



United Nations Environment Programme Chemicals

Antarctica REGIONAL REPORT

Regionally Based Assessment of Persistent

Substances

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UNITED NATIONS ENVIRONMENT PROGRAMME CHEMICALS



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ANTARCTICA REGIONAL REPORT

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GLOBAL ENVIRONMENT FACILITY

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UNEP Chemicals11-13, chemin des Anémones CH-1219 Châtelaine, GE Switzerland Phone: +41 22 917 1234 Fax: +41 22 797 3460 E-mail: <u>chemicals@unep.ch</u> http://www.chem.unep.ch

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PREFACE

This report forms a part of a global assessment of Persistent Toxic Substances, and covers one of twelve regions designated by the United Nations Environment Programme (UNEP). The Antarctic Regional Assessment was delegated to the Scientific Committee on Antarctic Research (SCAR), and SCAR in turn contracted the preparation of the assessment to the Science Training and Education Partnership.

Several people and organizations assisted with the preparation of the report. Foremost amongst these was Dr Peter Clarkson, Executive Secretary of SCAR. Useful advice was given by Drs David Walton, John Shears, Mike Meredith, Eric Wolff, David Peel and John King of the British Antarctic Survey, and I am also pleased to be able to acknowledge the earlier guidance of the late Dr Geof Cripps (also of BAS). Prof. Joan Albaiges (Barcelona) and other leaders and members of regional teams contributed to the PTS definitions used in Chapter 1.

Assembling the data was reliant on access to the peer-reviewed literature data. Christine Phillips, librarian at the British Antarctic Survey, and Shirley Sawtell, of the library at the Scott Polar Research Institute, provided invaluable help with access to material. A 'critical mass' was provided by the bibliography assembled by the Antarctic Environmental Officers Network (AEON) of the Council of Managers of National Antarctic Programmes (COMNAP). Mandy Dalton of the SCAR office re-formatted the final draft of the report and provided valuable additional material.

Finally, my thanks go to Paul Whylie at UNEP for his support and patience, and to Dr Hans Martin of Global Change Strategies International, who led the preparation of the Arctic regional assessment which formed the model for this report.

Julian Priddle Science Training and Education Partnership Barrington Cambridge UK

EXECUTIVE SUMMARY

Introduction

This assessment of persistent toxic substances (PTSs) in Antarctica forms part of a regionally-based global assessment. The Antarctic has been important in highlighting the pervasive nature of anthropogenic pollution. The discovery of DDT-related compounds in Antarctic biota in the 1960s and in the environment in the 1970s was a clear and well publicized indication of the global impact of human activities. At the same time, interest was focused on Antarctica as a key wilderness area. To some extent, this ignored the reality of significant human impact in the region, both through 'visible' local effects (such as the impacts of marine exploitation), and through the 'invisible' effects of global pollutant emissions.

This assessment of PTSs shows that Antarctica responds to activities both within the region and outside. The Antarctic environment is not pristine: there has been considerable but very localised human impact within the region. It is clear that pollutants are transported there from outside the region and that for many compounds this is the 'end of the line'. Polar regions could be a sink for some forms of low and mid-latitude pollution. However, in a global context, the region remains relatively uncontaminated, and provides an opportunity to monitor the health of the planet. Data presented here indicate the reality of this proposal and what needs to be done to make this practical.

Antarctica is unlike other regions covered by this global assessment. The continent is a barren wilderness with a very small, non-native population and with no industry or agriculture. The surrounding oceans support more life, but are still inhospitable and partially ice-covered.

Contaminant sources

Antarctica and the adjacent islands and ocean have a very small human population. Human presence in the region is concerned largely with scientific investigations. Logistics operations in support of these pelagic fisheries are an important operation in some parts of the region and tourism is increasingly becoming an important activity. Both of these may account for slight increases in emissions of some PTSs.

Pesticides are neither produced nor applied in the region. There appear to be no data suggesting that any permanent habitation in Antarctica is a local source of pesticide PTSs. No industrial compounds are manufactured in the region and where they are used and subsequently released, it is in very small quantities. Most data refer to PCBs, where relatively high levels of environmental and biotic contamination in small areas of the coastal marine ecosystem have been associated with accidental local release of lubricants and other PCBs. Accidental by-products, such as dioxins and PAHs, can again result from human activities. Data on PAHs in the marine ecosystem probably represent the most extensive record and include comprehensive studies of a small number of oil spillages.

Environmental levels

There is a range of data on levels of PTS in the abiotic environment in the region. In practice, sampling is patchy, and the full range of environmental media has not been sampled for any class of compound. There has been a decline in air concentrations of chlordane and heptachlor epoxide between the 1980s and 1990s, but both are present in the air only at pg m⁻³ concentrations. Data for total DDT concentration appears to have been of the order of 0.1 pg m⁻³, whilst concentrations had been as high as 100-200 pg m⁻³ in the early 1980s. The ratio of DDT to DDE also appears to be declined over the last two decades, but that this decline is not as significant as that seen for DDT. Current air concentrations of the compounds are ≤ 60 pg m⁻³ for HCB and ≤ 20 pg m⁻³ for γ -HCH.

There is a comparatively large amount of data for environmental levels of PCBs. Concentrations in air for individual compounds range from 0.1- 2.5 pg m⁻³. Overall, it seems likely there is no significant long-term trend. Analyses of PCB levels in marine sediments derive predominantly from locally contaminated sites, where concentrations may be 250-4300 ng g⁻¹, in contrast to background levels of 18-28 ng g⁻¹. The only data for environmental levels of dioxins and furans come from an area of contamination, but suggest that upper

limits for background air concentrations could be ≤ 0.12 pg m⁻³ for total PCDDs and ≤ 0.02 pg m⁻³ for PCDFs. The introduction to PAH to the region is a combination of global input, low-level and long-term natural and anthropogenic sources and catastrophic incidents with no long-term trend. Generally, uncontaminated seawater has PAH concentrations $\leq 1 \ \mu g \ kg^{-1}$. PAH concentrations in marine sediments vary from undetectable to 10 ng g⁻¹. At sites of local contamination, corresponding values can be much higher: >200 $\mu g \ kg^{-1}$ (for short periods) in seawater and $\geq 60 \ 000$ ng g⁻¹ in long-term contaminated sediments.

Levels in biota

In contrast to the apparent declines in environmental concentrations of pesticides, for some compounds there are increases in biological loadings. This is probably the case for dieldrin, and most likely for DDT. Concentrations of DDT and derivatives in endemic birds and mammals levels increased over the period from the early 1960s to the early 1980s. Typical values for high-latitude penguins, which accumulate their total DDT burden within the regions, were $\leq 300 \text{ ng g}^{-1}$ (lipid mass) in the mid 1990s. Overall, DDE predominates over DDT, which is consistent with the decline in DDT use worldwide. However, the ratio DDE:DDT has increased more rapidly in biotic samples than in the environment, suggesting that DDE is accumulating in the ecosystem.

Concentrations of HCB and HCH in marine biota are often lower than those for DDT, whereas recent atmospheric concentrations of these two compounds exceed those of DDT by an order of magnitude. For a similar suite of endemic birds and mammals, HCB concentration was 150 ng g⁻¹ lipid mass, and the range of γ -HCH concentrations was 17-103 ng g⁻¹ lipid mass.

PCBs have been shown to be an important local contaminant in the marine ecosystem, but there is a wide range of biotic data. Overall, there is a ten-fold variation in PCB loadings in benthic invertebrates between contaminated and uncontaminated sites. Away from contaminated sites, it is suggested that PCB concentration increases up the food chain, suggesting bioaccumulation.

Studies of PAH loadings in marine biota, especially benthic invertebrates, have been undertaken in response to specific pollution incidents and lower-level, persistent pollution. There are strong contrasts between animals from clean and contaminated sites and over a recovery period. For instance, limpets sampled soon after a major oil-fuel spillage had whole-tissue total PAH loading up to 125 000 ng g^{-1} DM, but this declined to about 180 ng g^{-1} DM two years later.

Major pathways of contaminant transport

With the exception of low-level and usually highly localised emissions of PTSs within the region, introduction of PTSs to Antarctica and the Southern Ocean comes entirely from extra-regional sources. The Antarctic continent and the peri-Antarctic islands are isolated from the rest of the world by an extensive ocean. Any form of overland transport of PTS such as transboundary river flow does not operate.

Over much of the height of the atmosphere, the circulation systems in the two hemispheres operate separately, and the timescale of exchange between these is long. For some PTS classes, it is possible to use data on composition to confirm the southern hemisphere origin of the source region. For instance, the predominant use of lindane in the southern hemisphere can be correlated with the high proportion of γ -HCH in air of total HCH. Transport in the atmosphere will be rapid and will be likely to reflect time-varying properties of the source. Some studies have been able to identify trends in concentration over a period of about a decade which agree with global estimates. On a shorter timescale, variation in PTS concentration in air can be correlated with conditions which will link that sampling site to likely extra-regional sources.

Ocean water from the neighbouring oceans can penetrate the ocean around Antarctica in two ways. First, southward flowing water at depths of about 2 km penetrates the Southern Ocean as a component of the so-called 'global ocean conveyor' circulation. Probably the most important input is from the North Atlantic via the southwards flow of North Atlantic Deep Water (NADW) which upwells into the ACC. This water will have accumulated any PTS load mainly in the northern hemisphere, and will have been isolated from the ocean surface for a considerable time. The surface circulation also exchanges with neighbouring oceans by the penetration of mesoscale eddies or core rings. The most intense exchange takes place where the southward flowing western boundary currents of the Indian and South Pacific Oceans, and to a lesser extent the South

Atlantic Oceans, meet the ACC. Various unique properties of the environment and ecosystem will modify the way in which PTSs are released and distributed once they have arrived in the region.

Preliminary assessment of regional capacity and needs

Data presented in the report arise from a wide range of studies, some of which are concerned with local issues, such as the fate of PAH following an oil spill, whilst others are designed to build an understanding of how PTS concentrations reflect global patterns and trends. The final assessment in the report is built around a series of questions which examine the suitability of future studies to form part of a global monitoring study:

Would continuation of the existing type and level of monitoring carried out in the region be adequate to underpin a future global monitoring study?

If not, is there a need for a new, coordinated monitoring programme?

Can existing national or multinational science programmes in the region sustain such a monitoring effort? Is the information currently available sufficient to design a more systematic monitoring programme?

Based on the current assessment, it is likely that future monitoring in the region would form an important component of a global assessment of PTSs. This will require the initiation of new systematic studies which make effective use of existing data. For most compounds, further research is needed to understand the dynamics of their input to the region, their deposition and storage and their dynamics in the environment and ecosystems.

Where existing data are too sparse to construct a time series or baseline, additional research will be needed in order to interpret the archive records preserved in snow and ice. Such samples potentially record time series of atmospheric concentrations with annual resolution over decades for some locations. However, their interpretation requires a good understanding of the current relationship between PTS levels in air and snowfall, and the relationship between regional air concentrations and the location and variability of extra-regional sources.

Key recommendations

- Following further quality control, existing data need to be archived in a way in which they can be used effectively in a global assessment
- Data on biotic loadings need to be assessed and brought to common bases in order to construct reliable pictures of spatial and temporal variability and of ecosystem effects
- Studies are needed to understand how PTSs are deposited in the region in snowfall and how this relates to the atmospheric content of PTSs and to physical conditions
- Studies are needed to understand the ways in which PTSs may be stored in different components of the abiotic environment and how these stores may subsequently be mobilised
- Models of atmospheric transport should be developed to include region-specific dynamics such as deposition in snowfall
- Back trajectory analysis should be undertaken where possible for all existing studies of air and cryosphere (snow and ice) concentrations, in order to understand temporal and spatial variability in the context of likely sources
- Existing data should be used to identify potential sites for inclusion in a global monitoring network and to define suitable samples for PTS analysis
- Agency support should be sought for routine sample collection and analysis to contribute to future global monitoring of PTSs
- With increasing exploitation of marine resources in the Southern Ocean, potential hazards to human health from consumption of krill, squid, fish and marine mammals need to be identified.

1 INTRODUCTION

1.1 OVERVIEW OF THE RBA PTS PROJECT

Following the recommendations of the Intergovernmental Forum on Chemical Safety, the UNEP Governing Council decided in February 1997 (Decision 19/13 C) that immediate international action should be initiated to protect human health and the environment through measures which will reduce and/or eliminate the emissions and discharges of an initial set of twelve persistent organic pollutants (POPs). Accordingly an Intergovernmental Negotiating Committee (INC) was established with a mandate to prepare an international legally binding instrument for implementing international action on certain persistent organic pollutants. These series of negotiations have resulted in the adoption of the Stockholm Convention in 2001. The initial 12 substances fitting these categories that have been selected under the Stockholm Convention include: aldrin, endrin, dieldrin, chlordane, DDT, toxaphene, mirex, heptachlor, hexachlorobenzene, PCBs, dioxins and furans. Beside these 12, there are many other substances that satisfy the criteria listed above for which their sources, environmental concentrations and effects are to be assessed.

Persistent toxic substances can be manufactured substances for use in various sectors of industry, pesticides, or by-products of industrial processes and combustion. To date, their scientific assessment has largely concentrated on specific local and/or regional environmental and health effects, in particular "hot spots" such as the Great Lakes region of North America or the Baltic Sea.

1.1.1 Objectives

There is a need for a scientifically-based assessment of the nature and scale of the threats to the environment and its resources posed by persistent toxic substances that will provide guidance to the international community concerning the priorities for future remedial and preventive action. The assessment will lead to the identification of priorities for intervention, and through application of a root cause analysis will attempt to identify appropriate measures to control, reduce or eliminate releases of PTS, at national, regional or global levels.

The objective of the project is to deliver a measure of the nature and comparative severity of damage and threats posed at national, regional and ultimately at global levels by PTS. This will provide the GEF with a science-based rationale for assigning priorities for action among and between chemical related environmental issues, and to determine the extent to which differences in priority exist among regions.

1.1.2 Results

The project relies upon the collection and interpretation of existing data and information as the basis for the assessment. No research will be undertaken to generate primary data, but projections will be made to fill data/information gaps, and to predict threats to the environment. The proposed activities are designed to obtain the following expected results:

- Identification of major sources of PTS at the regional level;
- Impact of PTS on the environment and human health;
- Assessment of transboundary transport of PTS;
- Assessment of the root causes of PTS related problems, and regional capacity to manage these problems;
- Identification of regional priority PTS related environmental issues; and
- Identification of PTS related priority environmental issues at the global level.

The outcome of this project will be a scientific assessment of the threats posed by persistent toxic substances to the environment and human health. The activities to be undertaken in this project comprise an evaluation of the sources of persistent toxic substances, their levels in the environment and consequent impact on biota and humans, their modes of transport over a range of distances, the existing alternatives to their use and remediation options, as well as the barriers that prevent their good management.

1.2 METHODOLOGY

1.2.1 Regional divisions

To achieve these results, the globe is divided into 12 regions namely: Arctic, North America, Europe, Mediterranean, Sub-Saharan Africa, Indian Ocean, Central and North East Asia (Western North Pacific), South East Asia and South Pacific, Pacific Islands, Central America and the Caribbean, Eastern and Western south America, Antarctica. The twelve regions were selected based on obtaining geographical consistency while trying to reside within financial constraints.

1.2.2 Management structure

The project is directed by the project manager who is situated at UNEP Chemicals in Geneva, Switzerland. A Steering Group comprising of representatives of other relevant intergovernmental organisations along with participation from industry and the non-governmental community is established to monitor the progress of the project and provide direction for the project manager. Each region is controlled by a regional coordinator assisted by a team of approximately 4 persons. The coordinator and the regional team are responsible for promoting the project, the collection of data at the national level and to carry out a series of technical and priority setting workshops for analysing the data on PTS on a regional basis. Besides the 12 POPs from the Stockholm Convention, the regional team selects the chemicals to be assessed for its region with selection open for review during the various workshops undertaken throughout the assessment process. Each team writes the regional report for the respective region.

1.2.3 Data processing

Data is collected on sources, environmental concentrations, human and ecological effects through questionnaires that are filled at the national level. The results from this data collection along with presentations from regional experts at the technical workshops, are used to develop regional reports on the PTS selected for analysis. A priority setting workshop with participation from representatives from each country results in priorities being established regarding the threats and damages of these substances to each region. The information and conclusions derived from the 12 regional reports will be used to develop a global report on the state of these PTS in the environment.

The project is not intended to generate new information but to rely on existing data and its assessment to arrive at priorities for these substances. The establishment of a broad and wide- ranging network of participants involving all sectors of society was used for data collection and subsequent evaluation. Close cooperation with other intergovernmental organizations such as UNECE, WHO, FAO, UNPD, World Bank and others was obtained. Most have representatives on the Steering Group Committee that monitors the progress of the project and critically reviews its implementation. Contributions were garnered from UNEP focal points, UNEP POPs focal points, national focal points selected by the regional teams, industry, government agencies, research scientists and NGOs.

1.2.4 Project funding

The project costs approximately US\$4.2 million funded mainly by the Global Environment Facility (GEF) with sponsorship from countries including Australia, France, Germany, Sweden, Switzerland and the USA. The project runs between September, 2000 to April, 2003 with the intention that the reports be presented to the first meeting of the Conference of the Parties of the Stockholm Convention projected for 2003/4.

1.3 SCOPE OF THE ANTARCTIC REGIONAL ASSESSMENT

Antarctica is unlike other regions covered by this assessment. The continent itself is a barren wilderness with a very small, non-native population and with no industry or agriculture. The surrounding oceans support more life, but are still inhospitable and partially ice-covered. Although various nations have made claims to Antarctic territory, these claims are held in abeyance. Human activities on land are regulated by the Antarctic Treaty. Because of the very small human population, the local introduction of pollutants is slight and, with a few notable exceptions, the effects can be demonstrated only within a few hundred metres of the source. This means that pollutant concentrations over much of the Antarctic environment are determined almost entirely by activities outside the region. Transport of pollutants into the Antarctic system will be mediated by atmospheric and oceanic processes.

Within the context of the present regionally-based assessment of persistent toxic substances (PTSs), the Antarctic region presents some incongruous features. Nearly all of the human activities which result in major deliberate or accidental release of PTSs in other regions are not undertaken in Antarctica and the Southern Ocean. Although local introduction of PTSs can be demonstrated, these introductions are minor in both their geographic scale and in the amounts of material involved. These introductions are predominantly accidental, and current environmental protection protocols probably mean that they will decline further.

These features of the region may at first sight suggest that inclusion of Antarctica in the assessment is a poor use of resources. However, this neglects the crucial value that data from almost-pristine environments can have in providing a means of monitoring global events. This value was first revealed in the 1960s when DDT and its congeners were detected in Antarctic marine biota, demonstrating the pervasiveness of some PTSs after a few decades of use. This message was underlined by the discovery of the effects of another group of anthropogenic compounds, the CFCs. Studies of ozone over the Antarctic continent were the first signal that the extensive use of these supposedly benign compounds was having a significant and unexpected global impact.

This report will detail the data relating to the occurrence of a number of PTSs, both in the environment and in biota. It will present the smaller dataset relating to the impacts of these materials in the region, and provide initial evaluation of the potential extra-regional sources for PTSs and how these are transported into the region. The capacity of the scientific programmes working in the region to monitor PTSs will be assessed in the context of the use of Antarctic data as a global monitor.

1.3.1 Existing assessments

Unlike the Arctic, where a coordinated assessment of environmental pollution has been undertaken recently (AMAP 1998), there is no comparable current overview of pollution in the Antarctic. A group of environmental officers from national Antarctic programmes has been formed under the aegis of the Council of Managers of National Antarctic Programmes (COMNAP). This group – AEON - has produced a summary of environmental monitoring activities in Antarctica (<u>http://www.comnap.aq/aeon</u>). This is a moderately comprehensive listing of summaries of monitoring activities, with bibliographies, and formed the starting point for developing this report.

Some other landmark publications have appeared over the last decade. The GESAMP survey State of the Marine Environment included a Southern Ocean assessment (Strömberg et al. 1990). Several research and

review papers were published together in 1992 in a special issue of *Marine Pollution Bulletin* (volume 25, combined issues 9-12, 1992) which brought together several key studies and reviews relating to pollution in the Antarctic marine environment. However, much of the literature, especially more modern results, are scattered through a range of journals and other publications. Although some recent papers provide data syntheses for certain groups of compounds or types of sample, no comprehensive summary for the region as a whole has been published. There is a single review for the Ross Sea area, published as a 'state of the environment report' by the New Zealand Antarctic Institute (Waterhouse et al. 2001). This review is comprehensive, and because it covers a geographic area where both PTS studies and human impact have been concentrated, provides an invaluable case study.

1.3.2 Inter-regional links and collaboration

It is impossible to consider an assessment of PTSs in any region without reference to other parts of the world. In the case of Antarctica, this is especially important because of two factors:

First, the overwhelming input of PTSs to the environment and biota derive from outside the region. Thus a regional assessment must take into account data from at least the adjacent Southern Hemisphere regions in order to place the regional data in a global context.

Second, most of the region is not under direct national jurisdiction (see section 1.4 below). Many countries participate in Antarctic research, and most of these are northern hemisphere nations.

This combination of circumstances resembles the situation in the Arctic, although at least the nation states involved there are not so widely dispersed in relation to the boundary of the region.

Thus both international and inter-regional collaboration are implicit in the compilation of this regional assessment, and will be absolutely essential if it is to be integrated effectively into a global assessment.

1.3.3 Omissions and weaknesses

The relatively short time for the preparation of this report and the lack of a solid foundation of regional assessment has meant that the report may not be as comprehensive as it might be. The literature base is small, but scattered.

Because the occurrence of pollutants in Antarctica is determined largely by transport from emission sources outside the region, knowledge of both sources and transport routes and mechanisms is vital to an understanding of persistent toxic substances at both a regional and global level. However, the scope for such an approach is limited by paucity of data, and this is a problem which cannot be solved from an Antarctic perspective alone. It will require a pan-regional approach.

1.4 METHODOLOGY

This initial report is based on material published in the peer-reviewed literature. This provides a crude index of the data quality, although it would be naïve to expect a uniform level of data quality across a wide range of journals and a wide period of time.

Several national scientific programmes have included assessment of PTSs, although the coverage has been patchy in time and space. For the most part, monitoring activities have been descriptive, especially focussed on the use of measurements in Antarctica and the Southern Ocean to provide baseline global data from a region wholly devoid of local production of PTSs, and with relatively trivial local contamination. A few studies have been motivated by local pollution incidents, and recent environmental legislation has prompted a more thorough assessment of some PTSs in the context of research and logistics activities. However, there has been no concerted campaign to establish an internationally-coordinated network for monitoring PTSs in Antarctica,

although there are bodies in the Antarctic research and logistics organizations which could provide the basis for such a network (SCAR and COMNAP, 1996, SCAR 2001).

Data from Antarctica have the potential to provide a useful baseline for global PTS levels. There are measurements of concentrations of a range of PTSs in the contemporary environment and biota, and records for a more limited suite of PTSs over longer timescales based on data archives derived from ice cores and other long-term records.

Preparation of the report was contracted by UNEP to the Scientific Committee on Antarctic Research (SCAR), the ICSU (International Council for Science) body which provides international coordination for scientific research in Antarctica (http://www.scar.org/). It has been based on literature data only, amplifying the COMNAP-AEON summary and adapting this to the UNEP regional report format. Because of the shortage of time and resources, the raw data have not been entered to the UNEP PTS questionnaires, but the data will be accessible via SCAR in due course.

1.5 GENERAL DEFINITIONS OF CHEMICALS

The UNEP regionally-based assessment of PTSs covers a total of twenty-six compounds, including the twelve persistent organic pollutants (POPs) covered under the Stockholm Convention. Data are not available for all compounds in the assessment list, and information is given in this section only for those where data are presented in this regional report. These are: aldrin, endrin, dieldrin, chlordane, DDT, heptachlor, mirex, toxaphene, hexachlorobenzene, PCBs, dioxins and furans, HCH (lindane), organic mercury, organic tin and polyaromatic hydrocarbons (PAHs). Toxicity data refer almost exclusively to organisms found outside the region.

1.5.1 Persistent Toxic Substances– Pesticides

1.5.1.1 <u>Aldrin</u>

Chemical Name: 1,2,3,4,10,10-Hexachloro-1,4,4a,5,8,8a-hexahydro-1,4-endo,exo-5,8-dimethanonaphthalene $(C_{12}H_8Cl_6)$. <u>CAS Number</u>: 309-00-2

Properties: Solubility in water: 27 μ g dm⁻³ at 25°C; vapour pressure: 2.3 x 10⁻⁵ mm Hg at 20°C; log K_{ow}: 5.17-7.4.

Discovery/Uses: It has been manufactured commercially since 1950, and used throughout the world up to the early 1970s to control soil pests such as corn rootworm, wireworms, rice water weevil, and grasshoppers. It has also been used to protect wooden structures from termites.

