment**

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## 1. Introduction

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” (ATSDR, 1995; Syracuse Research Corporation, 2000). 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, recognize 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 Stockholm Convention on POPs which was signed on 21 May 2001 on the basis of the decision 19/13 C made by the Governing Council of the United Nations Environment Programme (UNEP) on 7 February 1997. The following 12 POPs are included: aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene, polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and dibenzofurans;
- The United Nations Economic Commission for Europe (UNECE) protocol on POPs, which was signed in Aarhus (Denmark) on 24 June 1998. The following 16 POPs are included: pesticides (aldrin, chlordane, chlordecone, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex, toxaphene, hexachlorocyclohexane ( $\alpha$ -,  $\beta$ -, and  $\gamma$ -HCH); industrial chemicals (hexabromobiphenyl, polychlorinated biphenyls (PCBs); by-products or contaminants (dioxins, furans, polycyclic aromatic hydrocarbons PAHs).

According to the nature of sources, POPs can be divided in two major categories:

- Intentionally produced chemicals currently or once used in agriculture, disease control, manufacturing, or industrial processes. Examples include PCBs, which have been useful in a variety of industrial applications (e.g., in electrical transformers and large capacitors, as hydraulic and heat exchange fluids, and as additives to paints and lubricants) and DDT, which is still used to control mosquitoes that carry malaria in some parts of the world.
- Unintentionally produced chemicals, such as dioxins and PAHs, which result from some industrial processes and from incomplete combustion of organic matter (for example, municipal and medical waste incineration and backyard burning of trash).

While bans and phase-outs of the chemicals included in the first group occurred during the 1970s and 1980s in most developed countries, they were not in place in many developing countries. The Stockholm Convention requires signatory countries to develop National Implementation Plans (NIPs) [UNEP, 2001]. In some countries PCBs and organo-chlorine pesticides (OCPs) are still in use or loosely regulated and many countries will be faced with the legacy of past use of these persistent chemicals while fires probably constitute a significant source of atmospheric organic pollutants in the Southern Hemisphere

(Vasconcellos et al., 1998). Residues in soils, sediments and biota will pose a risk for wildlife and humans. Studies carried out during the last two decades emphasized that also relatively pristine environments are characterised by the presence of POPs, transported to cooler regions and globally distributed through a process of cold condensation. POPs follow successive volatilization and deposition steps from warmer areas towards cooler regions by a grasshopping behaviour. Areas with high elevation, high latitude and low temperatures are preferred regions for the condensation of long-range transported airborne contaminants (Wania and Mackay, 1993, 1995). This mechanism, confirmed by many studies carried out in remote polar and mountainous regions, explains the long-range atmospheric transport of POPs worldwide (Daly and Wania, 2005; Hung et al., 2002; Shen et al., 2004; Yang et al., 2007).

Complex mechanisms are involved in the continuous exchange of pollutants at the atmosphere-sea water interface. Therefore it is especially important to thoroughly know both the level of POPs concentration in aerosols, and processes occurring at the seawater surface.

The Polychlorobiphenyls (PCBs) form a class of non-polar semi-volatile organic compounds that includes 209 congeners divided into ten homolog classes. They are toxic, chemically very stable, and persistent in the environment. They also bio-accumulate in the food chains (Nishimura et al., 2004; Patandin et al., 1998). The Organo-chlorine pesticides (OCPs) form a numerous group of compounds; only 10–20 of these and their metabolites are routinely checked in monitoring studies. During the last decade, it has been found that some POPs are endocrine disrupters and threaten the health of both wildlife and humans. These pollutants are currently the subject of international negotiations intended to bring them under global agreements, with some being phased out and others being tightly controlled. For all these reasons, they are generally considered priority pollutants, so monitoring their concentration in the environment and their toxic effects on living organisms is of primary importance. Long-range atmospheric transport can move POPs away from source regions to more remote and pristine regions such as Antarctica, and makes them ubiquitous.

More recently, with increasing global and environmental awareness, it was realised that Antarctica provides a unique opportunity to study the transport, behaviour and effects of persistent atmospheric contaminants. In fact, the Stockholm Convention 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 SCAR, and the recently published report (UNEP 2002a) constitutes the first overview of sources, transport and impact of 26 organic compounds in Antarctica (including the 12 POPs of the Stockholm Convention).

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 of trace metal contamination and biomonitoring in

Antarctica have been published recently (Bargagli 2000, 2001). However, most available publications refer to specific groups of chemicals or specific regions, and many data on persistent contaminants in the Antarctic environment are 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 does not yet exist. 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. The reliability of analytical determinations of atmospheric contaminants is constantly improving and, although this and the following chapters are based on data published in peer-reviewed literature, it is impossible to assure a uniform quality level of data. Whenever possible, preference will be given to more recent papers, although comparisons with older data are essential.

## **2. POPs in the 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 emphasized that polar regions are also affected by 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 POPs concentration in the aerosol, and to know the processes occurring at the seawater surface.

Studies determining POPs in aerosols were carried out during the last decade, to define mechanisms and processes contributing to their presence in Antarctica, to identify sources and to discriminate local sources from long-range transport contributions. There is evidence that aerosol transport is the primary mechanism for long-range transport of POPs to Antarctica.

Montone et al. reported in 2003 that comparable levels of contamination in seawater from north and south of the Antarctic Convergence indicated that the atmosphere, not the water, was the dominant pathway for the transport of PCB compounds to the Antarctic. Previous studies by Tanabe (1983), Weber and Montone (1990) and Larsson et al (1992) provided further evidence of atmospheric transport of PCBs and organo-chlorine pesticides in the Antarctic environment. Concentrations reported by Montone et al of individual PCB congeners in air ranged from not detected to 33.2 pg m<sup>-3</sup>. Concentrations of PCBs were similar to those detected by Larsson (1992) and Kallenborn (1998), respectively in Ross Island and Signy Island, and by Montone and coworkers in Admiralty Bay area (Montone et al., 2001). The study also emphasized that PCB concentrations were related to meteorological conditions, as well as to the general synoptic atmospheric circulation of the region. In general higher levels of PCBs were observed when the frontal systems moved east over the Drake Passage and south of South America, causing a local increase in air temperature and surface winds from northwest, north and northeast. The possibility of atmospheric long-range

transport episodes from South America to Signy Island was also pointed out by Kallenborn in 1998, which determined PCB in ambient air at Signy Island over a period of 17 weeks and found that mean concentrations for single congeners were comparable to those in Arctic air.

The Montone results and other studies highlighted the predominance of lower chlorinated congeners in the PCB profiles of air samples associated with the frontal system. Further evidence of atmospheric transport of PCBs in the Antarctic environment was provided by Fuoco et al. (1996) whose studies of Antarctic lake sediment found high contributions of atmospheric particulate matter and concluded that it is the primary vehicle of transport and diffusion of PCB in the environment.

To establish PCB background air concentrations in oceanic regions and to assess their latitudinal distribution, PCBs data concentrations were collected during cruises such as the Atlantic cruise from the United Kingdom to Halley, Antarctica (Lohmann et al., 2004). Moreover Ockenden et al. (2001) monitored the PCBs in air at two sites in the southern hemisphere, one 'over land' and one 'over water'. They found that the highest concentrations were observed when temperatures were greater and air concentrations were higher over water than over land.

In addition to the Lohmann study other investigations were carried out to give evidence of POPs transport from the northern hemisphere to the southern. Investigations were carried out along transects from northern regions to the polar or sub-polar regions to reconstruct the trends in concentrations of POPs and to emphasize the potential contribution from the more anthropized regions. Transport processes were assessed on the base of concentration gradient and using the isomeric composition of some POPs. Hexachlorocyclohexanes (HCHs) were determined simultaneously in air and seawater during two cruises across the Atlantic Ocean between the Arctic Ocean (Ny-Alesund/Svalbard, 79°N; 12°E) and the Antarctic Continent (Neumayer Station/Ekstroem Ice Shelf, 70d°S; 8.2°W) in 1999/2000 (Lakaschus et al., 2002). The concentrations of  $\alpha$ -HCH and  $\gamma$ -HCH in air and surface waters of the Arctic exceeded those in Antarctica by 1-2 orders of magnitude. Average concentrations in surface seawater between 75°N and 80°N were  $315 \pm 184 \text{ pg L}^{-1}$  and  $137 \pm 49 \text{ pg L}^{-1}$  for  $\alpha$ -HCH and  $\gamma$ -HCH respectively. In the sea region of the southern fronts (50°S) the mean concentrations were  $3.9 \text{ pg l}^{-1}$  and  $0.8 \text{ pg l}^{-1}$   $\alpha$ -HCH and  $\gamma$ -HCH respectively. Between Cape Town and Neumayer Station the average gaseous concentrations of  $\alpha$ -HCH and  $\gamma$ -HCH were  $1.1 \text{ pg m}^{-3}$  and  $1.4 \text{ pg m}^{-3}$  and decreased further to  $0.36 \pm 0.03 \text{ pg m}^{-3}$  and  $0.15 \pm 0.04 \text{ pg m}^{-3}$  on the Ekstroem Ice Shelf at Neumayer Station. By comparison of results obtained from archived samples taken in 1987/1997 and those from 1999, a systematic decrease of  $\alpha$ -HCH was observed at all sampling locations. However, it must be emphasized that a different trend was observed for  $\gamma$ -HCH. In particular, the level of  $\gamma$ -HCH in surface seawater as a function of the time was constant in the tropical Atlantic region and the authors concluded that the tropical Atlantic acts as a sink for  $\gamma$ -HCH at present time (Lakaschus et al., 2002).

Dickhut and coworkers (2005) determined hexachlorobenzene (HCB), heptachlor,  $\alpha$ - and  $\gamma$ -HCH and heptachlor epoxide in air, seawater, sea ice, and snow. Samples were collected during the austral winter (September-October 2001) and summer (January-February 2002) along a transect in the Western Antarctic Peninsula. By comparison with previous studies they concluded HCB and HCH levels declined over the past 20 years, with a half-life of 3

years in Antarctic air. However, they observed that heptachlor epoxide levels did not decrease in Antarctic air over the past decade, possibly due to continued use of heptachlor in the southern hemisphere. They detected peak heptachlor concentrations in air coincident with air masses moving into the region from lower latitudes. Levels of lindane were 1.2-200 times higher in annual sea ice and snow compared to  $\alpha$ -HCH, likely due to greater atmospheric input of  $\gamma$ -HCH. On the basis of the ratio of  $\alpha/\gamma$ -HCH  $<1$  in Antarctic air, sea ice and snow they concluded that there is a predominance of influx of lindane versus technical HCH to the regional environment. However, they also observed that the  $\alpha/\gamma$ -HCH in seawater was  $>1$ , likely due to more rapid microbial degradation of  $\gamma$  - versus  $\alpha$  -HCH. Also this study concluded that the water/air fugacity ratios for HCHs demonstrate continued atmospheric influx of HCHs to coastal Antarctic seas, particularly during late summer (Dickhut et al., 2005).

An analogous study was carried out by Jantunen and coworkers (2004). The spatial distribution of  $\alpha$ -HCH and the net direction of air/water gas exchange were determined between November 1997 and February 1998. Air and water samples were collected between South Atlantic Ocean (South Africa) and Antarctica SANAE Base ( $70^{\circ}\text{S}$ ,  $3^{\circ}\text{E}$ ). The  $\alpha$ -HCH concentrations in air and surface water were much lower than in Arctic regions, consistent with the historically lower usage of technical HCH in the Southern Hemisphere. The water/air fugacity ratios of  $\alpha$ -HCH were lower than or equal to 1.0, indicating steady state or net deposition conditions. One analysis of the enantiomeric fractionation was also made. The results showed that the  $\alpha$ -HCH in water was enantioselectively metabolized and that the two isomers [ $(-)\alpha$ -HCH and  $(+)\alpha$ -HCH] in the air boundary layer reflected those in surface water, showing the bidirectional nature of gas exchange (Jantunen et al., 2004).

Montone and colleagues determined the atmosphere content of a large number of OC compounds (HCB, HCHs,  $pp'$ -DDE,  $pp'$ -DDD,  $pp'$ -DDT and 11 PCB) in a survey performed in November of 1995 in the open ocean between  $23^{\circ}\text{S}$  and  $62^{\circ}\text{S}$  (Montone et al., 2005). Air mass back trajectories were used to assess the origin of the air masses that arrived at the sampling point at low altitude. Organochlorine levels in the atmosphere ranged from not detected ( $<0.6$ ) to  $25.3 \text{ pg m}^{-3}$  for HCB,  $3.9\text{--}32.5 \text{ pg m}^{-3}$  for  $\Sigma\text{HCHs}$  ( $\alpha$ -HCH +  $\gamma$ -HCH),  $3.7\text{--}102.6 \text{ pg m}^{-3}$  for PDDTs ( $pp'$ -DDT +  $pp'$ -DDD +  $pp'$ -DDE) and  $46.2$  up to  $985.0 \text{ pg m}^{-3}$  for PCBs. The trend is similar to that detected between New Zealand and the Ross Sea (January to March 1990). However the mean concentration of HCB ( $15 \text{ pg m}^{-3}$ ) between latitudes  $47^{\circ}\text{S}$  and  $62^{\circ}\text{S}$  was remarkably lower than the values ( $60 \text{ pg m}^{-3}$ ) found by Bidleman et al. (1993). The HCH concentration was 10 times lower than the data of 1987 by Weber and Montone (1990). The mean concentration of Lindane ( $8.8 \text{ pg m}^{-3}$ ) was slightly higher than the value found along the transect from New Zealand to the Ross Sea, but three times below the values obtained by Larsson et al. (1992) and Kallenborn et al. (1998) at Ross Island and Signy Island, respectively. In agreement with conclusions of other authors, the study showed the HCH and DDT levels were significantly decreased in recent decades.

To study the transport of POPs from the northern hemisphere to the southern, cruises were carried out collecting aerosol and surface water samples where different classes of organic pollutants were determined. The content of polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), 1,1-dichloro-2,2-bis(4-chlorophenyl)ethene (4,4'-DDE), and polyaromatic hydrocarbons (PAHs) were determined from the island of Texel (The

Netherlands) to Walvis Bay (Namibia) and Cape Town (South Africa) (Booij et al. 2007). The concentrations of HCB range from 2 to 9  $\text{pg L}^{-1}$  in water and from 56 to 145  $\text{pg m}^{-3}$  in air. These values can be considered typical for background levels for seawater (5–27  $\text{pgL}^{-1}$ ) and air (4–140  $\text{pg m}^{-3}$ ) (Barber et al., 2005). Concentrations of 4,4'-DDE in water ranged from 0.3 to 1.4  $\text{pg L}^{-1}$ , which is similar to the values found in previous studies carried out in the North Atlantic (0.4–0.6  $\text{pg L}^{-1}$ ). Atmospheric 4,4'-DDE concentrations range from 0.1 to 0.9  $\text{pg m}^{-3}$  were somewhat smaller than the values of 1.3–6.3  $\text{pg m}^{-3}$  observed by Iwata et al. (1993) in the same area during one cruise carried out in April 1990.

During the same cruises the contents of polycyclic aromatic hydrocarbons (PAHs) and one emerging class of pollutants (polychlorinated naphthalenes, PCNs) were determined. The highest PAH concentrations occurred in the European samples, and in samples close to West Africa and South Africa. Consistently low PAH concentrations were measured in the southern hemisphere open ocean samples (190–680  $\text{pg/m}^3$ ). Concentrations showed a diurnal cycle, the day/night ratios of phenanthrene, 1-methylphenanthrene and fluoranthene were typically ~1.5–2.5:1. The mechanisms causing this pattern are not understood at present, but dynamic environmental processes are implicated. The highest PCN concentrations occurred in the European samples, but high values were also detected off the West African coast, and in the sample taken closest to South Africa (Jaward et al., 2004).

Choi and coworkers (2008) deployed air samplers for one year at the Korean polar research stations at Ny-Alesund, Norway (2005–2006) and King George Island, Antarctica (2004–2005) to assess levels and patterns of polychlorinated biphenyls (PCBs) and organo-chlorine pesticides (OCPs) in polar regions (Choi et al. 2008). The backward trajectories suggested that the Antarctic area was affected by long-range transport from source regions in the southern tip of South America. The results were consistent with the hypothesis of global fractionation and long-range transport. The authors also observed relatively high levels of PCB-11, averaging 60  $\text{pg m}^{-3}$ , suggesting an unusual source of PCB-11 to the Southern Hemisphere. The difference of concentration in term of  $\Sigma$  PCBs reflects the hemispheric distribution of global PCB emissions; the average level of  $\Sigma$ PCB (excluding three mono-CBs and PCB-11) was five times higher in the Arctic (95  $\text{pg.m}^{-1}$  range).

Further information on the impact of long-range transport and of local sources can be obtained from analysis of the PCB concentration in surface snow. The deposition and accumulation of PCB in the Antarctic snow/pack ice are in fact considered to be important steps in their transfer from the atmosphere to terrestrial and marine systems (Fuoco et al., 2001).

Gambaro et al (2005) increased the limited atmospheric database on PCB in remote areas by reporting PCB concentrations during the austral summer at a site in Terra Nova Bay, Antarctica and hypothesizing their possible sources. They reported that PCBs are present in the atmosphere essentially bound to aerosols  $<1 \mu\text{m}$ , and found that gas-phase concentration of individual PCB congeners in the air of Terra Nova Bay ranged from below the LOD to 0.25  $\text{pg m}^{-3}$ . The concentrations found were extremely low and confirm the still pristine characteristics of the Antarctic environment, even with respect to the values found in anthropized regions. The highest concentrations, of about 100  $\text{fg m}^{-3}$ , were observed for PCB<sub>2</sub>, PCB<sub>3</sub> and PCB<sub>28+31</sub> whereas the lowest concentrations, of few  $\text{fg m}^{-3}$ , were

observed for PCB34, PCB46+39, PCB67, PCB63, PCB77 and PCB85. Over 90% of the total PCB content was due to congener with one to four chlorine atoms and only about 10% with five to seven chlorines, whereas higher chlorinated PCBs were below detection limits. These results were in agreement with those reported by Montone et al. (2003).

There is evidence that other organic compounds may represent future emerging pollutants in polar regions. In particular, it must be noted that presence of PCNs, discussed above, and nitro-PAHs determined in pristine environments suggest that future monitoring actions must be taken for these classes of pollutants in polar regions (Vasconcelos et al, 1998; Vincenti et al, 2001). Indeed, the origin of Antarctic nitro-PAHs remains uncertain: while the abundance ratio of the nitro-naphtalene isomers supported the hypothesis of local direct emission, the relative high abundance of dinitro- with respect to mononitro-derivatives suggested that an efficient gas-phase nitration may take place on a substrate possibly transported from other continents.

In addition to atmospheric transport, local sources of PCB such as Antarctic Research Stations should be considered (Risebrough et al., 1990). The impact of scientific bases and related activities on the environment are more efficiently recorded by sediment analysis.

### **3. POPs in marine environment**

Few investigations have been carried out to determine POPs content in seawater; one recent investigation (Fuoco et al., 2005) 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  $\text{pg l}^{-1}$  and 150–400  $\text{pg l}^{-1}$ , 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 (Fuoco et al., 2005). Some data (Fuoco et al., 2009) were also obtained on the mixing process between two important water masses present in the area of the Ross Sea: the Modified Circumpolar Deep Water (MCDW) and the High Salinity Shelf Water (HSSW). Both move toward Cape Adere where they mix and where a water column profile of both PCB and PAH concentration was obtained. The intrusion of the relatively warmer MCDW in the colder HSSW was clearly evident from the very sharp change in the temperature at about 170 m depth from  $-1.5\text{ }^{\circ}\text{C}$  to  $+0.2\text{ }^{\circ}\text{C}$  (typical of MCDW). The temperature increase was in very good agreement with a sudden change observed also in the PCB and PAH presence, whose concentration increased by a factor of two in MCDW respect the surface water and about 20% respect the HSSW characterized by a temperature of about  $-1.9\text{ }^{\circ}\text{C}$ . This gradient of concentrations may be one experimental evidence that also the external oceanic circulation may contribute to the pollutant input in the Ross Sea basin, which happens in a period of the season when the ecosystem is particularly sensitive since the biological activity reaches its maximum.

In order to assess the spatial distribution of  $\alpha$ -HCH and the net direction of air/water gas exchange, between November 1997 and February 1998, surface and subsurface seawater samples were collected along one transect on the African side of the South Atlantic Ocean to Antarctica. The  $\alpha$ -HCH was predominately found in the dissolved phase with <0.5% on the particulate fraction. Concentrations of  $\alpha$ -HCH in surface water generally ranged from 5.1 to 19  $\text{pg l}^{-1}$ , with 28  $\text{pg l}^{-1}$  for one sample. A slight trend with latitude was noted in which concentrations reached its maximum between 47° and 51°S and again around 60°S, then declined toward Antarctica. The first maximum occurred near the Subantarctic Front and the Antarctic Polar Front, which were identified between 46–47°S and 50–51°S, respectively. The second maximum occurred near the spring ice edge. Ten samples at 25–80 m and two at 200 m depth were also taken during the expedition. Concentrations of  $\alpha$ -HCH ranged between 5.7 and 34  $\text{pg l}^{-1}$  in the 25–80 m depth and between 3.5 and 4.4  $\text{pg l}^{-1}$  at 200 m. The water/air fugacity ratios of  $\alpha$ -HCH were 1.0, indicating steady state or net deposition conditions (Jantunen et al, 2004). This confirms the important role of the atmosphere on the transport of organic pollutants.

Results reported by Fuoco et al. (1996), on surveys carried out in a large area of the Ross Sea and Victoria Land during summer campaign between 1988-1989 to 1991-1992, showed the most significant findings relevant to: the presence and distribution of PCBs in several environmental components. Particular emphasis was given to the effect of the seasonal formation/melting process of pack ice on the pollution level of surface seawater. In particular they reported results obtained on seawater samples collected before and after pack ice melting in the Gerlache Inlet and Wood Bay. The PCBs concentration in surface seawater ranged from 90 to 180  $\text{pg l}^{-1}$  before pack ice melting, it increased to 150-230  $\text{pg l}^{-1}$  after pack ice melting. The increase of PCB concentration higher than 1.3 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 its melting.