<u>Persistence/Fate</u>: Readily metabolized to dieldrin by both plants and animals. Biodegradation is expected to be slow and it binds strongly to soil particles, and is resistant to leaching into groundwater. Aldrin was classified as moderately persistent with half-life in soil and surface waters ranging from 20 days to 1.6 years.

Toxicity: Aldrin is toxic to humans; the lethal dose for an adult has been estimated to be about 80 mg kg⁻¹ body weight. The acute oral LD_{50} in laboratory animals is in the range of 33 mg kg⁻¹ body weight for guinea pigs to 320 mg kg⁻¹ body weight for hamsters. The toxicity of aldrin to aquatic organisms is quite variable, with aquatic insects being the most sensitive group of invertebrates. The 96-h LC₅₀ values range from 1-200 µg dm⁻³ for insects, and from 2.2-53 µg dm⁻³ for fish. The maximum residue limits in food recommended by FAO/WHO varies from 0.006 mg kg⁻¹ milk fat to 0.2 mg kg⁻¹ meat fat. Water quality criteria between 0.1 to 180 µg dm⁻³ have been published.

1.5.1.2 Dieldrin

<u>**Properties:**</u> Solubility in water: 140 μ g dm⁻³ at 20°C; vapour pressure: 1.78 x 10⁻⁷ mm Hg at 20°C; log K_{ow}: 3.69-6.2.

Discovery/Uses: It appeared in 1948 after World War II and used mainly for the control of soil pests such as corn rootworms, wireworms and catworms.

<u>Persistence/Fate:</u> It is highly persistent in soils, with a half-life of 3-4 years in temperate climates, and it bioconcentrates in organisms. The persistence in air has been estimated in 4-40 h.

Toxicity: The acute toxicity for fish is high (LC_{50} between 1.1 and 41 mg dm⁻³) and moderate for mammals (LD_{50} in mouse and rat ranging from 40 to 70 mg kg⁻¹ body mass - BM). However, a daily administration of 0.6 mg kg⁻¹ to rabbits adversely affected the survival rate. Aldrin and dieldrin mainly affect the central nervous system but there is no direct evidence that they cause cancer in humans. The maximum residue limits in food recommended by FAO/WHO varies from 0.006 mg kg⁻¹ milk fat and 0.2 mg kg⁻¹ poultry fat. Water quality criteria between 0.1 to 18 µg dm⁻³ have been published.

1.5.1.3 <u>Endrin</u>

Properties: Solubility in water: 220-260 μ g dm⁻³ at 25 °C; vapour pressure: 2.7 x 10-7 mm Hg at 25°C; log K_{OW}: 3.21-5.34.

Discovery/Uses: It has been used since the 1950s against a wide range of agricultural pests, mostly on cotton but also on rice, sugar cane, maize and other crops. It has also been used as a rodenticide.

<u>Persistence/Fate</u>: Is highly persistent in soils (half-lives of up to 12 y have been reported in some cases). Bioconcentration factors of 14 to 18 000 have been recorded in fish, after continuous exposure.

Toxicity: Endrin is very toxic to fish, aquatic invertebrates and phytoplankton; the LC_{50} values are mostly less than 1 µg dm⁻³. The acute toxicity is high in laboratory animals, with LD_{50} values of 3-43 mg kg⁻¹, and a dermal LD_{50} of 5-20 mg kg⁻¹ in rats. Long term toxicity in the rat has been studied over two years and a NOEL of 0.05 mg kg⁻¹ BM d⁻¹ was found.

1.5.1.4 Chlordane

<u>Chemical Name</u>: 1,2,4,5,6,7,8,8-Octachloro-2,3,3a,4,7,7a-hexahydro-4,7-methanoindene ($C_{10}H_6Cl_8$). <u>CAS</u> <u>Number</u>: 57-74-9

Properties: Solubility in water: 56 μ g dm⁻³ at 25°C; vapour pressure: 0.98 x 10⁻⁵ mm Hg at 25 °C; log K_{OW}: 6.00.

Discovery/Uses: Chlordane appeared in 1945 and was used primarily as an insecticide for control of cockroaches, ants, termites, and other household pests. Technical chlordane is a mixture of at least 120 compounds. Of these, 60-75% are chlordane isomers, the remainder being related to endo-compounds including heptachlor, nonachlor, diels-alder adduct of cyclopentadiene and penta/hexa/octachlorocyclopentadienes.

<u>Persistence/Fate</u>: Chlordane is highly persistent in soils with a half-life of about 4 years. Its persistence and high partition coefficient promotes binding to aquatic sediments and bioconcentration in organisms.

Toxicity: LC_{50} from 0.4 mg dm⁻³ (pink shrimp) to 90 mg dm⁻³ (rainbow trout) have been reported for aquatic organisms. The acute toxicity for mammals is moderate with an LD_{50} in rat of 200-590 mg kg⁻¹ BM (19.1 mg kg⁻¹ BM for oxychlordane). The maximum residue limits for chlordane in food are, according to FAO/WHO between 0.002 mg kg⁻¹ milk fat and 0.5 mg kg⁻¹ poultry fat. Water quality criteria of 1.5 to 6 µg dm⁻³ have been published. Chlordane has been classified as a substance for which there is evidence of endocrine disruption in an intact organism and possible carcinogenicity to humans.

1.5.1.5 <u>Heptachlor</u>

Properties: Solubility in water: 180 μ g dm⁻³ at 25°C; vapour pressure: 0.3 x 10⁻⁵ mm Hg at 20°C; log K_{ow}: 4.4-5.5.

<u>Production/Uses</u>: Heptachlor is used primarily against soil insects and termites, but also against cotton insects, grasshoppers, and malaria mosquitoes. Heptachlor epoxide is a more stable breakdown product of heptachlor.

Persistence/Fate: Heptachlor is metabolised in soils, plants and animals to heptachlor epoxide, which is more stable in biological systems and is carcinogenic. The half-life of heptachlor in soil is in temperate regions 0.75–2 y. Its high partition coefficient provides the necessary conditions for bioconcentration in organisms.

<u>**Toxicity</u>**: The acute toxicity of heptachlor to mammals is moderate (LD_{50} values between 40 and 119 mg kg⁻¹ have been published). The toxicity to aquatic organisms is higher and LC_{50} values down to 0.11 µg dm⁻³ have been found for pink shrimp. Limited information is available on the effects in humans and studies are</u>

inconclusive regarding heptachlor and cancer. The maximum residue levels recommended by FAO/WHO are between 0.006 mg kg⁻¹ milk fat and 0.2 mg kg⁻¹ meat or poultry fat.

1.5.1.6 <u>Dichlorodiphenyltrichloroethane (DDT)</u>

Chemical Name: 1,1,1-Trichloro-2,2-bis-(4-chlorophenyl)-ethane (C₁₄H₉Cl₅). CAS Number: 50-29-3.

Properties: Solubility in water: 1.2-5.5 μ g dm⁻³ at 25°C; vapour pressure: 0.2 x 10⁻⁶ mm Hg at 20°C; log K_{OW}: 6.19 for *pp*'-DDT, 5.5 for *pp*'-DDD and 5.7 for *pp*'-DDE.

Discovery/Use: DDT appeared for use during World War II to control insects that spread diseases like malaria, dengue fever and typhus. Following this, it was widely used on a variety of agricultural crops. The technical product is a mixture of about 85% *pp* '-DDT and 15% *op* '-DDT isomers.

<u>Persistence/Fate</u>: DDT is highly persistent in soils with a half-life of up to 15 years and of 7 days in air. It also exhibits high bioconcentration factors (in the order of 50 000 for fish and 500000 for bivalves). In the environment, the product is metabolized mainly to DDD and DDE.

<u>**Toxicity</u>**: The lowest dietary concentration of DDT reported to cause egg shell thinning was 0.6 mg/kg for the black duck. LC_{50} of 1.5 mg dm⁻³ for largemouth bass and 56 mg dm⁻³ for guppy have been reported. The acute toxicity of DDT for mammals is moderate with an LD_{50} in rat of 113-118 mg kg⁻¹ BM. DDT has been shown to have an oestrogen-like activity, and possible carcinogenic activity in humans. The maximum residue level in food recommended by WHO/FAO range from 0.02 mg kg⁻¹ milk fat to 5 mg kg⁻¹ meat fat. Maximum permissible DDT residue levels in drinking water (WHO) is 1.0 µg dm⁻³.</u>

1.5.1.7 <u>Toxaphene</u>

Chemical Name: Polychlorinated bornanes and camphenes (C₁₀H₁₀Cl₈). CAS Number: 8001-35-2

<u>Properties</u>: Solubility in water: 550 μ g dm⁻³ at 20°C; vapour pressure: 3.3 x 10⁻⁵ mm Hg at 25°C; log K_{OW} : 3.23-5.50.

Discovery/Uses: Toxaphene has been in use since 1949 as a nonsystemic insecticide with some acaricidal activity, primarily on cotton, cereal grains fruits, nuts and vegetables. It was also used to control livestock ectoparasites such as lice, flies, ticks, mange, and scab mites. The technical product is a complex mixture of over 300 congeners, containing 67-69% chlorine by weight.

<u>Persistence/Fate</u>: Toxaphene has a half life in soil from 100 d up to 12 y. It has been shown to bioconcentrate in aquatic organisms (BCF of 4 247 in mosquito fish and 76 000 in brook trout).

Toxicity: Toxaphene is highly toxic in fish, with 96-hour LC_{50} values in the range of 1.8 µg dm⁻³ in rainbow trout to 22 µg dm⁻³ in bluegill. Long term exposure to 0.5 µg dm⁻³ reduced egg viability to zero. The acute oral toxicity is in the range of 49 mg kg⁻¹ BM in dogs to 365 mg kg⁻¹ in guinea pigs. In long term studies NOEL in rats was 0.35 mg kg⁻¹ BM d⁻¹, LD₅₀ ranging from 60 to 293 mg kg⁻¹ BM. For toxaphene exists a strong evidence of the potential for endocrine disruption. Toxaphene is carcinogenic in mice and rats and is of carcinogenic risk to humans, with a cancer potency factor of 1.1 mg kg⁻¹ BM d⁻¹ for oral exposure.

1.5.1.8 <u>Mirex</u>

<u>Chemical Name</u>: 1,1a,2,2,3,3a,4,5,5a,5b,6-Dodecachloroacta-hydro-1,3,4-metheno-1H-cyclobuta[cd]pentalene (C₁₀Cl₁₂). <u>CAS Number</u>: 2385-85-5

Properties: Solubility in water: 0.07 μ g dm⁻³ at 25°C; vapour pressure: 3 x 10⁻⁷ mm Hg at 25°C; log K_{OW}: 5.28. **Discovery/Uses:** The use in pesticide formulations started in the mid 1950s largely focused on the control of ants. It is also a fire retardant for plastics, rubber, paint, paper and electrical goods. Technical grade preparations of mirex contain 95.19% mirex and 2.58% chlordecone, the rest being unspecified. The name 'Mirex' is also used to refer to bait comprising corncob grits, soya bean oil, and mirex.

<u>Persistence/Fate</u>: Mirex is considered to be one of the most stable and persistent pesticides, with a half-life is soils of up to 10 years. Bioconcentration factors of 2 600 and 51 400 have been observed in pink shrimp and fathead minnows, respectively. It is capable of undergoing long-range transport due to its relative volatility (VPL = 4.76 Pa; H = $52 \text{ Pa m}^3 \text{ mol}^{-1}$).

Toxicity: The acute toxicity of Mirex for mammals is moderate with an LD_{50} in rat of 235 mg kg⁻¹ and dermal toxicity in rabbits of 80 mg kg⁻¹. Mirex is also toxic to fish and can affect their behaviour (LC₅₀ (96 h) from 0.2 to 30 mg dm⁻³ for rainbow trout and bluegill, respectively). Delayed mortality of crustaceans occurred at 1 µg dm⁻³ exposure levels. There is evidence of its potential for endocrine disruption and possibly carcinogenic risk to humans.

1.5.1.9 <u>Hexachlorobenzene (HCB)</u>

<u>Chemical Name</u>: Hexachlorobenzene (C₆H₆). <u>CAS Number</u>: 118-74-1

<u>**Properties:**</u> Solubility in water: 50 μ g dm⁻³ at 20°C; vapour pressure: 1.09 x 10⁻⁵ mm Hg at 20°C; log K_{OW}: 3.93-6.42.

Discovery/Uses: It was first introduced in 1945 as fungicide for seed treatments of grain crops, and used to make fireworks, ammunition, and synthetic rubber. Today it is mainly a by-product in the production of a large number of chlorinated compounds, particularly lower chlorinated benzenes, solvents and several pesticides. HCB is emitted to the atmosphere in flue gases generated by waste incineration facilities and metallurgical industries.

Persistence/Fate: HCB has an estimated half-life in soils of 2.7-5.7 years and of 0.5-4.2 years in air. HCB has a relatively high bioaccumulation potential and long half-life in biota.

Toxicity: LC_{50} for fish varies between 50 and 200 µg dm⁻³. The acute toxicity of HCB is low with LD_{50} values of 3.5 mg g⁻¹ for rats. Mild effects of the [rat] liver have been observed at a daily dose of 0.25 mg kg⁻¹ BM. HCB is known to cause liver disease in humans (porphyria cutanea tarda) and has been classified as a possible carcinogen to humans by IARC.

1.5.1.10 Hexachlorocyclohexanes (HCH)

<u>Chemical Name</u>: 1,2,3,4,5,6-Hexachlorocyclohexane (mixed isomers) ($C_6H_6Cl_6$). <u>CAS Number</u>: 608-73-1 (γ -HCH, lindane: 58-89-9).

<u>Properties</u>: γ -HCH: solubility in water: 7 000 µg dm⁻³ at 20°C; vapour pressure: 3.3 x 10⁻⁵ mm Hg at 20°C; log K_{OW}: 3.8.

Discovery/Uses: There are two principle formulations: "technical HCH", which is a mixture of various isomers, including α -HCH (55-80%), β -HCH (5-14%) and γ -HCH (8-15%), and "lindane", which is essentially pure γ -HCH. Historically, lindane was one of the most widely used insecticides in the world. Its insecticidal properties were discovered in the early 1940s. It controls a wide range of sucking and chewing insects and has been used for seed treatment and soil application, in household biocidal products, and as textile and wood preservatives.

<u>**Persistence/Fate:**</u> Lindane and other HCH isomers are relatively persistent in soils and water, with half lives generally greater than 1 and 2 years, respectively. HCH are much less bioaccumulative than other organochlorines because of their relatively low liphophilicity. On the contrary, their relatively high vapour pressures, particularly of the α -HCH isomer, determine their long-range transport in the atmosphere.

<u>Toxicity</u>: Lindane is moderately toxic for invertebrates and fish, with LC_{50} values of 20-90 µg dm⁻³. The acute toxicity for mice and rats is moderate with LD_{50} values in the range of 60-250 mg kg⁻¹. Lindane resulted to have no mutagenic potential in a number of studies but an endocrine disrupting activity has been observed.

1.5.2 Persistent Toxic Substances - Industrial compounds

1.5.2.1 Polychlorinated biphenyls (PCBs)

<u>Chemical Name</u>: Polychlorinated biphenyls ($C_{12}H_{(10-n)}Cl_n$, where n is within the range of 1-10). <u>CAS Number</u>: Various (e.g. for Aroclor 1242, CAS No.: 53469-21-9; for Aroclor 1254, CAS No.: 11097-69-1);

<u>Properties</u>: Water solubility decreases with increasing chlorination: 0.01 to 0.0001 μ g dm⁻³ at 25°C; vapour pressure: 1.6-0.003 x 10⁻⁶ mm Hg at 20°C; log K_{ow}: 4.3-8.26.

Discovery/Uses: PCBs were introduced in 1929 and were manufactured in different countries under various trade names (e.g., Aroclor, Clophen, Phenoclor). They are chemically stable and heat resistant, and were used worldwide as transformer and capacitor oils, hydraulic and heat exchange fluids, and lubricating and cutting oils. Theoretically, a total of 209 possible chlorinated biphenyl congeners exist, but only about 130 of these are likely to occur in commercial products.

<u>Persistence/Fate</u>: Most PCB congeners, particularly those lacking adjacent unsubstituted positions on the biphenyl rings (e.g., 2,4,5-, 2,3,5- or 2,3,6-substituted on both rings) are extremely persistent in the environment. They are estimated to have half-lives ranging from three weeks to two years in air and, with the exception of mono- and di-chlorobiphenyls, > 6 y in aerobic soils and sediments. PCBs also have extremely long half-lives in adult fish, for example, an eight-year study of eels found that the half-life of CB153 was >10 y.

Toxicity: LC_{50} for the larval stages of rainbow trout is 0.32 µg dm⁻³ with a NOEL of 0.01 µg dm⁻³. The acute toxicity of PCB in mammals is generally low and LD_{50} values in rat of 1 g kg⁻¹ BM. IARC has concluded that

PCB are carcinogenic to laboratory animals and probably also for humans. They have also been classified as substances for which there is evidence of endocrine disruption in an intact organism.

1.5.3 Persistent Toxic Substances - Unintended by-products

1.5.3.1 <u>Polychlorinated dibenzo-p-dioxins (PCDDs) and Polychlorinated dibenzofurans (PCDFs)</u>

<u>Chemical Name</u>: PCDDs ($C_{12}H_{(8-n)}Cl_nO_2$) and PCDFs ($C_{12}H_{(8-n)}Cl_nO$) may contain between 1 and 8 chlorine atoms. Dioxins and furans have 75 and 135 possible positional isomers, respectively. <u>CAS Number</u>: Various (2,3,7,8-TetraCDD: 1746-01-6; 2,3,7,8-TetraCDF: 51207-31-9).

Properties: Solubility in water: in the range 0.43–0.0002 ng dm⁻³ at 25°C; vapour pressure: $2-0.007 \times 10^{-6}$ mm Hg at 20°C; log K_{ow}: in the range 6.60–8.20 for tetra- to octa-substituted congeners.

Discovery/Uses: They are by-products resulting from the production of other chemicals and from the low-temperature combustion and incineration processes. They have no known use.

<u>Persistence/Fate</u>: PCDD/Fs are characterized by their lipophilicity, semi-volatility and resistance to degradation (half life of TCDD in soil of 10-12 years) and to long-range transport. They are also known for their ability to bio-concentrate and biomagnify under typical environmental conditions.

Toxicity: The toxicological effects reported refers to the 2,3,7,8-substituted compounds (17 congeners) that are agonists for the AhR. All the 2,3,7,8-substituted PCDDs and PCDFs plus coplanar PCBs (with no chlorine substitution at the ortho positions) show the same type of biological and toxic response. Possible effects include dermal toxicity, immunotoxicity, reproductive effects and teratogenicity, endocrine disruption and carcinogenicity. At the present time, the only persistent effect associated with dioxin exposure in humans is chloracne. The most sensitive groups are foetus and neonatal infants.

Effects on the immune systems in the mouse have been found at doses of 10 ng kg⁻¹ BM d⁻¹, while reproductive effects were seen in rhesus monkeys at 1-2 ng kg⁻¹ BM d⁻¹. Biochemical effects have been seen in rats down to 0.1 ng kg⁻¹ BM d⁻¹. In a re-evaluation of the TDI for dioxins, furans (and planar PCB), the WHO decided to recommend a range of 1-4 TEQ pg kg⁻¹ BM, although more recently the acceptable monthly intake value has been set at 1-70 TEQ pg kg⁻¹ BM.

1.5.3.2 Polycyclic Aromatic Hydrocarbons (PAHs)

<u>Chemical Name</u>: PAHs is a group of compounds consisting of two or more fused aromatic rings. <u>CAS</u> <u>Number</u>:

Properties: Solubility in water: $0.00014 - 2.1 \text{ mg dm}^{-3}$ at 25°C; vapour pressure: from 0.0015×10^{-9} to $0.0051 \text{ mmHg at } 25^{\circ}\text{C}$; log K_{ow}: 4.79-8.20

Discovery/Use: Most of these are formed during incomplete combustion of organic material and the composition of PAHs mixture vary with the source(s) and also due to selective weathering effects in the environment.

Persistence/Fate: Persistence of the PAHs varies with their molecular weight. The low molecular weight PAHs are most easily degraded. The reported half-lives of naphthalene, anthracene and benzo(e)pyrene in sediment are 9, 43 and 83 hours, respectively, whereas for higher molecular weight PAHs, their half-lives are up to several years in soils/sediments. The BCFs in aquatic organisms frequently range between 100-2000 and it increases with increasing molecular size. Due to their wide distribution, the environmental pollution by PAHs has aroused global concern.

Toxicity: The acute toxicity of low PAHs is moderate with an LD_{50} of naphthalene and anthracene in rat of 490 and 18000 mg kg⁻¹ BM respectively, whereas the higher PAHs exhibit higher toxicity and LD_{50} of benzo(a)anthracene in mice is 10 mg kg⁻¹ BM. In *Daphnia pulex*, LC_{50} for naphthalene is 1.0 mg dm⁻³, for phenanthrene 0.1 mg dm⁻³ and for benzo(a)pyrene is 0.005 mg dm⁻³. The critical effect of many PAHs in mammals is their carcinogenic potential. The metabolic action of these substances produces intermediates that bind covalently with cellular DNA. IARC has classified benz[a]anthracene, benzo[a]pyrene, and dibenzo[a,h]anthracene as probably carcinogenic to humans. Benzo[b]fluoranthene and indeno[1,2,3-c,d]pyrene were classified as possible carcinogens to humans.

1.5.4 Organometals

1.5.4.1 Organotin compounds

<u>Chemical Name</u>: Organotin compounds comprise mono-, di-, tri- and tetrabutyl and triphenyl tin compounds. They conform to the following general formula $(n-C_4H_9)_n$ Sn-X and $(C_6H_5)_3$ Sn-X, where X is an anion or a group linked covalently through a hetero-atom. **CAS Number**: 56-35-9 (TBTO); 76-87-9 (TPTOH)

Properties: Solubility in water: 4 mg dm⁻³ (TBTO) and 1 mg dm⁻³ (TPTOH) at 25°C and pH 7; vapour pressure: 7.5 x 10^{-7} mm Hg at 20°C (TBTO) 3.5 x 10^{-8} mmHg at 50°C (TPTOH); log K_{ow}: 3.19 - 3.84. In sea water and under normal conditions, TBT exists as three species in seawater (hydroxide, chloride, and carbonate).

Discovery/Uses: They are mainly used as antifouling paints (tributyl and triphenyl tin) for underwater structures and ships. Minor identified applications are as antiseptic or disinfecting agents in textiles and industrial water systems, such as cooling tower and refrigeration water systems, wood pulp and paper mill systems, and breweries. They are also used as stabilizers in plastics and as catalytic agents in soft foam production. It is also used to control the shistosomiasis in various parts of the world.

Persistence/Fate: Under aerobic conditions, TBT takes 1 to 3 months to degrade, but in anaerobic soils may persist for more than 2 years. Because of the low water solubility it binds strongly to suspended material and sediments. TBT is lipophilic and tends to accumulate in aquatic organisms. Oysters exposed to very low concentrations exhibit BCF values from 1 000 to 6 000.

<u>**Toxicity</u></u>: TBT is moderately toxic and all breakdown products are even less toxic. Its impact on the environment was discovered in the early 1980s in France with harmful effects in aquatic organisms, such as shell malformations of oysters, imposex in marine snails and reduced resistance to infection (e.g. in flounder). Molluscs react adversely to very low levels of TBT (0.06-2.3 \mug dm⁻³). Lobster larvae show a nearly complete cessation of growth at just 1.0 \mug dm⁻³ TBT. In laboratory tests, reproduction in snails was inhibited when females exposed to 0.05-0.003 \mug dm⁻³ of TBT developed male characteristics. Large doses of TBT have been shown to damage the reproductive and central nervous systems, bone structure, and the liver bile duct of mammals.</u>**

1.5.4.2 Organomercury compounds

<u>Chemical Name</u>: The main compound of concern is methyl mercury (HgCH₃). <u>**CAS Number**</u>: 22967-92-6 <u>**Properties**</u>: Solubility in water: 0.1 g dm⁻³ at 21°C (HgCH₃Cl) and 1.0 g dm⁻³ at 25°C (Hg(CH₃)₂); vapour pressure: 8.5 x 10⁻³ mm Hg at 25°C (HgCH₃Cl); log K_{OW}: 1.6 (HgCH₃Cl) and 2.28 (Hg(CH₃)₂).

Production/Uses: There are many sources of mercury release to the environment, both natural (volcanoes, mercury deposits, and volatilization from the ocean) and human-related (coal combustion, chlorine alkali processing, waste incineration, and metal processing). It is also used in thermometers, batteries, lamps, industrial processes, refining, lubrication oils, and dental amalgams. Methyl mercury has no industrial uses; it is formed in the environment by methylation of the inorganic mercurial ion mainly by microorganisms in the water and soil.

Persistence/Fate: Mercury released into the environment can either stay close to its source for long periods, or be widely dispersed on a regional or even world-wide basis. Not only are methylated mercury compounds toxic, but highly bioaccumulative as well. The increase in mercury as it rises in the aquatic food chain results in relatively high levels of mercury in fish consumed by humans. Ingested elemental mercury is only 0.01% absorbed, but methyl mercury is nearly 100% absorbed from the gastrointestinal tract. The biological half-life of mercury is 60 days.

Toxicity: Long-term exposure to either inorganic or organic mercury can permanently damage the brain, kidneys, and developing foetus. The most sensitive target of low level exposure to metallic and organic mercury following short or long term exposures appears to be the nervous system.

1.6 DEFINITION OF THE ANTARCTIC REGION

Antarctica cannot be defined by national boundaries. The landmass south of 60° S is not under the jurisdiction of any nation – although claims of parts of the land mass are made by several nations, these claims are suspended under the Antarctic Treaty. In reaching a definition of the Antarctic region for this assessment, an initial functional description was used, based on the approximate northern boundary of the Southern Ocean, and this was then adjusted make it as relevant to the study without infringing the 'territory' of the neighbouring regions in the assessment.

For this assessment, a regional definition is required which encompasses the landmass, peri-Antarctic islands and the Southern Ocean from the Antarctic Polar Frontal Zone southwards to the coast of the continent. The definition suggested here is a region south of the boundaries of the region of the Southern Ocean, together with some peri-Antarctic islands which are typically included in Antarctic research. This area is delimited as follows:

All land and ocean in region south of the following boundary:

South of 50°S from 50°W to 30°E

South of $45^{\circ}S$ from $30^{\circ}E$ to $80^{\circ}E$

South of 55°S from 80°E to 150°E

South of 60°S from 150°E to 50°W

Île St Paul and Île Amsterdam 38°S, 77.5°E (administered by France)

Macquarie Island 54.5°S, 159°E (administered by Australia)

Gough Island 40°S, 10°W (administered by United Kingdom)

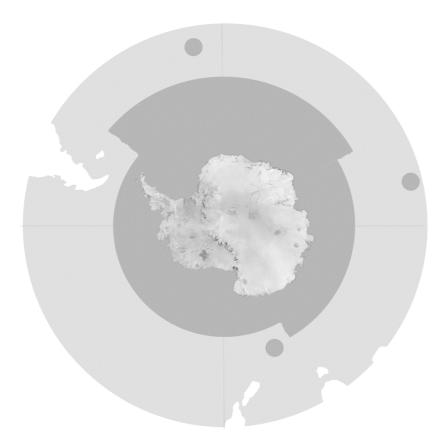


Figure 1-1. Map of the area covered by the Antarctic region. The Antarctic continent is shown in the centre of the image. The main darker grey area around it shows the boundary of the CCAMLR convention area. The three smaller circles indicate the positions of the island groups included in the regional definition but outside the CCAMLR area. Zero, 90 and 180 longitude, and outlines of southern South America, New Zealand and Australia are included for reference

This definition is amplified in the following text:

1. The Scientific Committee on Antarctic Research (SCAR) has a definition of its 'area of interest'. This definition uses the Antarctic Convergence (the northern boundary of the Antarctic Circumpolar Current) to

delimit the Southern Ocean and to include most of the peri-Antarctic islands. However, the SCAR area of interest specifically includes some islands which are located slightly to the north of this oceanographic boundary (see below 3).

2. The Commission for the Conservation of Antarctic Marine Living Resources (CCAMLR) has defined a similar oceanographic boundary for its area of jurisdiction. This definition is more convenient in that it is based on standard lines of latitude and longitude, corresponding to the UN Food and Agriculture Organization (FAO) Fishery Areas in the Southern Ocean.

2.1. The latitude of the boundary of the CCAMLR area varies with longitude, and can be summarised as follows:

From 50°W to 30°E the boundary is at 50°S

From 30°E to 80°E the boundary is at 45°S

From 80°E to 150°E the boundary is at 55°S

From 150°E to 50°W the boundary is at 60°S

3. The SCAR Area of Interest includes several islands and island groups which are sub-Antarctic in character but fall outside the notional boundary of the Antarctic Treaty (under which territorial claims are in abeyance). Of these, the following also fall outside the CCAMLR region boundary:

Île St Paul and Île Amsterdam 38°S, 77.5°E (administered by France)

Macquarie Island 54.5°S, 159°E (administered by Australia)

Gough Island 40°S, 10°W (administered by United Kingdom)

The following islands and island groups which are outside the Antarctic Treaty area fall within the CCAMLR area

Marion Island and Prince Edward Islands 46.8°S, 37.5°E (administered by South Africa)

Îles Crozet 46°S, 51°E (administered by France)

Îles Kerguelen 49°S, 69°E (administered by France)

Heard Island 53.5°S, 73.5°E (administered by Australia)

South Georgia 54.3°S, 36.6°W (administered by the United Kingdom)

South Sandwich Islands 56°S, 27°W (administered by the United Kingdom)

Bouvetøya 54.5°S, 3.5°W (administered by Norway)

4. The following nations undertake research programmes in this region and may contribute to the UNEP PTS assessment:

Argentina, Australia, Belgium, Brazil, Bulgaria, Canada, Chile, China, Ecuador, Finland, France, Germany, India, Italy, Japan, Korea, The Netherlands, New Zealand, Norway, Peru, Poland, Russia, South Africa, Spain, Sweden, Ukraine, The United Kingdom, The United States of America, Uruguay

1.7 PHYSICAL SETTING

Antarctica and the Southern Ocean is a remote region, with no indigenous human population and no industrial activity. Human activity is minimal, and mostly very localized. The overwhelming majority of PTS loading to the environment and biota derives from global rather than local input. The region defined in the previous section encompasses three components – the continental landmass, the surrounding circumpolar ocean, and a number of islands and island groups.

1.7.1 The terrestrial environment

The continent of Antarctica is a cold desert, and experiences an extreme climate. Temperatures in winter can drop below -50°C in the middle of the continent. The major differences in solar radiation between winter and summer have important consequences for climate and the environment, and for biota.

The landmass is mostly covered by an ice sheet which can exceed 4 km in thickness. Although Antarctica is the smallest continent, it has the highest mean elevation because of the thickness of the ice sheet. Beneath this ice sheet, parts of the land surface are below sea level, and geologically the continental landmass can be separated into two parts. The large and geologically ancient region of East Antarctica is predominantly a Precambrian shield. It lies to the south of Africa and Australia. South of South America is the geologically younger region known as West Antarctica, which comprises five separate crustal blocks.

The ice sheet has accumulated from snowfall over very long periods. The compacted snow and underlying ice provide a record of atmospheric composition, and this has been used to interpret variation in climate and atmospheric composition over hundreds of thousands of years. The temporal resolution of such records is dependent on accumulation rate. Typical snowfall over much of the continent is low, but in some areas close to the coast snow may be high enough to allow the resolution of annual or even seasonal variability (PAGES 1997).



Figure 1-2. Contrasting Antarctic landscapes. The left-hand panel shows an aerial view of the continental icecap, with the peaks of mountains (nunataks) emerging through the ice. The right-hand panel shows a botanist sampling from a moss-peat bank in the South Orkney Islands, where the climate is less extreme and lowland areas become snow-free in summer. The barren scree in the background is more typical scenery for much of the ice-free regions at the coast and on islands. (Photographs courtesy of the British Antarctic Survey)

Most exposed land comprises bare rock, and it is only in more hospitable regions close to the coast and on neighbouring islands that limited vegetation cover develops. Terrestrial ecosystems are simple for the most part, with vegetation dominated by cryptogams and the fauna limited to small invertebrate animals no more than a few millimetres in size. Soil development is poor. Inland water bodies may be more productive than the surrounding land, although their ecosystems are also very simple. Surface run-off can be locally intense on 'warm' days in summer, but there are no river systems comparable to those in the Arctic.

1.7.2 The marine environment

The Southern Ocean occupies a belt between 55-70°S. The more southerly part of this zone is covered by sea ice for all or part of the year. Water temperatures vary very slightly in both time and space. Summer temperatures may be as high as 3-4°C in the northern part of the Southern Ocean, decreasing to slightly below zero close to the continent. The annual range of water temperature is typically only a few degrees. Despite this

apparently hostile environment, the Southern Ocean supports a diverse biota, in strong contrast to Antarctic terrestrial ecosystems. The region supports a number of fisheries, some of which are of global importance. Previous episodes of marine resource exploitation, most notably whaling in the 20th century, resulted in catastrophic declines in stocks. Southern Ocean fisheries are now the subject of international conservation measures under the Convention for the Conservation of Antarctic Marine Living Resources (CCAMLR). In the case of whaling, the Southern Ocean has been declared a sanctuary area by the International Whaling Commission (IWC).

1.7.3 Islands

The region defined in 1.4 includes a wide variety of islands, from ice-covered islands close to the Antarctic continent to those at lower latitude where there is little or no permanent ice and snow cover and where terrestrial ecosystems are better developed. Many of these islands house research stations, so they contribute data to the PTS assessment even though they form a very small geographic component of the region. Useful introductions to the geography and ecology of these islands are given by King (1969) and Bonner & Walton (1985).



Figure 1-3. The marine and island environments. Left-hand panel shows a winter scene in a bay on the Antarctic Peninsula. The sea is covered with a layer of sea ice which is about 1 metre thick. An iceberg, calved from a floating ice shelf, is in the forground, whilst the mountains and land ice-cap are visible in the background. Right-hand panel shows a small part of a large penguin rookery on subantarctic Bird Island. The large population of marine birds and mammals are an indication of the productivity of the marine ecosystem. (Photographs courtesy of the British Antarctic Survey)

1.8 AN OUTLINE OF ENVIRONMENTAL REGULATION

The system for regulation of human activities and impacts in the region are dealt with in detail in a later chapter. However, a brief statement of the framework helps to provide a perspective for the next few chapters.

All of the Antarctic continent and many of the associated islands lie south of 60°S and are subject to the Antarctic Treaty. This treaty places any territorial claims in abeyance, and sets out a code governing national activities. Amongst other elements, all military activity is prohibited. Mineral exploitation has been effectively banned for the foreseeable future.

Until the last decade, nearly all human activity in the Antarctic Treaty area was concerned with scientific research and monitoring. In recent years, increase in other activities, especially in fisheries and tourism, has resulted in greater numbers of visitors to the region. However, the number of humans in the region remains small, and the majority visit in the southern summer and are restricted to a few locations.

Environmental protection within the Antarctic Treaty area is governed by a protocol to the treaty (see SCAR 1993). This protocol states that 'activities in the Antarctic Treaty area shall be planned and conducted so as to limit adverse impacts on the Antarctic environment and dependent and associated ecosystems'. The protocol includes provision for environmental impact assessment, which carries a monitoring component related to local activities. Any wastes containing PTS are required to be removed from the Antarctic (Annex III, Article 2). Some classes of material, including PCBs, are specifically prohibited under the protocol (Annex III, Article 7). Discharges of 'noxious substances' to the marine environment are prohibited (Annex IV, Article 4).

2 SOURCE CHARACTERISATION

2.1 INTRODUCTION

Antarctica and the adjacent islands and ocean, as defined in section 1.4, 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. The greatest impact can be expected where research is carried out at long-term stations, but even these typically have populations of less than 100 people. Pelagic fisheries are an important operation in some parts of the region (Figure 2-1), and tourism is also an increasingly important activity (Figure 2-2). Both of these may account for slight increases in emissions of some PTSs, but these will normally be highly dispersed.

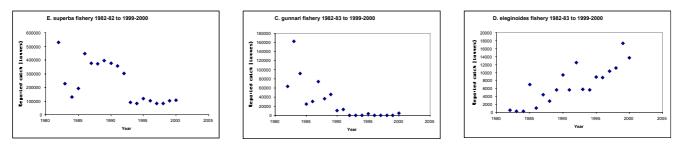


Figure 2-1. Fisheries patterns in the Southern Ocean during the last two decades of the 20th century. The fishery for krill, *Euphausia superba*, is one of the largest open-ocean crustacean fisheries in the world. Some fisheries, such as the mackerel icefish, *Champsocephalus gunnari*, have already been overexploited, whilst others are developing, such as that for toothfish, *Dissostichus elegenoides*. (Data courtesy of CCAMLR)

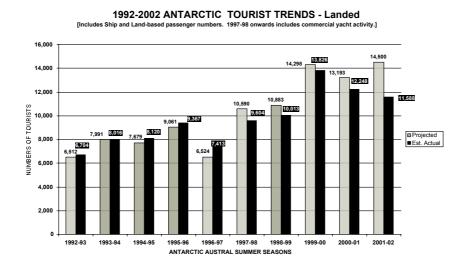


Figure 2-2. Tourism in Antarctica has increased rapidly since the mid-1970s. The figure shows reported and projected visits undertaken by operators who are members of the International Association of Antarctica Tour Operators. (Data courtesy of IAATO)

Human activity within the region can, and does, introduce small amounts of some PTSs into the environment. These releases are associated mainly with

Transport - air, sea and land vehicles

Use of some 'industrial' PTSs in machinery and in small engineering processes

Waste disposal, including incineration

With the exception of ship, aircraft and vehicle transport, both within the region and to and from the region, these releases are predominantly highly localised. Studies of PTSs around established research stations

typically detect the impact of these sites only within a few hundred metres. Even in a few extreme cases where the sites have been occupied for a long period, and were established when attitudes to environmental protection were very much more relaxed than under current requirements, no effects can be detected at distances greater than a kilometre.

A few pollution 'spillages' from maritime accidents and from coastal research stations have provided case studies which have allowed more detailed examination of the effects of local incidents. Most of these have been fuel releases, providing extensive data on local contamination by PAHs, their dispersal and fate in the local environment, and their impact on biota (e.g. Platt & Mackie 1979, Cripps 1990b, Pople et al. 1990, Kennicutt et al. 1991, Kennicutt & Sweet 1992, Cripps & Shears 1997, Smith & Simpson 1998).

The region cannot be considered to be a source of PTSs to adjacent regions. On the other hand there is compelling evidence that the overwhelming majority of loadings of most PTSs to the region derives from outside the Antarctic (e.g. Tatton & Ruzicka 1967, Peel 1975, Risebrough et al. 1976, Tanabe et al 1982, 1983, Focardi et al. 1991, 1992, Risebrough 1992, Bidleman et al. 1993, Oehme et al. 1995, Kallenborn et al. 1998). This aspect will be covered in section 4 of the report – here attention is confined to local inputs.

2.1.1 Persistent Toxic Substances – Pesticides

Pesticides are neither produced nor applied in the region. Trace contamination of aircraft and ships following decontamination en route to Antarctica, and contamination of materials imported to the region might also introduce very small amounts of pesticide. However, these amounts are only of concern in the context of possible degradation of data on global background levels, rather than being a significant input in their own right. There appear to be no data suggesting that any permanent habitation in Antarctica is a local source of pesticide PTSs in the way that can be demonstrated for some industrial compounds and unintended by-products.

2.1.2 Persistent Toxic Substances - Industrial Compounds

No materials in this category are manufactured in the region, and where they are used and subsequently released it is in very small quantities. These releases are trivial in a global context, but data for some compounds provide important means of defining the 'fingerprint' of release of PTSs from research stations. This information in turn allows the sampling strategy needed to be refined to capitalise on the value of Antarctica as means of monitoring global pollution levels and transport.

In this and subsequent sections of this chapter, reported values are as presented in the original published source. However, units have been brought to a common format to allow intercomparison – for instance $\mu g g^{-1}$ would be converted to ng g⁻¹ for consistency with ther data for a single PTS. The abbreviation 'nd' is used to indicate 'not detectable', although levels of detection are not given. More data on the geopgraphic location of samples can obtained in Appendices 1 and 2.

2.1.2.1 <u>Polychlorinated biphenyls (PCBs)</u>

The most comprehensive studies have been carried out close to the US McMurdo Station. This is the largest permanent human settlement in the region (excepting some land-based whaling stations on peri-Antarctic islands, operating mainly in the early-to-mid 20th century). The population of the station reached close to 1000 people over the summer season in the early 1970s, and this was supported by complex infrastructure and logistics. This period preceded the present-day rigorous attitudes to environmental protection in Antarctica, and the site was described by King (1969) as 'a sprawling conglomeration of huts on Ross Island which has all the makeshift qualities of a Yukon frontier town in the heyday of the Gold Rush'. It is not surprising that the long-period of such comparatively intense human activity has left a detectable imprint on the local environment.

This impact was first documented by Risebrough et al. (1990). They ascribed concentrations of PCBs in marine sediment close to the station as resulting from waste incineration and other local sources. The PCB

'spectrum' was more or less identical with Aroclor 1260 in all but one sample. Kennicutt et al. (1995) extended the sampling undertaken by Risebrough and colleagues. They were able to demonstrate the extent of the influence of the station, noting that PCB concentrations were high in sediment in Winter Quarters Bay, close to the station, but had decreased to background levels within a few hundred metres. Close to the station, the local input swamped the global signal. PCBs were detected in all sediment samples collected in the McMurdo Station area, ranging from 250-4300 ng g⁻¹, decreasing rapidly away from sources of contamination to background levels 18-28 ng g⁻¹.

The volume and type of activity at research stations, and the length and timing of occupation all combine to determine the impact on the local environment. Kennicutt et al. (1995) also studied the environment around another US research station. Palmer Station on the Antarctic Peninsula is another site with a long history of occupation, although the research station has never reached the large scale of the operation at McMurdo Station. A small number of sediment samples from the adjacent Arthur Harbour analysed for PCBs produced concentrations of 2.8-4.2 ng g⁻¹, similar to the values for uncontaminated sediments at McMurdo Station. PCBs were also examined in the tissues of limpets in Arthur Harbour. Concentrations were very low, except adjacent to the station where levels rose to 28-76 ng g⁻¹, with approximately equal amounts of penta-, hexa- and hepta-chlorobiphenyls. PCB emission from research stations may also affect the terrestrial environment. In an earlier study in the vicinity of Palmer Station, Risebrough et al (1976) had identified combustion-derived particulates from research stations as the source for elevated PCB concentrations in snow in the same area. Monod et al. (1992) studied PTSs in marine biota close to the French research station on the peri-Antarctic Kerguelen Islands during the 1970s. Highest levels were close to the research station, arising from refuse burning and leakage of PCBs from electrical equipment.

Overall, PCB emission from human habitation in Antarctica can be resolved as a pollution footprint in some cases, although typically the affected region is limited in its spatial extent, and environmental concentrations are still low in global terms, albeit higher than in nearby environments unaffected by local pollution.

2.1.3 Persistent Toxic Substances - Unintended by-products

The presence of unintended by-products again reveals the small but measurable local influence of human activity in the region, but the inputs have been extremely small with the exceptions of PAHs. The examples quoted below are primarily intended to define the extent of the effects of research stations and other sources, and their signal relative to global levels of these compounds, rather than to identify significant sources on a regional scale.

2.1.3.1 Polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs)

There are few data for this group of compounds in the region, and only one study documents evidence for local emission. Lugar et al. (1996) monitored ambient air at a series of sampling sites at McMurdo Station in 1992-94. Most frequent, most varied and highest levels of PCDDs and PCDFs were measured in a 'downtown' locations, where concentrations of total PCDDs were 0.12-1.8 pg m⁻³ and PCDFs were <0.02-2.77 pg m⁻³. The data suggest that various combustion sources beside the main solid waste incinerator contributed to the air loading of PCDDs and PCDFs. These levels are, again, low, and it is also uncertain how much they reflect the relatively uncontrolled approach to waste disposal operating even in the early 1990s. Contemporary regulation of waste disposal may mean that some of the waste-burning practices which might have contributed most to local PCDD and PCDF output are no longer typical of Antarctic operations.

2.1.3.2 Polycyclic Aromatic Hydrocarbons (PAHs)

Long-term human habitation, predominantly research stations but also land-based whale processing plants in the early-to-mid 20th century, provides sources of PAHs through hydrocarbon fuel spillage and as a by-product of combustion. As with industrial compounds such as PCBs, the level and extent of this contamination is small, and is mainly of interest because it enables the identification of those-areas in the region which cannot be considered free from local contamination.

Several authors have studied PAHs in the marine environment close to long-term human habitation. Platt and Mackie (1979, 1980) examined the local impact of a (by then disused) whaling station on the peri-Antarctic island of South Georgia. Both onshore and shipping activity would have been high in the heyday of operations, and environmental control lax. Platt and Mackie examined samples in a sediment profile extending back from the present to the early 1800s, and showed clearly the impact of the whaling station. Cripps (1990a) collected sediment and seawater samples from the same area and indicated that the whaling station continued to 'leak' PAHs although operations were then over. Total PAH concentrations up to 1.2 mg m⁻³ were measured in seawater close to derelict whaling stations at South Georgia.

Cripps (1990b) undertook a more systematic examination of contamination arising from Signy Research Station, South Orkney Islands: a small (about 20-person summer population) UK research station located in a cove on an island in the southern Scotia Sea. The station had been operating for approximately 40 years at the time of sampling. Total PAH concentrations in seawater and sediment were measured along a 3-km transect seawards from the station. PAH concentrations in seawater varied from 110-216 ng kg⁻¹, but showed no trend with distance from the station (in contrast to n-alkanes which decreased after distances >500 m from the station). PAH and alkane concentrations in the sediment both decreased with increasing distance from the station. Hydrocarbon pollution could be ascribed in part to known specific events in the operation of the station, including a small fuel spill in 1965. Cripps and Priddle (1995) also noted the temporal variability in PAH loading in known-age infaunal bivalves.

A few more significant spillages have occurred, predominantly through accidents with bunker fuel transfer or shipwreck or collision. Cripps and Shears (1997) followed the fate of an accidental spill of 1000 litres of diesel fuel at the UK Faraday Station, Galindez Island, Argentine Islands. Total PAH in seawater reached 222 µg kg⁻ on the day after the spill, and returned to 'background' levels within one week. However, seven months after the spill, PAH levels in limpets close to the station were still ten times higher than in those from an uncontaminated control site. This was ascribed to long-term, low-level input from the station, rather than from the spill itself.

The most notable pollution incident in region during the late 20th century was the sinking of the ship Bahia Paraiso close to the US Palmer Research Station, situated in an archipelago along the western coast of the Antarctic Peninsula. Kennicutt et al (1992a,b,c) quantified the extent and duration of the impact from this spillage, and how it compared with the longer-term low-level input from the research station. Local sources other than the shipwreck included diesel and other spillage on land, incineration and marine contamination. Marine sediment collected along a series of transects radiating from the station area had total PAH concentrations of nd - 11540 ng g⁻¹. Soils around the station had total PAH 800-86 000 ng g⁻¹. Other samples collected around the old Palmer research station included very high PAH contamination in one soil sample 345 000 ng g⁻¹. Kennicutt and co-workers also followed the course contamination in the marine environment from the Bahia Paraiso spillage, and found that contamination in the marine environment and marine biota declined after two years (Kennicutt and Sweet 1992, Kennicutt et al. 1995).

Kennicutt et al. (1995) summarised PAH data from the vicinity of McMurdo Station (see 2.1.2 above). Total PAH in the McMurdo area sediments 1990-91 and 1992-93 were below limit of detection to >6000 ng g⁻¹, with values up to 13 000 ng g⁻¹ in Winter Quarters Bay. Predominance of napthalene and phenanthrene in highly contaminated samples indicated contribution from spilt fuel. Pyrogenic PAH paralleled fuel PAH concentrations, suggesting a common origin. Fish tissue from the McMurdo area had PAH values up to 650 ng g^{-1} in contaminated areas.

Output of PAHs to the atmosphere results from evaporation and, predominantly, from combustion. Carrichia et al. (1995) measured particulate PAHs at a series of air-sampling stations set up within 200 m of the Italian research station at Terra Nova Bay in the Ross Sea. Measurements were undertaken during three consecutive summer seasons 1990-93. Overall, total PAH particulate concentrations were 15-700 pg m⁻³. Low air temperatures implied that most PAH were in particulate rather than vapour phase. Concentrations of individual compounds were low: 95% of the 11 compounds analysed were in the range 1-50 pg m^{-3} . The values resemble those from other remote monitoring sites, and are a hundred- to thousand-fold lower than particulate PAH in polluted urban areas. Electricity generation plant was considered to be the major source of particulate PAH.

Local contamination by PAH is probably the most common PTS impact of human activities in the region, and is probably also one of the best studied. Comprehensive sampling, with good spatial and temporal datasets in some of the major cases of single pollution incidents, provides a comprehensive picture of the extent and duration of PAH contamination around single localities. Some other sources of PAH, predominantly emissions from vehicles and aircraft, will have more widespread impact but would be expected to result in lower increases in concentration relative to the 'global' background.