Pesticides were determined by Dickhut et al. (2005) in the Antarctic Peninsula. The content of HCB, heptachlor,  $\alpha$  and  $\gamma$  HCH and heptachlor epoxide, were determined during the austral winter (September-October 2001) and summer (January-February 2002) in air, seawater, sea ice, and snow. The main aim was to estimate exchange at the air/water interface and to assess the accumulation on the pack ice. The content in air is discussed above in the atmosphere section. The HCH in surface water range from 1.65 to 4.54  $\text{pg l}^{-1}$  and from 0.9 to 10.5  $\text{pg l}^{-1}$  for the isomers  $\alpha$  and  $\gamma$  respectively. In addition to HCHs, heptachlor and heptachlor epoxide were also detected in the sea ice and snow samples. In spite of the higher air/water partition coefficients, these compounds were detectable in snow and sea ice. The presence of heptachlor and heptachlor epoxide in annual sea ice and snow is indicative of current atmospheric deposition of these pesticides to the Antarctic matrices, which is consistent with the observation that atmospheric heptachlor epoxide levels in the Antarctic have not declined over the past decade. The  $\alpha$ -HCH concentration for both sea ice and snow range from <0.04 to 2.18  $\text{pg l}^{-1}$ , while the  $\gamma$  HCH concentration range from 3.6 to 5.7  $\text{pg l}^{-1}$  and from 1.73 to 8.91  $\text{pg l}^{-1}$  for sea ice and snow respectively. The heptachlor and heptachlor epoxide concentrations in sea ice and snow are practically coincident, they range from <2.5 to 6.7  $\text{pg l}^{-1}$  and from <0.6 to 2.2  $\text{pg l}^{-1}$  for heptachlor and heptachlor epoxide respectively.

In order to describe the interaction between air and seawater, of particular importance is the

exchange of POPs at the water/atmosphere interface. The sea surface micro-layer is the widest environmental interface, where many important processes occur, including the accumulation of pollutants and other chemical substances, atmospheric particles, and microorganisms. A widely accepted conceptual model of the seawater surface is based on a multi-layer structure. The top layer (0.01 -0.001  $\mu\text{m}$ ) is formed –in remote areas- almost exclusively by naturally-derived surface active substances, whose chemical composition still has to be completely defined. There is a dynamic equilibrium, which involves the supply and removal of chemical substances. Supply processes include deposition from the atmosphere, bubble flotation and hydrodynamic renewal from sub-surface water, the latter being in turn affected by underlying water column. Removal processes include injection into the atmosphere in an enriched form as part of the marine aerosol produced by bursting bubbles. Most of the studies of POPs in the sea-surface micro-layer were undertaken in coastal environments. Very few samples have been analyzed from open oceans, 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.

The enrichment of PCBs and PAHs in the sea surface micro-layer (SML) and the depth profile of these pollutants in the water column were investigated at Gerlache Inlet. PCBs and PAHs showed a concentration range in the water column of 30-120  $\text{pg l}^{-1}$  and 150-400  $\text{pg l}^{-1}$ , respectively. In late summer there was observed a two-fold increase of PAH concentration in the first 20 cm of the water column (Sub-surface water, SSW). The mean concentrations in the surface micro-layer were 449 and 2726  $\text{pg l}^{-1}$  for PCBs and PAHs respectively. The estimated sampled sea-surface layer was about 100  $\mu\text{m}$ , while it can be assumed that POPs are confined in a very thin top layer of the SML of about 0.01-0.001  $\mu\text{m}$  thick, therefore an enrichment factor of  $10^5$ - $10^6$  for the sea-surface nano-layer was estimated. The authors also emphasized that the POPs concentration in seawater present high variability and their values were dependent on the suspended matter content (Fuoco et al., 2005).

During the Austral spring in 1998-1999 Cincinelli et al. (2005) measured PAHs concentration in the sea surface micro-layer (SML) and sub-surface layer (SSL) samples and in fresh snow collected in the coastal area of Terra Nova Bay. In dissolved phase, PAH concentration in SML varied from 4.67 to 7.79  $\text{ng l}^{-1}$  and from 2.24 to 4.01  $\text{ng l}^{-1}$  for SSL. The particulate PAH content of seawater ranged from 5.68 to 14.1  $\text{ng l}^{-1}$  in SML and from 1.65 to 3.65  $\text{ng l}^{-1}$  in SSL, therefore both for dissolved and particulate phases were enriched in PAHs. The PAH levels reported by Cincinelli were compared with those present in the literature for Antarctic seawater. Remarkable differences were observed on results reported by different authors. Cripps [1990] in a study carried out in the Bransfield Strait area, reported total PAH concentration lower than detection limit (50  $\text{ng l}^{-1}$ ) at 43% of the sampling stations, while a further 43.5% had values in the range 50-500  $\text{ng/l}$  and 13% 500-1700  $\text{ng/l}$ . In samples collected at the Signy research station (South Orkney Islands) the same author measured a total PAH content ranging from 50 to 200  $\text{ng l}^{-1}$ , depending on the distance from the coast. Higher contents of total PAHs, concentrations up to 9400  $\text{ng l}^{-1}$ , were observed by Comes and coworkers some years before in the Weddel Sea (Comes et al., 1987).

The coastal zones are directly exposed to marine air masses and coastal snow appears to be a very good collector of aerosol in those conditions in which all other expected aerosol contributions are minimal. Therefore organic compound concentrations in snow samples

depend on the different composition of marine aerosol with respect to the seawater and on the distance from the coast and altitude above sea level of the snow sampling site. In order to better understand this phenomenon, the Cincinelli and coworkers calculated the ratios between the concentration of organic compounds in snow and seawater samples using concentration data normalized by the concentration of sodium in the same matrices. They found similar PAH concentrations and pattern in snow samples collected after the same precipitation at different altitudes. Total PAH concentrations varied from 0.60 to 2.98 ng l<sup>-1</sup>, and the main PAH components were fluorene, anthracene, pyrene and chrysene; the same prevalent components detected in seawater samples. On the base of these results they hypothesize that chemicals found in the SML were transferred to the “fresh” snow samples by marine aerosols and were enriched particularly in the finest particles, a process that can be involved in the long-range transport of pollutants (Cincinelli et al., 2005).

Stortini et al. [2009] provided update data about PAHs concentrations in the SML and SSW samples from Antarctica coastal waters (Ross Sea, Antarctica) and identified the possible sources and partitioning of pollutants between the dissolved and particulate fraction, considering the results obtained on samples collected in 2001. The concentration found in SML and SSW samples collected at Gerlache Inlet were extremely low and confirmed the previous data by Cincinelli et al. (2005). The PAH concentrations in dissolved phase varied from 4.25 to 8.11 ng l<sup>-1</sup> for SML and from 2.14 to 2.85 ng l<sup>-1</sup> for SSW, while PAH content in sea water particulate ranged from 3.07 to 15.83 ng l<sup>-1</sup> in SML and from 2.81 to 4.66 ng l<sup>-1</sup> in SSW.

There are studies to identify sources of PAHs, either from petrogenic and pyrolytic origin, using ratios of specific PAH compounds (Azini et al., 2005 and Wang et al., 1999), Results reported by Fuoco et al. (2005) on the SML and SSW samples collected in the same area, during the 1997/1998 summer in the Gerlache Inlet area, showed LMW/HMW ratios indicating a petrogenic origin of PAHs.

The same authors (Fuoco et al, 2009) described the presence on PCBs and PAHs in seawater samples collected in a large area of the Ross Sea during various campaigns, especially comparing the result relative the 1997-98 and 2000-01 expeditions with the results obtained in 2003. A hypothesis was also made about a possible PAH source using the LMW/HMW ratio. The results highlighted a low and quite homogenous contamination of the area under investigation: the mean values of total PCBs and total PAHs were 50 pg l<sup>-1</sup> and 220 pg l<sup>-1</sup> respectively. The ratios LMW/HMW and PHE/ANT were calculated for all surface seawater samples collected in various areas of the Ross Sea, both near the coast and offshore. The low to high molecular weight PAH ratio was higher than 1, ranging from 1.6 to 3.2. Moreover, three samples had PHE/ANT values higher than 5, ranging from 6.3 to 12.0. Although this would seem to indicate a predominant petrogenic source of PAH contamination, the use of PAH ratios for source identification could be questionable in remote areas such as Antarctica. The petrogenic source might be due to either natural processes or be attributed to local sources related to anthropic activities, like micro spills and/or small leaks. Moreover, it is difficult to be sure that the levels of PAH measured in seawater samples could only be attributed to these contributions, because PAHs are known to be highly resistant to degradation processes, since their distribution pattern of the primary source may have been affected by the difference in the kinetic parameters controlling the photo-degradation reaction

of different isomers; therefore, the composition may be due to aged air masses reaching Antarctica by long-range transport.

Marine sediment is frequently used to reconstruct environmental pollution trends. Fuoco et al (1995) studied the distribution of PCBs in the sediment from Terra Nova Bay and Ross Sea gathered, during the 1990-1991 expedition. The relevant PCB concentrations ranged between 30-160  $\mu\text{g g}^{-1}$ , the variability was related to the particle size distribution. The depth profiles of PCB content in marine sediment samples collected in a few stations clearly show that PCBs are confined in a surface layer of about 10 cm. The data were confirmed by results successively presented (Fuoco et al., 1996).

Klanova et al. (2008) determined PCBs, OC pesticides and PAHs in sediment samples from James Ross Island. Sediment PCB concentrations ranged from 0.32 to 0.83  $\text{ng g}^{-1}$ , while they ranged from 0.14 to 0.76  $\text{ng g}^{-1}$  for HCHs, from 0.19 to 1.15  $\text{ng g}^{-1}$  for DDTs, and from 1.4 to 205  $\text{ng g}^{-1}$  for PAHs. The authors emphasized a prevalence of low-mass PAHs, less chlorinated PCBs, and more volatile chemicals. They explained this by the prevalent origin of POPs in Antarctica, namely, in particular in James Ross Island, the long-range atmospheric transport from populated areas of Africa, South America, and Australia.

Montone et al. (2001) determined PCBs in sediments of Admiral Bay on King George Island collected in the 1993/1994 austral summer. The individual concentrations of PCB congeners ranged from  $<0.05$  to 0.57  $\text{ng g}^{-1}$  dry weight, and the levels of total PCBs ranged from 2.03 to 5.91  $\text{ng g}^{-1}$  dry weight. These levels are comparable to those found in Antarctic sediments from pristine regions.

More data are available on environmental contamination deriving from the presence of scientific bases. Negri et al. (2006) examined the concentrations of total hydrocarbons (THC), PCBs, PAHs, in marine sediments off the Scott Base (NZ) and compared them with sediments near the highly polluted McMurdo Station (US) as well as less contaminated sites including Turtle Rock and Cape Evans. The THC concentration in sediments from Scott Base ranged from 3.0 to 134  $\mu\text{g g}^{-1}$ , 3 fold higher than the pristine site, Turtle Rock, but 10 fold lower than samples from McMurdo Station. The concentration of PAHs ranged from 0.1 to 2.1  $\mu\text{g g}^{-1}$ . PCB content varied between  $< 5$  and 373  $\text{ng g}^{-1}$ . The PCB concentrations for Turtle Rock were below the detection limit ( $<5 \text{ ng g}^{-1}$ ).

Curtosi et al (2007) reported the concentration of PAHs in sediment samples collected in two consecutive summer Antarctic expeditions at Potter Cove and on the peninsula, in the vicinity of Jubany Station (South Shetland Islands). Two- and 3-ring PAHs (methyl-naphthalene, 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 distribution 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 sediment PAH contents were assessed also in relation to the distribution in soils. The highest level in soil was detected in the upper layer of permafrost followed by a sharp decrease in depth, showing this layer is acting as a barrier for downward PAH migration. The authors observed a significant decrease in the soil content in summer 2005 (range  $12 \pm 1 - 153 \pm 22 \text{ ng g}^{-1}$ ) compared to summer 2004

(range  $162\pm 15$  -  $1182\pm 113$  ng g<sup>-1</sup>) contemporaneously was observed the accumulation in the marine sediment of the area. The PAH concentrations in surface sediment collected nearby the station increased drastically in 2005 (range:  $36\pm 3$  -  $1908\pm 114$  ng g<sup>-1</sup>) compared to 2004 (range:  $28\pm 3$  -  $312\pm 24$  ng g<sup>-1</sup>). Precipitation regime and water run off suggest that an important wash out of soil-PAHs occurred during the interval time between samplings. Results showed that the present PAH contamination level of Jubany Station was relatively low compared to other reported cases in Antarctica but also suggests that an increase in rain and in thawing processes caused by the global warming could result in an important soil-associated PAH mobilization with unpredictable consequences. The contents of aliphatic hydrocarbons (AHs) and PAHs were also measured in marine surface sediments around the Brazilian station at Admiralty Bay, during the summers of 1997/98 and 1999/2000 (Martins et al., 2004). Total aliphatic hydrocarbons ranged from 0.15 to 13.28  $\mu\text{g g}^{-1}$  (dry weight) while n-alkanes varied between 0.10 and 9.63  $\mu\text{g g}^{-1}$ . The distribution of n-alkanes showed significant quantities of long chain n-alkanes (n-C-22 to n-C-34) at sites near the Brazilian station that may be attributed to the station activities. A short chain n-alkanes sequence (n-C-12 to n-C-21) associated with diesel fuel Arctic (DFA) was present in all the samples. Total PAHs varied from 9.45 to 270.5 ng g<sup>-1</sup>. The higher PAHs level and the presence of an unresolved complex mixture only in sediment from the sewage outfall was considered as an indication of oil contamination at that location. A slight increase in PAHs near the Brazilian station since 1993 was attributed to the increase in the number of staff over recent years.

Some studies were carried out next to McMurdo Station (the largest scientific base in Antarctica). The more interesting area is Winter Quarters Bay, in consideration of its contamination problems. The concentration and the stable carbon isotopic composition of PAHs at McMurdo Station were determined in samples collected from land and from the sub-tidal area (Kim et al., 2006). PAHs in the study areas were characterized by high amounts of naphthalene and alkylated naphthalenes from petroleum products, the total concentration of PAHs ranged from 61 to 5024 ng g<sup>-1</sup>. Compositional assignments of origins were confirmed using compound specific stable carbon isotopic analysis. In the same area, Crockett and White (2003) determined the sediment concentrations of PCBs, metals, and hydrocarbon fuels. The main aim was to map the distribution of organic contaminants in WQB and assess the toxicity of sediments using a simple microbial test.

Studies of chemical contamination in Antarctica are commonly focused on POPs. However, some emerging pollutants exhibiting characteristics of persistence comparable to POPs should also be considered. Hale et al. (2006) highlighted the presence of polybrominated diphenyl ether (PBDE) in sediment next to McMurdo station. These compounds are used as flame retardant and are present in many modern polymer-containing products, e.g., home/office furnishings and electronics. BDE-209, the major constituent in commercial deca-PBDE products, was the dominant congener in sludge and dust, as well as aquatic sediments collected near the McMurdo wastewater outfall. Pattern and BDE-209 sediment concentration, in conjunction with its limited environmental mobility, suggested inputs from local sources. The total concentration of PBDEs ranged from 43.6 to 1820 ng g<sup>-1</sup>. The data indicate that reliance on wastewater maceration alone, as stipulated by the Protocol, may permit entry of substantial amounts of PBDEs and other chemicals to the Antarctic environment.

## **4. POPs in the terrestrial environment**

The analysis of polar snow and ice cores is one of the most suitable approaches for assessing (global or hemispheric) deposition of atmospheric contaminants and for reconstructing changes in atmospheric composition and climate history. The average annual precipitation on the Antarctic plateau is very low (usually 2- 4 g cm<sup>2</sup> year<sup>-1</sup>; Brownich and Parish, 1998), with the advantage that a 1-m ice core covers many years; however, this makes difficult to assess short-term variations in atmospheric deposition (Bargagli 2004). Risebrough et al. (1976) collected samples from a pit dug in a permanent snow-field on Doumer Island, close to the US Palmer Station and reported average concentration in surface snow of pp'-DDT (0.5 pg g<sup>-1</sup>), pp'-DDE (0.1 pg g<sup>-1</sup>), and total PCBs (0.15 pg g<sup>-1</sup>). Values increased in samples collected at 2-4 m depth (4, 0.27 and 1.2 pg g<sup>-1</sup> respectively), and then decreased at 5.5-6 m depth (2.1, 0.21 and 0.28 pg g<sup>-1</sup> respectively). The distribution pattern of pp'-DDT and pp'-DDE was similar, and the quantitative ratio between the two compounds was approximately 10 along the profile. The snow profile is not dated, but this is a region of high snow accumulation, with surface firn accumulation at about 1-2 m per year, so that the deepest snow in the Risebrough profile would be little more than a decade before the sampling (UNEP 2002). This would date the DDT and DDE peaks at no earlier than 1970. Tanabe et al. (1983) also measured DDT concentration in snow, collected close to the Syowa Station. Inland snow samples, both deep and shallow, showed similar levels of total DDT, suggesting similar deposition rate between the 1960s and the 1980s in contrast to the Risebrough et al. data. Total DDT content in snow samples was 9-17 pg total DDT dm<sup>-3</sup>. The bulk density of snow pack is not given, but this last concentration must still be substantially lower than the Douner Island values. Since the samples in the two studies cited here probably span similar time periods, the contrast between the two results points to a large amount of spatial variability in the deposition of DDT in Antarctic precipitation.

Tanabe et al. (1983) also analysed PCBs and HCH in snow samples collected close to Syowa Station. Overall snow sample concentration was 1.5-4.9 pg g<sup>-1</sup> and 0.2-1 pg g<sup>-1</sup> for total HCH and total PCBs, respectively. In ice (type not specified) total HCH and total PCBs concentration was 2.0- 2.2 pg g<sup>-1</sup> and 0.3-0.6 pg g<sup>-1</sup>, respectively. In contrast to Risebrough and co-workers, they found no significant variations in total DDTs, HCHs or PCBs between samples of surface and deep snow.

Fuoco (1996) analysed lake sediment and soil samples collected in a large area of Victoria Land during the 1988-1989, 1989-1990, 1990-1991, and 1991-1992 Italian expeditions. Total PCB mean concentration was 120 (CV 87%) and 60 (CV 38%) pg/g dry weight for lake sediment and soil samples, respectively. Since PCBs are generally adsorbed on the particle surface, the concentration of each sample (expressed in pg/g dry weight) was normalized by dividing it for the relevant calculated specific surface area (CS), expressed in square meters of surface per cubic centimetre of dry sample (m<sup>2</sup>/cm<sup>3</sup>), as obtained by particle size analysis. The mean normalized concentration was 240 (pg/g)/ (m<sup>2</sup>/cm<sup>3</sup>) dry weight for lake sediments (CV 27%); and 130 for soils (CV 18%). The much higher PCB concentration in lake sediment is probably due to the nature of Antarctic lakes, which form during the deglacial season from ice melting waters that are rich in atmospheric particulate matter trapped in the ice matrix during its formation. Lake sediments and soil samples also showed a PCB content that did not change significantly among sampling stations (the 95% confidence intervals of

the mean value for each matrix included the concentration of all the samples analysed). This low and quite homogeneous PCB contamination of the area under study may rule out any direct source of PCB pollution in Antarctica.

More recently, Fuoco and Ceccarini (2001) determined the concentration of selected PCB congeners in samples of recent snow and firn collected during the austral summer 1993–1994 in seven snowfields throughout northern Victoria Land. The pattern of PCB isomers in snow showed a predominance of lower chlorinated congeners and the pattern roughly reflects that reported for atmospheric PCBs at Signy Island and King George Island (Kallenborn et al, 1998; Montone et al, 2003). The sampling sites of surface snow throughout northern Victoria Land were located at different altitudes (from sea level to 3,000 m) and at varying distances from the sea, but total PCB concentration measured by Fuoco and Ceccarini showed no significant spatial variations (range 0.28–0.73 pg g<sup>-1</sup>; mean value 0.52 pg g<sup>-1</sup>). 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<sup>-1</sup>) in the deepest samples (presumably deposited around 1986–1988) than in surface snow (0.65 pg g<sup>-1</sup>). This result seems to corroborate previous findings by Risebrough et al. (1976), 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. The numerous studies performed on PCB congener patterns in Arctic air and snow show that their distribution is very similar, with lighter tri-chlorinated PCB homologues largely dominating the atmosphere and snow of northern sites (Macdonald et al. 2000).

Estimates of spatio-temporal variations in the rate of POP atmospheric deposition based on snow and firn data may contain large uncertainties due to meteorological conditions – which make it very difficult to select sampling sites representative of local atmospheric deposition, especially in terrains with blowing and drifting snow – and to the possible post-depositional release of some contaminants. Temperature variations may also affect the post-depositional loss of more volatile compounds, and this process may be accentuated under warmer climatic conditions. Despite the difficulty in making reliable comparisons between POP concentration in snow from regions with different climatic and environmental conditions, sampled in different years and under very different climatic and environmental conditions, and also complicated by the different approaches adopted for calculating the total amount of PCBs and HCHs (e.g. sum of different number of congeners; quantified as Aroclor mixtures; sum of  $\alpha$ -HCH and  $\gamma$ -HCH), Bargagli (2004) came to some conclusions. In the first half of the 1990s, average PCB concentrations in Victoria Land snow (0.5 pg g<sup>-1</sup>) corresponded to the mean value measured by Melnikov et al. (2003) in snow from the Ob-Yenisey River watershed, and were about 8 times lower than the average 4.1 pg g<sup>-1</sup> reported by Macdonald et al. (2000) for Canadian Arctic snow.

Deger et al. (2003) analysed an ice-core sample taken from the Mackeller Peninsula in the Antarctic region on February 2002 for organo-chlorine pesticide endosulfan. Endosulfan has been withdrawn from the registered use in many countries, however it is still manufactured and used especially in developing countries. Despite restrictions on its use, endosulfan and its major metabolite endosulfan sulphate, which is of particular concern as it is extremely toxic to mammals and more persistent than its isomeric parent compound, continue to be detected in the environment even in remote areas. Endosulfan sulphate was determined in the ice-core

sample at a concentration of  $0.3 \text{ ng g}^{-1}$ . This result supports the findings of other researchers reporting its presence, even at higher concentrations (up to  $136 \mu\text{g l}^{-1}$ ) in remote areas as European remote mountain lakes (Vilanova et al, 2001) and Russian and Canadian Arctic (Boyd-Boland et al, 1996).

Human activities in Antarctica release a number of persistent organic atmospheric contaminants. To ascertain whether Palmer Station (Anvers Island) was a significant source of PCBs, Risebrough et al. (1976) collected four samples of surface snow at distances of 0.5–1.5 km from the station. They found high particulate contents, principally soot, and concentration of total PCBs ranging from 4 to  $10 \text{ pg g}^{-1}$  (i.e. 8–20 times higher than those measured in snow from the same region at Doumer Island). 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 (UNEP 2002).