2.1.4 Organometals

There are very few data for environmental levels of organometals in the region, and of these none provide definitive indication of local impact rather than larger-scale contamination. Measured environmental levels of methyl-mercury (MeHg) are low (DeMora et al. 1993) and typically account for about 10% of total gaseous mercury. Analysis of total mercury in snow suggests limited local contamination (Dick et al. 1990), and similar conclusions can be reached for other heavy metals such as lead (Suttie & Wolff 1993). Analysis of time-series from snow cores suggest that atmospheric deposition of mercury in the region has increased over the last few decades (Sheppard et al. 1991, Görlach & Boutron 1992) but again it is difficult to separate local and global sources.

2.2 SUMMARY - SOURCE CHARACTERISATION

The very small amount of human activity in the region means that local sources are both limited and localised. The region cannot be considered to be a source to PTSs to adjacent regions.

There are no demonstrable sources of pesticides within the region. Use of some industrial PTSs in the region has resulted in local contamination. Within this group, PCBs are the best documented. Local contamination arises directly from leakage and spillage, and from incineration.

The presence of unintended by-products such as PCDDs, PCDFs and PAHs results from local activity associated especially with long-term operations in the regions. Again, incineration and transport emissions are the key means of introducing these PTSs to the local environment, along with spillages in the case of PAHs.

Data for sources of organometals are scarce, although some studies of mercury and lead suggest that there is limited local contamination.

In all cases where systematic spatial and temporal analyses have been undertaken, such as studies of PCBs and PAHs in the marine environment, results indicate that local sources are highly localised.

3 ENVIRONMENTAL LEVELS, TOXICOLOGICAL AND ECOTOXICOLOGICAL CHARACTERISATION

3.1 INTRODUCTION

This chapter presents data on the levels of PTSs in the environment and in biota. Where there are sufficient data, comment is made on temporal variability, and in the case of biota if there are indications of concentration of PTSs in particular parts of the foodweb. Toxological data are sparse, and generally have been obtained from research experiments rather than systematic monitoring programmes. A summary is presented here to indicate the range of information available.

3.2 LEVELS AND TRENDS – ABIOTIC ENVIRONMENT

There is a range of data on levels of PTS in the abiotic environment in the region, potentially based on samples from the following media:

Atmosphere - vapour and particulate phases

Seawater and sea ice

Marine sediments

Terrestrial soils and lake sediments

Precipitation, run-off and terrestrial water bodies

Snow and land ice

In practice, sampling is patchy, and the full range of environmental media has not been sampled for any class of compound. The location and timing of sampling is often determined by logistic and scientific constraints. This may make it difficult to generalize from relatively sparse datasets to make statements of regional or global relevance. There are no data at all for some of the compounds considered in this assessment. There is often a wide range of measured concentrations, and this sometimes reflects the spatial variability of the impact of minor local sources (discussed in Chapter 2) against a low-level 'global' background, as well as temporal changes in both local and extra-regional sources.

The duration and frequency of sampling is rarely adequate for the description of temporal trends. These have been constructed for a few PTS, such as DDT, and these typically agree with global trends, indicating the overwhelming impact of extra-regional emissions as opposed to local input.

Samples from some media provide temporal information in the form of so-called 'archive' samples. Examples are dated sediment series and snow and ice cores. The utility of these data may be restricted by analytical constraints, but in some cases these have the potential to provide important time-series data. Such samples could be exploited to remedy the lack of time-series data for many of the PTSs considered here.

3.2.1 Persistent Toxic Substances – Pesticides

Pesticides are neither manufactured nor applied within the region. The presence of these PTSs in environmental samples is an indicator of extra-regional output. Levels for individual compounds will reflect both the 'global' levels and the transport pathways into different environments within the region. Time series can be constructed for a few pesticides, and these may be comparable with extra-regional trends.

3.2.1.1 Chlordane

3.2.1.1.1 Concentrations in air

Chlordane concentration in air has been measured in three studies, two of which are geographically extensive. Bidleman et al. (1993) undertook a shipborne sampling campaign along a transect from New Zealand to Ross Sea, January to March 1990. Mean concentration of chlordanes plus nonachlors was 1.8 pg m⁻³. As with all compounds measured along this section, concentrations were lowest at Ross Sea end of transect, demonstrating the expected gradient from low-latitude source regions to lower concentrations at high latitude. Their Table 3 shows published values for a range of PTSs in samples from the region collected between 1980 and 1990, and demonstrates apparent decline in all compounds. Kawano et al. (1985) undertook a similar, transect-based sampling programme in the eastern Indian Ocean and in the Southern Ocean south of western Australia during December 1983-January 1984. The Southern Ocean samples comprise data integrated over long transects of 4 and 2 degrees of latitude respectively. Chlordane (sum of cis-chlordane, trans-chlordane and trans-nonachlor) concentrations were 4.8 and 7.5 pg m⁻³ at the northern and southern sites in the Southern Ocean respectively. Finally, Kallenborn et al. (1998) provide air concentration data for a sample site in the southwest Atlantic sector. A seventeen-week sampling campaign was undertaken from December 1994 – April 1995 at Signy Island. The concentration range for chlordanes was 0.04-0.9 pg m⁻³.

The two earlier studies in the early-mid 1980s cover an extensive area and together suggest typical air concentrations of chlordanes over the Southern Ocean of 2-8 pg m⁻³. Although the data of Kallenborn et al. come from a different location in the region, it is unlikely that it would be significantly 'cleaner' than the earlier sample sites. Kallenborn et al. identified the sources of their sampled air, with highest levels coinciding with storm tracks originating in South America. This suggests that all of the studies discussed here can be taken to be broadly comparable, and that there has probably been a decline in air concentrations of chlordanes in the region as a whole between the early 1980s and the late 1990s. Smaller-scale spatio-temporal variability could be linked directly to atmospheric links between the sampling site and sources of contaminated air.

3.2.1.2 Heptachlor and derivatives

3.2.1.2.1 Concentrations in air

Bidleman et al. (1993) measured heptachlor epoxide concentrations in air along an oceanic transect from New Zealand to Ross Sea, January to March 1990. Mean concentration along the transect was 0.52 pg m⁻³, with lowest concentrations at the Ross Sea end of transect. As with chlordane, data reviewed by Bidleman and colleagues suggests a decline in air concentration during the 1980s and early 1990s, but there are no more recent data to assess whether this decline has progressed further.

3.2.1.3 <u>Dichlorodiphenyltrichloroethane (DDT)</u>

DDT and its congeners were some of the first PTSs to be analyzed in Antarctic environmental samples, with positive records from analyses of marine biota in the 1960s and from snow samples in the early 1970s.

3.2.1.3.1 Concentrations in air

There have been several geographically extensive sampling programmes using shipboard sampling on transects from mid-latitudes to the Antarctic coast. Tanabe et al. (1982a,b) undertook air and surface water sampling on an Antarctic supply voyage between Japan and the Syowa Research Station in 1980-81. Total DDT (p,p' DDT, p,p' DDE and o,p' DDT) levels did not show much spatial variability through the study, and Southern Ocean levels ranged from 0.11-0.23 ng m⁻³.

In a later paper, Tanabe et al. (1983) report a similar sampling programme in the environs of Syowa Station and on research voyages in the Indian and Southwest Pacific sectors of the Southern Ocean. Air samples were

collected around Syowa 1981-82, and on two extensive voyages in 1980-81 and 1982. Data along a N-S section from Mauritius to Syowa show marked decline in total air DDT, but DDD-DDT ratio changed little. A year-round sampling campaign at Syowa indicated marked seasonality, with total DDT concentrations higher in summer and lower in winter.

Kawano et al. (1985) collected samples of marine air sampled from ship in the eastern Indian Ocean and in the Southern Ocean south of western Australia during December 1983-January 1984. Total DDTs were 8.4 and 11 pg m⁻³ at the northern and southern sites in the Southern Ocean.

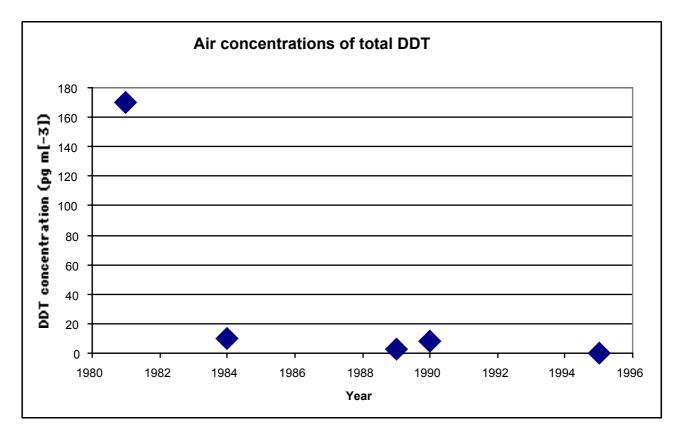


Figure 3-1. Time series of total DDT in air samples from Antarctica. Data sources are cited in the text.

Bidleman et al. (1993) measured a mean air concentration of p,p' DDE plus p,p' DDT of 0.81 pg m⁻³ during a shipborne transect between New Zealand and the Ross Sea during January-March 1990. Concentrations were lowest at the Ross Sea end of the transect. They also review the data for the region between 1980-90, and suggest a decrease in atmospheric DDT concentration. However, they note that the DDT:DDE ratio of 1.5 suggests fresh DDT was still then reaching the region. The decline in DDT in the region, identified by Bidleman et al. (1993) from a range of published data, agrees with the global decline in the same period (Tatsukawa et al. 1990).

In addition to shipborne sampling of marine air, other studies have made measurements on land, albeit close to the coast. Larsson et al. (1992) carried out a monitoring study at Ross Island in 1988-90. They recorded mean air concentration values of DDT+DDE of 3 pg m⁻³. Kallenborn et al. (1998) analyzed air samples at Signy Island from December 1994 –April 1995. Total DDT compounds were present at concentrations of 0.07-0.4 pg m⁻³. This site is closer to potential sources of DDT than is the Ross Sea region, so it would seem likely that the low values recorded in this survey represent a genuine continuation of the decline documented by Bidleman et al. (1993).

3.2.1.3.2 Concentrations in seawater and sea ice

Surface seawater samples collected on an extensive programme in the Indian Ocean and Western Pacific sectors (Tanabe et al.1982a,b) showed little spatial variability. Southern Ocean levels were 5-58 pg dm⁻³. Tanabe et al. (1983) measured DDT in seawater close to Syowa station, and found that concentrations varied

from 1.3-21 pg total DDT dm⁻³. The study included water samples under fast ice and at the outer margins of pack- total DDT was lower under fast ice. This and differences in PCB composition suggest that sedimenting particles are an important process scavenging some compounds from surface seawater.

3.2.1.3.3 Concentrations in precipitation, run-off and terrestrial water bodies

Tanabe et al. (1983) measured DDT concentrations in lake water. Concentrations were similar to those in seawater, varying from 1.3-21 pg total DDT dm⁻³.

3.2.1.3.4 Concentrations in snow and land ice

George & Frear (1966) failed to detect DDT in water and snow sampled around McMurdo Station, although they did detect it in marine mammals and birds. Peterle (1969) provides the first positive record of DDT in Antarctic snow, although Peel (1975) suggests that these values were probably 50 times too high. Risebrough et al. (1976) provide more comprehensive data for DDT concentrations in snow. They collected snow samples during January-February 1975 at from a pit dug in a permanent snow-field on Doumer Island, close to the US Palmer Station and the smaller Chilean Yelchio Station. Concentration of pp'DDT increased with snow depth (i.e. from younger to older snow), ranging from 0.5 pg g^{-1} in the top 0.5 m, rising to 4 pg g^{-1} at 3.5-4 m depth and then declining to 2 pg g^{-1} at 5.5-6 m depth. Concentrations of pp'DDE also increased down the snow profile, and showed a similar shaped distribution. The ratio of p, p"DDT to p, p"DDE was approximately 10 throughout 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 (David Peel pers comm). This would date the DDT and DDE peaks at no earlier than 1970. Tanabe et al. (1983) also measured DDT concentrations 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. Overall snow samples were 9-17 pg total DDT dm⁻³. The bulk density of snow pack is not given, and will be significantly less than 1 kg dm⁻³, but these last concentrations 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.

3.2.1.3.5 Spatial and temporal variability

Overall, snow and air samples provide time series data for DDT deposition in the Antarctic environment, although these data are clearly also affected by other sources of variability. Data for concentrations in air show a marked decline over the sampling period (Figure 3-1). In 1995 the 'background' atmospheric concentration of DDT in the Antarctic and Southern Ocean appears to have been of the order of 0.1 pg m⁻³, whilst concentrations had been as high as 100-200 pg m⁻³ in the early 1980s. Data from snow sampling potentially extend this time series back to the 1960s-70s, when atmospheric concentrations were probably even higher. The ratio of DDE to DDT also appears to be increasing. Risebrough et al. (1976) estimated a ratio of approximately 0.1 for samples of snow which probably span the period 1965-75, whilst Bidleman et al. (1983) calculated a ratio of 0.33. This conforms with the decrease in addition of new DDT to the southern hemisphere atmosphere, although it is clear that fresh DDT continued to reach the region in the 1980s

3.2.1.4 <u>Hexachlorobenzene (HCB)</u>

3.2.1.4.1 Concentrations in air

Bidleman et al. (1993) carried out measurements along their shipborne transect between New Zealand and the Ross Sea, January to March 1990. Mean air concentration of HCB was 60 pg m⁻³. Concentrations were lowest at Ross Sea end of the transect. Their Table 3 demonstrates an apparent decline in HCB concentration over their entire sampling area between 1980 and 1990, but this does not include more samples specific to the region.

3.2.1.5 Hexachlorocyclohexanes (HCH)

3.2.1.5.1 Concentrations in air

Tanabe et al. (1982a,b) collected air and surface seawater samples during an Antarctic supply voyage between Japan and the Syowa Research Station in 1980-81. Highest total HCH concentrations were encountered in the northern hemisphere. Levels were low in air over the Southern Ocean, with a concentration range of 90-170 pg m⁻³. The authors provide detailed discussion of patterns of concentration and characterisation in relation to production and sources. They suggest that HCH composition in Southern Ocean samples corresponded with lindane use in the southern hemisphere. In a later study, Tanabe et al. (1983) sampled both along two extensive cruise tracks and around a coastal Antarctic research station. Air concentrations of HCH were measured along a N-S section from Mauritius to the Syowa Station. There was a marked decline in total HCH towards the southern end of the section, although there was an HCH peak at about 63°S. HCH isomeric composition changed along the transect, with increasing importance of γ HCH south of 63°S. The paper describes regional variation, suggesting that air samples taken off Syowa derived from air over the Atlantic, whilst those taken in Southern Ocean locations south of Australia derived from more contaminated air over the Indian Ocean. A year-round sampling campaign at Syowa indicated marked seasonality in total HCH. Concentrations were higher in summer and lower in winter.

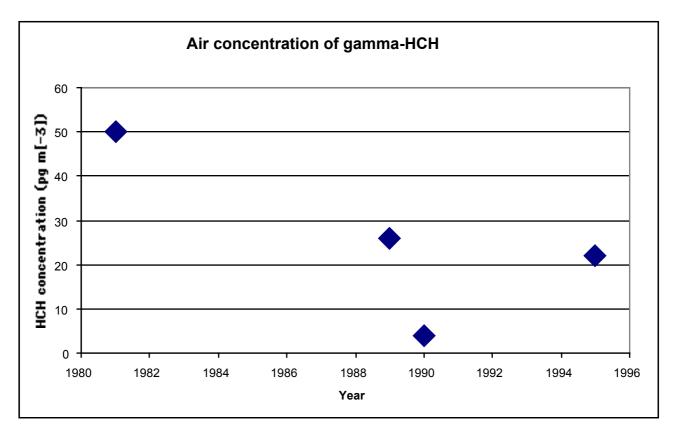


Figure 3-2. Time series of concentration of γ -HCH in Antarctic air samples. Data sources are cited in the text.

Bidleman et al. (1993) found mean air concentrations of α - and γ -HCH 4 and 3.8 pg m⁻³ respectively along a transect between New Zealand and the Ross Sea. As with other PTSs in this study, concentrations were lowest at the Ross Sea end of the transect.

Larsson et al. (1992) carried out a study of various PTSs at Ross Island in 1988-90. The mean air concentration of γ -HCH was 26 pg m⁻³. Highest concentrations occurred in summer – the variation over the period from March to December was 0.5-118 pg m⁻³. Kallenborn et al. (1998) report data from a seventeen week sampling campaign at Signy Island, December 1994 – April 1995. Mean air concentration of γ -HCH was 22 pg m⁻³.

3.2.1.5.2 Concentrations in seawater and sea ice

Tanabe et al. (1982a,b) collected surface seawater samples during an Antarctic supply voyage between Japan and the Syowa Research Station in 1980-81. Lowest levels were found in the Southern Ocean, where concentrations in surface seawater ranged from 260-920 pg dm⁻³. Tanabe et al. (1983) measured HCH concentrations in seawater close to Syowa station, where concentrations varied from 210-930 pg dm⁻³ total HCH. Total HCH concentrations were similar in water samples under fast ice and at outer margins of pack ice, in contrast to data for DDT and PCBs.

3.2.1.5.3 Concentrations in precipitation, run-off and terrestrial water bodies

Tanabe et al. (1983) found that lake water and seawater had similar concentrations, varying from 210-930 pg dm⁻³ total HCH.

3.2.1.5.4 Concentrations in snow and land ice

Inland snow samples collected by Tanabe et al. (1983), both deep and shallow, showed similar levels of total HCH, suggesting similar deposition rate since 1960s. Overall snow sample concentrations were 1500-4900 pg dm⁻³ total HCH. In ice (type not specified) total HCH concentrations were 2000-2200 pg dm⁻³.

3.2.1.5.5 Spatial and temporal variability

In a review of data for the 1980s and early 1990s, Bidleman et al. (1993) demonstrated a decline in HCH air concentrations in the region. Taken with the later data from Kallenborn et al. (1998), this decline appears to be sustained, but seems to be less dramatic than the decrease in DDT over the same period (Figure 3-2), and indicates that input of HCH to the region continues. Air concentrations of γ -HCH of about 20 pg m⁻³ have been recorded as mean values from studies in different parts of the region from the late 1980s through to the mid 1990s. In contrast the lowest recorded levels range from undetectable to about 0.5 pg m⁻³. As Tanabe et al. (1983) point out, there is also considerable spatial variability in atmospheric concentrations of HCH, reflecting differences in source regions and atmospheric transport.

3.2.2 Persistent Toxic Substances - Industrial Compounds

In contrast to pesticides, some industrial compounds have been used within the region, although the quantities used and the resulting contamination remain very low and typically highly-localised. Environmental levels are available only for PCBs.

3.2.2.1 Polychlorinated biphenyls (PCBs)

3.2.2.1.1 Concentrations in air

Tanabe et al. (1982a) measured PCBs in air samples on Antarctic supply voyages between Japan and the Syowa Research Station in 1980-81. Unlike other PTSs analysed in the study, PCB concentrations showed no north-south gradient, although this is at variance with other similarly extensive studies reported here. For instance, Tanabe et al. (1983) report an extensive sampling programme in the environs of Syowa Station and on research voyages in the Indian and Southwest Pacific sectors of the Southern Ocean1980-82. Along a N-S section from Mauritius to Syowa there was a marked decline in total air PCBs. A year-round sampling campaign at Syowa indicated marked seasonality in PCBs - concentrations were higher in summer and lower in winter.

Two more recent studies have been carried out in the south-west Atlantic sector of the region. Kallenborn et al. (1998) conducted a seventeen-week air-sampling campaign on Signy Island from December 1994 –April 1995. Many data were close to detection limits. Concentrations for single PCBs were 0.02-17 pg m⁻³. Ockenden et

al. (2001) established two air-monitoring sites - one in the Falkland Islands (outside the region covered by this report) and at Halley Research Station on the eastern coast of the Weddell Sea. PCBs were monitored throughout 1999. Particulate concentrations were generally below the limit of detection. Vapour-phase concentrations were higher at the Falklands site than at Halley. Higher concentrations at each site coincided with higher temperatures. Concentrations over land were lower than over the adjacent ocean. The authors note that PCB concentrations in the Southern Ocean region were generally higher than in the Arctic. Halley data for mean vapour-phase concentrations for individual PCBs were: PCB 28 2.5 pg m⁻³, PCB 52 <0.1 pg m⁻³, PCB 101 0.25 pg m⁻³, PCB 138 0.4 pg m⁻³, PCB 153 0.3 pg m⁻³, PCB 180 0.2 pg m⁻³.

3.2.2.1.2 Concentrations in seawater and sea ice

Data for surface seawater showed concentrations varying from 35-69 pg dm⁻³ total PCBs (Tanabe et al. 1983). Total PCB concentrations were similar under fast ice and at the outer margins of the pack ice.

3.2.2.1.3 Concentrations in marine sediments

Sampling of marine sediments for PCBs has typically been undertaken in regions of known contamination. Most work has been carried out in the vicinity of McMurdo Research Station in the Ross Sea. Risebrough et al. (1990) found typical total PCB concentration in surface sediment of 500 ng g⁻¹. Composition was identical with Aroclor 1260 in all but one sample. Kennicutt et al. (1995) also sampled PCBs in sediment from Winter Quarters Bay, near the McMurdo Station. They confirmed that the composition corresponded to Aroclor 1260, with little evidence for degradation. PCBs were detected in all sediment samples collected at McMurdo, with total PCB concentrations ranging from 250-4300 ng g⁻¹. Concentrations decreased rapidly away from sources of contamination and the authors describe background levels of 18-28 ng g⁻¹. Risebrough et al. (1990) also measured PCTs (polychlorinated terphenyls) in the contaminated sediments from McMurdo. PCTs were present at levels of 30-1200 ng g⁻¹, with a composition similar to Aroclor 5460. Kennicutt et al. (1995) also analysed three sediment samples from Arthur Harbour, on the Antarctic Peninsula. These samples had total PCB concentrations of 2.8-4.2 ng g⁻¹, values similar to background concentrations at 'clean' sites in the Ross Sea.

3.2.2.1.4 Concentrations in precipitation, run-off and terrestrial water bodies

Tanabe et al. (1983) measured PCB concentrations in a range of samples, including lake water. Lake water and seawater had similar concentrations, varying from 40-70 pg dm⁻³ total PCBs.

3.2.2.1.5 Concentrations in snow pack and land ice

Risebrough et al. (1976) measured total PCB concentration in snow collected from a deep pit in a permanent snow-field on Doumer Island. Snow samples were collected during January-February 1975. PCB concentrations also showed a peak value of 1.2 pg g⁻¹ at 3.5-4 m depth, and ranged from 0.05-0.8 pg g⁻¹ elsewhere in 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 present profile would be little more than a decade before the sampling (David Peel pers comm). Tanabe et al. (1983) also measured concentrations in snow. Inland snow samples, both deep and shallow, showed similar levels of total PCBs, suggesting similar deposition rate at this site between the 1960s and 1980s. Overall concentrations in snow samples were 0.2-1 pg g⁻¹. Ice (type not specified) had total PCB concentrations of 0.3-0.6 pg g⁻¹.

3.2.2.1.6 Temporal and spatial variability

There is a comparatively large amount of data for environmental levels of PCBs, and a dataset that covers the same time-span as the information for DDT and HCH. However, the data on air concentrations of PCBs are too variable to establish any temporal trends. The large-scale geographic trend seen in the study by Ockenden et al. (2001) suggests that air concentrations reflect extra-regional

output and that these concentrations will decrease with increasing latitude. Overall, it seems likely that either air concentrations exhibits high spatial variability, or that there is no significant long-term trend, comparable for instance to that seen in DDT. Data from two analyses of snow samples suggest that there was probably only slight variability over the period 1960-80. Data on PCB concentrations in sediments from 'clean' sites are too few to provide information on temporal trends

3.2.3 Persistent Toxic Substances - Unintended by-products

3.2.3.1 Polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs)

3.2.3.1.1 Concentrations in air

Lugar (1993) and Lugar et al. (1996) report the results of monitoring ambient air around McMurdo Station during 1992-93 and 1993-94 austral summers. Measurements were made at sites clearly exposed to local contamination. Measured concentrations of total PCDDs were 0.12-1.8 pg m⁻³ and PCDFs were <0.02-2.77 pg m⁻³. These appear to be the only data for environmental levels of PCDDs and PCDFs, and the signal is clearly dominated by local contamination. Taking the lowest recorded values, upper limits for background air concentrations could be suggested as ≤ 0.12 pg m⁻³ for total PCDDs and ≤ 0.02 pg m⁻³ for PCDFs.

3.2.3.2 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are probably the PTS which have been analysed most commonly in the region, especially in connection with low-level contamination by long-term human activity in the region, alongside the occasional more serious accidental release of fuel-oil (see Chapter 2).