In soils where oil spills have occurred, toxic PAHs may accumulate in very high concentration. In a sample collected near Old Palmer Station, Kennicutt et al. (1992) measured a concentration of  $345,000 \text{ ng g}^{-1}$  dry wt. In contaminated soil samples from an area near the Scott base for the storage of drums of engine oil, PAH concentration ranged from 41 to  $8,105 \text{ ng g}^{-1}$  dry wt. (Aislabie et al. 1999). As reported in other surveys performed on Antarctic soils, sample concentration of naphthalene and other PAHs indicative of spilled fuel always exceed those of pyrogenic PAHs (from high-temperature combustion); nevertheless, 11 of the 16 PAHs on the USEPA Priority Pollutant List were detected. Hydrocarbons had migrated to lower depths, and the highest concentration occurred at 2–10 cm deep subsurface soils. Mazzera et al. (1999) surveyed PAH concentration in surface soils at McMurdo Station during peak summer activity. The maximum value was measured for naphthalene, acenaphthalene, acenaphthylene and fluoranthene ( $27,000 \pm 2,600$ ,  $17,800 \pm 1,270$ ,  $15,700 \pm 6,300$  and  $13,300 \pm 430 \text{ ng g}^{-1}$  dry wt, respectively), especially in soils from unpaved roadbeds near the gasoline pumps for seawater intake. This polluted site was a potential source of the high level of PAHs found in sediment samples from McMurdo Sound by Kennicutt et al. (1995). However, available data on Antarctic soils show that PAH pollution is highly localised, and concentration in samples from control areas is usually below detection limits. In the environment around Davis Station, Green and Nichols (1995) found very low concentration, and the content of individual PAHs around a fuel deposit only exceeded  $1 \text{ ng g}^{-1}$  dry wt. 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.

Aislabie (2004) reviewed the properties of Antarctic soils; the sources and types of hydrocarbons that accumulate in the soils following fuel spills and the effects of the hydrocarbons on physical, chemical, and biological soil properties.

Comparisons between temperature profiles of hydrocarbon contaminated and pristine sites at Scott Base and Marble Point indicate that during sunny weather, when soils are snow-free, the daily maximum surface temperature of hydrocarbon-contaminated soils is often warmer (by up to ca.  $10 \text{ }^\circ\text{C}$ ) than adjacent pristine sites (Balks et al., 2002). The higher temperatures at the hydrocarbon contaminated sites were attributed to decreased soil surface albedo due to surface darkening by hydrocarbons. In contrast, at a Bull Pass site where hydrocarbons

contaminated the subsurface, no difference in soil temperature was detected between a pristine and hydrocarbon-contaminated soil. There is potential for hydrocarbons to affect soil moisture regimes. Hydrocarbon-contaminated soils were weakly hydrophobic, whereas no evidence of hydrophobicity was detected at pristine sites.

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.

Lichens and mosses are cryptogamic organisms with a number of features in common. They lack root systems, have a high cation-exchange capacity (CEC), and depend largely on atmospheric deposition for their nutrient supply. Mosses and lichens therefore have elemental compositions reflecting in an integrated way gaseous, dissolved and particulate elements in atmospheric deposition (Bargagli 1998). Lichens and mosses are the principal component of terrestrial flora in many ecosystems of continental Antarctica and can play a very important role as bio-monitors of persistent contaminant deposition around scientific stations and in field camps.

Owing to their slow growth rates and long life cycles (probably of up to some 100 years), lichens behave as long-term integrators of persistent atmospheric pollutants; the analysis of 50- to 60-year-old specimens may yield information about DDT and other POP deposition. As a rule, concentration of local and long-range transported contaminants in *lichen thalli* is much higher than that in the atmosphere or snow, and this makes analytical determinations easier. The average content of HCB, HCH, DDTs and PCBs in lichens and mosses collected in 1985 and 1988 in the Antarctic Peninsula and northern Victoria Land ranged from 0.2–9.9 ng g<sup>-1</sup> dry wt. (Bacci et al. 1986; Focardi et al. 1991; i.e. three orders of magnitude higher than those in Antarctic snow).

Borghini (2005) measured organo-chlorine pollutants in soils and mosses from Victoria Land. Total PCB concentration in mosses ranges between 23 and 34 ng g<sup>-1</sup> dry wt. These values are in the same order of magnitude as those reported for the moss *Hylocomium splendens* in Norway, e.g. 6.7–52 ng g<sup>-1</sup> dry wt. (Lead et al., 1996). Previously reported PCB concentration in Antarctic mosses collected in the same sampling area ranges from <5 to 16 ng g<sup>-1</sup> dry wt. (Focardi et al., 1991).

The concentration ranges of 4,4'-DDE and 4,4'-DDT were 1.1–7.9 and 0.54–0.91 ng g<sup>-1</sup> dry wt., respectively. Similarly to PCB, these compounds exhibit a rather uniform distribution of concentration with less than one order of magnitude of variation. Higher concentrations of 4,4'-DDE were found in all samples, which is consistent with a long-range transport as being responsible for the transformation of 4,4'-DDT to 4,4'-DDE after release into the environment. Previous studies of these two pesticides in Antarctic moss samples showed concentration of 0.2–0.5 ng g<sup>-1</sup> dry wt. for both compounds (Focardi et al., 1991).

HCB exhibited rather uniform concentration, 0.85–1.9 ng g<sup>-1</sup> dry wt.. Previously reported HCB concentrations in Antarctic mosses were 0.3–0.8 ng g<sup>-1</sup> dry wt. (Focardi et al., 1991).

α-HCH and γ-HCH are the major HCHs found in the samples. They involved the largest concentration ranges of all OC analyzed, 0.43–4.0 and 0.18–1.6 ng g<sup>-1</sup> dry wt., respectively. The concentration of these two pesticides in previous Antarctic moss studies encompassed 0.2–1.1 and 0.4–1.7 ng g<sup>-1</sup>, respectively. In all cases except Granite Harbour, α-HCH is found

in higher concentration than the  $\gamma$ -isomer. The high proportion of the  $\alpha$ -isomer is consistent with previous observations in other remote sites (Atlas and Giam, 1981; Harner et al., 1999; van Drooge et al., 2001) as these areas currently reflect past usage of  $\alpha$ -HCH enriched technical mixtures and only pure lindane ( $\gamma$ -HCH) is presently found in the areas under higher anthropogenic influence (Harner et al., 1999).

Soil PCB concentration varied between 0.36 and 0.59 ng g<sup>-1</sup> dry wt. These values were similar to those reported in lake sediments of Arctic regions, 0.12–0.60 ng g<sup>-1</sup> dry wt. (Gubala et al., 1995; Allen-Gil et al., 1997). 4,4'-DDE and 4,4'-DDT range between 0.053–0.086 and <0.005–0.020 ng g<sup>-1</sup> dry wt. Again, the higher abundance of 4,4'-DDE over 4,4'-DDT precludes that their occurrence may be due to recent spillages. Among soil HCH, only the isomer  $\alpha$ -HCH was found above limit of detection between <0.01 and 0.026 ng g<sup>-1</sup>. As for moss samples, the dominance of the  $\alpha$ -isomer is consistent with the observations in remote sites (Atlas and Giam, 1981; Harner et al., 1999; van Drooge et al., 2001). HCB ranged between 0.034 and 0.17 ng g<sup>-1</sup> dry wt. These concentrations are also similar to those reported in Arctic lake sediments (Allen-Gil et al., 1997). These low values of the Antarctic mosses and soils reflect the absence of local pollution sources near the sampling sites and are consistent with the lower use of organo-chlorine compounds in the southern hemisphere.

The Antarctic continent does not have stream–river drainage systems, Antarctic lakes are thus the main sinks for water and solutes from the surrounding environment. Depending on their origin, the presence of a perennial ice cover, exposed rocks and soils in the watershed, seabirds and distance from the sea, the water may show very different characteristics – from almost distilled to salt-rich brine which does not freeze in winter. Despite this variability, waters, sediments and the biota are natural integrators of soluble elements and compounds deposited in the watershed, and these matrices may play a very important role as indicators of the impact of local human activities and/or of long-term changes in climatic conditions and biogeochemical processes.

Burgess and Kaup (1997) discussed human impacts on lake systems in the Larsermann Hills region. In this region Ellis-Evans et al. (1997) found remarkable changes in microbial communities in a lake located near a scientific station, built only four years earlier. Although the concentration of persistent contaminants in these and other Antarctic lakes affected by human activities has not yet been determined, there is evidence that lake sediments in northern Victoria Land accumulate higher concentration of PCBs than soil or marine sediments (Fuoco et al. 1996).

Li guang (2005) determined the accumulation flux profiles and temporal trends of organo-chlorine pesticides such as DDT and HCH in two lake cores from King George Island, West Antarctica. 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. In the lake core sediments without glacier melt water input, the accumulation flux of DDT shows a gradual decline trend after the peak in 1960s. This striking difference in the DDT flux profiles between the two lake cores is most likely caused by the regional climate warming and the resulted discharge of the DDT stored in the Antarctic ice cap into the lakes in the Antarctic glacier frontier, as already reported by Fuoco et al. (1996) for PCBs.

Negoita (2003) measured concentration of hexachlorobenzene (HCB),  $\alpha$ -,  $\beta$ - and  $\gamma$ -

hexachlorocyclohexane (HCH) isomers, o,p'- and p,p'-isomers of DDT and 28 PCB congeners in eleven soil samples and one lichen collected on the Eastern coast of Antarctica from 5 Russian stations. The concentration of OCPs and PCBs was highly variable for different pollutants and between the research stations. This is due to the particular characteristics of the areas from where samples were taken and to the different pollution pathways. For samples with low concentration of PCBs (range 0.20–0.41 ng g<sup>-1</sup> dry weight) and pesticides (0.86–4.69 ng g<sup>-1</sup> and 0.11–1.22 ng g<sup>-1</sup> dry weight for HCHs and DDTs, respectively), atmospheric long-range transport from Africa, South America or Australia was suggested as the sole source of contamination. The profile of PCB congeners was dominated by the more volatile tri, tetra- and penta-PCBs congeners, thus supporting the long-range transport hypothesis. Four samples contained a moderate level of PCBs (range 1.98–6.94 ng g<sup>-1</sup> dry weight) and a variable concentration of pesticides ( $\gamma$ -HCH, p,p'-DDT and o,p'-DDT being the main contaminants). For samples with high concentration of PCBs (range 90.26–157.45 ng g<sup>-1</sup>) and high concentration of pesticides, the presence of high molecular weight PCB congeners such as: 153, 180, 187, 170 etc, strongly suggests a local source of PCBs rather than atmospheric transport. Therefore authors suggested that on a local scale, biotic focussing of pollutants, due to bird activities (nesting and excrement) can cause high contamination levels and become more significant than contaminant input via abiotic pathways.

Kim et al. (2006) analyzed samples from McMurdo Station for PAH molecular and stable carbon isotopic compositions to discern the origins of contaminants in the area. Total PAH concentrations ranged from 664 ng g<sup>-1</sup> to 74,267 ng g<sup>-1</sup> dry wt for soil samples. Elevated PAH contamination on land was found in areas where fuels were stored and in areas of parking and heavy traffic in central McMurdo Station. The mean total PAH concentrations in the samples from the four sites of known contamination sources on land (the fuelling stations, the old oil tanks, the helipad and the machine shop) differed by about a factor of two from 17,567 ng g<sup>-1</sup> in 1999 to 38,326 ng g<sup>-1</sup> in 2001. The large changes in PAH concentrations observed at the fuelling stations and the machine shop are presumably due to on-going contamination. At the sites of old oil storage tanks and the helipad, statistically significant changes in total PAH concentrations between the two different samplings were not observed. On-going introduction of fuel PAHs at the fuelling station and the machine shop were confirmed by the “freshness” of the spills as indicated by the alkylnaphthalenes to total PAH ratios.

Curtosi et al. (2007) sampled soil in two consecutive summer Antarctic expeditions at Potter Cove and peninsula, in the vicinity of Jubany Station (South Shetland Islands). Total PAH concentration in soil samples obtained during the first sampling (January 2004) were generally low although higher than those shown at a reference site located in a pristine area far from direct influences (fumes or spills) from the station. Total PAH concentrations in surface soil of all sampling sites were significantly lower than values at 75-cm depth. Surface values (19–42 ng/g dw) were approximately one order of magnitude lower than those measured at 75-cm depth (162 and 1052 ng/g dw). The second striking feature was the difference between PAH pattern in surface soil when compared with 75-cm depth samples. At surface, even though phenanthrene was predominant, ranging between 8 and 27% of the total PAH concentrations, several other PAHs were present at appreciable levels: naphthalene (1–16%), fluoranthene (4–16%), acenaphthylene (1–9%) and benzo(a)pyrene (4–11%). On the contrary, a great prevalence of phenanthrene was found (66–85% of the total PAHs) at a

depth of 75 cm and also the other 3-ring PAHs fluorene and anthracene are enhanced at 75-cm depth in comparison with those observed at surface. PAHs with lower molecular weights (as naphthalene and 2-methylnaphthalene) also showed an important enrichment at 75-cm depth in 2004 sampling campaign. The second sampling (February 2005) revealed in the surface layer, levels of PAHs similar to those observed 1 year earlier, with the exception of one sampling site located very close to the main buildings of the station where concentration of PAHs (552 ng/g) was notoriously higher than 1 year before. However, this increase is associated with a diesel spillage which occurred a few months earlier in the fuel storage tanks located close to the sampling site. Total PAH concentrations increased progressively with depth into the active layer at most sites showing the highest values at 200–205-cm depth layer, corresponding to the layer just above permafrost. However, values of total PAHs found at 75-cm depth during the second sampling were all significantly lower than those registered during the first sampling year.

Klånova (2008) measured levels of persistent organic pollutants in solid environmental matrices of James Ross Island collected in 2005. James Ross Island is a large island (2500 km<sup>2</sup>) off the southeast coast of the Antarctic Peninsula (64°10'S, 57°45'W). The influence of previous scientific expeditions operating in the island on its fragile environment was found negligible and, as a new polar station was completed in February 2006; those results can serve as an initial point for the evaluation of an anthropogenic impact of new research station in following years, and related to the scientific program of the station. Soil and sediment samples from James Ross Island were analysed for their PCB, OCP and PAH contents. Soil concentrations ranged between 0.51 and 1.82 ng g<sup>-1</sup> for seven indicator PCB congeners, between 0.49 and 1.34 ng g<sup>-1</sup> for HCH congeners, between 0.51 and 3.68 ng g<sup>-1</sup> for the sum of p,p'-DDT, DDE, and DDD, and between 34.9 and 171 ng g<sup>-1</sup> for the sum of 16 EPA PAHs. Sediment levels ranged from 0.32 to 0.83 ng g<sup>-1</sup> for PCBs, from 0.14 to 0.76 ng g<sup>-1</sup> for HCHs, from 0.19 to 1.15 ng g<sup>-1</sup> for DDTs, and from 1.4 to 205 ng g<sup>-1</sup> for PAHs. A prevalence of lower molecular weight PAH compounds (phenanthrene and fluoranthene), less chlorinated PCB congeners (the pattern dominated by tri- and tetra-chlorinated congeners) as well as other more volatile chemicals as HCB in the soil and sediment samples indicates that the long-range atmospheric transport is the most probable source of contamination in the James Ross Island. In general, PCB and OCP levels measured in this research project were consistent with those obtained from the Ross Sea and Victoria Land (Fuoco et al., 1996) or less contaminated soil samples from the East Antarctic (Negoita et al., 2003), rather than from heavily contaminated sites in the Winter Quarters Bay where the PCB levels in sediments were as high as several mg g<sup>-1</sup> (Risebrough et al., 1990). PAH levels were similar to those in the marine surface sediments collected in Admiralty Bay (Martins et al., 2004) but smaller than the soil levels measured in the Scott Base Research Station, the Marble Point or the Wright Valley (Aislabie et al., 1999), or the sediment in Winter Quarters Bay (Cleveland et al., 1997) being as high as tens of mg g<sup>-1</sup>.

However, the soil samples from the Whisky Bay area showed a different pattern with a higher amount of less volatile PAH compounds indicating a presence of local sources of pollution. Similarly, the river sediment sample from the same sampling area as well as one of the sediment samples from the Solorina Valley showed the same results. Contamination with the chlorinated compounds seems to be more uniform; only the northern regions (Lachman Cape) exhibited a higher concentration ratio of the more chlorinated PCBs than the rest of the island. Higher POP levels in the matrices collected from northern and western parts of the

island also generally support the hypothesis of the long-range atmospheric transport of POPs to the Antarctic.

## **5. POPs in the Antarctic food web**

Antarctica is protected by the Protocol on Environmental Protection, which came into force in January 1998. Marine pollution can still occur, however, as a result of oil spills, sewage and garbage release, long range transport of contaminants and introduction of exotic organisms (Barnes, 2007). Contamination of Antarctic benthic organisms can occur from human waste, atmospheric transport, upwelling, volcanic output and geothermal activity. Polychlorinated biphenyls are imported through human activities locally or in more temperate regions and can then be biomagnified (Corsolini & Focardi 2000). Organochlorine pesticides are imported through the atmosphere thousands of km away from industrialized and densely populated areas (Risebrough 1977, Iwata et al., 1993; Halsall et al., 2001). A number of benthic species have been surveyed for such contaminants and some have unexpectedly high levels (Kennicutt et al. 1995; Bargagli 2005). Hydrocarbon contamination may derive from atmospheric transport or local contamination from research and old whaling stations and ships (Platt 1978; Green & Nichols 1995). Of particular note is the Bahia Paraiso spill in January 1989 offshore of the US Palmer Station on the Antarctic Peninsula, where an estimated 600 000 l of petroleum were lost (Penhale et al. 1997). The oil spill had varying effects depending on habitat and species. Toxic effects were most evident on intertidal organisms, such as limpets and macroalgae, and in seabirds, such as cormorants and Adelie penguins. No evidence of impact could be found for subtidal species and marine mammals.

Sewage release occurs at coastal research stations, of which there are currently 43 winter-over and 28 summer-only ([www.comnap.aq](http://www.comnap.aq)). Ships in Antarctic waters are also allowed to release food waste and sewage at a distance of 12 nautical miles from land and ice shelves. Release of oil, noxious liquids and garbage is prohibited, although it has happened in the past, usually offshore of research and whaling stations (Lenihan & Oliver 1995; Barnes, 2007). Sewage release results in the introduction of non-native microbes, trace elements, nutrients, organics and particulates. Antarctic stations are required to monitor the quality of their sewage effluent, but published data on the effects on benthic communities is largely limited to Australia's Casey Station and the United States' McMurdo Station (Dayton & Robilliard 1971; Kennicutt et al. 1995; Lenihan & Oliver 1995; Stark et al. 2003; Conlan et al. 2004). In the past, raw sewage was released; treatment is beginning to be implemented at some stations, and up to 2005, 26 of 43 permanent stations, 8 of 28 summer stations and 0 of 4 field station were equipped with wastewater treatment (Thompson, 2005). However, past pollution is still evident decades after release and may take centuries to millennia to degrade.

On the other hand the degradation of deposited POPs is very slow in the Polar Regions due to the low temperatures and winter darkness. Ice can entrap POPs and release them into the environment, when it melts (Fuoco et al., 1991), allowing them to enter the trophic webs, which in Antarctica is relatively simple and short: animals at the top of the food webs depend on a few key species, such as the Antarctic silverfish (*Pleuragramma antarcticum*) and Antarctic krill (*Euphausia superba*), which are the prime food source for several bird species and marine mammals, which depend on them either directly or indirectly (Corsolini, 2008).

Also, concentration of persistent contaminants in organs and tissues of Antarctic organism may not reflect exposure. These organisms tend to be slow-growing and long-lived; as food availability (and the uptake of persistent contaminants) exhibits strong seasonal variability, concentration of contaminants in their organs and tissues may vary in relation to the sampling period and feeding behaviour.

During the last three decades, a number of papers have been published on concentrations 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 dry mass, total lipid content, etc.). Also it is lacking an internationally accepted agreement on the meaning of “total PCBs” and “total PAHs”, in terms of the compounds whose individual concentration is included in the calculation of the total content (Fuoco et al., 2009). 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.

Literature data on persistent contaminant concentration will be reported according to the following scheme:

- Krill and pelagic food webs,
- Benthic and epibenthic organisms in the neritic province,
- Seabirds and seals breeding in Antarctica.

The names of all organisms mentioned are reported in the note at the end of this section.

Also, a summary data table listing the reviewed data according to contaminants is available at the end of this section.

The pelagic environment in the oceanic province shows two different food webs: one in permanently ice-free zones (dominated by copepods, salps and small euphausiids) and another in the seasonal pack-ice zone, in which krill (*Euphausia superba*) and the short food chain diatoms–krill–whales (or seals or penguins) are the dominant element. The relatively high efficiency of short food chains in the transfer of organic matter to top predators tends to reduce the amplification of pollutant loadings (biomagnification), but this effect is partly counterbalanced by the long lifespan (i.e. exposure time) of Antarctic marine organisms. Several species of seabirds and marine mammals migrate to lower latitudes (some even reach the Northern Hemisphere) during the austral winter; these seasonal migrations further complicate the interpretation of bioaccumulation data because migrating species reflect the integrated input of persistent contaminants (inside and outside the Southern Ocean).

The neritic province includes nearshore waters and ice shelves where phytoplankton may show intense and brief blooms. Due to the low biomass of zooplankton, however, most algal cells sink and become food for very rich benthic communities (sponges, hydroids, tunicates,

polychaetes, molluscs, actinarians, echinoderms, amphipods and fish). Many invertebrates are suspension-feeders, grow slowly, have long lifecycles, and can survive long period of starvation at negligible metabolic cost. They constitute an important link between primary producers (phytoplankton and benthic macroalgae) and notothenioid fish, which are in turn eaten by birds and marine mammals. As leopard seals and killer whales may eat penguins and seals, food webs on Antarctic continental shelves can become rather complex and long, thereby enhancing the biomagnification of persistent contaminants.

### 5.1 Pelagic plankton

Joiris and Overloop (1991) analysed organochlorine residues in samples of particulate matter (mainly phytoplankton) from the Indian sector of the Southern Ocean. They found that PCB concentration referred to by samples dry weight ( $0.7 \mu\text{g/g}$  dry wt.) was similar to that of temperate zones. Whereas values expressed per water volume unit were seven times lower ( $1.2 \mu\text{g m}^{-3}$ ) than North Sea ones ( $8.8 \mu\text{g m}^{-3}$ ) due to the low phytoplankton density. Thus, the authors suggested the need to adopt a different system of units in order to correctly express the contamination level of a marine area and to identify mechanisms responsible for persistent contaminant accumulation. In netplankton (mainly zooplankton) samples from the same zone, PCB concentration was comparable to that in phytoplankton on a dry weight basis ( $0.7 \mu\text{g/g}$  dry wt.), lower on a lipid weight basis ( $5.8 \mu\text{g/g}_{\text{lw}}$ ), and much higher when expressed per unit seawater volume ( $27.2 \mu\text{g m}^{-3}$ ). Very low concentrations of lindane, heptachlor epoxide, dieldrin, DDE and DDT were detected in various netplankton samples, while these compounds were undetectable in bulk phytoplankton. The high DDT/DDE ratio indicated that Antarctic organochlorines had originated recently in the Southern Hemisphere, and suggested a possible increase in Antarctic contamination by POPs.