3.2.3.2.1 Concentrations in air

Most studies refer to the marine environment, and there are few data on atmospheric loadings. Carrichia et al. (1995) determined concentrations of particulate PAH in during austral summers 1990-91, 1991-92 and 1992-93 within 200 m of the Italian research station at Terra Nova Bay, Ross Sea. Low air temperatures implied that most PAH were in particulate rather than vapour phase, and the results suggested that local sources dominated. Concentrations of individual compounds were low - 95% of the 11 compounds analysed were in the range 1-50 pg m⁻³. Overall, total PAH particulate concentrations in air were 15-700 pg m⁻³.

3.2.3.2.2 Concentrations in seawater and sea ice

There are several studies which report PAH in seawater (see review by Cripps, 1992b, for a summary of earlier data). Cripps (1989, 1990a) found that total PAH in surface seawater at South Georgia varied from 0.05-1.19 μ g dm⁻³, and he obtained similar data for a more geographically extensive study in the late 1980s (total PAH in seawater 0.1-1.2 μ g dm⁻³) with highest values close to derelict whaling stations at South Georgia, which are identifiable sources of long-term PAH contamination (see also Platt & Mackie 1979, 1980). Cripps (1990a) reviewed a short time-series of seawater data from the seas around South Georgia and suggested, on the basis of four sampling efforts (1973-90), that local input dominated and there was no significant change over time.

There are also data for supposedly uncontaminated sites. Cripps (1994) found the mean value for total PAH in surface seawater from the Bransfield Strait region to be 0.23 μ g dm⁻³ (range <0.05-1.7 μ g dm⁻³). Cripps (1990b) reported a more localised study close to the Signy Research Station. Total PAH concentrations in seawater varied from 0.11-0.22 μ g dm⁻³. These data showed no trend with distance from the station, suggesting that local contamination was not high enough to establish a concentration gradient in the well mixed coastal waters. Similarly, Cripps (1992a,b) demonstrated that there is little recognizable temporal or spatial pattern in total PAH levels in Southern Ocean samples from a range of locations (Atlantic sector of the Southern Ocean, Bransfield Strait, Weddell Sea and Ross Sea /Terra Nova Bay). The overall range of seawater concentrations in the studies reviewed by Cripps (1992b) was undetectable-9.4 μ g dm⁻³ total PAH.

Local fuel oil spillage can lead to dramatic but short-lived elevation in seawater PAH concentrations. Cripps & Shears (1997) monitored an accidental spill of 1000 dm³ of diesel fuel at Faraday Station, Galindez Island, Argentine Islands. Total PAH in seawater reached 222 μ g dm⁻³ on the day after the spill, but returned to 'background' levels within one week.

3.2.3.2.3 Concentrations in marine sediments

Marine sediments offer a different view of PAH input to the Southern Ocean. Several authors have noted that PAHs in these sediments does not appear to degrade significantly (Platt & Mackie 1979, 1980; Cripps 1990a; Kennicutt et al. 1995) or to disperse (Kennicutt et al. 1995). Thus sediments preserve records of local PAH input. Most seawater samples are indicative of much larger-scale inputs, and the signal of local PAH pollution events appears only to last for a few days in seawater (e.g. Cripps & Shears 1997). Typically, many studies have concentrated on known sources of continuous, low-level pollution or on the effects of transient events. Many such studies use transects leading away from the source of pollution in order to define the spatial scale of contamination, by identifying samples with putative baseline concentrations. In a few cases, the historical record within dated sediment cores has also been used.

Not unexpectedly, there is a large volume of data for marine sediments in the vicinity of research stations. Kennicutt et al. (1995) determined total PAH in sediments close to McMurdo in 1990-91 and 1992-93, where levels ranged from undetectable to $>6000 \text{ ng g}^{-1}$ (all values expressed on dry mass basis), with values up to 13 000 ng g⁻¹ in Winter Quarters Bay. Predominance of napthalene and phenanthrene in highly contaminated samples indicated that the main contribution came from spilt fuel. Pyrogenic PAH paralleled fuel PAH concentrations, suggesting a common origin. Kennicutt et al. (1992a, 1995) report data from the vicinity of Palmer Research Station on the Antarctic Peninsula, reflecting both the long-term, low-level input from research stations in the Arthur Harbour area and the fuel spillage arising from a shipwreck (Kennicutt et al. 1991). Marine sediment collected along a series of transects radiating from the current station area had total PAH nd - 11 540 ng g⁻¹, of which napthalenes nd - 9 500 ng g⁻¹, fluorenes nd - 3700 ng g⁻¹, and phenathrenes $nd - 3700 \text{ ng g}^{-1}$. Total PAH in marine sediment close to the old Palmer station was up to 60 000 $ng g^{-1}$. Kennicutt et al. (1991) provide a detailed description of the spatial extent and fate of PAH from the grounding of the Bahia Paraiso January in 1989, when an estimated 600 000 dm³ of Diesel Fuel Arctic were released. The spill dispersed rapidly in the high-activity environment. Time series of intertidal sediments show decline in total PAH from 700-1700 ng g⁻¹ in early February to about 500 ng g⁻¹ in early March. Composition of PAHs in sediment samples indicated complex sources, including fuel and other oils, weathered components, and combustion products. Cripps (1990b) measured sediment total-PAH concentrations along a 3-km transect seawards from Signy Research Station, South Orkney Islands. Total PAH concentrations in the surface sediment decreased with increasing distance from the station, from 300 ng g⁻¹ close to station to about 10 ng g⁻¹ 500 m away. Hydrocarbon pollution would have been associated with the station activities, including a small spill in 1965.

Green et al. (1992) sampled around Davis Station, and found PAH in all environmental and biotic samples, but at low levels (parts per trillion). Very high levels were recorded in basin sediments from Ellis Fjord (2240-7270 ng g⁻¹), in comparison with well mixed oxic sediments, suggesting long-term accumulation of PAH in anoxic sediments. The PAH composition suggested that local input dominates, predominantly derived from hydrocarbon fuels, rather than global sources of combustion products.

3.2.3.2.4 Concentrations in terrestrial soils and lake sediments

There are a few analyses of terrestrial environmental samples, again typically from close to research stations. Kennicutt et al. (1992a) determined PAH in soil from contaminated areas around the old Palmer station, and detected very high PAH contamination in one soil sample with a concentration of 345 000 ng g⁻¹. Green & Nichols (1995) found that PAHs were present throughout the environment around Davis station in both soils and marine sediments - predominantly napthalenes, fluorenes and phenanthrenes. However, concentrations were typically very low, and often close to limits of detection. Concentrations of individual PAHs only exceeded 1 ng g⁻¹ (dry mass) around the fuel depot and at the sewage outfall.

3.2.3.2.5 Summary of data

The information on environmental levels of PAHs is extensive, although many data relate to local sources which are unrepresentative of the region as a whole. Baseline levels can be estimated for some environmental media. Generally, uncontaminated seawater has PAH concentrations $\leq 1 \ \mu g \ dm^{-3}$. PAH concentrations in marine sediments vary from undetectable to about 10 ng g⁻¹. At sites of local contamination, corresponding values can be much higher: >200 $\mu g \ dm^{-3}$ (for short periods) in seawater and >60 000 ng g⁻¹ in long-term contaminated sediments. Levels in contaminated soils can be even higher than this, but again the extent of such contamination is very limited.

There appears to be no temporal trend in the environmental loading of PAHs. This is expected, because PAH output has a long history, and the introduction to PAH to the region is an irregular combination of global input, low-level and long-term natural and anthropogenic sources, and catastrophic incidents.

3.2.4 Organometals

Input of organometals to the Antarctic environment probably derives from a complex combination of sources, some of which may be considered 'global' whilst others are local, predominantly low-level but long-term and often widely dispersed. Studies of heavy metal concentrations in snow and ice cores provide records of natural and anthropogenic changes in atmospheric loadings over varying timescales, but do not distinguish orgaznometals from other forms. Boutron & Patterson (1986) measured lead concentration changes in an Antarctic ice core spanning the Wisconsin-Holocene transition, and identified climatic and tectonic factors determining atmospheric particulate lead loading. Vandal et al. (1993) provide similar information on variations in mercury deposition to Antarctica over the past 34 000 years. Comparison of Greenland and Antarctic cores reveals interhemispheric differences in atmospheric lead concentrations (Murozumi et al. 1969). Shorter timescale studies have pinpointed the effects of local and global input of lead (Görlach & Boutron 1992; Wolff 1992; Suttie & Wolff 1993; Wolff & Peel 1994; Wolff et al.1994, 1999; Barbante et al. 1998).

3.2.4.1 Organotin compounds (OTs)

There are no data on the presence of organotin compounds in the Southern Ocean environment. It is quite likely that these compounds will have been used to some extent as anti-fouling on ships working within the Southern Ocean, but this would represent a very minor input. Such anti-fouling would not be applied within the region.

3.2.4.2 Organomercury compounds

Despite a moderately extensive literature on the occurrence of mercury in a range of environmental samples, there are few studies which provide independent measurements of organo-mercury compounds. DeMora et al. (1993) collected 196 air samples at Scott Base and Arrival Heights on Ross Island 1987-1989. Dimethylmercury was typically about 10% of total gaseous mercury, with mean value for all three years of 0.04 ng m⁻³ (range nd-0.63 ng m⁻³).

3.2.5 Overall conclusions – environmental levels and trends

Data have been presented for a subset of the suite of PTSs covered by the regional assessment. For those pesticides where adequate data are available, environmental levels are typically low and time series reflect the history of pesticide use outside the region. For chlordane, concentrations in air over the Southern Ocean in the 1990s were 0.04-0.9 pg m⁻³, decreasing from 2-8 pg m⁻³ in the early-mid 1980s. Data for atmospheric DDT concentrations suggest a more dramatic decline. In 1995 the 'background' atmospheric concentrations had been as high as 100-200 pg m⁻³ in the early 1980s. Data from snow samples suggest that levels in the 1960s and 1970s might have been even higher. By contrast, HCH does not appear to have decreased by such a large amount. Air concentrations of γ -HCH of about 20 pg m⁻³ have been recorded as mean values from studies in different parts of the region from the late 1980s through to the mid 1990s.

Whereas pesticides can be clearly identified as being extra-regional in origin, industrial compounds may be released within the region (albeit at low levels). There is a comparatively large amount of data for environmental levels of PCBs, and a dataset that covers the same time-span as the information for DDT and HCH. However, data on air concentrations of PCBs are too variable to establish any temporal trends, and it seems likely that either air concentrations exhibits high spatial variability, or that there is no significant long-term trend, comparable for instance to that seen in DDT. Furthermore, data from two analyses of snow samples suggest that there was probably only slight variability over the period 1960-80. Air concentrations for single PCBs in the studies reported here were 0.02-17 pg m⁻³. Data on PCB concentrations at such sites were in the range 2.8-4.2 ng g⁻¹, whereas samples from contaminated sites were 250-4300 ng g⁻¹.

Data for 'unintended by-products' are sparse, with the exception of PAHs. For dioxins and furans, upper limits for background air concentrations could be suggested as ≤ 0.12 pg m⁻³ for total PCDDs and were ≤ 0.02 pg m⁻³ for PCDFs. Sources of PAHs are complex, involving local and global sources. Baseline levels can be estimated for some environmental media. Generally, uncontaminated seawater has PAH concentrations ≤ 1 µg dm⁻³. PAH concentrations in marine sediments vary from undetectable to about 10 ng g⁻¹. At sites of local contamination, corresponding values can be much higher: >200 µg dm⁻³ (for short periods) in seawater and $\geq 60\ 000$ ng g⁻¹ in long-term contaminated sediments. Levels in contaminated soils can be even higher than this, but again the extent of such contamination is very limited.

3.3 LEVELS AND TRENDS – BIOTA

Data on PTS loadings in Antarctic biota are often patchy, and typically result from one-off studies rather than systematic monitoring effort. The terrestrial ecosystem is poorly developed, and there are no large plants or animals. Most data for terrestrial biota are derived from analysis of lichens and bryophytes (e.g. Bacci et al. 1986). It is likely that the processes by which pollutants reach these organisms and accumulate are complex, and will vary from one PTS to another and from one site to another. Many study sites will be at coastal and island sites, where many research stations are located and where ecosystem development is maximal. The presence of some pollutants, such as PAH and organometals, will undoubtedly often include a significant local component associated with long-term human habitation close to the site. The presence of land-breeding marine birds and mammals will also provide a strong linkage between the terrestrial community and the marine ecosystem at coastal locations. It should also be noted that most of the terrestrial vegetation is very slow-growing, and that biomass often accumulates in the absence of significant grazing and slow microbial breakdown. Thus vegetation samples used for PTS analysis may represent decades of accumulation.

The marine ecosystem provides very different conditions in the context of measurements of PTSs in biota. In the pelagic system, vegetation comprises microscopic phytoplankton with very short turnover times. Zooplankton, however, tend to be large and often long-lived. Predators include cephalopods, fish, birds and mammals. With the exception of cephalopods, these predators are typically long-lived. Many species of birds and mammals migrate to lower latitudes, or even into the high-latitude northern hemisphere, in the austral winter, so that their pollutant loading will integrate input from both outside and within the region in the case of PTS with long turnover times. Even at lower levels in the food web, the mobility of pelagic organisms means that they will integrate environmental PTS loading over large spatial and temporal scales. The pelagic ecosystem is dominated by short food chains which transfer primary production to top predators with relatively high efficiency (Priddle et al. 1998). This would tend to reduce the amplification of pollutant loadings resulting from biomagnification in more complex food webs. However, Van den Brink (1997) points out that coldcondensation implies that polar regions will be a sink for the most volatile pollutants, and that these may then be present at higher environmental levels than at lower latitudes. On this basis, animals occupying a specific trophic niche in a polar ecosystem may have higher PTS loading than the corresponding species in a temperate or tropical ecosystem.

Benthic marine organisms have also been sampled for a range of PTS. Their restricted mobility and contact with substrate makes them more useful as monitors of local pollution. However, again organisms tend to be slow-growing and long-lived, so that some pollutants will tend to be accumulated over long periods of time.

Feeding and growth exhibit strong seasonal patterns, implying that capacity for uptake of PTS by benthic animals will vary through the year. Interpretation of PTS loading in known-age individuals can be complex (Cripps & Priddle 1995).

There are no data on PTS loadings in humans living in the region. As noted already, there are no indigenous peoples, and those persons present in the region typically spend no more than a few months to a year there.

Reporting units vary widely in the published data. Here, the only alterations to values have been to bring them to common concentration units. The tissue basis of the measurement (ie fresh mass, dry mass, total lipid, or a particular organ) have been stated where these are clear from the original published source, but there has been attempt to inter convert values (eg bring all data to a whole organism dry mass or total lipid basis). Where no tissue basis has been given, concentration per unit of fresh mass of whole organism or tissue has been assumed. The level of comparability of different values is indicated where possible. Full 'scientific' binomial names and accepted English language equivalents are given in Appendix 3.

3.3.1 Persistent Toxic Substances – Pesticides

No pesticides are manufactured or applied in the region, and all input comes from extra-regional sources.

3.3.1.1 <u>Aldrin and Dieldrin</u>

3.3.1.1.1 Marine ecosystem

There are only a few reports of dieldrin concentrations in biota, and these are widely separated in space and time. Joiris & Overloop (1989, 1991) and Joiris & Holsbeek (1992) found consistent levels of dieldrin of 9 ng g^{-1} DM in particulate material (predominantly phytoplankton) sampled from the Indian Ocean sector and the southwest Atlantic sector of the Southern Ocean between 1987-89. Joiris & Overloop (1989, 1991) note that aldrin was undetectable in the same samples.

Remaining data come mainly from samples from birds and mammals. Tatton & Ruzicka (1967) analysed samples of marine animals from Signy Island, collected in the mid-1960s. Penguin, seabird, fish and krill tissues were taken remote from the small research station. Measured levels of dieldrin ranged from not detectable-9 ng g⁻¹. Donnewald et al. (1979) measured levels of PTSs in penguin subcutaneous fat at Paradise Bay, northern Antarctic Peninsula, in January-February 1973. Concentrations of dieldrin were 11-62 ng g⁻¹ fat. Schneider et al. (1985) measured dieldrin in adipose tissue from seals and birds collected along the ice shelf in the Weddell Sea in austral summer 1980-81. Overall levels were low, although high levels of dieldrin was undetectable in all crabeater and Weddell seal samples. Gardner et al. (1985) analysed eggs from a total of 24 species of seabirds sampled at Marion and Gough Islands and islands off the South African coast. Lowest levels were found in birds at Marion Island. The range of dieldrin concentrations was 0.1-15.9 ng g⁻¹. Highest levels were found in Antarctic skua and wandering albatross. Finally, Van den Brink (1997) gives data on dieldrin concentrations in various tissues from Adelie penguins collected in 1991-92. Concentrations in subcutaneous fat ranged from not-detectable – 40 ng g⁻¹ lipid mass.

3.3.1.1.2 Summary

If these samples can be treated as comparable, they suggest that there has been a gradual increase in dieldrin levels in birds, although levels remain low compared with the loadings of some other pesticides. However, a trend based on such few samples must be treated with considerable caution. There are too few data on organisms other than birds and mammals to indicate whether dieldrin concentrations differ significantly between different trophic levels in the marine food web.

3.3.1.2 <u>Endrin</u>

3.3.1.2.1 Marine ecosystem

Donnewald et al. (1979) measured endrin concentrations of 20-90 ng g^{-1} fat in 30 samples of subcutaneous fat from gentoo penguin, at Paradise Bay, Antarctic Peninsula, in January-February 1973. This appears to be the only published record for this PTS in biota in the region.

3.3.1.3 Chlordane

3.3.1.3.1 Marine ecosystem

Data for chlordane are patchy, and will not support any description of temporal or spatial variability. Kennicutt et al (1995) determined chlordane compounds in benthic biota sampled at McMurdo 1990-91 and 1992-93 Compounds identified include alpha-chlordane and trans- and cis-nonachlor. Weber & Goerke (1996) analysed tissues from various species of fish, especially *Chaenocephalus aceratus*, *Chamsocephalus gunnari* and *Gobionotothen gibberifrons* collected between 1987 and 1991. Concentrations were similar in liver and adipose tissue for all species, and tissue concentrations were not related to body size. Concentrations of transnonachlor 0.5-6 ng g⁻¹ extractable organic matter. Luckas et al. (1990) noted that Weddell seal blubber showed high levels of transnonachlor. Van den Brink (1997) could not detect transnonachlor in fat samples from Adelie penguins, but found mean levels of 51 and 168 ng g⁻¹ lipid in Cape petrels and Southern fulmars respectively. This again suggests that those species which range widely accumulate much of their PTS burden outside the region, and will exhibit higher levels.

3.3.1.4 Heptachlor and derivatives

3.3.1.4.1 Marine ecosystem

Tatton & Ruzicka (1967) collected various samples of marine biota from Signy in the mid-1960s, remote from the small research station. Samples included tissues from penguin, seabirds, fish and krill. Measured levels of heptachlor epoxide (metabolite of heptachlor) ranged from not detectable-730 ng g⁻¹, with the highest levels in skua fat. Joiris & Overloop (1989, 1991) and Joiris & Holsbeek (1992) measured an average heptachlor epoxide concentration of 27 ng g⁻¹ DM in particulate material (predominantly phytoplankton) sampled from the Indian Ocean sector and the southwest Atlantic sector of the Southern Ocean between 1987-89. Heptachlor itself was undetectable in the same samples.

These few data do not allow any generalisation about the occurrence of heptachlor and its derivatives in Antarctic marine biota, except to note the likely predominance of the metabolite heptachlor epoxide over the parent compound, which would be expected on the basis of the extra-regional origin of the PTS.

3.3.1.5 <u>Dichlorodiphenyltrichloroethane (DDT)</u>

The detection of DDT and its derivatives in marine biota from the early 1960s onwards was a powerful demonstration of the pervasiveness of global pollution by this class of PTS (Sladen et al. 1963; George & Frear 1966; Tatton & Ruzicka 1967; Conroy & French 1974 – see also review by Hidaka, & Tatsukawa 1981). This long and relatively comprehensive data series means that there is probably better information for DDT and its derivatives than for any other class of PTS.

3.3.1.5.1 Terrestrial ecosystem

There is only one set of data for the terrestrial biota. Bacci et al. (1986) analysed a suite of lichen and moss samples collected in 1985 from Port Lockroy, Galindez Island and Rothera Point. Concentrations of p,p' DDE varied from 0.1-0.6 ng g⁻¹, and p,p' DDT was 0.08-0.9 ng g⁻¹. These plants could have accumulated their PTS loading over a long period, and the routes by which they received DDT could have included atmospheric deposition, marine aerosol (sites are close to the coast) and perhaps bio-transport.

3.3.1.5.2 Marine ecosystem - plankton

There are data for several trophic levels in the more complex marine ecosystem. Łukowski & Ligowski (1987) sampled plankton diatoms in 1983-84 in Admiralty Bay, King George Island and from around South Orkney Islands. Concentrations of p,p' DDE ranged from not detectable-14.0 ng g⁻¹ (fresh mass). Highest levels were found in Admiralty Bay samples. Joiris & Overloop (1989, 1991) found that p,p' DDE and p,p' DDT were undetectable in bulk phytoplankton samples collected over a wide area of the Southern Ocean in 1987-89.

Eukowski (1978a) analysed p,p' DDE, p,p' DDD and p,p' DDT in samples of krill from Drake Passage, Bransfield Strait and Scotia Sea February-March 1976. Measurements were made on homogenised whole animals, and total DDT was 20-65 ng g⁻¹ (fresh mass). Variability was linked to age of animals in individual samples and to geographic location. Higher DDT proportion (i.e. non metabolised) and higher levels in the west of the sampling area suggests that this region experienced higher environmental loading. A second study also includes data for Antarctic krill, collected at about the same time at the Antarctic Peninsula. Risebrough et al. (1976) present data for a single sample of krill collected in October 1975. This contained p,p' DDE 14 ng g⁻¹ lipid mass, p,p' DDT 19 ng g⁻¹ lipid mass, which is broadly comparable with the data of Eukowski (1978a). The ratio of p.p' DDE to p,p' DDT in these studies indicates that a high proportion of unmetabolised DDT entered the ecosystem at this time.

3.3.1.5.3 Marine ecosystem - fish

Five studies provide data on DDT loadings in fish. Monod et al. (1992) found that DDT was very low or not detectable in fish sampled at Îles Kerguelen in 1971 and 1975. Subramanian et al. (1983) sampled *Pagothenia bernachii* in the vicinity of Syowa Research Station in the early 1980s. Whole fish concentrations of total DDT averaged 0.7 ng g⁻¹ fresh mass. Their data suggested that DDT continued to accumulate over the fishes' lifetime. Larsson et al. (1992) measured levels of DDT in the liver of *Pagothenia bernachii* sampled at Ross Island. The mean concentration of DDT was 10 ng g⁻¹ fat weight. Weber & Goerke (1996) sampled various species of fish off the Antarctic Peninsula between 1987 and 1991, especially *Chaenocephalus aceratus, Chamsocephalus gunnari* and *Gobionotothen gibberifrons*. Concentrations of *p.p*' DDE were 2-40 ng g⁻¹ EOM (extractable organic matter) and were one to two orders of magnitude lower than in North Sea fish. Concentrations were similar in liver and adipose tissue for all species, and concentrations were not related to body size (in contrast to the conclusions of Subramanian et al. 1983).

Focardi et al. (1992) present data for a range of fish species, but mainly *Chionodraco hamatus* and *Pagothenia bernacchii*, sampled in 1987-88 and 1989-90. Concentrations in liver were about ten times the levels in muscle, and ranged from 25.0 (range 17.2-31.9) to 52.7 (23.5-75.6) ng g⁻¹ DM for *p.p*' DDE in the two species, and 14.6 (8.5-21.0) to 8.1 (5.3-15.3) ng g⁻¹ DM for *p.p*' DDT. Data in the different studies are presented on different tissue and mass bases. Despite this, it appears that DDT levels in Antarctic fish increased over the

period from the mid 1960s to the late 1980s, although they remain low compared with polluted sites elsewhere. Where data on the ratio of p,p' DDE to p.p' 'DDT are available, they appear to be similar to data for krill.

3.3.1.5.4 Marine ecosystem – birds and mammals

Analyses of DDT and derivatives in various tissues from marine birds and mammals provide the largest body of data, although there is considerable inter-species variability potentially masking temporal and spatial trends. The samples from the 1960s and early 1970s comprise tissue samples from seals, penguins and seabirds (Sladen et al. 1963; George & Frear 1966; Tatton & Ruzicka 1967; Conroy & French 1974). Many of these studies detected DDT in only some of the animals sampled. Tatton & Ruzicka (1967) analysed samples from Signy Island, remote from the small research station, collected in mid 1960s. For a diverse range of samples, measured levels of *p.p* ' DDE ranged from 1-26 000 ng g^{-1} fresh mass, *p.p* ' TDE from not detectable-18 ng g^{-1} , *p.p* ' DDT from1-2500 ppm. Subcutaneous fat in skuas had the highest levels, which is consistent both with its extensive dispersal outside the breeding season and its carrion diet.

Conroy & French (1974) found no DDT or DDE in Emperor penguins from the Weddell Sea (collected in 1971) but found that p,p' DDE in giant petrels from Signy Island (1968-69) increased with age. Liver concentration of p,p' DDE in giant petrels ranged from 20 ng g⁻¹ (fresh mass) at 80 days age to 30 ng g⁻¹ (fresh mass) at 5-15+ years old. There was no p,p' DDT except in one sample. It seemed likely that the giant petrels accumulated most of their pollutant load outside the Antarctic. Monod et al. (1992) found that DDE present was in all birds sampled at Îles Kerguelen in 1971 and 1975, but DDD and DDT were present only in penguins and albatross. Risebrough et al. (1976) collected data for three pygoscelid penguin species at the Antarctic Peninsula from January 1970-January 1975. Concentrations of p,p' DDE ranged from 66-380 ng g⁻¹ lipid mass with no evidence for significant interspecies or temporal variation. Donnewald et al. (1979) measured average levels of DDT and related compounds in penguins at the northern part of the Antarctic Peninsula in 1973. Concentrations were p.p' DDE: nd-460 ng g⁻¹ fat, p,p' DDT : nd-87 ng g⁻¹ fat, and p,p' DDD: <10 ng g⁻¹ fat. Note that in this range of samples from the 1960s to 1970s, the ratio of p,p' DDE to p,p''DDT is high, with DDT being undetectable in some samples and the ratio in others being 5-10.

Eukowski (1983a,b) measured levels of DDT and derivatives in penguins and seabirds at Admiralty Bay (King George Island, South Shetland Islands) in the late 1970s. In adult penguins p,p' DDE and trace amounts of p,p' DDT were found, but p,p' DDE only in the eggs. There was no significant difference between species. Penguin fat concentrations of p,p' DDE plus p,p' DDT ranged from 340-550 ng g⁻¹ (fresh mass). In flighted seabirds, p,p' DDE predominated, reaching levels of 400-8 000 ng g⁻¹ (fresh mass) in fat tissue. *Oceanites oceanicus* (storm petrel) had the highest levels, and is the species with the most wide-ranging migration outside breeding season. It may also accumulate DDT residues by scavenging on fat from carcasses. The author suggests that the low level of DDT relative to DDE in these samples indicates little input of 'new' DDT, coupled with the persistence of DDE.

Schneider et al. (1985) sampled adipose tissue from a range of seals and birds collected along the ice shelf in the Weddell Sea in austral summer 1980-81. Overall ranges were p,p' DDE 46-3370 ng g⁻¹ lipid mass, p.p' DDT 7-953 ng g⁻¹ lipid mass. Levels are still relatively low in these samples, and p,p' DDE continued to be found at higher levels than p,p' DDT. The highest levels were found in south polar skuas, which migrate out of the region. Karolewski et al. (1987) also analysed adipose tissue from five Antarctic seal species (collected at King George Island 1979-1981). Highest overall level was in leopard seal -p,p' DDT 158-164 ng g⁻¹ (fresh mass), p,p' DDE 267-456 ng g⁻¹ (fresh mass). DDT was undetectable in elephant, Weddell, crabeater and fur seals. Concentrations of p,p' DDE varied from species to species, from 5-36 ng g⁻¹ (fresh mass) in crabeater seal to 54-69 ng g⁻¹ (fresh mass) in Weddell seal. Contrasts between species reflect feeding ecology. The leopard seal is an apex predator feeding mainly on penguins and other seals, the Weddell seal feeds on fish and squid, whilst the crabeater seal feeds on krill.

Luke et al. (1989) provide a comprehensive picture of DDT loadings in Antarctic seabirds, based on analyses of eggs from 15 species of seabirds at Davis and Casey stations (1981-83) on the coast of Eastern Antarctica, and from Macquarie Island (1978-83). DDE concentrations varied markedly – Adelie and Emperor penguins from Davis showed very low levels of 4 and 10 ng g^{-1} fresh mass respectively, whilst Gentoo, Royal and Rockhopper penguins from Macquarie were 40, 40 and 20 ng g^{-1} fresh mass respectively. Differences relate both to

geography and diet. Data for flighted birds - petrels, albatross and skua - were more variable, and can also be related to range and diet. Petrels breeding near Davis have limited dispersal and had p,p' DDE levels 10-20 ng g⁻¹ fresh mass (similar to Davis penguins). By contrast, birds such as storm petrels and giant petrels which spend much of their life outside the Southern Ocean had higher levels – Wilson's storm petrel from Davis and Casey had p.p' DDE 60-1800 ng g⁻¹ fresh mass, giant petrels from Macquarie p,p' DDE 170-1530 ng g⁻¹ fresh mass (the northern race having higher loadings than the southern race). There was apparently consistent increase in p,p' DDE levels in giant petrel eggs over the period of sampling – southern race 360 ng g⁻¹ fresh mass in1978, 430 in 1979 and 620 in1983, and northern race 810 ng g⁻¹ fresh mass in 1979 and 950 in 1983. Gardner et al. (1985) also measured DDT in eggs from 24 species of seabirds sampled at Marion and Gough Islands and islands off the South African coast. Lowest levels were found in birds at Marion Island. Concentrations of p,p' DDE ranged from 9-589 ng g⁻¹, and p,p' DDT from 2-70 ng g⁻¹. Highest levels were found in Antarctic skua and wandering albatross. Subramanian et al. (1986) recorded p,p' DDE concentrations of 119-804 ng g⁻¹ lipid mass in Adelie penguins collected in 1981 close to Syowa Research Station.

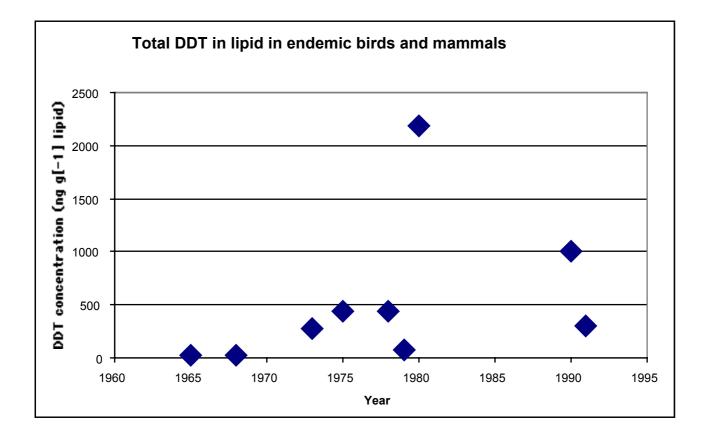


Figure 3-3. Time series of concentration of total DDT in lipid in endemic marine birds and mammals sampled in Antarctica from 1965-95. Data sources are cited in the text.

Van den Brink (1997) analysed DDT and derivatives in Cape petrels from King George Island, sampled in 1991 (about a decade after the study of Łukowski, 1983b, in the same area). These later data from a range of tissues showed mean level of total DDT 3000 ng g⁻¹ (lipid mass). These data appear to indicate little reduction in DDT loadings to seabirds between the late 1970s and the early 1990s. Van den Brink's data on Adelie penguins can be compared to data from Tatton & Ruzicka (1967), Conroy & French (1974) and Łukowski (1983a), although the samples are more widely spread. Van den Brink's data indicate mean tissue concentrations of about 300 ng g⁻¹ (lipid mass), which is higher than the earliest data for penguins but comparable to data from the late 1970s.

Finally, there is also a small dataset for seal tissue which can be compared with the earliest records from the region. Luckas et al. (1990) examined samples of seal blubber from various locations, including four Weddell seals collected in the Weddell Sea. Mean levels were p,p' DDE 67 ng g⁻¹ blubber fresh mass, p,p' DDD 4 ng g⁻¹

¹ blubber fresh mass, p,p' DDT 35 ng g⁻¹ blubber fresh mass. These levels appear to be slightly higher than data for animals collected in the 1960s.

3.3.1.5.5 Summary – trends in DDT levels in the marine ecosystem

Overall, data for birds and mammals endemic to the region suggest that levels of DDT and derivatives increased over the period from the early 1960s to the early 1980s (Figure 3-3). Since the mid-1980s, levels appear to have fallen slightly, but less so than might be expected from regional and global environmental data (Bidleman et al.1993, and Tatsukawa et al.1990 respectively). It is difficult to assess whether the ratio of DDE to DDT concentrations has changed significantly over the same period, against a background of inter-species and other sources of variability. Many of the first measurements provide only a crude estimate of the DDE:DDT ratio, because of a combination of low levels as the pesticide spread into the region, and poor analytical resolution. It is clear that DDE has always predominated in biota, even though Bidleman et al (1993) suggested that significant input of fresh DDT was still evident in environmental samples collected in 1990. For data from biota reviewed here, DDE:DDT varied widely, and it is not easy to construct a temporal pattern. The 1960s data of Tatton & Ruzicka (1967) suggest that DDE:DDT ratio was about 10, even taking into account species ranging outside the region. Commenting on data from the late 1970s, Lukowski (1983a,b) pointed out that the high DDE:DDT ratio indicated that little new DDT was represented in biotic loadings. The extensive study by Gardner et al. (1989) in the early 1980s also suggests a DDE:DDT ratio of 10, although data on highlatitude seals from Luckas et al. (1990) gave a DDE:DDT ratio of 2. Data from most recent samples of endemic penguins, (Van den Brink 1997) suggests that DDE:DDT ratio may have risen to 20. Taken together, these data are indicative of the persistence of DDE in the biota and environment, despite a significant fall in the input of 'new' DDT and DDE from outside the region.

For the marine ecosystem as a whole, it is clear that DDT and its derivatives are persistent, despite significantly reduced input to the region over the course of the period of sampling (mid 1960s to early 1990s). There do not appear to be major differences in tissue loadings between different levels in the marine ecosystem, when only those top predators which are endemic to the region are considered (Figure 3-4). This may reflect the short food chains typical of the Southern Ocean pelagic ecosystem.

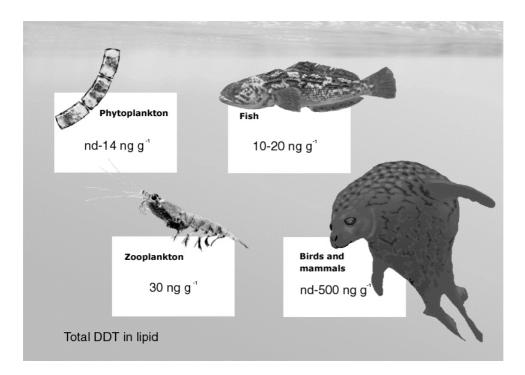


Figure 3-4. Concentration of total DDT in lipid at various levels of the Antarctic marine food web. Levels in top predators such as birds and mammals are highly variable, but significant bioaccumulation of DDT at the top of the food web does not appear to be taking place. Data combined from sources cited in the text

3.3.1.6 <u>Toxaphene (Polychlorobornanes and camphenes)</u>

3.3.1.6.1 Marine ecosystem

High levels of toxaphene were found in blubber of Weddell seals from the Weddell Sea by Luckas et al. (1990). This appears to be the only published record. The presence of toxaphene in animals which typically had low levels of other PTSs (such as HCB, HCH, DDT) may indicate that toxaphene contamination in the Antarctic marine ecosystem is widespread. However, it is hard to imagine that the many other studies of top predators in the region would have failed to detect the compound.

3.3.1.7 <u>Mirex</u>

3.3.1.7.1 Marine ecosystem

There is little information on levels of mirex and its degradation product photomirex in Antarctic biota. Weber & Goerke (1996) claim the first record. They present data for various species of fish collected between 1987 and 1991off the Antarctic Peninsula, especially *Chaenocephalus aceratus, Chamsocephalus gunnari* and *Gobionotothen gibberifrons*. Concentrations were similar in liver and adipose tissue for all species, and concentrations were not related to body size. Concentrations of mirex were 0.5-12.5 ng g⁻¹ extractable organic matter. Van den Brink (1997) analysed subcutaneous fat from three species of seabird. Adelie penguins had an average mirex concentrations were probably overestimated). Levels were higher for two species of flighted seabirds which have greater dispersal. Cape petrels had an average mirex concentration of 2328 ng g⁻¹ fat, and photomirex 508 ng g⁻¹ fat. These last data suggest that top predators feeding outside the region may accumulate high mirex burdens, whilst fish and endemic avian predators have lower loadings, of the order of \leq .100 ng g⁻¹ fat for endemic birds. The paucity of data precludes any statement on spatial or temporal variability.

3.3.1.8 Hexachlorobenzene (HCB)

3.3.1.8.1 Terrestrial ecosystem

Bacci et al. (1986) measured HCB concentrations of 0.30-2.16 ng g⁻¹ dry mass in lichen and moss samples collected 1985 from Port Lockroy, Galindez Island and Rothera Point. This appears to be the sole record for the terrestrial ecosystem.

3.3.1.8.2 Marine ecosystem - plankton

Data for the more complex marine ecosystem cover a range of trophic levels. –Lukowski & Ligowski (1987) sampled plankton diatoms in 1983-84 in Admiralty Bay, King George Island and from around South Orkney Islands. HCB was present only at trace concentrations or was undetectable.

3.3.1.8.3 Marine ecosystem - fish

Weber & Goerke (1996) sampled various species of fish off the Antarctic Peninsula, especially *Chaenocephalus aceratus, Chamsocephalus gunnari* and *Gobionotothen gibberifrons* between 1987 and 1991. Concentrations of HCB were about 20 ng g⁻¹ EOM (extractable organic matter), similar to levels found in North Sea fish and interpreted as result of cold condensation increasing environmental levels. Focardi et al. (1992) present data for other fish species sampled in the Ross Sea region in 1987-90. Most data refer to two species, *Chionodraco hamatus* and *Pagothenia bernacchii*, and HCB concentrations in the liver were 8.4 (range 5.0-12.2) ng g⁻¹ DM and 3.4 (1.2-6.5) ng g⁻¹ DM respectively. Allowing for the fact that data from the two

studies are expressed on different tissue bases (EOM and tissue dry mass respectively), their results are broadly similar.

3.3.1.8.4 Marine ecosystem – birds and mammals

Birds and mammals are important top predators in the marine ecosystem, and five studies summarise the data on HCB levels in these animals. The earliest data are for penguins sampled at the Antarctic Peninsula in 1973. Donnewald et al. (1979) found HCB concentrations in subcutaneous fat ranging from 87-600 ng g^{-1} fat. Luke et al. (1989) analysed eggs from 15 species of seabirds at Davis and Casey stations (1981-83) on the coast of Eastern Antarctica, and from Macquarie Island (1978-83). Levels of HCB were similar in all penguin eggs (10-20 ng g^{-1} fresh mass). Petrels, albatross and skua data were more variable, and this variability can be related to range and diet. Petrels breeding near Davis have limited dispersal and had HCB levels similar to Macquarie penguins (mean 40 ng g^{-1} fresh mass). By contrast, birds such as storm petrels and giant petrels, which spend much of their life outside the Southern Ocean had higher levels – Wilson's storm petrel from Davis and Casey had HCB 50-180 ng g^{-1} fresh mass, giant petrels from Macquarie HCB 50-260 ng g^{-1} fresh mass (the northern race having higher loadings than the southern race).

Van den Brink (1997) analysed HCB in uropygial gland oil in birds from the Antarctic, sub-Antarctic and Europe. Antarctic and sub-Antarctic birds showed higher levels of HCB than those found in European samples. Adelie penguin and petrels were sampled at Hop Island in February 1994, and Antarctic petrels from King George Island. HCB varied from 268-2253 ng g⁻¹ lipid mass. Schneider et al. (1985) present data for adipose tissue from seals and seabirds collected along the ice shelf in the Weddell Sea in austral summer 1980-81. Overall range of HCB concentrations was 42-1330 ng g⁻¹ lipid mass. Luckas et al. (1990) determined HCB concentration in samples of blubber from four Weddell seals collected in the Weddell Sea. Mean level was 4 ng g⁻¹ blubber fresh mass.

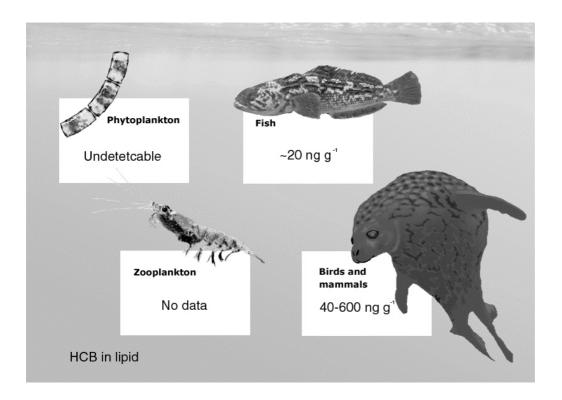


Figure 3-5. Concentration of HCB in lipid at various levels of the Antarctic marine food web. Levels in top predators such as birds and mammals are highly variable, but significant bioaccumulation of HCB at the top of the food web does not appear to be taking place. Data combined from sources cited in the text.

3.3.1.8.5 Summary

The data presented here are too patchy to define spatial or temporal trends. Levels in terrestrial plants may be very low, and interestingly HCB could not be detected in marine phytoplankton. HCB has been detected in fish, birds and mammals, but tissue loadings are highly variable. High levels in some bird species may indicate that most of the pollution load is accumulated outside the region (e.g. Luke et al. 1989). Certainly, low levels in endemic species such as some penguins (Luke et al. 1989) and Weddell seals (Luckas et al. 1990) suggest that this is the case.

3.3.1.9 Hexachlorocyclohexanes (HCH)

3.3.1.9.1 Terrestrial ecosystem

Bacci et al. (1986) provide the only data for the terrestrial ecosystem. They analysed lichen and moss samples collected 1985 from Port Lockroy, Galindez Island and Rothera Point. Concentrations of α -HCH were 0.2-1.15 ng g⁻¹ dry mass, and γ -HCH 0.4-1.7 ng g⁻¹ dry mass. The authors speculate that the predominance of γ -HCH indicates pollution by what were then newer forms of the insecticide. However, these plants are often very long-lived and will accumulate their pollution loading over decades.

3.3.1.9.2 Marine ecosystem - plankton

Eukowski & Ligowski (1987) sampled plankton diatoms in 1983-84 in Admiralty Bay, King George Island and from around South Orkney Islands. Concentrations were α -HCH 0.3-8.0 ng g⁻¹ (fresh mass), β -HCH not detectable, and γ -HCH 0.7-26.0 ng g⁻¹ (fresh mass). Highest levels were in the Admiralty Bay samples, collected closer to land than other samples. The authors speculate that glacial melt may release HCH and other compounds stored in snow, acting as a 'delay loop' between the time of local deposition in snowfall and subsequent release to the marine environment. In this case, the compounds released at the time of sampling may have originated at the time of maximum pesticide use. Joiris & Overloop (1989, 1991) and Joiris and Holsbeek (1992) found broadly similar levels in bulk samples of particulate matter (phytoplankton) from several parts of the Southern Ocean. Their average value for lindane concentration in these samples was 19 ng g⁻¹ DM. Comparing these data with the 'fresh-mass' data of Eukowski & Ligowski (1987) suggests that the values of Joiris and co-workers are representative of uncontaminated open ocean systems, and that higher HCH concentrations characterise coastal ecosystems with contamination by terrestrial run-off.

3.3.1.9.3 Marine ecosystem - fish

Larsson et al. (1992) measured an average lindane concentration of 30 ng g^{-1} fat weight in the liver of the fish *Pagothenia bernachii*.

3.3.1.9.4 Marine ecosystem – birds and mammals

Three studies report HCH concentrations in birds and seals, which are important top predators in the marine ecosystem. Schneider et al.(1985) analysed adipose tissue from seals and seabirds collected along the ice shelf in the Weddell Sea in austral summer 1980-81. Overall range of lindane (γ -HCH) concentrations was 17-103 ng g⁻¹ lipid mass. Karolewski et al. (1987) sampled adipose tissue from five Antarctic seal species, collected at King George Island (1979-1981). Highest overall levels were in leopard seal, an apex predator which will disperse widely in the Antarctic winter, with total HCH 24-26 ng g⁻¹ (fresh mass). For other species, total HCH varied from 8 ng g⁻¹ (fresh mass) in elephant seal to 18 ng g⁻¹ (fresh mass) in fur seal. Contrasts between species reflect feeding ecology and dispersal. Luckas et al. (1990) included data for Weddell seals in their analysis of pinniped PTS loadings. Mean levels were α -HCH 0.4 ng g⁻¹ blubber fresh mass, γ -HCH 0.3 ng g⁻¹ blubber fresh mass.

3.3.1.9.5 Summary

There are no local sources of HCH, so the relatively low levels seen in marine and terrestrial biota represent extra-regional input. Concentrations in marine biota appear to be similar, irrespective of trophic level – indeed concentrations in endemic seals appear to be lower in some cases than in fish or phytoplankton. The predominance of γ -HCH agrees with the dominance of this compound in environmental samples. The small number of studies, and the natural variability within and between samples, precludes any statement on the temporal trends in HCH contamination of biota.

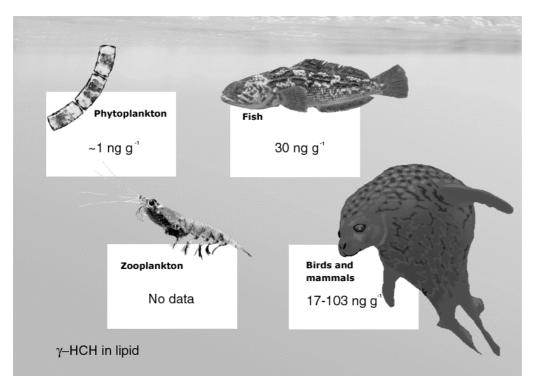


Figure 3-6. Concentration of γ -HCH in lipid at various levels of the Antarctic marine food web. Data combined from sources cited in the text.

3.3.2 Persistent Toxic Substances - Industrial Compounds

3.3.2.1 Polychlorinated biphenyls (PCBs)

3.3.2.1.1 Terrestrial ecosystem

Bacci et al. (1986) analysed a suite of lichen and moss samples collected in 1985 from Port Lockroy, Galindez Island and Rothera Point. Concentrations of total PCBs were <5 [detection limit]-16 ng g^{-1} dry mass (DM). These plants, which are slow-growing and long-lived, would have received their PCB input over a long period from atmospheric deposition and marine aerosol.

3.3.2.1.2 Marine ecosystem - plankton

For the marine ecosystem, there are data for phytoplankton from a series of bulk samples of particulate material over a large area of the Southern Ocean in 1987-89 (Joiris & Overloop 1989, 1991, Joiris & Holsbeek 1992). Total PCB concentrations measured in these samples were up to 750 ng g⁻¹ dry mass.

Several studies report PCB levels in invertebrates and fish, which will accumulate their entire PCB loading within the region and will probably be sensitive to local inputs. Many data for invertebrates refer to benthic taxa, but there is a single record for krill, a dominant component of the pelagic ecosystem. Risebrough et al.

(1976) analysed a single sample of krill collected in October 1975 at the Antarctic Peninsula. These animals contained total PCBs at a concentration of 3 ng g^{-1} lipid mass.

3.3.2.1.3 Marine ecosystem - fish

Larsson et al. (1992) analysed the fish *Pagothenia bernachii* and found total PCBs in the liver 70 ng g⁻¹ fat weight. Subramanian et al. (1983) also studied *Pagothenia bernachii* – their analysis of whole fish gave total PCB concentration of 0.17 ng g⁻¹ fresh mass. Monod et al. (1992) analysed various marine biota around the research station on Îles Kerguelen. Fish showed levels of total PCB 70-280 ng g⁻¹, close to the station, but significantly lower offshore.

Weber & Goerke (1996) analysed various species of fish in the Antarctic Peninsula region, especially *Chaenocephalus aceratus, Chamsocephalus gunnari* and *Gobionotothen gibberifrons* collected between 1987 and 1991. Concentrations were similar in liver and adipose tissue for all species, and concentrations were not related to body size. Concentrations of individual compounds were measured: PCB-153 0.5-7.4 ng g⁻¹ EOM (extractable organic matter), PCB-138 0.2-2.5 ng g⁻¹ EOM, and PCB-180 <0.1-4 ng g⁻¹ EOM. Comparison of levels for 1987 and 1991 suggested that loadings of PCBs increased during this time, despite decreased production and use at lower latitudes. They concluded that increasing Antarctic levels reflected global redistribution.