Kennicutt (1995) measured PAH in limpet tissues and in bivalve tissues (*L. elliptical*) at Mc Murdo Station and at Palmer Station (West Antarctica) and found that samples from McMurdo Sound were highest in Winter Quarter Bay (WQB) (where there is an abandoned disposal site) and decreased with distance from WQB. However, PAH concentrations were only occasionally above the method detection limit (MDL estimated by Kennicutt in this study to be  $\sim 150\text{-}200 \text{ ng g}^{-1}$  for the sum of all PAH), even in WQB, and were in all cases predominantly naphthalenes. PAH at distant locations were near or below the MDL. In general, limpets from Arthur Harbor exhibited low total PCB concentration with no clear spatial or temporal distribution. However, intertidal limpets collected adjacent to Old Palmer and Palmer Stations were elevated in total PCB concentration (56.9, 29.3, 28.5, and  $75.7 \text{ ng g}^{-1}$ , respectively). In limpets collected in the vicinity of Palmer Station, PCBs profile is similar to that of a mixture of Aroclors 1254 and 1260. In contrast, limpets collected near Old Palmer Station contained a predominance of PCB congeners with six and seven chlorines, characteristic of Aroclor 1260. The predominance of high molecular weight congeners strongly suggests a local source of PCBs rather than atmospheric transport. Indeed abandoned dump sites with solid wastes were burned near Old Palmer Station and Palmer Station. Lube oil, transmission fluid, and various greases are also common. Fuel spills occur due to leakage from drains, leaks from full pipelines, overfilling of day tanks, and failure of fuel containers. Visiting ships are a source of contamination too, and oil sheens are a common feature when ships are in port.

No significant differences were observed in the total PCB concentration between organisms

collected in the vicinity of Arthur Harbor during 1989 (mean =  $18.3 \pm 8.5 \text{ ng g}^{-1}$ , n = 4) and 1991 (mean =  $14.0 \pm 4.2 \text{ ng g}^{-1}$ , n = 5). In most cases, subtidal limpet PCB concentration was lower than in the intertidal, suggesting a runoff source. Except for locations directly adjacent to the station, the PCB level in limpets in Arthur Harbor was comparable to that in bivalve tissues (*L. elliptica*) collected at remote locations in Mc Murdo Sound. PCB concentrations in bivalve tissues from Winter Quarters Bay (400 and  $430 \text{ ng g}^{-1}$ ) and the sewage outfall (380 and  $410 \text{ ng g}^{-1}$ ) were 20-80 times higher than the PCB levels in bivalves from more remote areas of McMurdo Sound (mean =  $9.8 \text{ ng g}^{-1}$ ). DDT and its derivatives, DDD and DDE, were also detected in sediments and organisms from McMurdo Sound and Arthur Harbor. Other toxic organic compounds occasionally detected at very low concentration in sediments and organisms included  $\alpha$ - and  $\gamma$ -hexachlorohexane, hexachlorobenzenes,  $\alpha$ -chlordane, and trans- and cis-nonachlor.

Corsolini and Focardi (2000) measured mean PCB concentration (the sum of 50 congeners) in Ross Sea phytoplankton (mainly diatoms) and mixed zooplankton (copepods, amphipods and krill) of 1 and  $4.2 \text{ ng g}^{-1}$  wet wt. respectively. Although the percentage of each congener was a small percentage of the total PCB content (<10 %) in seawater, phytoplankton showed a remarkable increase in PCBs 153, 138, 180 and 195.

Polybrominated diphenyl ethers (PBDE) are, together with PAHs, between the substances being considered for inclusion in the Stockholm Convention other than the so called *dirty dozen*. Chiuchiolo et al. (2004) measured brominated diphenyl ethers (BDEs), organic compounds produced for use as flame retardants and exactly BDE-47, -99, and -100, in sea ice algae and water column plankton, collected in the Palmer Long-Term Ecological Research (LTER) region west of the Antarctic Peninsula during late austral winter and midsummer, 2001-2002. BDEs were 100-1000 times higher in ice algae and 2-10 times higher in phytoplankton than the most abundant organochlorine pesticide, hexachlorobenzene (HCB), reflecting the current production and use of BDEs versus organochlorine pesticides. Moreover, lower vapor pressures of BDEs versus HCB render the former more easily condensed out of the atmosphere and incorporated into sea ice. However, concentration of HCB and BDEs was significantly lower in summer plankton than in ice algae indicating lower atmospheric inputs, removal from the water column, and/or biodilution of persistent organic pollutants at the base of the food web during summer. The level of  $\gamma$ -HCH (<0.06-5.6  $\text{ng/g}_{\text{lipid}}$ ), heptachlor epoxide (<0.04-5.5  $\text{ng/g}_{\text{lipid}}$ ), p,p'-DDT (<0.04-16.4  $\text{ng/g}_{\text{lipid}}$ ), and p,p'-DDE (<0.03-5.2  $\text{ng/g}_{\text{lipid}}$ ) in plankton measured in this study was almost 2 orders of magnitude lower than the concentration previously reported for plankton samples taken during 1987 in the Indian Ocean sector of the Antarctica (Joiris and Overloop, 1991). Similarly, lower concentration of  $\alpha$ -HCH,  $\gamma$ -HCH and DDTs was measured in phytoplankton in this study than previously in the Antarctic Peninsula region (Lukowski and Ligowski, 1987 and 1988). 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  $\Sigma\text{HCH}$  ( $\alpha$ - +  $\gamma$ -HCH) in Antarctic plankton over time yields an estimated environmental half-life of 2 yr for HCHs in coastal Antarctic surface waters.

Hale (2008) measured PBDEs in 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*) obtained from October to December 2003 in 11 sites 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 sediments and biota within 0.1 km of McMurdo. PBDEs in invertebrates within 0.5 km of the outfall were also elevated (mean 356 ng/g, std. dev. 196, n = 11).

## 5.2 Krill (*Euphausia superba*)

In the Southern Ocean, the marginal ice zone is the nursery ground for *E. superba* (by far the dominant herbivore), which channels organic matter produced by nanoplankton and diatoms to cephalopods, fish, seabirds, seals and baleen whales. Krill has a number of unique characteristics – its life cycle closely matches seasonal cycles of primary productivity, adults are larger than other pelagic herbivorous crustaceans (up to 6.2 cm long), they have an unusually high metabolic rate and swimming speed, adapt to whatever food is available, and survive notwithstanding the low food supply in winter (Bargagli, 2005). A salient characteristic of euphausiids, especially of *E. superba*, is the formation of dense aggregations which vary considerably in area (from a few to 1,000 m<sup>2</sup> and sometimes even many square kilometres), density (from 0.5 to several kg m<sup>-3</sup>) and depth (usually in the upper 100–200 m of the water column; Knox 1994). In view of these characteristics and its central position in the Antarctic pelagic food chain, krill has been of extreme interest to man since the onset of sealing in the 18th century. Despite intensive research, however, secondary productivity by krill and its total biomass in the Southern Ocean are still unknown. Estimates based on its annual consumption by predators (40, 100, 40, 25 and 15x10<sup>6</sup> tonnes (t) by reduced whale stocks, seals, squid, birds and fish respectively; Knox 1994) give an idea of annual krill production and of its role in transferring metals and POPs to higher levels of the Antarctic pelagic food chain.

In a krill sample collected in 1975 along the Antarctic Peninsula, Risebrough et al (1976) measured p,p'-DDE, p,p'-DDT and total PCBs: 14, 19 and 3 ng g<sup>-1</sup> by lipid mass. The DDE:DDT ratio indicated a high proportion of unmetabolised DDT. Overall, data for birds and mammals endemic to the Antarctic region showed an increase in DDT and derivatives from the early 1960s to the early 1980s (UNEP 2002a). However, Bidleman et al. (1993) reported that significant input of fresh DDT was still evident in 1990 samples.

Sen Gupta et al. (1996) measured average concentration of total-HCH ( $\alpha+\gamma$  isomers=0.154 ng g<sup>-1</sup> dry wt.), total PCBs (sum of CB-101 CB-136 CB-151 CB-118 CB-153 CB-138 = 0.152 ng g<sup>-1</sup> dry wt., dominant PCB congeners were PCB-138 and PCB-136) and total DDT (p,p'-DDT + o,p'-DDT + p,p'-DDE + o,p'-DDE = 0.037 ng g<sup>-1</sup> dry wt.) in samples of *E. superba* collected in December 1987–January 1988 at about 70° S and 12° E. The dominant isomers and metabolites of DDT, p,p'-DDT and p,p'-DDE occurred in almost equal percentages in krill.

Corsolini et al. (2002) measured average p,p'-DDE and HCB concentration (0.86±0.98 and 0.37±0.17 ng g<sup>-1</sup> wet wt. respectively) in krill samples collected from the Ross Sea (71°20'S–72° 33'S/170° 22'E–178° 04'E) in January 2000. Average PCB concentrations in these samples were much higher (167±85 ng g<sup>-1</sup> wet wt.), and congener- specific PCB profiles showed a prevalence of low-chlorinated isomers (tetra-PCBs accounted for most of the

residue). This pattern differed from that usually detected in organisms from low and mid latitudes, and it was likely due to global fractionation at high latitudes. Isomer patterns in organisms from the Ross Sea were similar to those of Kanechlor, a technical mixture mostly used in Japan and other eastern Asian countries, roughly located at the longitude of the Ross Sea (Corsolini et al. 2002). On a lipid weight basis, concentrations of total polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (DFs) in the same krill samples (Kumar et al. 2002) were  $27 \text{ pg g}^{-1}$ , and those of non- and mono-ortho-substituted polychlorinated biphenyls (dioxin-like PCBs) were  $0.9 \text{ ng g}^{-1}$ .

Chiuchiolo (2004) noticed that concentrations of HCB (juvenile and adult krill) and BDEs (juvenile krill) were not significantly different from their primary food source (ice algae, phytoplankton), and BDEs were significantly lower in adult krill versus phytoplankton, indicating no biomagnification of HCB or BDEs 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.

Corsolini (2006) measured Organochlorine Pesticides in krill sampled at Ross Sea in Terra Nova Bay, during 2000, 2001/02 and found concentrations of HCB, HCHs and DDTs  $0.23 \pm 0.01$ ,  $0.28 \pm 0.04$  and  $0.18 \pm 0.03$  respectively while chlordanes (CHLs) were below the detection limit ( $\text{MDL} < 0.02 \text{ ng/g wet wt}$ ). Mean PBDE concentrations were  $0.20 \text{ ng/g}$  in krill whole body and  $5.60 \text{ ng/g}$  on a lipid basis. PCB levels were higher with one order of magnitude than PBDEs levels.

Bengstone (2008) studied persistent organohalogen contaminants (POCs) in the eastern Antarctic sector. Samples were collected during January and February 2006 and originated from 12 sampling stations. They were analysed for >100 organohalogen compounds including chlorinated pesticides, polychlorinated biphenyls (PCBs), polybrominated organic compounds and polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs). The suspected naturally occurring organohalogen, 2,4,6-tribromoanisole (TBA) as well as  $\alpha$ -HCH; o,p'-DDE; o,p'-DDD; p,p'-DDD; p,p'-DDT; penta-chlorobenzene (PeCB); HCB; heptachlor-exo-epoxide; heptachlor; trans-nonachlor, mirex and toxaphene congeners Tox-26 (B8-1413), Tox-40+41 (B8-1414+ B8-1945) and Tox-50 (B8-2229) were quantified in all samples analysed whilst PCB-101,  $\gamma$ -HCH, p,p'-DDE cis-nonachlor, Tox-42a (B8-806) and Tox-44 (B8-2229) were quantified in  $\geq 75\%$  of samples analysed. Organochlorine pesticides dominated measured krill contaminant burdens with hexachlorobenzene (HCB) as the single most abundant compound quantified:  $4.37 \text{ ng/g}_{\text{lw}}$  (lipid weight) or  $0.2 \text{ ng/g}_{\text{ww}}$  (wet weight). HCB concentrations were comparable to those detected at this trophic level in both the Arctic and temperate northwest Atlantic, lending support to the hypothesis that HCB will approach global equilibrium at a faster rate than other POCs. Para, para'-dichlorodiphenylethane (p,p'-DDE) was detected at notable concentrations:  $2.6 \text{ ng/g}_{\text{lw}}$   $0.13 \text{ ng/g}_{\text{ww}}$ . In contrast to the Arctic, PCBs did not feature prominently in contaminant burdens of Antarctic krill:  $1.2 \text{ ng g}^{-1}_{\text{lw}}$  and  $0.05 \text{ ng/g}_{\text{ww}}$ , dominant PCB congeners were PCB-18, PCB-28, PCB-31 and PCB-153. The major commercial polybrominated diphenyl ether (PBDE) congeners -99 and -47 were quantified at low background levels ( $0.67 \text{ ng/g}_{\text{lw}}$ ,  $0.03 \text{ ng/g}_{\text{ww}}$  and  $0.35 \text{ ng/g}_{\text{lw}}$ ,  $0.007 \text{ ng/g}_{\text{ww}}$  respectively) with clear concentration spikes observed at around  $70^\circ\text{E}$ , in the vicinity of modern, active research stations. The suspected naturally occurring brominated organic compound, 2,4,6-tribromoanisole (TBA), was a ubiquitous contaminant in all samples

whereas the 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).

### 5.3 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 are now affecting their populations. Among the most widespread are fishing activities and the by-catch of cetaceans, environmental pollution, and ocean noise pollution from active sonar systems. Climate warming would reduce the seasonal sea-ice cover, primary productivity and the availability of krill on which most Antarctic whales feed.

The killer whale (*Orcinus orca*) is probably the main exception, as it feeds on squid, fish, cephalopods, birds, seals and other cetaceans.

Baleen whales have often been used to biomonitor the distribution of POPs in the Northern and Southern hemispheres (e.g. Tanabe et al. 1983; O'Shea and Brownell 1994). Although minke whales have a wide range of migratory areas, there is no evidence of hybridisation between populations in the two hemispheres. In general, POP concentrations in whales from the Southern Ocean are much lower than in those from the northern Pacific. This is likely due to lower environmental contamination in the Southern Hemisphere and to the different feeding behaviour of northern and southern minke whales. However, data by Aono et al. (1997) show that 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. The predominant DDT compound was p,p'-DDE; it 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. The composition of HCH isomers in the diet and blubber of southern whales differed from that in the diet and blubber of northern whales; according to Aono et al. (1997), this suggests that lindane was being used to a greater extent in countries of the Southern Hemisphere than in those of the Northern Hemisphere.

Aono (1997) measured an increase in PCBs concentration in the blubber of *Balaenoptera acutorostrata* in the period 1984–1991 and 1984–1993 respectively, but did not notice any trend in levels of tDDT, HCB and HCHs.

Khuran (2008) measured PCBs, DDTs, CHLs, HCB and HCHs in blubber from Antarctic Type C killer whales and found that mean concentrations in all groups of POPs were significantly higher in adult males than in females. Type C whales had anyway the lowest mean concentrations for all groups of POPs, except for HCB. For example, the mean  $\Sigma$ PCB and  $\Sigma$ DDT concentrations in adult male Type C whales, relative to those from other five killer whale groups, ranged from 0.23% to 12% and from 0.12% to 20%, respectively. Conversely, mean HCB concentrations measured in Type C whales were comparable to others. PCB patterns in the blubber of the Antarctic Type C killer whales were also very different from those of the other killer whale populations, primarily due to a high relative abundance of higher chlorinated congeners (particularly PCB 149 and PCB 170) in Type C whales. Because point sources of pollution in Antarctica are relatively rare, the PCBs acquired by the biota from the region are generally the lower molecular weight congeners that can be transported via the atmosphere or ocean (Wania and Mackay 1993). However,

certain areas in McMurdo Sound have been documented to contain high, but patchy concentrations of the anthropogenically introduced Aroclor 1260 (one of several technical mixtures of PCBs) that contains the higher chlorinated congeners (Risebrough et al. 1990, Geochemical and Environmental Research Group 2003). Although it is not currently known if Type C whales are resident in Antarctica or whether they migrate to lower latitudes during the winter, migration could increase their exposure to pollutants. Regardless, Type C killer whales have the lowest levels of POPs (except HCB) of any killer whale population studied to date. In contrast POP concentrations in adult male Type C killer whales were found to be several times (5 to 90-fold) higher than those of male Antarctic minke whales sampled in western Antarctica (1992/1993, n = 20; Aono et al. 1997) and to the single Antarctic minke whale biopsied in 2006 (Khran 2008). 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.

#### **5.4 Coastal benthic organisms**

Although Antarctic seaweed does not have the trophic significance of phytoplankton, it contributes to primary productivity in coastal ecosystems and provides suitable habitats for a variety of animals. Some of the dominant species in Antarctica are *Iridaea cordata* in the infralittoral zone, *Leptosomia simplex* in the lower intertidal zone, *Phyllophora antarctica* at intermediate depths, and the largest Antarctic brown alga *Himantothallus grandifolius* down to depths of 25–30 m.

Montone et al. (2001) determined concentrations of PCB congeners in *Desmarestia sp.* samples collected from various locations at Admiralty Bay (King George Island). Total PCB concentrations ranged from 0.46 to 3.86 ng g<sup>-1</sup> dry wt., and the predominance of low-molecular weight congeners indicated that there were no significant local sources of PCBs at Admiralty Bay.

Unlike shelf waters around the other continents, 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*, *T. pennellii*, *T. scotti*, *T. hansonii*). Notothenioids also include a few pelagic species such as *Pleuragramma antarcticum* and species living on the undersurface of ice (e.g. *Pagothenia borchgrevinkii*). Besides notothenioids, Antarctic waters contain plunderfish, dragonfish and icefish (about 50 species), which are mostly pelagic or semipelagic and prey on crustaceans and fish (Eastman 1999).

*Trematomus bernacchii* is an ideal bioindicator of local contamination because it has restricted home ranges and is ubiquitous. *T. bernacchii* has been used as a bioindicator of POPs in marine ecosystems adjacent to scientific stations such as McMurdo (Larsson et al. 1992; Kennicutt et al. 1995), Terra Nova Bay (Focardi et al. 1992, Bargagli 2005) and Syowa (Subramanian et al. 1983). Comparisons among the results of these studies are difficult because some refer to the whole body content, while others refer to different tissues and/or are expressed on different mass bases. In general, DDTs, PCBs, PAHs and other POPs have always been detected; average concentrations were in the same range as those previously reported for krill and were significantly lower than those usually detected in fish from other

seas. *T. bernacchii* viscera from WQB and Cinder Cones were analyzed for PAH. The fish tissues from WQB were higher than the controls,  $656 \pm 319$  and  $200 \pm 72$  ng g<sup>-1</sup> (n = 6), respectively. The PAH were predominantly naphthalenes with occasional phenanthrenes present. Traces of pyrogenic PAH were detected, suggesting that some of the PAH could be due to sediments entrained in the fish viscera (Kennicutt 1995).

TEQs (2378-tetrachlorodibenzo-p-dioxin equivalents) were determined for the clams (*L. elliptica*) collected near McMurdo via bioassays. Values ranged from non-detected to 0.25 and from 1.16 to 1.66 ng g<sup>-1</sup>, from control sites and contaminated sites respectively (Kennicutt 1995).

Concentrations of three highly toxic non-ortho coplanar PCB congeners (77, 126 and 169) were always extremely low (<0.5 pg g<sup>-1</sup> wet wt.) in the muscle tissue of *T. bernacchi* from Terra Nova Bay (Bargagli et al. 1998d).

High average concentrations of PAH metabolites were measured in the bile of *Notothenia coriiceps* samples collected near Palmer Station and the Bahia Paraiso wreckage (McDonald et al. 1992).

Analysis of organochlorine compounds in fish species from the Antarctic Peninsula (Weber and Goerke 1996) showed that HCB concentrations (20 ng g<sup>-1</sup> wet wt.) were as high as those in *Limanda limanda* from the North Sea, and bioaccumulation was attributed to the cold-condensation process. Levels of DDT and PCB congeners (153, 138 and 180) were from one to two orders of magnitude lower than in North Sea fish. However, POPs in samples from the Antarctic Peninsula generally increased between 1987 and 1991.

The Antarctic silverfish (*Pleuragramma antarcticum*) 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 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 (Eastman 1993). Average PCB, HCB, and p,p'-DDE concentrations in adult *P. antarcticum* samples from the Ross Sea were 348, 4.85 and 2.01 ng g<sup>-1</sup> wet wt. respectively (Corsolini et al. 2002). 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.

Kumar (2002) analysed two species of Antarctic fishes (*Trematomus pennelli*, *Chionodrodraco hamatus*) collected in 1994–1995 and found PCDD/DFs total concentration of 11–17 pg/g with 2378-TCDF, 23478-PeCDF and OCDD as the major congeners and dioxin-like PCBs (4 non-ortho and 8 mono-ortho PCBs) plus two di-ortho (congeners 170 and 180) concentration of 6.2 ng/g with pentachlorobiphenyls 118,170 and 180 as the predominant ones.

Goerke (2004) noticed that two benthic fish species (*Gobionotothen gibberifrons*, *Chaenocephalus aceratus*) feeding on benthos invertebrates and fish reflected significantly increasing concentrations within a decade (1987–1996), while a benthopelagic species (*Champsocephalus gunnari*) feeding on krill did not. 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.

Borghesi (2008) reported results on the accumulation of polybrominated diphenyl ethers (PBDEs), mono- and non-ortho-polychlorobiphenyls (PCBs), polychlorodibenzodioxins (PCDDs) and polychlorodibenzofurans (PCDFs) in the tissues of two species of Antarctic fish (*Chionodraco hamatus* and *Trematomus bernacchii*). 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<sup>-1</sup> wet wt in *C. hamatus* muscle to 789.9 pg g<sup>-1</sup> wet wt in *T. bernacchii* liver and were lower than the levels of PCBs. PCBs were the main organochlorine compounds detected and their concentrations ranged from 0.3 ng g<sup>-1</sup> wet wt in *C. hamatus* muscle to 15.1 ng g<sup>-1</sup> wet wt in *T. bernacchii* liver. TEQ concentrations resulted higher in *C. hamatus* than in *T. bernacchii* and were due mainly to PCDDs.

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.

Hale (2008) found that two rock cod (*T. bernacchii*) from the vicinity of the wastewater outfall site contained the highest ΣPBDE6 concentrations, 1520 and 1840 ng/g by lipid weight.