3.3.2.1.4 Marine ecosystem – birds and mammals

There is a comparatively large body of data on PCB concentrations in tissues of birds and mammals, which are dominant members of the Antarctic marine ecosystem. These animals provide data which compare PCB levels with similar top predators in the Arctic and elsewhere (e.g. Ballschmitter et al. 1981; Luckas et al 1990; Oehme et al. 1995; Van den Brink 1997) but the data are highly variable. Different species have differing body mass and lifespans, and may sometimes be sampled in extreme physiological states which could affect tissue concentrations. They occupy different trophic levels in the food web, and may be endemic to the region or may disperse widely outside the breeding season. All of these factors can influence exposure to PCBs, and interspecies variability will probably be much greater that any small or medium-scale spatial variability in environmental PCB concentrations. Luke et al. (1989) failed to detect PCBs in bird tissues they analysed, and Donnewald et al. (1979) found that total PCB concentrations in subcutaneous fat in pygoscelid penguins was 14-87 ng g⁻¹ fat. On the other hand, Monod et al. (1992) detected PCBs in all seabird species examined, and found highest levels in blue-eyed shag, with fat concentrations up to 51 000 ng g⁻¹ lipid mass.

Van den Brink (1997) suggests that top predators in polar ecosystems represent a 'sink' for volatile PTSs such as PCBs. He measured high PCB levels in uropygial gland oil from Antarctic and sub-Antarctic seabirds - Adelie penguin and petrels sampled at Hop Island in February 1994, and Antarctic petrels from King George Island. Total PCB (suite of 30 compounds) ranged from 204-1588 ng g⁻¹ lipid. Antarctic petrels had the highest levels of the Antarctic seabirds sampled, and this is a comparatively widely-dispersed species.

Subramanian et al. (1986) measured total PCBs in Adelie penguins collected in 1981 close to the Syowa research Station, and found a range of concentrations in subcutaneous fat from 28.8-124 ng g⁻¹ lipid mass. Eukowski et al. (1987) analysed subcutaneous fat and liver from three pygoscelid penguin species and four seabirds from the breeding colony on King George Island. Total PCBs reached highest concentrations in *Oceanites* (storm petrel), which forage extensively outside the region. Concentration in fat was 15000 ng g⁻¹ (fresh mass), and in liver 1800 ng g⁻¹ (fresh mass). Lowest levels were found in penguins, which are more or less restricted to the Southern Ocean. Concentrations in fat were 150-720 ng g⁻¹ (fresh mass), and in liver 60-290 ng g⁻¹ (fresh mass). This contrast between different taxa is mirrored in the data of Focardi et al. (1997) for birds sampled over the period 1987-92 at Ross Island. Adelie penguins had average total PCB concentration in the liver of 690 ng g⁻¹ (dry mass), whilst the corresponding value for skuas was 2 540 ng g⁻¹ (dry mass).

Levels of PCBs have been measured in the eggs of several seabird species. Risebrough et al. (1976) measured total PCB levels in eggs from five species of pygoscelid penguins collected at the Antarctic Peninsula during 1970-75. The range of concentrations was were 21-180 ng g^{-1} lipid mass with no evidence for significant interspecies or temporal variation. Gardner et al. (1985) analysed eggs from a total of 24 species of seabird

sampled at sub-Antarctic Marion and Gough Islands and islands off the South African coast. The lowest PCB levels were found in birds at Marion Island. For the whole study, the range of total PCB concentrations was 5-1450 ng g^{-1} . Highest levels were found in Antarctic skua and wandering albatross – both species which disperse widely.

Seal blubber has been another tissue analysed for PCBs. Luckas et al. (1990) sampled four Weddell seals in the Weddell Sea, and found mean levels of individual PCBs 3-9 ng g⁻¹ blubber fresh mass and total PCBs 78 ng g⁻¹ blubber fresh mass. Oehme et al. (1995) detected coplanar (non-ortho substituted) PCBs (CB-77, CB-126, CB-169) in blubber samples from female fur seals at Bird Island in December 1987.

3.3.2.1.5 Marine ecosystem - benthos

Benthic invertebrates, especially molluscs, have been used in studies of local PCB pollution of the marine environment. These animals are either sedentary or have only limited dispersal, and feed on suspended or deposited particulate material. Kennicutt et al. (1995) measured PCB concentrations in marine animals from Arthur Harbour (1989-93) and McMurdo Sound. Tissue concentrations of PCBs were low in Arthur Harbour limpets, except adjacent to research stations where levels were 28-76 ng g⁻¹, with approximately equal amounts of penta-, hexa- and hepta-chlorobiphenyls. At McMurdo, bivalves showed high levels of PCB contamination close to the station (380-430 ng g⁻¹), but not at remote sites (5-22 ng g⁻¹).

3.3.2.1.6 Summary

Overall, PCB levels in Antarctic marine biota are highly variable. Many of the benthic marine invertebrates sampled have been collected close to local sources of PCB contamination, and may show levels of total PCB of 300-500 ng g⁻¹, whereas tissue concentrations in animals from uncontaminated sites may be less that 10% of these levels. Similarly, liver PCB concentrations in fish sampled in contaminated environments were 70-200 ng g⁻¹, whereas those from uncontaminated sites were significantly less. Weber & Goerke (1996) suggest that fish from uncontaminated areas showed increasing PCB levels with time, but this was based on a short sampling period.

Birds and mammals which are endemic to the region, such as pack ice seals and penguins, have relatively low PCB loadings. They probably do not respond to local PCB 'hotspots' in the way that fish and benthic invertebrates appear to. Penguin liver total PCB concentrations were typically not detectable to 300 ng g⁻¹ (fresh mass), and levels in seal blubber were about 100 ng g⁻¹ (fresh mass). Birds and mammals that forage extensively outside the region clearly encounter higher environmental PCB levels, and these animals may have tissue PCB concentrations as high as 50 000 ng g⁻¹ (fresh mass).

With the wide variety of samples analysed for PCBs, and the spatial and temporal variability of environmental levels, it is not easy to generalise regarding trends in these data. Focardi et al. (1995) suggest that PCB concentration increases up the food chain, and they cite their own data as follows: Weddell seal 585 (407-750) ng g⁻¹ FM (skin biopsy), Adelie penguin 101 (56-188) ng g⁻¹ FM, south polar skua 1162 (885-1676) ng g⁻¹ FM, fish (two spp) 21 (15-44) and 36 (18-77) ng g⁻¹ FM. However, inclusion of other data presented here would not necessarily support this simple picture. The data for phytoplankton presented by Joiris & Overloop (1989, 1991) and Joiris & Holsbeek (1992) suggest that PCB levels at the base of the food web can be high. Subramanian et al. (1983) speculate that PCBs do not accumulate indefinitely in fish, but reach an equilibrium loading.

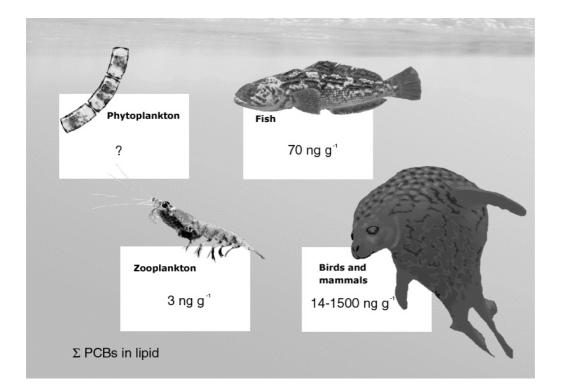


Figure 3-7. Concentration of total PCB in lipid at various levels of the Antarctic marine food web. Values for concentration in phytoplankton appear anomalous, and have not been included in this summary. Data combined from sources cited in the text.

3.3.3 Persistent Toxic Substances - Unintended by-products

3.3.3.1 Polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs)

3.3.3.1.1 Marine ecosystem – birds and mammals

Two studies report data for PCDD and PCDF concentrations in seal blubber, and make comparisons with samples from other parts of the world. Bignert et al. (1989) failed to detect these compounds in blubber from crabeater seals, a species associated with the pack ice in the high-latitude Southern Ocean. Oehme et al. (1995) used more sensitive analytical methods to measure these compounds in blubber from fur seals, sampled at Bird Island in 1987. PCDD/PCDF were present at levels around 2 pg TEQ g⁻¹ blubber. These are significantly lower levels than Arctic pinnipeds, and PCDD-PCDF congener patterns were also different.

3.3.3.2 Polycyclic Aromatic Hydrocarbons (PAHs)

3.3.3.2.1 Marine ecosystem - plankton

Measurements of PAH in biota have concentrated on elements of the marine ecosystem around sites of persistent or one-off contamination (e.g. Platt & Mackie 1979, 1980; Kennicutt & Sweet 1992). There are few measurements in the pelagic system – Cripps (1989) measured PAH concentrations of 5.75 ng g⁻¹ DM in Antarctic krill, the 'keystone' zooplankter in the pelagic ecosystem in many parts of the Southern Ocean. Cripps (1994) analysed samples of particulates from Bransfield Strait region. These samples were predominantly phytoplankton, and concentrations of individual PAH compounds ranged from undetectable to 427 ng g⁻¹ DM. Cripps discusses dietary uptake and accumulation of PAH by krill, and suggests that PAH concentrations in krill may be consistent with phytoplankton ration, although not all compounds in phytoplankton are found in krill, and vice versa.

3.3.3.2.2 Marine ecosystem - benthos

Because of the focus on local pollution, the majority of biotic samples are from benthic organisms. Such studies require careful design and sampling strategy. Dhargalkar & Bhosle (1987) examined nine taxa of benthic marine macroalgae collected in the Vestfold Hills region. They found high variability in total hydrocarbon content, and concluded that here was uncertainty over use of the data to monitor local pollution. Kennicutt et al. (1991) showed that macroalgae exposed to chronic oil pollution cleaned rapidly within a few days.

In the case of single pollution incidents, carefully designed sampling strategies have been used effectively to monitor the spatial extent and duration of PAH exposure. Kennicutt et al. (1991, 1995) and Kennicutt & Sweet (1992) undertook extensive sampling of intertidal limpets in response to the grounding of the *Bahia Paraiso* and the subsequent release of 600 000 litres of Diesel Fuel Arctic (DFA). Sampling covered an area within 6 km radius of the wreck to west of Arthur Harbour, Anvers Island, from one day after the spill until 2 years later. Intertidal limpets were contaminated with DFA over a period of 6-7 weeks. Total PAH loading in whole tissue samples reached 125 000 ng g⁻¹ DM in the initial phase of the spill, and declined to about 180 ng g⁻¹ DM two years later. Closest sites showed peak total PAH tissue concentration for intertidal limpets soon after the spill 125 000 ng g⁻¹ DM. This decreased about ten-fold over the 7 weeks following the spill. At more distant sites, limpet tissue concentrations were typically 500-50 000 ng g⁻¹ DM at the time of spill, declining to 35-400 ng g⁻¹ DM two years later. Data for the locality are also available for uncontaminated limpets prior to the spill, and these animals typically had low PAH (<1000 ng g⁻¹), although background contamination from the nearby research station was evident (Kennicutt et al. 1992, 1995). Total PAH in limpet tissues collected adjacent to the new station ranged from 15-2900 ng g⁻¹. Napthalenes predominated, with concentrations of 15-1090 ng g⁻¹. Remote from the station, levels were lower.

Cripps & Shears (1997) undertook a similar study in response to an accidental spill of 1000 litres diesel fuel at Faraday Station, Galindez Island, Argentine Islands. Total PAH concentration in seawater reached 222 μ g dm³ on the day after the spill, and returned to 'background' levels within one week. Limpets were found dead after the spill. Surviving animals had elevated PAH levels, but these levels were low compared with the Arthur Harbour samples - 90 ng g⁻¹ 30 d after the spill. Seven months after the spill, PAH levels in limpets close to the station were still ten times higher than those from an uncontaminated control site. This was ascribed to long-term, low-level input from the station, rather from the spill itself. On the basis of these two studies, it appears that limpets from uncontaminated sites in the Southern Ocean will have PAH tissue concentrations of <100 ng g⁻¹.

Other benthic molluscs have also been sampled. Kennicutt et al. (1991) also analysed the infaunal bivalve *Laternula* as part of their sampling campaign associated with the *Bahia Paraiso* sinking. Animals sampled near the wreck had tissue total PAH 17 500 ng g⁻¹ DM, and 1200 ng g⁻¹ DM more distant from wreck (central Arthur Harbour). Cripps & Priddle (1995) measured PAH loading in another bivalve, *Yoldia eightsii*, from the vicinity of Signy Research Station. Total PAH loading increased with age, from 1 to 21 ng per animal over the age range 5-50 years respectively. However, tissue concentration declined with age, from 25 down to 5 ng g⁻¹ (fresh tissue mass) over the same age range. Tissue loading varied seasonally, being highest in October (end of winter) and lowest in December (mid-summer), which might reflect metabolic changes. Although these tissue concentrations were probably affected by local pollution from the research station, they are consistent with the very low background values found in Southern Ocean biota.

The feeding ecology of the molluscs cited here probably means that they will be very effective indicators of local pollution. Other parts of the food web will probably accumulate lower amounts. Kennicutt et al. (1995) analysed fish tissue from the vicinity of McMurdo station. They found PAH concentrations up to 650 ng g⁻¹ in contaminated areas.

3.3.3.2.3 Summary – patterns and trends

The data do not indicate that there is a consistent temporal trend in PAH contamination. Background levels in a range of biota are low, and do not appear to have changed markedly over three decades of sampling. The

spatial pattern of PAH contamination in marine biota – and indeed the spatial pattern of sampling - is dominated by local pollution incidents.

3.3.4 Organometals

Data on organometals are scarce, although there is a large body of data on heavy metal concentrations in a range of terrestrial and marine biota.

3.3.4.1 Organomercury compounds

3.3.4.1.1 Marine ecosystem

Honda et al. (1987) note the low bio-accumulation of Hg resulting from the short food chain and low concentrations in seawater. Joiris & Holsbeek (1992) provide data on methyl mercury (MeHg) concentrations in Antarctic fish and seabirds, collected over an extensive area from 1986-90. Methyl mercury was typically about 50% of the total Hg load. Data for fish are derived from whole animals, and cover 10 species – MeHg concentrations ranged from 0.03-0.55 μ g g⁻¹ dry mass (DM). Data for birds come from three different tissues from three species. MeHg levels in muscle were 0.13-0.39 μ g g⁻¹ DM, in liver 0.3-1.3 μ g g⁻¹ DM and in kidney 0.34-0.78 μ g g⁻¹ DM.

3.4 TOXICOLOGY

Research laboratories in the region are not normally equipped to undertake rigorous toxicological testing, whilst maintaining most Antarctic organisms in outside the region requires highly-sophisticated controlledenvironment facilities. Because of this, and because of low levels of PTSs in the environment and biota, there has been little toxicological research. The following summary is intended simply to indicate some of the approaches which have been used to investigate the interaction between different organisms of PTS which occur in the Antarctic environment. It is not practical here to provide the sort of quantitative data which would be available for other regions.

3.4.1 Anecdotal evidence for environmental impact –ecological and physiological data

The distribution of organisms relative to sources of pollution or areas affected by PTSs provides an index of sensitivity. As an example, Lenihan et al. (1990) related the distribution of the infaunal bivalve *Laternula* in relations to hydrocarbon contamination of sediments in Winter Quarters Bay, McMurdo Sound. They demonstrated an inverse relationship between bivalve numbers and hydrocarbon contamination. In a later study, Lenihan et al. (1995) conducted 'transplant' experiments, where communities were moved along a pollution gradient and their composition monitored.

Pople et al. (1990) and Smith & Simpson (1998) used community composition changes at polluted and control sites to follow the impact of an oil spill at Macquarie Island in 1987. Contemporary studies of the impact were followed up two years later.

3.4.2 Physiological data for organism response

Enzyme activities provide a sensitive index of the response of organisms to exposure to PTSs. Focardi et al. (1992a,b, 1997) have undertaken extensive research on the activity of mixed function oxidase in vertebrates in response to PTS levels. Viarengo et al. (1993) describe the role of metallothionein in the homeostasis and detoxification of heavy metals in the Antarctic scallop *Adamussium colbecki*.

3.4.3 Data on metabolism and breakdown of pollutants

Concerns arising from local pollution incidents, especially fuel oil spillages, have prompted studies of the rates at which natural communities metabolise such materials. Kennicutt et al. (1990) examined the capacity for microbial bioremediation following the *Bahia Paraiso* spillage. They found low densities of hydrocarbon-metabolizing bacteria – turnover time for hexadecane was more than 2 years. Similar investigations have been carried out by Kerry (1990, 1993) in studies of experimental oil spills on soils.

3.4.4 Experimental exposure tests

Various studies have tested the effects of exposure of organisms to artificially elevated levels of PTS. Some of these experiments have been used single compounds, whilst others have used 'raw' pollutants such as diesel fuel. Kennicutt et al.(1990) carried out experiments which demonstrated no significant effect of the watersoluble fraction of diesel fuel on photosynthesis of macroalgae. Other studies involving artificial PAH exposure have been carried out by Ogrodowczyk (1981), Lenihan et al., (1995), McDonald et al. (1995) and Yu et al. (1995). These have covered a range of organisms from krill to fish. Ogrodowczyk (1981) exposed krill and fish to crude oil, and found krill to be especially sensitive. McDonald et al. (1995) tested the effects of injection of fish with benzo[a]pyrene or Arctic diesel fuel.

Bystrzejewska et al. (1989) and Łukowski et al. (1989) tested the effects of various PTS compounds on the photosynthetic rate of marine phytoplankton. Bystrzejewska et al. showed that very low levels of Arochlor 1254 (0.01-1 ppm) may stimulate carbon incorporation, but that respiration also increases. This balance is reversed at concentrations from 1-50 ppm. The study by Łukowski et al. tested the effects of Arochlor 1254, Arochlor 1242, p,p' DDE, p,p' DDT and lindane added to natural marine phytoplankton assemblage at range of final concentrations 0.1-50 ppm. Lindane inhibited photosynthesis at all concentrations, and effectively stopped it at 50 ppm. Of remaining compounds, decreasing order of toxicity were Arochlor 1242, p,p' DDE, p,p' DDT, Arochlor 1254. The authors note that under conditions of ice melt, when chlorinated hydrocarbons can be released rapidly following gradual accumulation over winter, levels of some pesticides may reach concentrations shown to inhibit photosynthesis in this study.

3.5 SUMMARY - ENVIRONMENTAL LEVELS, TOXOLOGICAL AND ECOTOXOLOGICAL CHARACTERISATION

Data on PTS levels in the environment derive from a range of samples, including components of the cryosphere. Comprehensive datasets are available for only a few PTSs.

Concentrations in air of several pesticides, including chlordane and DDT, appear to have declined during the period from the early-mid 1980s to the late 1990s, although this trend is not evident in data for HCH.

There is a comparatively large amount of data on PCB concentrations in the environment. Concentrations in air are highly variable in space and time, and no long-term trend can be seen. Several studies have quantified PCBs in marine sediments close to known sources of contamination. Concentrations in these sediments are typically 100 to 1000 times values in adjacent uncontaminated samples, suggesting that background concentrations in the marine environment are very low.

PAHs in environmental samples arise from local and global contamination. For many studies, local inputs dominate environmental levels. Again, systematic studies show that PAH contamination in the marine environment remains restricted spatially, and that contamination ascribed to one-off events declines over time. No long-term trend in baseline levels can be identified.

Levels of PTSs in biota derive almost entirely from the marine ecosystem. There are no data for PTS concentrations in people, and such measurements would anyway be irrelevant.

In the case of marine birds and mammals, concentration data for most PTSs vary in a way which probably reflects the degree to which they are exposed to these compounds when migrating outside the region.

There is evidence for some pesticides in the assessment, such as dieldrin and especially DDT, that concentrations in marine biota are increasing over time, despite the decrease in environmental levels. Tissue concentrations of pesticides in marine birds and mammals remain low compared with levels in similar species from regions with greater environmental pollution, and migrant species may show higher concentrations than predominantly endemic species.

Levels of PCBs in biota are highly variable, indicating the dominant role of localised contamination in determining tissue PCB loadings in some components of the marine ecosystem. There appears to be little evidence for bioaccumulation of PCBs in marine biota.

Measurements of PAHs in biota have concentrated on elements of the marine ecosystem close to know sites of long-term and/or one-off contamination. Because of the highly variable input to local systems, no temporal trend can be seen. Background levels in biota are low.

Toxological data are sparse, and generally have been obtained from research experiments rather than systematic monitoring programmes. Some experimental exposure tests indicate that environmental levels of some pesticides may occasionally rise to levels show to affect phytoplankton growth.

4 MAJOR PATHWAYS OF CONTAMINANT TRANSPORT

4.1 INTRODUCTION

With the exception of low-level, and usually highly localised, emissions of PTSs within the region, introduction of PTSs to Antarctica and the Southern Ocean comes entirely from extra-regional sources. The Antarctic continent and the peri-Antarctic islands are isolated from the rest of the world by an extensive ocean. Any form of overland transport of PTS, such as transboundary river flow, does not operate. Although 'biotransport' is an important process in determining the PTS loadings of some marine species, particularly marine birds and mammals, it is only atmospheric and oceanic transport which constitute major pathways for PTS input to the region.

The following brief discussion of atmospheric and oceanic transport of PTSs into the region is intended to be general. It does not deal specifically with distinctions between different PTSs in their physico-chemical properties (such as vapour pressure and volatility, solubility, susceptibility to scavenging by precipitation), in their turnover time in the environment, nor to the possible specific source regions. All of these factors will determine the way in which an extra-regional PTS signal is translated into environmental or biotic concentrations within the region. At the end of the chapter, some local factors which might modulate the signal of extra-regional transport are highlighted.

4.2 ATMOSPHERIC TRANSPORT

Atmospheric circulation at mid-latitudes in the southern hemisphere is dominated by the westerly flow between subtropical highs and the subpolar lows. Cyclone tracks typically spiral towards the Antarctic, carrying air from lower latitudes into the region. Several studies of PTS concentrations in air have been carried out along north-south gradients. Bidleman et al. (1993) carried out air sampling along a transect from New Zealand to the Ross Sea. Concentrations of a range of PTS were lower at the Ross Sea end of the transect. Tanabe et al. (1982 a,b) report the results of a similar transect between the northern hemisphere and the Antarctic continent. Their data for spatial variability vary between compounds - HCH showed a marked north-south gradient in air concentrations whilst this was not the case for PCBs or DDT. Ockenden et al. (2001) sampled air at Halley station on the Weddell Sea coast, and at the Falkland Islands. Vapour-phase PCB concentrations were consistently lower at Halley. Tanabe et al. (1983) present data from an extensive survey involving two northsouth transects together with year-round monitoring at a station on the Antarctic coast. Along a transect from Mauritius in the Indian Ocean to the Syowa station on the Antarctic coast, they found a decline in air concentration of DDT, HCH and PCBs. They interpreted zonal differences in air PTS concentrations on the basis of likely atmospheric circulation trajectories – air sampled at the Syowa station probably originated over the south Atlantic Ocean and carried low PTS loadings compared with air sampled over the Southern Ocean south of Australia which would have originated in more contaminated air from the Indian Ocean region. Kallenborn et al. (1998) similarly identify trajectories from South America to the site in the northern Weddell Sea where they monitored airborne PTS concentrations. Barbante et al. (1998) suggested that lead carried in atmospheric aerosol could be traced along trajectories between South America and the Atlantic sector of East Antarctica, and Australia and the Pacific sector.

For some PTSs, the north-south gradient also appears in biotic loadings found during geographically extensive studies (e.g. Gardner et al. 1985; Luke et al. 1989). However, other sources of variability typically obscure such an effect.

Over much of the height of the atmosphere, the circulation systems in the two hemispheres operate separately, and the timescale of exchange between these is long. For some PTS classes, it is possible to use data on composition to confirm the southern hemisphere origin of the source region. For instance, Tanabe et al. (1982b) suggested that the differences in HCH composition between the northern part of their transect (off the Pacific coast of Asia) and the Southern Ocean samples could be explained by the higher use of 'technical HCH' in Asia, whilst lindane use in the southern hemisphere was demonstrated by the high proportion of γ -HCH in air samples from the Southern Ocean.

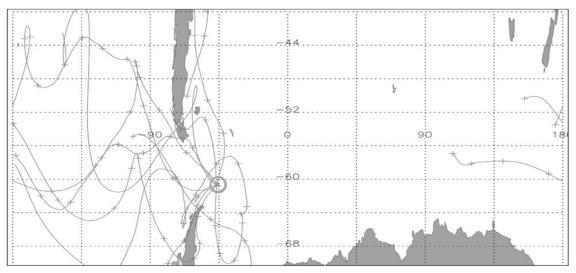


Figure 4-1. Air-mass back trajectories (900 hPa) for Signy Island (ringed), the site of the study by Kallenborn et al. (1998). The trajectories were calculated for successive ten-day periods in December 1999-March 2000. Note the wide variety of trajectories, and consequently of source regions for air reaching the sampling site. Figure provided by Dr John King (British Antarctic Survey), using facilities at the British Atmospheric Data Centre.