Cod collected at Cinder Cones contained ΣPBDE6 at 311 ng/g. This is more than 10-fold greater than levels in biota at other sites far from McMurdo. For comparison, a 2006 study by Corsolini of krill, rock cod, and penguin eggs at Terra Nova Bay (200 km from McMurdo) reported much lower ΣPBDE6 concentrations (3.06 to 5.81 μg/kg). Corsolini attributed the dominance of the more volatile congeners to their preferential long-range transport. Hale instead suggested that the 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.

De Wit et al. (2006) recently reviewed published levels in a variety of Arctic environmental matrices. Despite greater PBDE use in the Northern Hemisphere and the proximity of population centers, the levels in Antarctic sediments and biota found by Hale far exceeded the majority of Arctic values (Gouin et al, 2006). Overall, BDE-209 in the Antarctic sediments was widely distributed (quantifiable in 6 of 11 samples) and generally exceeded ΣPBDE6. As BDE-209 has limited volatility and long-range transport potential, its distribution here points to contributions from local sources. These results illustrate that without additional precautions, an increased human presence in Antarctica may further compromise the continent's pristine status. Direct discharge of largely untreated wastewaters, as still practiced at some Antarctic research bases, can result in the release of substantial amounts of contaminants. Even wastewaters subjected to modern treatment, as now performed at the McMurdo and Scott research bases, contain detectable concentrations of persistent, bioaccumulative pollutants such as PBDEs.

## 5.5 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, Adélie, Chinstrap and Gentoo penguins. Only Emperor (*Aptenodytes forsteri*) and Adélie (*Pygoscelis adeliae*) penguins are true continental birds, because the other two species are found exclusively in the northern Antarctic Peninsula. Other birds which breed successfully along Antarctic coasts include the South Polar skua (*Catharacta maccormicki*) and some species of procellariiforms such as the snow petrel (*Pagodroma nivea*), cape pigeon (*Daption capensis*), Antarctic petrel (*Thalassoica antarctica*) and Wilson's storm petrel (*Oceanites oceanicus*).

Donnewald et al. (1979) found HCB concentrations in subcutaneous fat of penguins sampled on the Antarctic Peninsula ranging from 87 to 600 ng/g fat. Luke et al. (1989) analysed eggs from 15 species of seabirds at Davis and Casey stations (1981–1983) on the coast of Eastern Antarctica, and from Macquarie Island (1978–1983). Levels of HCB were similar in all penguin eggs (10–20 ng/g fresh mass).

In order to evaluate the potential input of xenobiotics through diet, Corsolini et al. (2003) determined POP concentrations in the stomach content of Adélie penguins at Edmonson Point (northern Victoria Land). They found that the mean concentration of HCB, p,p'-DDE and PCBs from one foraging trip were 1,412, 1,508 and 303 ng g<sup>-1</sup> wet wt. respectively. Stomach contents richer in euphausiids had generally higher xenobiotic concentrations, and this was attributed to the effective release of particulate materials containing POPs from melting ice and their adsorption on the body surface of crustaceans. Although dioxin-like PCBs (i.e. those with either meta or para chlorine substitutions or with one chlorine in the ortho position) were detected in all stomach content samples, the estimated toxicity for Adélie penguins was very low. 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. Besides variations in their diet, van den Brink et al. (1998) showed that during the breeding season penguins utilise different fat stores at different times, thereby contributing to seasonal fluctuations of organochlorine levels in blood and uropygial oil.

Despite all these factors causing strong variability in contaminant levels, Adélie and Emperor penguins are useful biomonitors of persistent contaminants in Antarctic marine ecosystems because of their distribution around the continents (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. Studies on POP accumulation in penguins began in the 1970s. Risebrough et al. (1976) assessed chlorinated hydrocarbon concentrations in penguin eggs from different zones of the Antarctic Peninsula and compared these with data from penguins on sub-Antarctic islands. The results proved, for the first time, that POPs in the Antarctic environment did not derive from local human activity and that the atmosphere (rather than oceanic water masses) is the main pathway of transport of PCB and DDT compounds to the continent. Tanabe et al. (1986) examined the mother-to-egg transfer in Adélie penguins of PCB isomers and congeners and of p,p'-DDE. 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. In subsequent years several papers were published on POP

concentrations in penguin eggs (e.g. Luke et al. 1989; Focardi et al. 1992 c; Court et al. 1997; Kumar et al. 2002) and in various organs, tissues and feathers (e.g. Subramanian et al. 1986; Focardi et al. 1995; Inomata et al. 1996; Sen Gupta et al. 1996; Corsolini and Focardi 2000). 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 (e.g. Court et al. 1997; Wanwimolruk et al. 1999) that the liver of Adélie penguins has a low capacity to detoxify PCBs and chlorinated pesticides.

Sen Gupta et al. (1996) measured average concentrations of t-HCH ( $\alpha+\gamma$  isomers=108 pg g<sup>-1</sup> dry wt.), total PCBs (sum of CB-101 CB-136 CB-151 CB-118 CB-153 CB-138 = 109 pg g<sup>-1</sup> dry wt., dominant PCB congeners were PCB-138 and PCB-136) and total DDT (p,p'-DDT + o,p'-DDT + p,p'-DDE + o,p'-DDE = 33 pg g<sup>-1</sup> dry wt.) in penguin feathers collected in December 1987–January 1988 at Dakshin Gangotri 70° S and 12° E.

Van der Brink (1997) measured HCB and  $\Sigma$ PCB (here defined as the sum of the following congeners: 31, 28, 45, 52, 44, 66, 101, 97, 87, 110, 151, 107, 149, 118, 146, 153, 105, 141, 179, 138, 182, 183, 128, 174, 177, 180, 170, 196, 194 and 206) concentrations in birds restricted to the Antarctic region during summer and winter (Adelie Penguin (n = 12), Snow Petrel (n = 4), Antarctic Petrel (n = 5) and Southern Fulmar (n = 18)) and birds wintering in sub-antarctic region (Cape Petrel breeding at Hop Island (n = 3) and Cape Petrel breeding at K. George Island (n = 6)) compared with birds living in temperate areas at the northern hemisphere during summer and in sub-tropical regions during winter (Common Tern (n=6)). Of these three categories of birds, the first one showed relatively low  $\Sigma$ PCB levels but higher HCB levels. The second one has  $\Sigma$ PCB concentrations significantly higher whereas HCB concentrations are also higher, but not significantly. The third category has relatively high levels of  $\Sigma$ PCB, but HCB concentrations are extremely low. Therefore the trend for  $\Sigma$ PCB is that species further away from potential sources (e.g. species confined to the Antarctic continent all year) have low concentrations while for HCB the pattern is different and can be explained by the cold-condenser or the global-distillation effect (Calamari et al., 1991; Simonich and Hites, 1995). HCB is relatively volatile (Bidleman, 1984), it has a high environmental half-life and it accumulates in species at higher trophic levels (Mackay et al., 1992). The species in this study with relatively high HCB levels, are confined to the cold Antarctic region for at least a major part of the year whereas the Common Tern which inhabits temperate to sub-tropical areas throughout the year, where HCB apparently evaporates before it enters the food web, has extremely low concentrations.

Goerke (2004) studied Adelie penguins, (*Pygoscelis adeliae*), 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.

Corsolini (2007) measured POP concentrations in three species of penguins: Adélie penguin (*Pygoscelis adeliae*), Chinstrap penguin (*Pygoscelis antarctica*) and Gentoo penguin (*Pygoscelis papua*) and found that 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. Dissimilar ecological or metabolic features may be involved; the diverse timing of reproduction steps can be responsible for those differences; moreover, Adélie penguins feed on krill (a fatty resource) more abundantly than the other two species during the rearing period.

Zhang (2007) analysed eggs of skuas, penguins and giant petrel and found that the concentration accumulation of POPs was in the order of  $\Sigma\text{PCB} > \Sigma\text{DDT} > \text{HCB} > \Sigma\text{HCH}$ . The lower accumulation of HCHs in the seabird eggs, compared to other POPs, might be due to the decreased use of HCHs in agriculture and easy degradation relative to that of PCBs, DDTs and HCBs. In the eggs of skuas, concentration levels of  $\Sigma\text{PCB}$  (the total of PCB101, PCB118, PCB138, PCB153, PCB180 and PCB194) ranged from 91.9 to 515.5 ng/g,  $\Sigma\text{DDT}$  (p,p'-DDT + p,p'-DDE) 56.6 to 304 ng/g, HCB 6.5 to 70.5 ng/g, and  $\Sigma\text{HCH}$  ( $\alpha + \gamma$  isomers) <0.5 to 2.0 ng/g. In the penguin eggs, concentrations of  $\Sigma\text{PCB}$  ranged from 0.5 to 0.8 ng/g,  $\Sigma\text{DDT}$  2.0 to 10.1 ng/g, HCB 6.0 to 10.2 ng/g, and  $\Sigma\text{HCH}$  0.1 to 0.4 ng/g. In the eggs of giant petrel, concentrations of  $\Sigma\text{PCB}$  ranged from 48.1 to 81.7 ng/g,  $\Sigma\text{DDT}$  12.7 to 53.7 ng/g,  $\Sigma\text{HCB}$  4.2 to 8.8 ng/g and  $\Sigma\text{HCH}$  0.5 to 1.5 ng/g. These results agreed well with those from the similar study by Weichbrodt et al, (1999) for the average accumulation levels of  $\Sigma\text{HCH}$ ,  $\Sigma\text{DDT}$ , and  $\Sigma\text{PCB}$  in Antarctic skua eggs. The average concentration was brown skua > South Polar skua > giant petrel > penguin. The major foods of the brown skua were penguin eggs and infants, also they liked to forage for human waste. South Polar skuas prey on fishes, zooplankton, and small-sized birds; they also eat corpses of penguins and seals as a supplement. Penguins cannot fly and their major food is Antarctic krill, fishes and shrimps. They are also preyed upon by skua and giant petrels. Giant petrels prey on zooplankton, cephalopods, and fish. From the prey-predator relationship it could be seen that the accumulation of PCBs and OCPs in the seabirds was the result of their position in the food chain.

Taniguchi (2008) collected data for chlorinated pesticides, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) in subcutaneous fat samples from Brown skuas, three species of penguins: Adélie (*Pygoscelis adeliae*); Chinstrap (*Pygoscelis Antarctica*); and Gentoo (*Pygoscelis papua*) and opportunistic samples of Antarctic tern (*Sterna vittata*) Snowy sheathbill (*Chionis alba*) and Blue-eyed shag (*Phalacrocorax atriceps*) and concluded again that except for HCHs and HCB, the concentrations of most chlorinated pesticides were significantly higher in skuas than in the other species of birds. In contrast, comparable concentrations of HCB were found in skuas ( $573 \pm 278 \text{ ng g}^{-1}_{\text{lw}}$ ), penguins ( $373 \pm 177 \text{ ng g}^{-1}_{\text{lw}}$ ), terns ( $601 \pm 256 \text{ ng g}^{-1}_{\text{lw}}$ ), shags ( $161 \text{ ng g}^{-1}_{\text{lw}}$ ) and sheathbills ( $282 \text{ ng g}^{-1}_{\text{lw}}$ ): 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 ( $\text{ng g}^{-1}$  by lipid weight) 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.

Geisz (2008) compared data on DDT concentration of Adélie penguin (*Pygoscelis adeliae*) eggs and found that p,p'-DDE levels have not declined in the Palmer population of Adélie penguins in more than 30 years. In contrast,  $\Sigma$ DDT decreased significantly from 1975 to 2003 in Arctic seabird eggs.  $\Sigma$  DDT in the fat of Adélie penguins from Cape Crozier measured in 2006 was significantly higher than that measured by Sladen (1964). p,p'-DDT/p,p'-DDE ratios <1.0 for several Antarctic organisms, including Adélie penguin eggs, suggest contamination by old DDT. Indeed, the p,p'-DDT/p,p'-DDE ratio measured in Adélie penguins has significantly declined since 1964, indicating a predominance of old rather than new sources of  $\Sigma$ DDT in the Antarctic. Two independent measurements of  $\Sigma$ DDT indicate that  $14 \text{ kg} \cdot \text{y}^{-1}$   $\Sigma$ DDT is currently being released into the Antarctic marine environment due to glacier ablation.

### 5.6 Skua and other birds breeding in Antarctica

Birds breeding along Antarctic coasts are almost exclusively marine species, and each species is uniform across very large coastal regions. 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.

Among marine organisms breeding in Antarctica, the South Polar skua (*Catharacta maccormicki*) combines the traits of the species more exposed to the bioaccumulation of persistent contaminants. Skuas are opportunistic top predators, and during the breeding season in Antarctica they adopt a wide range of feeding tactics that enable them to prey or scavenge on all profitable marine or terrestrial food resources according to their temporal and spatial availability (Pezzo et al. 2001). Many skuas nest close to penguin rookeries, and Adélie penguins are an important component of their diet. However, in areas such as the Larsemann Hills (Princess Elizabeth Land) where there are no breeding penguins, the snow petrel (*Pagodroma nivea*), together with other seabirds, various marine foods and refuse (meat, fish and vegetable remains) from nearby stations, becomes the major dietary component of skuas. 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 (Bargagli, 2005). 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 biomonitoring surveys of Antarctic wildlife identified the South Polar skua and brown skua (*C. lonnbergi*) as the species with the highest concentrations of persistent contaminants (e.g. Risebrough and Carmignani 1972; Gardner et al. 1985).

Since the South Polar skua is a top predator and scavenger and has one of the longest migration paths in more polluted marine environments, average concentrations of DDTs ( $369 \text{ ng g}^{-1}$  wet wt.) and PCBs ( $908 \text{ ng g}^{-1}$  wet wt.) in its eggs at Cape Bird (Ross Island; Court et al. 1997) 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. However, studies by Focardi et al. (1992) showed that values of MFO (Mixed Function Oxidases) activity were very low in

penguins, while South Polar skua values corresponded to those of certain Northern Hemisphere gulls. Although the two species seem to have different metabolisms and although skuas accumulate most organochlorines in regions north of the Antarctic Convergence, the prevalent PCB congener in penguin and skua samples was the same (22'44'55', a hexachlorobiphenyl; Court et al. 1997). As 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*; Furness and Hutton 1979).

Kumar et al. (2002) determined concentrations of polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (DFs) and dioxin-like PCBs in the liver of polar bears from the Alaskan Arctic, in the liver of Weddell seals, and in the eggs of Adélie penguins and South Polar skuas. Skua eggs had the highest concentrations of total PCDD/DFs (mean=181 pg g<sup>-1</sup>), and estimated concentrations of 2378-tetrachlorodibenzo-p-dioxin equivalents (TEQs) of PCDDs, PCDFs and dioxin-like PCBs in skua eggs (mean=344 pg g<sup>-1</sup>) were higher than in the liver of polar bears (mean=120 pg g<sup>-1</sup>). These concentrations were close to values which 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 (Kemler et al. 2000).

Lin Tao (2006) investigated the presence of perfluorinated chemicals (PFCs) in Adélie penguin (*Pygoscelis adeliae*) blood, unhatched Adélie penguin eggs and whole blood of South Polar skua collected during 1995-2005. PFCs have been used as surfactants in industrial and commercial products for over 50 years. PFCs are incredibly resistant to breakdown and perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) are being considered for inclusion in the Stockholm Convention. PFOS was found in the blood of elephant seals from Antarctica at concentrations ranging from <0.08 to 3.52 ng/ml. 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 distribution of these compounds on a global scale even if contamination levels in the Antarctic is still low.

Bustnes (2006) compared organochlorines (OCs) levels in Antarctic and Arctic avian top predators analyzing blood sampled from the wing vein of south polar skuas (142 skuas, 73 females and 69 males) breeding at Svarthamaren (71° 53' S, 05° 10' E) in Dronning Maud Land (Antarctica) in December 2001 and January 2002. Svarthamaren is the largest breeding colony of Antarctic petrels (*Thalassoica antarctica*) in the world, with about 250,000 pairs. This petrel colony supports a breeding population of 80-90 pairs (250 individuals) of south polar skuas. Svarthamaren is approximately 200 km from the open sea, and during the breeding season skuas feed on the eggs and young of petrels (Brooke et al., 1999). South polar skuas had 8% and 29% of the blood OCs concentrations (45 ng/g, ww) found in glaucous gulls and great black-backed gulls (158 ng/g) living in the northern hemisphere. PCBs (here the sum of congeners: CB-101, -99, -118, -153, -138, -180, and -170), p,p'-DDE, and oxychlorane concentrations were much lower in the skuas. The level of the semivolatile HCB instead was relatively high (7 ng/g) and Mirex (an insecticide and flame retardant) was the dominant OC in south polar skuas. To record changes in OC concentrations in south polar skuas during the breeding season, a subsample (n = 66) was recaptured after 2 weeks, and new blood samples were taken. In skuas, the mean levels of most OCs increased by about 30% between the two blood samplings, and the mirex level increased by nearly 60%. The

increases in HCB and mirex seem to be more related to local exposure than to lipid dynamics, suggesting that skuas are accumulating these compounds during the breeding season at Svarthamaren. 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 northern hemisphere, which could mean 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.

Bustnes (2007) again examined relationships between fitness components and concentrations of OCs in this species. Using principal component analyses (PCA) this study found associations between concentrations of OCs and fitness components in Antarctic birds; i.e. the timing of the reproduction and hatching mass of chicks were both adversely related to the mothers' blood residues of OCs. Such changes may affect population parameters in long-lived birds; i.e. late hatching may result in poor reproductive output and poor body condition of chicks at hatching may reduce their survival probability. An important question issued by the author is whether OC levels in female blood provide a suitable measure of the effect potential of the OCs: 1) in relation to factors affecting timing of reproduction, which is probably mostly related to OC levels in sensitive tissues of the females and, 2) in relation to chick hatching mass, which is probably mostly related to maternal transfer of OCs to the eggs. Several bird studies suggest that concentrations of OCs in blood are well correlated to levels in sensitive tissues (Marsili et al., 1996; Henriksen et al., 1998), and also a good measure of OCs sequestered into the seabird eggs (Verreault et al., 2006). However, some individuals may have eaten lipid-rich meals, which temporarily increase blood lipids (up to 4%), with a corresponding increase in OC values. Similarly, temporarily low blood lipid levels will result in OC values that are poorly related to the body burden (Bustnes et al., 2005). In general the lipid values in seabird blood vary between 0.3 and 0.8%, and within this range the repeatability of OC measurements among individuals is high (Bustnes et al., 2001, 2005). Bustnes suggested that individuals with extreme lipid values should be removed as outliers in studies where potential effects are studied.

### 5.7 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<sup>6</sup> 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. Investigations on organochlorine concentrations in organs and tissues of Antarctic seals began in the 1980s (e.g. Kawano et al. 1984; McClurg 1984; Schneider et al. 1985).

Concentrations of p, p'-DDT (160 ng g<sup>-1</sup> wet wt.), p, p'-DDE (from 267 to 456 ng g<sup>-1</sup> wet wt.) and HCH (25 ng g<sup>-1</sup> wet wt.) were much higher in the adipose tissue of leopard seals collected in 1979-1981 at King George Island than in that of four other species of seals

(Karolewski et al. 1987). This may be due to the fact that the leopard seal is a top predator and that it disperses widely in the Southern Ocean during the austral winter. In blubber samples from Ross seals, McClurg (1984) detected low DDT, PCB and dieldrin concentrations and found no relationships between residue levels and sex or size (age) of animals.

Bacon et al. (1992) analysed concentrations of organochlorines and polychlorinated biphenyls in pinniped milk samples from the Arctic, Antarctic, California and Australia. Concentrations of 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, Bacon et al. (1992) found a similar ratio pattern for PCB congeners 153, 138 and 180 in pinnipeds throughout the world. They concluded that it is not the levels which shape the profiles, but rather how the pollutants react in metabolic systems. As in the milk of Antarctic fur seals, average DDT, PCB, HCB and HCH concentrations in samples of Weddell seal blubber from various Antarctic locations (e.g. Kawano et al. 1984; Schneider et al. 1985) are from one to three orders of magnitude lower than average values in the blubber of Arctic seals (e.g. Becker 2000). Toxaphene and chlordane components in chromatograms of Weddell seal samples were found to exceed the intensity of PCB signals (Luckas et al. 1990), and the  $\gamma$ HCB/ $\alpha$ HCH ratio was  $>1$  while in Arctic samples it was always  $<1$ . Focardi et al (1995a) found a relationship between PCB concentrations and trophic levels of marine organisms from Terra Nova Bay. Concentrations of PCBs and of three highly toxic non-ortho coplanar PCBs, were much higher in the Weddell seal than in penguins or fish.

Jarman (1992) analyzing  $\Sigma$ DDT,  $\Sigma$ PCB and dieldrin in Antarctic fur seal (*Arctocephalus gazella*) milk in comparison with marine mammals and bird eggs from the Arctic, Antarctic, Australia, and the East and West Coasts of North America found that the concentration of  $\Sigma$ DDT was about ten times lower in Antarctic fur seal milk than in Northern fur seal milk,  $\Sigma$ PCB was about 25 times lower whereas dieldrin was only about 2 times lower in samples from Antarctica.

Vetter (2003) highlighted that samples of Weddell seals blubber from King George Island (the region with the mildest climate in the Antarctic) showed the lowest DDT (11 to 19 ng/g) and PCB (1 to 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 of the same species from other sites in Antarctica (located between 69°S and 78°S). This suggests a wide variability of organohalogen levels in the Antarctic, depending on the geographic site. This raises the question whether high proportions of organohalogens are being deposited on the Antarctic continent where they are not available to marine organisms and clearly demonstrates that it is complicated to derive time trends in concentrations of POPs in biota from different reference sites in the Antarctic.

Goerke (2004) studied the Weddell seal (*Leptonychotes weddellii*), and southern elephant seal (*Mirounga leonine*), feeding at higher levels in the food web on fish and cephalopods, and found that they biomagnified most compounds by up to 2 orders of magnitude relative to krill. In these top predators p,p'-DDE attained the highest concentrations with 0.2  $\mu\text{g g}^{-1}$  EOM (extractable organic matter). However, hexachlorobenzene (HCB) was the predominant pollutant in all other animals studied. It is noteworthy that HCB levels in Weddell seals and

in southern elephant seals were considerably lower than in their dominant prey, the pelagic fishes *Pleuragramma antarcticum* (Plotz, 1986; Plotz et al., 2001) and *Gymnoscopelus nicholsi* and the squid *Psychroteuthis glacialis* (Daneri and Carlini, 2002). The same result was found for ringed seals (*Phoca hispida*), and harbour seals (*Phoca vitulina*), in the northern hemisphere (Muir et al., 1988; Ruus et al., 1999; Fisk et al., 2001). 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. Top predators are generally thought to represent indicators of biomagnified POPs. However, the selective elimination of hexachlorobenzene in pinnipeds demonstrates that biomonitoring should not be confined to single taxa.

The example of extremely low HCB levels in seals and experimental evidence on PCB patterns being related to PCB elimination in marine animals of different systematic position (Goerke and Weber, 2001) showed that changes in POP composition between various species of the same community are also controlled by elimination capacities. Hence, a cluster analysis classifying the investigated species on the basis of their POP concentrations revealed groups of similar ecological and systematic status. Pelagic fish (*Trematomus eulepidotus*, *G. nicholsi*, *P. antarcticum*, *C. gunnari*) and squid (*P. glacialis*) were in the same set as their prey, Antarctic krill, whereas Adelie penguins and the seals were separated in two further groups.

Miranda Filho (2007) analysed blubber samples (n = 129) from live and apparently healthy female and male pups, juveniles and adults of *M. leonine* (elephant seal) caught at Elephant Island in the Antarctica Peninsula (61°13'S-55°23'W) during 1997/1998, 1998/1999, and 1999/2000 austral summers. He found that DDT compounds and PCBs are the most accumulated POPs in the blubber of elephant seals. The relative importance of other OC pesticides in blubber tissue, such as mirex, methoxychlor, dieldrin, and -HCH, indicates that pesticides used either currently or in the recent past in countries in the southern hemisphere are the sources of contamination in the Antarctic region. 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.

Kawano (2007) measured extractable organohalogen PCBs, DDTs and chlordane compounds (CHLs) in blubber of Weddell seal caught at Syowa Station (69° 00'S, 39° 35'E) from 1980 to 1982 and found that the age-trend accumulation of EOBr (extractable organobromine) and EOI (extractable organoiodine) was similar to man-made organochlorine compounds. Percent compositions of known organic chlorine in EOCl also increased gradually with aging. However, their values were less than 1%. This implied that many other, unknown organic halogen compounds were present in Weddell seals and there are many unidentified compounds in Antarctic marine organisms. It is reasonable to hypothesize that, Antarctic organisms might be forced to produce unique natural organic compounds containing halogen atoms. Actual antifreeze glycoproteins were found in the blood serum of fish specimens from the Antarctic marine environment (DeVries and Wohlschlag, 1969). Recently, halogenated natural products have been tentatively identified in five species of Antarctic sponges (Vetter & Janussen, 2005). Their estimated concentrations ranged from pg/g to µg/g. The high abundance of these compounds relative to known anthropogenic

pollutants suggested a natural origin.

## **5.8 Note: Common and scientific names of organisms**

### **1 Invertebrates**

Antarctic Krill *Euphausia superba*

Antarctic Limpet *Nacella concinna*

Antarctic Soft-shell Clam *Laternula elliptica*

### **2 Fish**

Antarctic Silverfish *Pleuragramma antarcticum*

Blackfin Icefish *Chaenocephalus aceratus*

Blunt Scalyhead *Trematomus eulepidotus*

Emerald Rockcod *Trematomus bernacchii*

Humped Rockcod *Gobionotothen gibberifrons*

Icefish *Chionodraco hamatus*

Lanternfish *Gymnoscopelus nicholsi*

Mackerel Icefish *Chamsocephalus gunnari*

Sharp-Spined Notothenia *Trematomus pennellii*

### **3 Birds**

Adélie Penguin *Pygoscelis adélieae*

Antarctic Petrel *Thalassoica antarctica*

Antarctic Tern *Sterna vittata*

Blue-eyed Shag (cormorant) *Phalacrocorax atriceps*

Brown (or Antarctic) Skua *Catharacta lönnbergi*

Cape Petrel *Daption capensis*

Chinstrap Penguin *Pygoscelis antarcticum*

Gentoo Penguin *Pygoscelis papua*

Giant Petrel *Macronectes giganteus*

Snow Petrel *Pagodroma nivea*

Snowy Sheathbill *Chionis alba*

Southern Fulmar *Fulmarus glacialisoides*

South Polar Skua *Catharacta maccormicki*

### **4 Mammals**

Antarctic (or Southern) Fur Seal *Arctocephalus gazellae*

Killer Whale *Orcinus orca*

Leopard Seal *Hydrurga leptonyx*

Minke Whale *Balaenoptera acutorostrata*

Southern Elephant Seal *Mirounga leonina*

Weddell Seal *Leptonychotes weddellii*

## 6. Summary Data Tables

### Atmosphere data

Chemical	Sample	Concentration	Year	Locations	Reference
PCBs (sum of 10 congeners)	Marine atmosphere	12.1 - 92.6 pg m <sup>-3</sup>	1995-1996	Admiralty Bay	Montone et al., 2003
PCBs	Lower atmosphere	15.2 pg m <sup>-3</sup>		Ross Island	Larsson et al., 1992
DDE p,p' DDT p,p'	Lower atmosphere	1 pg m <sup>-3</sup> 2 pg m <sup>-3</sup>		Ross Island	Larsson et al., 1992
HCH γ -	Lower atmosphere	25.8 pg m <sup>-3</sup>		Ross Island	Larsson et al., 1992
PCBs (sum of 22 congeners)	Ambient air sample	5 – 131 pg m <sup>-3</sup>	1994-1995	Signy Island	Kallenborn et al., 1998
CHLs (Σ trans-Chlordane, cis -Chlordane, trans-Nonachlor, cis - Nonachlor)	Ambient air sample	0.08 – 3.26 pg m <sup>-3</sup>	1994-1995	Signy Island	Kallenborn et al., 1998
HCH α- HCH β- HCH γ -	Ambient air sample	<0.9 – 8.4 pg m <sup>-3</sup> <1.5– 6.9 pg m <sup>-3</sup> 1.5 – 59 pg m <sup>-3</sup>	1994-1995	Signy Island	Kallenborn et al., 1998
DDTs (Σpp'-DDT, p,p'-DDE, and p,p'-DDD, op'-DDT, o,p'-DDE, and o,p'-DDD)	Ambient air sample	<0.2 – 6.67 pg m <sup>-3</sup>	1994-1995	Signy Island	Kallenborn et al., 1998
PCBs (sum of 10 congeners)	Marine atmosphere	12.1 - 42.9 pg m <sup>-3</sup>	1993-1994	Admiralty Bay	Montone et al., 2001
HCH α- HCH γ -	Air 20m above sea level	0.36 pg m <sup>-3</sup> 0.15 pg m <sup>-3</sup>	1999-2000	Neumayer Station	Lakaschus et al., 2002

HCH $\alpha$ - HCH $\gamma$ -	Air 20m above sea level	0.3-0.21 $\text{pg m}^{-3}$ 0.1-69 $\text{pg m}^{-3}$	1999-2000	Cruises across the Atlantic Ocean between the Arctic Ocean and Antarctica	Lakaschus et al., 2002
HCH $\alpha$ - HCH $\gamma$ -	Marine atmosphere	<0.05 – 0.49 $\text{pg m}^{-3}$ <0.02 – 2.98 $\text{pg m}^{-3}$	2001-2002	Western Antarctica Peninsula	Dickhut et al., 2005
HCB	Marine atmosphere	<5 – 32.1 $\text{pg m}^{-3}$	2001-2002	Western Antarctica Peninsula	Dickhut et al., 2005
Heptachlor Heptachlor epoxide	Marine atmosphere	<1 – 19.1 $\text{pg m}^{-3}$ <0.3 – 20.7 $\text{pg m}^{-3}$	2001-2002	Western Antarctica Peninsula	Dickhut et al., 2005
HCB	Atmosphere	56-145 $\text{pg m}^{-3}$	2001	Cruise from the Netherland to Cape Town South Africa	Booij et al. 2007
4,4' DDE	Atmosphere	<0.1-0.9 $\text{pg m}^{-3}$	2001	Cruise from the Netherland to Cape Town South Africa	Booij et al. 2007
PAHs	Atmosphere	190-3730 $\text{pg m}^{-3}$	2001	Cruise from the Netherland to Cape Town South Africa	Jaward et al. 2004a
PCNs (polychlorinated naphthalenes)	Atmosphere	0.3-86 $\text{pg m}^{-3}$	2001	Cruise from the Netherland to Cape Town South Africa	Jaward et al. 2004a
PCBs (sum of 29 congeners)	Atmosphere	12-360 $\text{pg m}^{-3}$	2001	Cruise from the Netherland to Cape Town South Africa	Jaward et al. 2004b
HCB	Atmosphere	4.8-100 $\text{pg m}^{-3}$	2001	Cruise from the Netherland to Cape Town South Africa	Jaward et al. 2004b
HCH $\alpha$ - HCH $\gamma$ -	Atmosphere	<0.1-11 $\text{pg m}^{-3}$ <3.6-100 $\text{pg m}^{-3}$	2001	Cruise from the Netherland to Cape Town South Africa	Jaward et al. 2004b
DDE p,p' DDT p,p'	Atmosphere	<1.5-47 $\text{pg m}^{-3}$ <2.2-5.4 $\text{pg m}^{-3}$	2001	Cruise from the Netherland to Cape Town South Africa	Jaward et al. 2004b
HCH $\alpha$ -	Marine atmosphere	0.3 – 1.7 $\text{pg m}^{-3}$	1997-1998	Cruise to South African Base	Jantunen et al., 2004
HCH $\alpha$ -	Marine atmosphere	6.6 –40 $\text{pg m}^{-3}$	1989-1990	Ross Sea	Iwata et al., 1993
HCH $\alpha$ - HCH $\gamma$ -	Marine atmosphere	4 $\text{pg m}^{-3}$ 3.8 $\text{pg m}^{-3}$	1990	From New Zealand to Ross Island	Bidleman et al., 1993
HCB	Marine atmosphere	60 $\text{pg m}^{-3}$	1990	From New Zealand to Ross Island	Bidleman et al., 1993

CHLs ( $\Sigma$ Chlordanes plus Nonachlors)	Marine atmosphere	1.8 pg m <sup>-3</sup>	1990	From New Zealand to Ross Island	Bidleman et al., 1993
DDTs ( $\Sigma$ pp'-DDT, p,p'-DDE)	Marine atmosphere	0.81 pg m <sup>-3</sup>	1990	From New Zealand to Ross Island	Bidleman et al., 1993
HCB	Marine atmosphere	21.9-25.3 pg m <sup>-3</sup>	1995	61°16' S 55°07' W 62°11' S 58°63' W 61°18' S 55°05' W	Montone et al., 2005
HCH $\alpha$ - HCH $\gamma$ -	Marine atmosphere	3.3-4.5 pg m <sup>-3</sup> <2.7 – 4.6 pg m <sup>-3</sup>	1995	61°16' S 55°07' W 62°11' S 58°63' W 61°18' S 55°05' W	Montone et al., 2005
DDE p,p' DDD p,p' DDT p,p'	Marine atmosphere	<2.5-5.2 pg m <sup>-3</sup> <2.7 pg m <sup>-3</sup> <2.7 pg m <sup>-3</sup>	1995	61°16' S 55°07' W 62°11' S 58°63' W 61°18' S 55°05' W	Montone et al, 2005
PCBs (sum of 11 congeners)	Marine atmosphere	52.6-69.9 pg m <sup>-3</sup>	1995	61°16' S 55°07' W 62°11' S 58°63' W 61°18' S 55°05' W	Montone et al., 2005
PCBs (sum of 31cong) PCBs (sum of coplanar) PCBs (sum of 206 cong) PCB-11 (average)	Atmosphere	2.10-8.07 pg m <sup>-3</sup> 0.18-0.91 pg m <sup>-3</sup> 45.21-117.80 pg m <sup>-3</sup> 60 pg m <sup>-3</sup>	2004-2005	King Sejong Station on King George Island	Choi et al., 2008
PCBs (sum of 78 congeners)	Atmosphere	0.63-1.78 pg m <sup>-3</sup>	2003-2004	Northern Victoria Land	Gambaro et al., 2005
Nitro-PAHs	Atmosphere	1-200 fg m <sup>-3</sup>	2000	Terra Nova Bay	Vincenti et al., 2001

## Marine environment data

Chemical	Sample	Concentration	Year	Locations	Reference
PCBs (sum of 7 congeners)	SML* SSW*	427 pg l <sup>-1</sup> 48 pg l <sup>-1</sup>	1997-1998	Gerlache Inlet, Ross Sea	Fuoco et al., 2005
PAHs (sum of 14)	SML* SSW*	2300 pg l <sup>-1</sup> 325 pg l <sup>-1</sup>	1997-1998	Gerlache Inlet, Ross Sea	Fuoco et al., 2005
PCBs (sum of 7 congeners)	Surface sea water	55 - 84 pg l <sup>-1</sup> 23 pg l <sup>-1</sup> 36 - 53 pg l <sup>-1</sup>	1997-1998 2000-2001 2002-2003	Ross Sea and Terranova Bay	Fuoco et al., 2009
PAHs (sum of 14)	Surface sea water	122 - 330 pg l <sup>-1</sup> 328 - 360 pg l <sup>-1</sup> 96 - 281pg l <sup>-1</sup>	1997-1998 2000-2001 2002-2003	Ross Sea and Terranova Bay	Fuoco et al., 2009
HCH α-	Surface water Middle Depth water (25-200 m)	5.1 - 19 pg l <sup>-1</sup> 3.5 - 34 pg l <sup>-1</sup>	1997-1998	Cruise to South African Base	Jantunen et al., 2004
HCH α- HCH γ -	Sea water (11 m depths)	3.4 – 5.3 pg l <sup>-1</sup> 0.7 – 0.9 pg l <sup>-1</sup>	1999-2000	Lat S 61 - 66	Lakaschus et al., 2002
HCH α- HCH γ -	Sea water (11 m depths)	2 – 689 pg l <sup>-1</sup> 1.4 – 230 pg l <sup>-1</sup>	1999-2000	Cruises across the Atlantic Ocean between the Arctic Ocean and Antarctica	Lakaschus et al., 2002
PCBs	Surface water before PIM* and after PIM*	100 -160 pg l <sup>-1</sup> ; 150 -180 pg l <sup>-1</sup> 140 pg l <sup>-1</sup> ; 180 pg l <sup>-1</sup> 90 - 180 pg l <sup>-1</sup> ; 160 - 230 pg l <sup>-1</sup>	1989-1990 1990-1991 1991-1992	Gerlache Inlet and Wood Bay	Fuoco et al., 1996
HCH α- HCH γ -	Surface water	1.65 - 4.54 pg l <sup>-1</sup> 0.9 -10.5 pg l <sup>-1</sup>	2001-2002	Western Antarctica Peninsula	Dickhut et al., 2003
HCH α- HCH γ -	Sea ice	<0.04 - 2.18 pg l <sup>-1</sup> 3.6 - 5.7 pg l <sup>-1</sup>	2001-2002	Western Antarctica Peninsula	Dickhut et al., 2003
Heptachlor Heptachlor epoxide	Sea ice	<2.5 – 5.8 pg l <sup>-1</sup> <0.6 – 2.2 pg l <sup>-1</sup>	2001-2002	Western Antarctica Peninsula	Dickhutv, 2003

HCB, 4,4'	Surface seawater	1.9-9.0 pg l <sup>-1</sup>	2001	From Texel (the Netherland) to Cape Town South Africa	Booij et al. 2007
DDE	Surface seawater	<0.3-1.4 pg l <sup>-1</sup>	2001	From Texel (the Netherland) to Cape Town South Africa	Booij et al. 2007
PAHs (sum of 13)	Dissolved phase SML* Dissolved phase SSL* Particulate phase SML* Particulate phase SSL*	4.67 - 7.79 ng l <sup>-1</sup> 2.24 – 4.01 ng l <sup>-1</sup> 5.68 – 14.1 ng l <sup>-1</sup> 1.65 – 3.65 ng l <sup>-1</sup>	1998-1999	Terra Nova Bay	Cincinelli et al., 2005
PAHs	Seawater	50-200 ng l <sup>-1</sup>		Signy Research Station	Cripps, 1990
PAHs	Seawater	Up to 9400 ng l <sup>-1</sup>	1987	Weddel Sea	Comes et al., 1987
PAHs (sum of 13)	Dissolved phase SML* Dissolved phase SSL* Particulate phase SML* Particulate phase SSL*	4.25 – 8.11 ng l <sup>-1</sup> 2.14 – 2.85 ng l <sup>-1</sup> 3.07 – 15.83 ng l <sup>-1</sup> 2.81 – 4.66 ng l <sup>-1</sup>	2000-2001	Gerlache Inket, Ross sea	Stortini et al., 2009
PCBs (total)	Marine sediment	80 pg g <sup>-1</sup> dry wt 150 (pg g <sup>-1</sup> ) / (m <sup>2</sup> cm <sup>-3</sup> )	1988-1992	Ross sea	Fuoco et al., 1996
PCBs (sum of 7 congeners)	Marine sediment	0.4 - 0.5 ng g <sup>-1</sup>	2005	James Ross Island	Klanova et al., 2008
HCH γ -	Marine sediment	0.2 -0.3 ng g <sup>-1</sup>	2005	James Ross Island	Klanova et al., 2008
DDTs (sum of p,p'DDT, DDD, DDE)	Marine sediment	0.3 – 0.6 ng g <sup>-1</sup>	2005	James Ross Island	Klanova et al., 2008
HCB	Marine sediment	2 - 4 ng g <sup>-1</sup>	2005	James Ross Island	Klanova et al., 2008
PAHs (sum of 16 USEPA priority pollutants)	Marine sediment	20-50 ng g <sup>-1</sup>	2005	James Ross Island	Klanova et al., 2008
PCBs (sum of 13 congeners)	Marine sediment	0.47 – 2.47 ng g <sup>-1</sup> dry wt	1993-1994	Admiralty Bay	Montone et al., 2001
PCBs	Marine sediment	<5 –40 μg g <sup>-1</sup> 220-373 ng g <sup>-1</sup> <5 ng g <sup>-1</sup>	2002	Scott Base Mc Murdo Base Turtle Rock, Cape Evans	Negri et al., 2006

PAHs (from oil)	Marine sediment	110 – 370 ng g <sup>-1</sup> 1100 – 2100 ng g <sup>-1</sup> 70 – 360 ng g <sup>-1</sup>	2002	Scott Base Mc Murdo Sewage Outfall Turtle Rock, Cape Evans	Negri et al., 2006
PAHs (from combustion)	Marine sediment	15 – 30 ng g <sup>-1</sup> 270 – 550 ng g <sup>-1</sup> 10 – 30 ng g <sup>-1</sup>	2002	Scott Base Mc Murdo Sewage Outfall Turtle Rock, Cape Evans	Negri et al., 2006
PBDEs (sum of 6 congeners)	Sediment	<d.l.-677 ng g <sup>-1</sup> (TOC basis)	2003	McMurdo Sound	Hale et al., 2008
PAHs (sum of 25)	Marine sediment	28 –312 ng g <sup>-1</sup> dry wt 36 –1908 ng g <sup>-1</sup> dry wt	2004 2005	Potter Cove (South Shetland Islands)	Curtosi et al., 2007
PAHs (sum of 25)	Marine surface sediment	9.45 – 270.5 ng g <sup>-1</sup>	1997-1998 and 1999- 2000	Admiralty Bay (around the Brazilian Station)	Martins et al., 2004
PAHs	Marine benthic sediment	1077 – 2053 ng g <sup>-1</sup> 621 – 5024 ng g <sup>-1</sup>	2000 2001	McMurdo Station	Kim et al., 2006
PCBs	Marine sediment	250-4300 ng g <sup>-1</sup>		Winter Quarters Bay	Crockett and White, 2003
PAHs	Marine sediment	360-13000 ng g <sup>-1</sup>		Winter Quarters Bay	Crockett and White, 2003

## Terrestrial environment data

Chemical	Sample	Concentration	Year	Locations	Reference
DDE p,p' DDT p,p'	Surface snow	0.1 pg g <sup>-1</sup> 0.5 pg g <sup>-1</sup>	1975	Antarctic peninsula	Risebrough et al., 1976
PCBs (total)	Surface snow	0.2 pg g <sup>-1</sup>	1975	Antarctic peninsula	Risebrough et al., 1976
DDE p,p' DDT p,p'	2-4m deep snow	0.3 pg g <sup>-1</sup> 4 pg g <sup>-1</sup>	1975	Antarctic peninsula	Risebrough et al., 1976
PCBs (total)	2-4m deep snow	1.2 pg g <sup>-1</sup>	1975	Antarctic peninsula	Risebrough et al., 1976
DDE p,p' DDT p,p'	5.5-6 m deep snow	0.2 pg g <sup>-1</sup> 2.1 pg g <sup>-1</sup>	1975	Antarctic peninsula	Risebrough et al., 1976
PCBs (total)	5.5-6 m deep snow	0.3 pg g <sup>-1</sup>	1975	Antarctic peninsula	Risebrough et al., 1976
PCBs (total)	Shallow and deep snow	0.2-1 pg g <sup>-1</sup>	1980-1982	Syowa Station	Tanabe et al., 1983
HCH	Shallow and deep snow	1.5-4.9 pg dm <sup>-3</sup>	1980-1982	Syowa Station	Tanabe et al., 1983
PCBs (total)	Ice	0.3-0.6 pg g <sup>-1</sup>	1980-1982	Syowa Station	Tanabe et al., 1983
HCH	Ice	2-2.2 pg dm <sup>-3</sup>	1980-1982	Syowa Station	Tanabe et al., 1983
PCBs (total)	Lake sediment	120 pg g <sup>-1</sup> dry wt 240 (pg g <sup>-1</sup> ) / (m <sup>2</sup> /cm <sup>3</sup> )	1988-1992	Victoria Land	Fuoco et al., 1996
PCBs (total)	Soil	60 pg g <sup>-1</sup> dry wt 130 (pg g <sup>-1</sup> ) / (m <sup>2</sup> cm <sup>-3</sup> )	1988-1992	Victoria Land	Fuoco et al., 1996
PCBs (total)	Snow (surface down to 2.5 deep)	0.28-0.73 pg g <sup>-1</sup>	1993-1995	Hercules Nèvé	Fuoco and Ceccarini, 2001
Endosulfan sulfate	Ice core	300 pg g <sup>-1</sup>	2002	Mackeller Peninsula	Deger et al., 2003
PCBs (total)	Surface snow	4-10 pg g <sup>-1</sup>	1975	Palmer Station	Risebrough et al., 1976
PAHs	Soil	345,000 ng g <sup>-1</sup> dry wt	1989-1993	Old Palmer Station	Kennicutt and Champ, 1992
PAHs (sum of 16 USEPA priority pollutants)	Soil	41-8,105 ng g <sup>-1</sup> dry wt	1998	Scott Base	Aislabie et al., 1999
PCBs (total)	Mosses	23-34 ng g <sup>-1</sup> dry wt	1999	Victoria Land	Borghini et al., 2005

DDE p,p' DDT p,p'	Mosses	1.1-7.9 ng g <sup>-1</sup> dry wt 0.6-0.9 ng g <sup>-1</sup> dry wt	1999	Victoria Land	Borghini et al., 2005
HCB	Mosses	0.9-1.9 ng g <sup>-1</sup> dry wt	1999	Victoria Land	Borghini et al., 2005
HCH α- HCH γ -	Mosses	0.4-4 ng g <sup>-1</sup> dry wt 0.2-1.6 ng g <sup>-1</sup> dry wt	1999	Victoria Land	Borghini et al., 2005
PCBs (total)	Soil	0.4-0.6 ng g <sup>-1</sup> dry wt	1999	Victoria Land	Borghinv, 2005
DDE p,p' DDT p,p'	Soil	0.05-0.09 ng g <sup>-1</sup> dry wt < 0.005-0.02 ng g <sup>-1</sup> dry wt	1999	Victoria Land	Borghini et al., 2005
HCB	Soil	0.034-0.17 ng g <sup>-1</sup> dry wt	1999	Victoria Land	Borghini et al., 2005
HCH α- HCH γ -	Soil	0.03 ng g <sup>-1</sup> dry wt < 0.01 (LOD)	1999	Victoria Land	Borghini et al., 2005
PCBs (28 congeners)	Soil	0.2 –157 ng g <sup>-1</sup> dry wt	1998	5 Russians Station	Negoita et al., 2003
PCBs (28 congeners)	Lichen	3.3 ng g <sup>-1</sup> dry wt	1998	5 Russians Station	Negoita et al., 2003
HCHs (sum α,β,γ,δ)	Soil	0.9 –43.1 ng g <sup>-1</sup> dry wt	1998	5 Russians Station	Negoita et al., 2003
HCHs (sum α,β,γ,δ)	Lichen	59.7 ng g <sup>-1</sup> dry wt	1998	5 Russians Station	Negoita et al., 2003
HCB	Soil	0.02 –25.3 ng g <sup>-1</sup> dry wt	1998	5 Russians Station	Negoita et al., 2003
HCB	Lichen	0.3 ng g <sup>-1</sup> dry wt	1998	5 Russians Station	Negoita et al., 2003
DDE p,p' DDT p,p'	Soil	0.03 –3.2 ng g <sup>-1</sup> dry wt 0.04-14.9 ng g <sup>-1</sup> dry wt	1998	5 Russians Station	Negoita et al., 2003
DDE p,p' DDT p,p'	Lichen	0.40 ng g <sup>-1</sup> dry wt 0.71 ng g <sup>-1</sup> dry wt	1998	5 Russians Station	Negoita et al., 2003
HCH α- HCH γ -	Snow	<0.04-2.18 pg l <sup>-1</sup> 1.73 – 8.91 pg l <sup>-1</sup>	2001-2002	Western Antarctica Peninsula	Dickhut et al., 2003
Heptachlor Heptachlor epoxide	Snow	<2.5 – 6.70 pg l <sup>-1</sup> <0.63 – 1.12 pg l <sup>-1</sup>	2001-2002	Western Antarctica Peninsula	Dickhut et al., 2003
PAHs (sum of 25)	Soil	10 – 1182 ng g <sup>-1</sup> dry wt 12 – 552 ng g <sup>-1</sup> dry wt	2004 2005	Potter Cove (South Shetland Islands)	Curtosi et al., 2007
PAHs		1724 – 46479 ng g <sup>-1</sup> 664 – 74267 ng g <sup>-1</sup>	1999 2001	McMurdo Station	Kim et al., 2006
PCBs (7 congeners)	Soil Sediment (lake and river)	0.5-2 ng g <sup>-1</sup> 0.4 – 0.8	2005	James Ross Island	Klanovav, 2008

HCH $\gamma$ -	Soil Sediment (lake and river)	0.5-1.3 ng g <sup>-1</sup> 0.1 – 0.7	2005	James Ross Island	Klanova et al., 2008
DDTs (sum of p,p' DDT, DDD, DDE)	Soil Sediment (lake and river)	0.5-3.7 ng g <sup>-1</sup> 0.1 - 1.3	2005	James Ross Island	Klanova et al., 2008
HCB	Soil Sediment (lake and river)	4 –8 ng g <sup>-1</sup> 1 - 4	2005	James Ross Island	Klanova et al., 2008
PAHs (sum of 16 USEPA priority pollutants)	Soil Sediment (lake and river)	35-170 ng g <sup>-1</sup> 5 - 200	2005	James Ross Island	Klanova et al., 2008

### Food web data

Chemical	Target Species	Concentration	Year	Locations	Reference
CHLs ( $\Sigma$ Oxychlordane, trans-Chlordane, cis-Chlordane, trans-Nonachlor)	Southern Elephant seals blubber	38.56 ng g <sup>-1</sup> lipid wt males 34.53 ng g <sup>-1</sup> lipid wt females 31.20 ng g <sup>-1</sup> lipid wt juveniles 18.09 ng g <sup>-1</sup> lipid wt pups	1997-1998 1998-1999 1999-2000	Elephant Island	Miranda-Filho et al., 2007
CHLs ( $\Sigma$ Oxychlordane, trans-Chlordane, cis-Chlordane, trans-Nonachlor)	Weddel seal blubber	15.5 ng g <sup>-1</sup> wet wt	1994	King George Island	Vetter et al., 2003
CHL : oxychlordane CHL : Trans-nonachlor	South polar skuas blood	1.3 ng g <sup>-1</sup> wet wt, 400 ng g <sup>-1</sup> lipid wt 0.2 ng g <sup>-1</sup> wet wt, 100 ng g <sup>-1</sup> lipid wt	2001-2002	Svarthamaren in Dronning Maud Land	Bustnes et al., 2006
CHL : Trans-nonachlor	<i>C. gunnari</i> , <i>G. gibberifrons</i> , <i>C. aceratus</i> liver	1.1 $\pm$ 0.4 ng/g <sub>EOM</sub>	1987	Antarctic peninsula	Weber and Goerke, 1996

CHLs	Minke whale ( <i>Balaenoptera acutorostrata</i> )	27 ng g <sup>-1</sup> wet wt 29 ng g <sup>-1</sup> wet wt 31 ng g <sup>-1</sup> wet wt 41 ng g <sup>-1</sup> wet wt	1984/85 1988/89 1990/91 1992/93		Aono et al., 1997
CHLs	Type C Killer whales blubber	1300 ng g <sup>-1</sup> lipid wt	2005 and 2006	McMurdo Sound	Khuran et al. 2008
DDE p, p'	<i>C. gunnari</i> , <i>G. gibberifrons</i> , <i>C. Aceratus</i> liver	4.7 ± 2.4 ng g <sup>-1</sup> <sub>EOM</sub>	1987	Antarctic peninsula	Weber and Goerke, 1996
DDE p, p'- (p, p'-DDT nd)	Adelie penguin eggs	58.5-755 ng g <sup>-1</sup> lipid wt 73.0-176 ng g <sup>-1</sup> lipid wt	2004 2006	Palmer Archipelago Cape Crozier, Ross Island	Geisz et al., 2008
DDE p,p'	Krill	0.7 ng/g <sub>EOM</sub>	1986	Weddel sea, Elephant island and Shetland islands	Goerke et al., 2004
DDE p,p'	Adélie penguin blood Chinstrap penguin blood Gentoo penguin blood	8.2±3.3 ng g <sup>-1</sup> wet wt 6.8 ±4.2 ng g <sup>-1</sup> wet wt 4 ±3.1 ng g <sup>-1</sup> wet wt	2004	Lenie Field Station, Admiralty Bay, King George Is	Corsolini et al., 2007
DDE p,p'-	South polar skuas blood	6.8 ng g <sup>-1</sup> wet wt 2000 ng g <sup>-1</sup> lipid wt	2001-2002	Svarthamaren in Dronning Maud Land	Bustnes et al., 2006
DDE p,p' DDT p,p'	Leopard seals	267-456 ng g <sup>-1</sup> wet wt 160 ng g <sup>-1</sup> wet wt	1979-1981	King George Island	Karolewski et al., 1987
DDE p,p'	Krill	0.86±0.98 ng g <sup>-1</sup> wet wt	1999/2000	Ross Sea	Corsolini et al., 2002
DDE p,p'	<i>Pleurogramma antarcticum</i>	1.77±0.37 ng g <sup>-1</sup> wet wt (larva) 2.01±1.48 ng g <sup>-1</sup> wet wt (adult)	1999/2000	Ross Sea	Corsolini et al., 2002
DDE p,p' DDTs (ΣDDE,DDT,DDD)	Krill	0.13 ng g <sup>-1</sup> wet wt, 2.6 ng g <sup>-1</sup> lipid wt 0.18 ng g <sup>-1</sup> wet wt, 3.5 ng g <sup>-1</sup> lipid wt	2005/06	12 sampling stations (NE sector)	Bengstone et al., 2008
DDE p,p' DDT p,p'	Krill	14 ng g <sup>-1</sup> lipid wt 19 ng g <sup>-1</sup> lipid wt	1975	Antarctic peninsula	Risebrough et al., 1976
DDE p,p'-	<i>L. weddellii</i> blubber <i>M. leonine</i> blubber	110 ng g <sup>-1</sup> <sub>EOM</sub> 118 ng g <sup>-1</sup> <sub>EOM</sub>	1995 1996	Waters around Elephant Island	Goerke et al., 2004

DDE p,p'-	<i>P. Adeliae</i>	3.5 ng g <sup>-1</sup> <sub>EOM</sub>	1995	Waters around Elephant Island	Goerke et al., 2004
DDE p,p'-	<i>C. gunnari</i> liver <i>G. nicholsi</i> muscle <i>P. eulepidotus</i> liver <i>P. antarcticum</i> muscle	4 ng g <sup>-1</sup> <sub>EOM</sub> 7.5 ng g <sup>-1</sup> <sub>EOM</sub> 6.2 ng g <sup>-1</sup> <sub>EOM</sub> 3 ng g <sup>-1</sup> <sub>EOM</sub>	1996 1996 2000 2000	Waters around Elephant Island	Goerke et al., 2004
DDTs (Σ p,p'-DDE+ p,p'-DDT)	<i>Pygoscelis papua</i> eggs Giant petrel eggs Brown skua eggs	2.0-10.1 ng g <sup>-1</sup> 12.7-53.7 ng g <sup>-1</sup> 56.6-304 ng g <sup>-1</sup>	2001-2002	Fildes Peninsula adjacent to Great Wall Station of China	Zhang et al., 2007
DDTs (Σ p,p'-DDT, p,p'-DDE, and p,p'-DDD)	Antarctic fur seal milk	8 ng g <sup>-1</sup> 3.8 ng g <sup>-1</sup>	1985 1984	South Georgia Island	Jarman et al., 1992
DDTs (Σ p,p'-DDT, p,p'-DDE, and p,p'-DDD)	Weddel seal blubber	14.1 ng g <sup>-1</sup> wet wt	1994	King George Island	Vetter et al., 2003
DDTs (Σ p,p'-DDT, p,p'-DDE, and p,p'-DDD, op'-DDT, o,p'-DDE, and o,p'-DDD)	Southern Elephant seals blubber	192.85 ng g <sup>-1</sup> lipid wt males 182.59 ng g <sup>-1</sup> lipid wt females 123.50 ng g <sup>-1</sup> lipid wt juveniles 79.95 ng g <sup>-1</sup> lipid wt pups	1997-1998 1998-1999 1999-2000	Elephant Island	Miranda-Filho et al., 2007
DDTs	Brown skua fat tissue Penguins fat tissue Antarctic tern fat tissue Blue-eyed shag fat tissue Snowy sheatbill fat tissue	6118 ± 3813 ng g <sup>-1</sup> lipid wt 193 ± 16 ng g <sup>-1</sup> lipid wt 524 ± 205 ng g <sup>-1</sup> lipid wt 374 ng g <sup>-1</sup> lipid wt 468 ng g <sup>-1</sup> lipid wt	1997-1998	Brazilian and Polish Antarctic Station on King George Island.	Taniguchi et al., 2008
DDTs	krill	0.037 ng g <sup>-1</sup> dry wt	1987/88	Dakshin Gangotri (70° S and 12° E)	Sen Gupta, 1996
DDTs	Penguin feathers	0.033 ng g <sup>-1</sup> dry wt	1987/88	Dakshin Gangotri (70° S and 12° E)	Sen Gupta et al., 1996
DDTs	Minke whale ( <i>Balaenoptera acutorostrata</i> )	110 ng g <sup>-1</sup> wet wt 120 ng g <sup>-1</sup> wet wt 130 ng g <sup>-1</sup> wet wt 180 ng g <sup>-1</sup> wet wt	1984/85 1988/89 1990/91 1992/93		Aono et al., 1997

DDTs	Krill	0.18 ng g <sup>-1</sup> wet wt	2000-2001/02	Ross Sea in Terra Nova Bay	Corsolini et al., 2006
DDTs	Type C Killer whales blubber	4300 ng g <sup>-1</sup> lipid wt	2005 and 2006	McMurdo Sound	Khram et al., 2008
Dieldrin	Southern Elephant seals blubber	10.25 ng g <sup>-1</sup> lipid wt males 9.12 ng g <sup>-1</sup> lipid wt females 7.94 ng g <sup>-1</sup> lipid wt juveniles 4.28 ng g <sup>-1</sup> lipid wt pups	1997-1998 1998-1999 1999-2000	Elephant Island	Miranda-Filho et al., 2007
Dieldrin	Antarctic fur seal milk	10 ng g <sup>-1</sup> 17 ng g <sup>-1</sup>	1985 1984	South Georgia Island	Jarman et al., 1992
Dieldrin	Weddel seal blubber	4.6 ± 0.5 ng g <sup>-1</sup> wet wt	1994	King George Island	Vetter et al., 2003
Endosulfan (Σendosulfan, endosulfan-sulfate)	Southern Elephant seals blubber	3.02 ng g <sup>-1</sup> lipid wt males 2.68 ng g <sup>-1</sup> lipid wt females 1.99 ng g <sup>-1</sup> lipid wt juveniles 0.90 ng g <sup>-1</sup> lipid wt pups	1997-1998 1998-1999 1999-2000	Elephant Island	Miranda-Filho et al., 2007
HCB	<i>Pygoscelis papua</i> eggs Giant petrel eggs Brown skua eggs	6.0-10.2 ng g <sup>-1</sup> 4.2-8.8 ng g <sup>-1</sup> 6.5-70.5 ng g <sup>-1</sup>	2001-2002	Fildes Peninsula adjacent to Great Wall Station of China	Zhang et al., 2007
HCB	Brown skua fat tissue Penguins fat tissue Antarctic tern fat tissue Blue-eyed shag fat tissue Snowy sheatbill fat tissue	573 ± 278 ng g <sup>-1</sup> lipid wt 373 ± 177 ng g <sup>-1</sup> lipid wt 601 ± 256 ng g <sup>-1</sup> lipid wt 161 ng g <sup>-1</sup> lipid wt 282 ng g <sup>-1</sup> lipid wt	1997-1998	Brazilian and Polish Antarctic Station on King George Island.	Taniguchi et al., 2008
HCB	South polar skuas blood	7.2 ng g <sup>-1</sup> wet wt 2300 ng g <sup>-1</sup> lipid wt	2001-2002	Svarthamaren in Dronning Maud Land	Bustnes et al., 2006
HCB	Southern Elephant seals blubber	11.20 ng g <sup>-1</sup> lipid wt males 8.58 ng g <sup>-1</sup> lipid wt females 8.89 ng g <sup>-1</sup> lipid wt juveniles 4.60 ng g <sup>-1</sup> lipid wt pups	1997-1998 1998-1999 1999-2000	Elephant Island	Miranda-Filho et al., 2007
HCB	Krill	0.37±0.17 ng g <sup>-1</sup> wet wt	1999/2000	Ross Sea	Corsolini et al., 2002
HCB	<i>Pleurogramma antarcticum</i>	2.46±2.24 ng g <sup>-1</sup> wet wt (larva) 4.85±5.49 ng g <sup>-1</sup> wet wt (adult)	1999/2000	Ross Sea	Corsolini et al., 2002

HCB	Sea ice algae	15.9 ± 6.2 ng g <sup>-1</sup> lipid wt	2001/2002	Region west of the Antarctic Peninsula	Chiuchiolo et al., 2004
HCB	Minke whale ( <i>Balaenoptera acutorostrata</i> )	110 ng g <sup>-1</sup> wet wt 100 ng g <sup>-1</sup> wet wt 92 ng g <sup>-1</sup> wet wt 130 ng g <sup>-1</sup> wet wt	1984/85 1988/89 1990/91 1992/93		Aono et al., 1997
HCB	Krill	0.2 ng g <sup>-1</sup> wet wt, 4.37 ng g <sup>-1</sup> lipid wt	2005/06	12 sampling stations (NE sector)	Bengstone et al., 2008
HCB	Krill	0.23 ng g <sup>-1</sup> wet wt	2000-2001/02	Ross Sea in Terra Nova Bay	Corsolini et al., 2006
HCB	Krill	1 ng g <sup>-1</sup> EOM	1986	Weddel sea, Elephant island and Shetland islands	Goerke et al., 2004
HCB	<i>Champscephalus gunnari</i> , <i>Gobionotothen gibberifrons</i> , <i>Chaenocephalus aceratus</i> liver	20 ± 6.9 ng g <sup>-1</sup> EOM	1987	Antarctic peninsula	Weber and Goerke, 1996
HCB	Adelie Penguin (n = 12) Snow Petrel (n = 4) Antarctic Petrel (n = 5) Southern Fulmar (n = 18) Cape Petrel: Hop Island (n = 3) Cape Petrel: K. George Island (n = 6)	620 ng g <sup>-1</sup> lipid wt 478 ng g <sup>-1</sup> lipid wt 268 ng g <sup>-1</sup> lipid wt 518 ng g <sup>-1</sup> lipid wt  1808 ng g <sup>-1</sup> lipid wt  2253 ng g <sup>-1</sup> lipid wt	February 1994 January 1991	Hop Island      K. George Island	Van der Brink et al., 1997
HCB	<i>L. weddellii</i> blubber <i>M. leonine</i> blubber	7.5 ng g <sup>-1</sup> EOM 5 ng g <sup>-1</sup> EOM	1995 1996	Waters around Elephant Island	Goerke et al., 2004
HCB	<i>P. Adeliae</i>	25 ng g <sup>-1</sup> EOM	1995	Waters around Elephant Island	Goerke et al., 2004

HCB	<i>C. gunnari</i> liver <i>G. nicholsi</i> muscle <i>P. eulepidotus</i> liver <i>P. antarcticum</i> muscle	5 ng g <sup>-1</sup> EOM 10 ng g <sup>-1</sup> EOM 10 ng g <sup>-1</sup> EOM 10 ng g <sup>-1</sup> EOM	1996 1996 2000 2000	Waters around Elephant Island	Goerke et al., 2004
HCB	Adélie penguin blood Chinstrap penguin blood Gentoo penguin blood	6.7±6.1 ng g <sup>-1</sup> wet wt 3.6 ±1.9 ng g <sup>-1</sup> wet wt 2.7 ±1.4 ng g <sup>-1</sup> wet wt	2004	Lenie Field Station, Admiralty Bay, King George Is	Corsolini et al., 2007
HCB	Type C Killer whales blubber	740 ng g <sup>-1</sup> lipid wt	2005 and 2006	McMurdo Sound	Khran et al., 2008
HCH	Leopard seals	25 ng g <sup>-1</sup> wet wt	1979-1981	King George Island	Karolewski et al., 1987
HCH	Brown skua fat tissue Penguins fat tissue Antarctic tern fat tissue Blue-eyed shag fat tissue Snowy sheatbill fat tissue	1.22-3.11 ng g <sup>-1</sup> lipid wt 12.3 ± 9.1 ng g <sup>-1</sup> lipid wt <0.12–2.60 ng g <sup>-1</sup> lipid wt 1.33 ng g <sup>-1</sup> lipid wt <0.12 ng g <sup>-1</sup> lipid wt	1997-1998	Brazilian and Polish Antarctic Station on King George Island	Taniguchi et al., 2008
HCH	Weddel seal blubber	0.7 ±0.2ng g <sup>-1</sup> wet wt	1994	King George Island	Vetter et al., 2003
HCHs (Σ α-HCH+γ-HCH)	Pygoscelis <i>papua</i> eggs Giant petrel eggs Brown skua eggs	0.1-0.4 ng g <sup>-1</sup> 0.5-1.5 ng g <sup>-1</sup> < 0.5-2 ng g <sup>-1</sup>	2001-2002	Fildes Peninsula adjacent to Great Wall Station of China	Zhang et al., 2007
HCHs (Σ-α,-γ)	Southern Elephant seals blubber	2.20 ng g <sup>-1</sup> lipid wt males 1.61 ng g <sup>-1</sup> lipid wt females 1.24 ng g <sup>-1</sup> lipid wt juveniles 0.81 ng g <sup>-1</sup> lipid wt pups	1997-1998 1998-1999 1999-2000	Elephant Island	Miranda-Filho et al., 2007
HCH α-	Weddel seal blubber	0.8 ±0.1 ng g <sup>-1</sup> wet wt	1994	King George Island	Vetter et al., 2003
HCH β-	South polar skuas blood	0.1ng g <sup>-1</sup> wet wt <100 ng g <sup>-1</sup> wet wt	2001-2002	Svarthamaren in Dronning Maud Land	Bustnes et al., 2006
HCHs	krill	0.154 ng g <sup>-1</sup> dry wt	1987/88	Dakshin Gangotri (70° S and 12° E)	Sen Gupta et al., 1996
HCHs	Penguin feathers	0.108 ng g <sup>-1</sup> dry wt	1987/88	Dakshin Gangotri (70° S and 12° E)	Sen Gupta et al., 1996

HCHs	Minke whale ( <i>Balaenoptera acutorostrata</i> )	3.7 ng g <sup>-1</sup> wet wt 1.8 ng g <sup>-1</sup> wet wt 2.1 ng g <sup>-1</sup> wet wt 2.7 ng g <sup>-1</sup> wet wt	1984/85 1988/89 1990/91 1992/93		Aono et al., 1997
HCHs	Krill	0.28 ng g <sup>-1</sup> wet wt	2000- 2001/02	Ross Sea in Terra Nova Bay	Corsolini et al., 2006
HCH α- HCH β- HCH γ -	Krill	0.01 ng g <sup>-1</sup> wet wt, 0.28 ng g <sup>-1</sup> lipid wt 0.01 ng g <sup>-1</sup> wet wt, 0.16 ng g <sup>-1</sup> lipid wt 0.01 ng g <sup>-1</sup> wet wt, 0.13 ng g <sup>-1</sup> lipid wt	2005/06	12 sampling stations (NE sector)	Bengstone et al., 2008
HCHs	Type C Killer whales blubber	< LOQ	2005 and 2006	McMurdo Sound	Khran et al., 2008
Mirex	Brown skua fat tissue Penguins fat tissue Antarctic tern fat tissue Blue-eyed shag fat tissue Snowy sheatbill fat tissue	2210 ± 1590 ng g <sup>-1</sup> lipid wt 90.6 ± 70.6 ng g <sup>-1</sup> lipid wt 260 ± 58 ng g <sup>-1</sup> lipid wt 89.2 ng g <sup>-1</sup> lipid wt 149 ng g <sup>-1</sup> lipid wt	1997-1998	Brazilian and Polish Antarctic Station on King George Island	Taniguchi et al., 2008
Mirex	South polar skuas blood	20.7 ng g <sup>-1</sup> wet wt 6500 ng g <sup>-1</sup> lipid wt	2001-2002	Svarthamaren in Dronning Maud Land	Bustnes et al., 2006
Mirex	Southern Elephant seals blubber	24.28 ng g <sup>-1</sup> lipid wt males 29.30 ng g <sup>-1</sup> lipid wt females 19.41 ng g <sup>-1</sup> lipid wt juveniles 8.42 ng g <sup>-1</sup> lipid wt pups	1997-1998 1998-1999 1999-2000	Elephant Island	Miranda-Filho et al., 2007
Mirex	Krill	0.18 ng g <sup>-1</sup> EOM	1986	Weddel sea, Elephant island and Shetland islands	Goerke et al., 2004
Mirex	<i>L. weddellii</i> blubber <i>M. leonine</i> blubber	6.5 ng g <sup>-1</sup> EOM 13 ng g <sup>-1</sup> EOM	1995 1996	Waters around Elephant Island	Goerke et al., 2004
Mirex	<i>P. Adeliae</i>	0.6 ng g <sup>-1</sup> EOM	1995	Waters around Elephant Island	Goerke et al., 2004

Mirex	<i>C. gunnari</i> liver <i>G. nicholsi</i> muscle <i>P. eulepidotus</i> liver <i>P. antarcticum</i> muscle	0.6 ng g <sup>-1</sup> EOM 1.8 ng g <sup>-1</sup> EOM 2 ng g <sup>-1</sup> EOM 0.9 ng g <sup>-1</sup> EOM	1996 1996 2000 2000	Waters around Elephant Island	Goerke et al., 2004
PAHs	Limpet	ng g <sup>-1</sup> dry wt	1989-1993	McMurdo station Palmer Station	Kennicutt et al., 1995
PAHs	<i>T. bernacchii</i> viscera	656±319 and 200±72 ng g <sup>-1</sup>	1989-1993	McMurdo station Palmer Station	Kennicutt et al., 1995
PAHs	Brown skua fat tissue Penguins fat tissue Antarctic tern fat tissue Blue-eyed shag fat tissue Snowy sheatbill fat tissue	3375 ± 1588 ng g <sup>-1</sup> lipid wt 1588 ± 654 ng g <sup>-1</sup> lipid wt 5744 ± 2546 ng g <sup>-1</sup> lipid wt 3961 ng g <sup>-1</sup> lipid wt 4090 ng g <sup>-1</sup> lipid wt	1997-1998	Brazilian and Polish Antarctic Station on King George Island.	Taniguchi et al., 2008
PBDEs (sum of 3 congeners)	Sea ice algae, Water column plankton	5460 ±3840, 7110 ± 5910, and 1350 ± 1070 ng g <sup>-1</sup> lipid wt	2001/2002	Region west of the Antarctic Peninsula	Chiuchiolo et al., 2004
PBDE -99 PBDE -47	Krill	0.03 ng g <sup>-1</sup> wet wt, 0.67 ng g <sup>-1</sup> lipid wt 0.007 ng g <sup>-1</sup> wet wt, 0.35 ng g <sup>-1</sup> lipid wt	2005/06	12 sampling stations (NE sector)	Bengstone et al., 2008
PBDEs	Krill	0.20 ng g <sup>-1</sup> wet wt (whole body) 5.60 ng g <sup>-1</sup> lipid wt	2000- 2001/02	Ross Sea in Terra Nova Bay	Corsolini et al., 2006
PBDEs	Adélie penguin blood Chinstrap penguin blood Gentoo penguin blood	291 ±477 ng g <sup>-1</sup> wet wt 108 ±105 ng g <sup>-1</sup> wet wt 117 ±108 ng g <sup>-1</sup> wet wt	2004	Lenie Field Station, Admiralty Bay, King George Is	Corsolini et al., 2007
PBDEs	Type C Killer whales blubber	112 ng g <sup>-1</sup> lipid wt	2005 and 2006	McMurdo Sound	Khran et al., 2008
PBDEs (sum of 6 congeners)	Rock cod	1520 and 1840 ng g <sup>-1</sup> lipid wt  356 ng g <sup>-1</sup> lipid wt  311 ng g <sup>-1</sup> lipid wt	2003	Close to McMurdo wastewater outfall Within 0.5 km from McMurdo wastewater outfall Cinder Cones	Hale et al., 2008
PBDEs (sum of 7 congeners)	Penguin (eggs)	0.29 ±031 ng g <sup>-1</sup> wet wt	2000-	Ross Sea in Terra Nova	Corsolini et al., 2006

congeners			2001/02	Bay	
PBDEs (sum of 7 congeners)	Rockcod (muscle) Rockcod (wb)	0.05 ±0.02 ng g <sup>-1</sup> wet wt 0.16 ±0.01ng g <sup>-1</sup> wet wt	2000- 2001/02	Ross Sea in Terra Nova Bay	Corsolini et al., 2006
PBDEs (sum of 9 congeners)	<i>C. hamatus</i> (n = 6) (muscle and liver tissue)	0.16 ±0.08 ng g <sup>-1</sup> wet wt 0.21 ±0.12ng g <sup>-1</sup> wet wt	2005	Ross sea	Borghesi et al., 2006
PBDEs (sum of 9 congeners)	<i>T. bernacchii</i> (n = 6) (muscle and liver tissue)	0.35 ±0.11 ng g <sup>-1</sup> wet wt 0.79 ±0.25 ng g <sup>-1</sup> wet wt	2005	Ross sea	Borghesi et al., 2006
PCBs	Bivalve tissues ( <i>L. elliptica</i> )	400 and 430 ng g <sup>-1</sup> (WQB) mean = 9.8 ng g <sup>-1</sup> (McMurdo Sound)	1989-1993	Winter Quarter Bay and McMurdo Sound	Kennicutt et al., 1995
PCBs	Limpet	mean = 18.3 ng g <sup>-1</sup> dry wt (1989) mean = 18.3 ng g <sup>-1</sup> dry wt (1991)	1989-1993	McMurdo station Palmer Station	Kennicutt et al., 1995
PCBs	Krill	167.40±84.69 ng g <sup>-1</sup> wet wt	1999/2000	Ross Sea	Corsolini et al., 2002
PCBs	<i>Pleurogramma antarcticum</i>	503.85±8.53 ng g <sup>-1</sup> wet wt (larva) 348.18±299.05 ng g <sup>-1</sup> wet wt (adult)	1999/2000	Ross Sea	Corsolini et al., 2002
PCBs (sum of 9 congeners)	<i>Pygoscelis papua</i> eggs Giant petrel eggs Brown skua eggs	0.5 – 0.8 ng g <sup>-1</sup> 48.1-81.7 ng g <sup>-1</sup> 91.9-515.5 ng g <sup>-1</sup>	2001-2002	Fildes Peninsula adjacent to Great Wall Station of China	Zhang et al., 2007
PCBs (non ortho coplanar)	<i>T. bernacchi</i> muscle	<0.0005 ng g <sup>-1</sup> wet wt		Terranova Bay	Bargagli et al., 1998
PCBs (sum of 50 congeners)	Mixed zooplankton (copepods, amphipods and krill)	4.2 ng g <sup>-1</sup> wet wt		Ross Sea	Corsolini and Focardi, 2000
PCBs (sum of 50 congeners)	Phytoplankton (mainly diatoms)	1 ng/ g <sup>-1</sup> wet wt		Ross Sea	Corsolini and Focardi, 2000
PCBs (Σ 28, 153, 138, 180)	Weddel seal blubber	2.0 ng g <sup>-1</sup> wet wt	1994	King George Island	Vetter et al., 2003
PCB 153 PCB 138 PCB 180	Krill	0.1 ng g <sup>-1</sup> EOM 0.08 ng g <sup>-1</sup> EOM 0.04 ng g <sup>-1</sup> EOM	1986	Weddel sea, Elephant island and Shetland islands	Goerke et al., 2004

PCB 153 PCB 138 PCB 180	<i>C. gunnari</i> , <i>G. gibberifrons</i> , <i>C. aceratus</i> liver	$1.0 \pm 0.5 \text{ ng g}^{-1}$ EOM $0.4 \pm 0.2 \text{ ng g}^{-1}$ EOM $0.4 \pm 0.3 \text{ ng g}^{-1}$ EOM	1987	Antarctic peninsula	Weber and Goerke, 1996
PCB 153	<i>L. weddellii</i> blubber <i>M. leonine</i> blubber	$10 \text{ ng g}^{-1}$ EOM $8 \text{ ng g}^{-1}$ EOM	1995 1996	Waters around Elephant Island	Goerke et al., 2004
PCB 153	<i>P. Adeliae</i>	$2 \text{ ng g}^{-1}$ EOM	1995	Waters around Elephant Island	Goerke et al., 2004
PCB 153	<i>C. gunnari</i> liver <i>G. nicholsi</i> muscle <i>P. eulepidotus</i> liver <i>P. antarcticum</i> muscle	$0.5 \text{ ng g}^{-1}$ EOM $0.9 \text{ ng g}^{-1}$ EOM $0.8 \text{ ng g}^{-1}$ EOM $0.5 \text{ ng g}^{-1}$ EOM	1996 1996 2000 2000	Waters around Elephant Island	Goerke et al., 2004
PCBs	Brown skua fat tissue Penguins fat tissue Antarctic tern fat tissue Blue-eyed shag fat tissue Snowy sheatbill fat tissue	$19,720 + 9620 \text{ ng g}^{-1}$ lipid wt $256 + 125 \text{ ng g}^{-1}$ lipid wt $613 + 187 \text{ ng g}^{-1}$ lipid wt $282 \text{ ng g}^{-1}$ lipid wt $297 \text{ ng g}^{-1}$ lipid wt	1997-1998	Brazilian and Polish Antarctic Station on King George Island.	Taniguchi et al., 2008
PCBs	<i>Desmarestia</i> sp.	$0.46 - 3.86 \text{ ng g}^{-1}$ dry wt	1993/94	Admiralty Bay (King George Island)	Montone et al., 2001
PCBs	Krill	$0.152 \text{ ng g}^{-1}$ dry wt	1987/88	Dakshin Gangotri (70° S and 12° E)	Sen Gupta et al., 1996
PCBs	Penguin feathers	$0.109 \text{ ng g}^{-1}$ dry wt	1987/88	Dakshin Gangotri (70° S and 12° E)	Sen Gupta et al., 1996
PCBs	Minke whale ( <i>Balaenoptera acutorostrata</i> )	$38 \text{ ng g}^{-1}$ wet wt $76 \text{ ng g}^{-1}$ wet wt $97 \text{ ng g}^{-1}$ wet wt $96 \text{ ng g}^{-1}$ wet wt	1984/85 1988/89 1990/91 1992/93		Aono et al., 1997
PCBs	Krill	$0.05 \text{ ng g}^{-1}$ wet wt $1.2 \text{ ng g}^{-1}$ lipid wt	2005/06	12 sampling stations (NE sector)	Bengstone et al., 2008
PCBs	Krill	$1.67 \text{ ng g}^{-1}$ wet wt (whole body)	2000-2001/02	Ross Sea in Terra Nova Bay	Corsolini et al., 2006
PCBs	Krill	$3 \text{ ng g}^{-1}$ lipid wt	1975	Antarctic peninsula	Risebrough et al., 1976

PCBs	Pelagic netplankton (mainly zooplankton)	350 ng g <sup>-1</sup> dry wt 27200 ng m <sup>-3</sup>	1987	Indian sector of Southern Ocean	Joiris and Overloop, 1991
PCBs	Pelagic phytoplankton	700 ng g <sup>-1</sup> dry wt 1200 ng m <sup>-3</sup>	1987	Indian sector of Southern Ocean	Joiris and Overloop, 1991
PCBs	Type C Killer whales blubber	1600 ng g <sup>-1</sup> lipid wt	2005 and 2006	McMurdo Sound	Khran et al., 2008
PCBs (sum of 15 congeners)	South polar skuas blood	9.0 ng g <sup>-1</sup> wet wt 2700 ng g <sup>-1</sup> lipid wt	2001-2002	Svarthamaren in Dronning Maud Land	Bustnes et al., 2006
PCBs (sum of 25 congeners)	Southern Elephant seals blubber	56.09 ng g <sup>-1</sup> lipid wt males 49.92 ng g <sup>-1</sup> lipid wt females 39.82 ng g <sup>-1</sup> lipid wt juveniles 56.09 ng g <sup>-1</sup> lipid wt pups	1997-1998 1998-1999 1999-2000	Elephant Island	Miranda-Filho et al., 2007
PCBs (non ortho)	Adélie penguin blood Chinstrap penguin blood Gentoo penguin blood	227 ±363 ng g <sup>-1</sup> wet wt 201 ±153 ng g <sup>-1</sup> wet wt 719 ±1264 ng g <sup>-1</sup> wet wt	2004	Lenie Field Station, Admiralty Bay, King George Is	Corsolini et al., 2007
PCBs (sum of 23 congeners)	<i>C. hamatus</i> (n = 6) (muscle and liver tissue)	0.35 ±0.30 ng g <sup>-1</sup> wet wt 2.20 ±0.95 ng g <sup>-1</sup> wet wt	2005	Ross Sea	Borghesi et al., 2008
PCBs (sum of 23 congeners)	<i>T. bernacchii</i> (n = 6) (muscle and liver tissue)	1.65 ±1.40 ng g <sup>-1</sup> wet wt 15 ±9.20 ng g <sup>-1</sup> wet wt	2005	Ross Sea	Borghesi et al., 2008
PCBs (sum of 30)	Adelie Penguin (n = 12) Snow Petrel (n = 4) Antarctic Petrel (n = 5) Southern Fulmar (n = 18) Cape Petrel: Hop Island (n = 3) Cape Petrel: K. George Island (n = 6)	469 ng g <sup>-1</sup> lipid wt 270 ng g <sup>-1</sup> lipid wt 235 ng g <sup>-1</sup> lipid wt 204 ng g <sup>-1</sup> lipid wt  706 ng g <sup>-1</sup> lipid wt  1588 ng g <sup>-1</sup> lipid wt	February 1994      January 1991	Hop Island        K. George Island	Van der Brink, 1997
PCBs (sum of 56 congeners)	Penguin (eggs)	24.9 ±21.6 ng g <sup>-1</sup> wet wt	2000- 2001/02	Ross Sea in Terra Nova Bay	Corsolini et al., 2006
PCBs (sum of 56 congeners)	Rockcod (muscle) Rockcod (wb)	6.35 ±4.8 ng g <sup>-1</sup> wet wt 9.25 ±8.04 ng g <sup>-1</sup> wet wt	2000- 2001/02	Ross Sea in Terra Nova Bay	Corsolini et al., 2006

PCBs (sum of congeners detected)	Antarctic fur seal milk	68 ng g <sup>-1</sup> 33 ng g <sup>-1</sup>	1985 1984	South Georgia Island	Jarman et al., 1992
PCBs (tetra, penta, hexa, hepta, octa, nona-CBs)	Adélie penguin blood Chinstrap penguin blood Gentoo penguin blood	9.8±3.8 ng g <sup>-1</sup> wet wt 4.5 ±2.4 ng g <sup>-1</sup> wet wt 3.4 ±1.6 ng g <sup>-1</sup> wet wt	2004	Lenie Field Station, Admiralty Bay, King George Is	Corsolini et al., 2007
PCBs dioxin like	South polar skua eggs (n=5)	139 ng g <sup>-1</sup> wet wt 1440 ng g <sup>-1</sup> lipid wt	1998/99	Terra Nova Bay	Kumar et al., 2002
PCBs dioxin like	Adelie penguin eggs (unhatched) (n=5)	3.3 ng g <sup>-1</sup> wet wt 30 ng g <sup>-1</sup> lipid wt	1995/96	Edmonson Point (74°20'56.7" S and 165°08'10.03" E)	Kumar et al., 2002
PCBs dioxin like	Weddell seal liver (n=1)	2.9 ng g <sup>-1</sup> wet wt 106 ng g <sup>-1</sup> lipid wt	1995/96	Edmonson Point (74°20'56.7" S and 165°08'10.03" E)	Kumar et al., 2002
PCBs dioxin like plus 170 and 180	<i>T. pennelli</i> (n=6) <i>C. hamatus</i> (n=2)	2.2·10 <sup>-4</sup> ng g <sup>-1</sup> wet wt, 0.01 ng g <sup>-1</sup> lipid wt 1.4·10 <sup>-3</sup> ng g <sup>-1</sup> wet wt, 0.02 ng g <sup>-1</sup> lipid wt	1994/95	Terra Nova Bay	Kumar et al., 2002
PCBs non and mono-ortho-substituted (dioxin like)	Krill	0.03 ng g <sup>-1</sup> wet wt 0.88 ng g <sup>-1</sup> lipid wt	1994/95	Ross Sea	Kumar et al., 2002
PCDD/DFs	South polar skua eggs (n=5)	0.02 ng g <sup>-1</sup> wet wt 0.18 ng g <sup>-1</sup> lipid wt	1998/99	Terra Nova Bay	Kumar et al., 2002
PCDD/DFs	Adelie penguin eggs (unhatched) (n=5)	2.6·10 <sup>-3</sup> ng g <sup>-1</sup> wet wt 0.02ng g <sup>-1</sup> lipid wt	1995/96	Edmonson Point (74°20'56.7" S and 165°08'10.03" E)	Kumar et al., 2002
PCDD/DFs	Weddell seal liver (n=1)	0.2·10 <sup>-3</sup> ng g <sup>-1</sup> wet wt, 8.9·10 <sup>-3</sup> ng g <sup>-1</sup> lipid wt	1995/96	Edmonson Point (74°20'56.7" S and 165°08'10.03" E)	Kumar et al., 2002
PCDD/DFs	<i>T. pennelli</i> (n=6) <i>C. hamatus</i> (n=2)	2.2·10 <sup>-4</sup> ng g <sup>-1</sup> wet wt, 0.01 ng g <sup>-1</sup> lipid wt 1.4·10 <sup>-3</sup> ng g <sup>-1</sup> wet wt, 0.02 ng g <sup>-1</sup> lipid wt	1994/95	Terra Nova Bay	Kumar et al., 2002
PCDDs (sum of 7 congeners)	<i>C. hamatus</i> (n = 6) (muscle and liver tissue)	0.01 ±0.009 ng g <sup>-1</sup> wet wt 0.02 ±0.006 ng g <sup>-1</sup> wet wt	2005	Ross Sea	Borghesi et al., 2006

PCDDs (sum of 7 congeners)	<i>T. bernacchii</i> (n = 6) (muscle and liver tissue)	0.006 ±0.003 ng g <sup>-1</sup> wet wt 0.01 ±0.008 ng g <sup>-1</sup> wet wt	2005	Ross Sea	Borghesi et al., 2006
PCDDs and DFs	Krill	0.85·10 <sup>-3</sup> ng g <sup>-1</sup> wet wt, 0.027 ng g <sup>-1</sup> lipid wt	1994/95	Ross Sea	Kumar et al., 2002
PCDFs (sum of 10 congeners)	<i>C. hamatus</i> (n = 6) (muscle and liver tissue)	0.01 ±0.006 ng g <sup>-1</sup> wet wt 0.02 ±0.01 ng g <sup>-1</sup> wet wt	2005	Ross Sea	Borghesi et al., 2008
PCDFs (sum of 10 congeners)	<i>T. bernacchii</i> (n = 6) (muscle and liver tissue)	0.02 ±0.014 ng g <sup>-1</sup> wet wt 0.03 ±0.014 ng g <sup>-1</sup> wet wt	2005	Ross Sea	Borghesi et al., 2008
PFOS	Southpolar skua blood eggs	<0.24-1.36 ng/ml 2.1-3.1 ng g <sup>-1</sup>	1998-1999		Lin Tao et al., 2006
TEQs	South polar skua eggs (n=5)	0.03 ng g <sup>-1</sup> wet wt, 0.34 ng g <sup>-1</sup> lipid wt	1998/99	Terra Nova Bay	Kumar et al., 2002
TEQs	Adelie penguin eggs (unhatched) (n=5)	5.9·10 <sup>-3</sup> ng g <sup>-1</sup> wet wt, 0.05 ng g <sup>-1</sup> lipid wt	1995/96	Edmonson Point (74°20'56.7" S and 165°08'10.03" E)	Kumar et al., 2002
TEQs	Weddell seal liver (n=1)	0.65·10 <sup>-3</sup> ng g <sup>-1</sup> wet wt, 0.02 ng g <sup>-1</sup> lipid wt	1995/96	Edmonson Point (74°20'56.7" S and 165°08'10.03" E)	Kumar et al., 2002
TEQs	Krill	0.2·10 <sup>-4</sup> ng g <sup>-1</sup> wet wt, 0.58·10 <sup>-3</sup> ng g <sup>-1</sup> lipid wt	1994/95	Ross Sea	Kumar et al., 2002
TEQs	<i>T. pennelli</i> (n=6) <i>C. hamatus</i> (n=2)	0.1·10 <sup>-4</sup> ng g <sup>-1</sup> wet wt, 0.6·10 <sup>-3</sup> ng g <sup>-1</sup> lipid wt 0.2·10 <sup>-3</sup> ng g <sup>-1</sup> wet wt, 2.4·10 <sup>-3</sup> ng g <sup>-1</sup> lipid wt	1994/95	Ross Sea	Kumar et al., 2002
TEQs (TCDD toxic equivalent)	Bivalve tissues ( <i>L. elliptica</i> )	1.16 -1.66 ng g <sup>-1</sup> (WQB) nd-o.25 ng g <sup>-1</sup> (McMurdo Sound: control site)	1989-1993	Winter Quarter Bay and McMurdo Sound	Kennicutt et al., 1995

## **7. References**

### **1. Introduction**

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