From these and similar data, the source areas for atmospheric transport of PTS to Antarctica can be identified as the being predominantly in the southern hemisphere continents. Some large-scale spatial variability in vapour-phase PTS concentrations within the region can be explained in the context of likely airflow trajectories (Tanabe et al. 1983). Over longer timescales, and as the production of some PTSs ceases or diminishes significantly, larger-scale processes will dominate, and interhemispheric concentration gradients may be reduced as atmospheric loadings equilibrate on a global scale.

Whilst we can identify the likely sources of PTS entering the region, and thus the atmospheric pathways along which they travel, it is less clear how these compounds are deposited. The PTS load in particulates is typically low (Bidleman et al. 1993, Ockenden et al. 2001). The dynamics of scavenging of PTS by snowfall are poorly understood (Tanabe et al 1983).

4.3 OCEANIC TRANSPORT

The circulation pattern of the Southern Ocean is unique. The Antarctic Circumpolar Current (ACC) is the largest current system in the world ocean, transporting about 100 Sverdrup (1Sv = 1 million m³ s⁻¹). This current system consists of several cores (jets) which extend from the surface to the ocean floor. This circumpolar flow plays a large role in isolating the Antarctic continent from the rest of the world ocean.

Ocean water from the neighbouring oceans can penetrate the Southern Ocean in two ways. First, southward flowing water at depths of about 2 km penetrates the Southern Ocean as a component of the so-called 'global ocean conveyor' circulation. Probably the most important input is from the North Atlantic, via the southwards flow of North Atlantic Deep Water (NADW) which upwells into the ACC. This water will have accumulated any PTS load mainly in the northern hemisphere, and will have been isolated from the ocean surface for a considerable time.

The surface circulation exchanges with neighbouring oceans by the penetration of mesoscale eddies or core rings. These packets of surface ocean water – typically only a few hundred metres in depth, will carry the signal of more recent PTS loading from riverine-coastal and atmospheric input. The most intense exchange of eddies takes place where the southward flowing western boundary currents of the Indian and South Pacific Oceans, and to a lesser extent the South Atlantic Oceans, meet the ACC. This mixing process is probably most effective off South Africa, where the Agulhas Current flowing along the eastern African coast meets the

northward edge of the Southern Ocean in an area where interchange between Indian Ocean water and Subtropical Convergence-Southern Ocean water is high.

The balance between these inputs is hard to quantify. The flux of NADW into the Southern Ocean is probably of the order of 10-15 Sv. Using concentrations of dissolved PTSs in seawater of ng m⁻³ to μ g m⁻³, annual input via NADW would introduce PTS to the Southern Ocean in 10 kg to 10 tonne quantities annually. Exchange of surface water between the Southern Ocean and western boundary currents is very much more difficult to quantify, because it involves processes which are highly variable in space and time. Taking the diameter of a typical core ring as 50 km, and its depth as 100 m, then the volume of water contained within it is about 6 × 10¹⁰ m³. If we assume that one core ring enters the Southern Ocean at each of the three main eddy formation sites each week, this gives an annual transport of 10^{13} m³ y⁻¹. This number seems large, but is equal to an average transport rate of less than 1 Sv – about 10% of the NADW flux. Concentrations of PTS in surface seawater would be expected to be slightly higher, but despite this the importance of this transport route into the region is probably small.

4.4 THE TIME-SCALE OF TRANSPORT

It appears relatively easy to determine the physical processes which dominate the transport of PTSs into the region, and for atmospheric transport it is possible to determine by back-trajectories the likely source region. In considering the implications of these transport mechanisms, especially in the context of the use of the region as a global 'barometer', it is also important to understand the timescale of the transport processes. This in turn will determine how changes in extra-regional emissions will be reflected in environmental loadings within the region.

As noted already, the timescale of processes in the ocean is likely to be long, and will smooth out signals of extra-regional environmental variability. Midwater flux dominates transport at least in terms of volume, if not PTS loading. It is likely that the NADW injected into the ACC will have spent several years (at least) isolated from the ocean surface. The second proposed mechanism involving eddy exchange with western boundary currents, will bring in water carrying a signal of more recent inputs both from the atmosphere and from riverine or coastal sources. However, this process would still be relatively slow, and once within the Southern Ocean the exchange time would again be a matter of years to decades. To provide a measure of the timescale, the time for a packet of water to travel once around the ACC is about eight years. That said, there do appear to be regional differences in loading of some PTS in ocean water which are sufficiently well-defined to be evident as spatial variability in biotic PTS concentrations (Łukowski 1978).

By contrast, transport in the atmosphere will be more rapid and will be more likely to reflect time-varying properties of the source. Bacci et al. (1986) suggest that what were then newly introduced insecticides dominated the HCH signal in terrestrial biota, suggesting relatively rapid transport between source and deposition. In a review of time-series data of atmospheric PTS concentrations, Bidleman et al. (1993) were able to identify trends in concentration over a period of about a decade which agreed with global estimates. On a shorter timescale, Kallenborn et al. (1998) were able to explain peaks in PTS concentration in air in the northern Weddell Sea, by relating them to weather conditions which would have brought in potentially contaminated air from South America. There are also seasonal variations in air PTS loadings, which can again be related in part to extra-regional changes (Tanabe et al. 1983).

In addition to the time-varying responses to extra-regional events, the atmosphere-ocean system within the region exhibits strong interannual to decadal scale variability which may further influence the impact of changes in PTS inputs. The most conspicuous feature of this variability is the so-called Antarctic Circumpolar Wave – a coupled variation in atmospheric and ocean circulation which is quasi-cyclical with a period of about four years (Murphy et al. 1995, White and Peterson 1996).

4.5 LOCAL MODULATION OF EXTRA-REGIONAL INPUTS

Although this chapter is concerned with long-range transport, it is important to emphasise that the input of PTS from outside the region will be modified by various processes within the region. Because extra-regional sources constitute the only source for most PTSs found in the region, these local processes are best viewed as the end-members of transport routes. They determine how the environment and biota finally receive the PTSs carried into the region.

Various unique properties of the environment and ecosystem will modify the way in which PTSs are released and distributed once they have arrived in the region. Physical features include:

- Low temperatures which reduce or eliminate subsequent evaporation of volatile PTSs
- The importance of snowfall in overall precipitation
- The capacity of snow and ice to act as reservoirs for PTSs over timescales which potentially range from years to centuries
- The effects of sea ice in isolating the surface ocean from atmospheric inputs for part of the year

Ecosystem features include:

- The low biomass, simplicity, and restricted geographical extent of the terrestrial ecosystem, including the absence of large herbivores and predators
- The very close integration of marine and terrestrial ecosystems at coastal and island locations
- Poor development of soils in ice-free areas
- The intense seasonaility of primary production and other metabolic processes in both terrestrial and aquatic ecosystems, which will in turn influence the temporal variability of the susceptibility of biota to PTSs in the environment
- Slow metabolic and growth rates, contributing to long residence times of PTSs in biological reservoirs

4.6 SUMMARY – REGIONAL RESPONSE TO EXTRA-REGIONAL SOURCES

Almost all of the PTSs present in the Antarctic environment and biota come from sources outside the region. They reach the region predominantly via atmospheric and oceanic transport. Other physical mechanisms are missing or unimportant. Spatial and temporal variability in airborne PTS concentrations can be linked to source variability and patterns of airflow and storm tracks. Similar variability in seawater will be masked by stronger mesoscale variability.

The region probably represents a sink for most, if not all, of the PTS compounds considered in this assessment. Physical conditions favour the accumulation of PTSs, and militate against their 're-export' from the region. Both physical and biological factors imply that the lifetime of many PTSs in the environment and in biota will be prolonged.

5 PRELIMINARY ASSESSMENT OF THE REGIONAL CAPACITY AND NEEDS

5.1 INTRODUCTION

Preceding chapters have shown that:

- For the most part, the levels of PTSs in the Antarctic region are typically very low
- For all PTSs covered by this assessment, there is no local production
- For a very few, there has been local pollution of the environment but this is typically highly localised, with a very few sites affected and spatial scale of significant contamination less than one kilometre
- There is an increasingly rigorous approach to minimizing environmental impact associated with most human activities in the region
- Most sources of PTSs in the region are extra-regional, and this has probably always been the case for all PTSs in all but a few localities
- Monitoring of PTSs in the environment and in biota is patchy and inconsistent, and is commonly linked to assessment of the impact of local activities or single pollution incidents
- For some PTSs, time series of environmental concentration can be constructed, and these show a strong relationship to use and release of these compounds either globally or at least throughout the Southern Hemisphere
- Again, for only a small subset of the PTSs in this assessment, and a subset of the monitoring studies, the broad geographic location of extra-regional sources can be identified
- Some factors complicate the interpretation of data on PTS levels in biota, including physiological effects, environmental influences on exposure, and the degree of endemism of some animals in the marine food web

Given some of the caveats stated above, it is clear that the Antarctic region offers the opportunity to monitor globally averaged pollutant loadings in the absence of any significant widespread local contamination. The first question to be asked is whether this facility to monitor extra-regional PTS levels has value in a global context. If this is so, then other questions follow:

Would continuation of the existing type and level of monitoring carried out in the region be adequate?

If not, is there a need for a new, coordinated monitoring programme?

Can existing national or multinational science programmes in the region sustain such a monitoring effort?

Is the information which currently available sufficient to design a more systematic monitoring programme? In particular:

Can existing data be used to assign valid monitoring sites?

Can existing data be used to identify optimum sample media?

- Is there an adequate understanding of the transport of PTS into the region?
- Is there an adequate understanding of environmental factors which give rise to local temporal and spatial variability in the levels of PTSs?

Can PTSs be prioritised for a future monitoring study?

5.2 CURRENT STATUS – DATA, REGULATION AND CAPACITY

5.2.1 The levels of PTSs in the Antarctic region

The measurements on which this report is based come from a variety of sites and media from the Antarctic continent and its surrounding ocean and islands, collected over a period of more than thirty years. For all PTSs measured, the levels are overwhelmingly low in comparison with those from lower latitude regions. In a few cases, intense local contamination has led to higher levels, and these have attracted public attention (e.g. Risebrough 1992).

5.2.2 Local sources – production

No production of any PTS takes place, or has ever taken place, within the region. This may seem to be a redundant statement, but the fact needs to be re-stated in the context of discussion later in this chapter.

5.2.3 Local sources – contamination

As shown in Chapter 3, both continuous low-level release and one-off pollution incidents have resulted in local input of some PTSs to the environment and biota. For the most part, the level of contamination is still very low by comparison with emissions in more industrialised regions, and the resulting contamination remains highly localised. However, in a near-pristine environment such as Antarctica and the Southern Ocean, any contamination is conspicuous, and is now usually perceived as unacceptable even where its impact is slight.

Local sources of pesticides can be discounted, although trace amounts may have been introduced to the region as a consequence of logistics operations (for instance application to aircraft or ships whilst entering the region from outside).

PCBs have been introduced to the environment close to long-term human habitation. The concentrations are well documented, and can be shown to be restricted to a kilometre-scaled area in even the worst cases (Kennicutt et al. 1995).

Combustion products arise from poorly controlled burning of waste, and from other procedures (Risebrough et al. 1976, Carrichia et al. 1995, Kennicutt et al. 1995). There are few data for dioxins and furans, but these again indicate that the levels are low and highly localised (Lugar et al. 1996).

PAHs probably constitute the largest category of local pollution, because of the widespread use of petroleum fuels for logistics; technical problems with fuel storage and transfer; emissions from vehicles and generation plant; and occasional accidental spillages. These last events leave a clear local signal in the environment and biota, although this again is spatially-restricted and can be seen to decrease over time (at least in the marine environment where most systematic monitoring has taken place) (Cripps 1990, 1992, Kennicutt et al. 1991, Green & Nichols 1995).

There are insufficient data to establish whether local sources of organometals may contribute to environmental and biotic levels.

It should be stressed that some of the local sources documented here date back two or three decades, when environmental procedures were less rigorous that at present (see next section). In time, the local contamination associated with research stations will decline. PAHs are probably the exception to this generalisation. Although facilities for fuel handling have improved greatly, the amount of shipping in particular has increased in the region.

5.2.4 Current environmental controls and regulation

Although previous human activities in the region have caused local long-term environmental impact, current activities within the region are subject to rigorous control and scrutiny. Public and governmental concern over environmental pollution were fuelled by several regional issues in the 1970s and 1980s. These included the publication of an increasingly large body of evidence of the penetration of PTSs into the region, the demonstration of the effects of CFCs (chloro-fluorocarbons) on the stratospheric ozone layer over the Antarctic interior, and the possibility of mineral extraction within the region. These raised the profile of environmental concerns within the region, at the time that the Antarctic Treaty was open for re-negotiation. As a result, environmental protection now forms a very much more conspicuous and well-regulated element of human activities in the region. With regard to environmental controls and regulation, the region comprises three distinct types of area, or 'divisions'.

5.2.4.1 Environmental control within the Antarctic Treaty area

The Antarctic Treaty (Washington, USA, in December 1959) refers specifically to all areas of land and ice shelves (the seaward extension of the continental ice cap) situated south of 60°S latitude. This delineation encompasses the entire continental landmass of Antarctica, and some of the peri-Antarctic islands and island groups.

The Antarctic Treaty receives scientific advice from SCAR, which has at present a Group of Specialists on Environmental Affairs and Conservation, and from the Scientific Committee of the Commission for the Conservation of Antarctic Marine Living Resources (SC-CCAMLR). The implementation of environmental standards and procedures is the responsibility of national programmes. Their coordinating body, the Committee of National Antarctic Programmes (COMNAP) hosts a network for environmental officers working within national programmes (AEON - <u>http://www.comnap.aq/aeon)</u>.

5.2.4.1.1 Environmental Protocol to the Antarctic Treaty

Environmental protection within the Antarctic Treaty area is governed by a protocol to the treaty. This protocol states that 'activities in the Antarctic Treaty area shall be planned and conducted so as to limit adverse impacts on the Antarctic environment and dependent and associated ecosystems'. The protocol includes provision for environmental impact assessment, which carries a monitoring component related to local activities. Any wastes containing PTSs are required to be removed from the Antarctic (Annex III, Article 2). Some classes of material, including PCBs, are specifically prohibited under the protocol (Annex III, Article 7).

It should be noted that, although the Antarctic Treaty refers only to land and shelf-ice areas, the Environmental Protocol does cover marine pollution with a separate annex, as well as specific articles in other annexes (e.g. Annex III, article 5). Discharges of 'noxious substances' to the marine environment are prohibited (Annex IV, Article 4), although no specific categorisation of these noxious substances is provided within the annex. In practical terms, the protocol defers to MARPOL 73/78 (see next section). The Environmental Protocol to this Treaty, and its annexes, (SCAR 1993) details agreed measures to protect the environment and biota within the Treaty Area. Many of the provisions of this protocol reflect the nature of human activity within the Treaty Area, which is still dominated by scientific studies carried out from permanent research stations and by expedition groups operating in field camps. The Antarctic Treaty system has an Environmental Protection Committee (established under Article 11 of the Environmental Protocol) which considers a range of scientific and technical issues arising from the Environmental Protocol, including:

The collection, archiving exchange and evaluation of information related to environmental protection,

The state of the Antarctic environment, and

The need for scientific research, including environmental monitoring, related to implementation of the Protocol

(Environmental Protocol Article 12, 1I-k).

5.2.4.2 Environmental controls in land areas outside the Antarctic Treaty area

The second 'division' of the region comprises those peri-Antarctic islands included in the regional definition (and mostly in the SCAR 'region of interest' – see section 1.4 of this report). Environmental regulation in these areas is the responsibility of the nations administering them. They may have explicit territorial waters or exclusive economic zones in which special environmental measures apply. The list of these territories, and their national administration, is:

Île St Paul and Île Amsterdam 38°S, 77.5°E (administered by France)

Macquarie Island 54.5°S, 159°E (administered by Australia)

Gough Island 40°S, 10°W (administered by United Kingdom)

Marion Island and Prince Edward Islands 46.8°S, 37.5°E (administered by South Africa)

Îles Crozet 46°S, 51°E (administered by France)

Îles Kerguelen 49°S, 69°E (administered by France)

Heard Island 53.5°S, 73.5°E (administered by Australia)

South Georgia 54.3°S, 36.6°W (administered by the United Kingdom)

South Sandwich Islands 56°S, 27°W (administered by the United Kingdom)

Bouvetøya 54.5°S, 3.5°W (administered by Norway)

5.2.4.3 Environmental controls in the Southern Ocean

The final 'division' of the region is the open ocean, both within and outside the Antarctic Treaty area (bounded to the north by latitude 60°S). Environmental regulation in this division falls under the normal conventions applying to the high seas. An Antarctic Treaty body, the Commission for the Conservation of Antarctic Marine Living Resources (CCAMLR) regulates fisheries in the region, and this includes a strong ecosystem monitoring component (see http://www.ccamlr.org/). However, CCAMLR does not have an explicit pollution monitoring remit, although it does follow some issues which emanate from fisheries operations, such as the disposal at sea of plastic debris.

5.2.4.3.1 International Convention for the Prevention of Pollution from Ships, 1973, as modified by the Protocol of 1978, (MARPOL 73/78)

The MARPOL Convention is a combination of two treaties adopted in 1973 and 1978. It covers all technical aspects of pollution from ships, except the disposal of waste into the sea by dumping, and applies to ships of all types. The Convention has five annexes covering oil, chemicals, sewage, garbage, and harmful substances carried in packages, portable tanks, freight containers, etc.

5.2.4.4 Stockholm Convention On Persistent Organic Pollutants

This convention was adopted at the December 2000 meeting in Johannesburg of the intergovernmental negotiating committee for an international legally binding instrument for implementing international action on certain persistent organic pollutants. The objective of this Convention is to protect human health and the environment from persistent organic pollutants. The selected list of PTSs is of direct relevance to the UNEP assessment of PTSs. The Convention was opened for ratification signatures on 23 May 2001. The eventual status of this convention in this region, with relation to the Antarctic Treaty and its Environmental Protocol, is uncertain.

5.2.5 Extra-regional sources of PTSs

Chapter 4 provides a brief summary of transport routes into the region, and demonstrates that extra-regional areas are the predominate sources of all PTSs. It is clear that airborne transport provides a larger and more rapid route for bringing PTS into the region than does oceanic transport.

5.2.6 Motivation and strategy for monitoring PTS in the environment and in biota

The data presented in Chapter 3 of this report derive from a very diverse set of studies, undertaken for several different reasons. The motivation, and resulting strategy, for such research determines both the current value of the data and their potential value to future studies (see section 5.3 below). There are four main motives for undertaking PTS-related research in the region.

5.2.6.1 Assessing existing and potential environmental impact

A substantial quantity of the research carried out on PTSs in the region, especially within the last two decades, has been intimately connected to assessing the impact of scientific and logistic operations (and to a lesser extent fisheries and tourism). This has been both in the context of existing operations and in performing impact assessments for planned operations and projects (a requirement of the Environmental Protocol – see 5.2.4.1 above). Such assessments may provide the basis for long-term monitoring programmes, because they establish protocols for repeat sampling. However, the pollutants of primary concern are those which may be associated with the operations, such as PAHs and other combustion products. As a result, complete categories of PTSs such as pesticides will be likely to be excluded.

5.2.6.2 <u>Response to pollution incidents</u>

A few recent pollution incidents have provoked well-planned and coordinated studies of the extent and fate of pollutants and their effect on biota. All the incidents have been fuel spills, of which that resulting from the grounding of the *Bahia Parsaiso* was the largest and has been the best studied (Kennicutt et la. 1991, 1995). Again, the coverage of pollutant classes in these studies is very restricted. Time-series sampling programmes, which follow the fate of the pollution event over time, using repeat sampling in the environment and biota, provide an especially valuable picture of the way in which pollutants are retained and transformed within the system. Almost all of these incidents have been in the marine environment, or have had their main impact there. However, the fate of some accidental spillages, and of some deliberate experimental applications, have been assessed in the terrestrial ecosystem (e.g. Kerry 1990, 1993).

5.2.6.3 Using Antarctica as a global monitoring site

As noted throughout this report, the region is not pristine. However, contamination levels over nearly all of the region are low, and local sources are small and easily identified. Most of the PTS input to the region comes from extra-regional sources. These conditions suggest that samples from Antarctic environments and biota can be used to monitor PTS levels on a hemispheric or global scale. Several studies have used this approach, and the data calibrate well with other estimates of time series of PTS release, for example the resemblance of Antarctic air concentrations of DDT to global estimates (e.g. Bidleman et al. 1993). However, for these studies to realise their full value, they must be complemented with a good understanding of how individual PTSs reach the region, how their concentrations in environment and biota will be modified by local processes, and ultimately whether they will accumulate in the system (cf Champ et al. 1992).

5.2.6.4 Curiosity-driven research

Many of the studies of PTSs in biota have been concerned with fundamental problems of how organisms in extreme environments cope with environmental stresses – either actual or potential. These are typically 'one-off' studies, and may sometimes be difficult to relate to the way organisms are exposed to PTS in the natural

environment. Many such studies are undertaken in research stations within the region, where facilities for maintaining organisms and for undertaking large-scale experiments may be less satisfactory than those found in larger laboratories specialising in environmental studies in other regions.

5.2.7 Time series of environmental PTS concentration

The large variety of measurements of PTS in the region often makes it difficult to construct time-series, which must ultimately be the basis of any attempt to undertake global monitoring. Time series can be constructed for air concentrations for DDT, HCH and PCBs, and these can be calibrated against estimates of global temporal change. For other PTSs, and for many other environmental media, the sampling is simply too inconsistent and/or the data too variable to construct a historical data series. The opportunity for recovering PTSs from high-resolution environmental 'archive' samples in snow and ice has been used in the past (e.g. Risebrough et al. 1976, Tanabe et al. 1983), and may prove a potential means of increasing the scope of PTS data for the last 4-5 decades.

5.2.8 Identifying the geographic location of extra-regional sources

Knowledge of transport trajectories and spatial and temporal variability in airborne concentrations of some PTSs has enabled some studies to identify the likely extra-regional sources of PTSs (Section 4.2) (e.g. Kallenborn et al. 1998). It should be possible to specify these in more detail when the pattern of emissions in the source regions are better understood, and from there to refine models of airborne transport. The same cannot be said of oceanic transport, where a more complex pattern of influx and different mixing scales will smooth out details which could link environmental levels in the region to sources outside.

5.2.9 Factors complicating the interpretation of data on PTS levels in biota

In the introduction to Section 3.2, various factors which affect the relation between environmental PTS loadings and the loadings in biota were discussed. These again place constraints on the use of data for monitoring, both locally and globally. Perhaps most importantly, the wide variation in PTS loadings in avian and mammalian top predators in the marine ecosystem is seen to be determined in part by the degree to which different species forage outside the region. Such variability makes the construction of temporal or spatial patterns difficult.

5.3 THE VALUE OF ANTARCTIC PTS MEASUREMENTS IN A GLOBAL CONTEXT

In the introduction to this chapter, it was noted that the Antarctic offers a potential site for conducting monitoring of global PTS levels. This is because there is no production of these compounds in the region, and very low and localised contamination. This section of the chapter is concerned with evaluating the potential value and implications of an Antarctic compo0nent of a global monitoring survey. This assessment is conducted as a series of questions. The first question to ask is whether such a survey is needed at all.

5.3.1 The value of monitoring PTS globally from the Antarctic

In earlier parts of this chapter, we saw that Antarctica has a potential use as a 'barometer' for larger-scale changes in PTS levels, although much of the research to date had been undertaken for other reasons. Such a barometer is a useful component of a global monitoring effort, because it provides a control for other estimates of emissions. Also, the polar regions are likely to be the ultimate sinks for many volatile PTSs, so for this reason alone monitoring in the Antarctic is important in order to understand their fate on a global scale. Champ et al. (1992) provide a discussion on the value of such an approach. They note that existing environmental studies in polar regions have yet to yield an in-depth understanding of processes, and thus make it impossible to estimate human impacts on polar ecosystems. They go on question the value of polar environmental data in a

global context, but do not reach any firm conclusion. Risebrough (1992) – writing in the same special volume – highlights the importance of some Antarctic studies in relation to global problems, and emphasises the need for consistent measurement strategy if long-term or geographically extensive patterns are to be identified.

If we accept that we need to continue to follow the fate of PTSs on a global scale, and that an Antarctic measurement programme forms a key component of such an effort, then other questions follow:

5.3.1.1 Suitability of existing monitoring programmes

As noted in Sections 5.2.6-9 above, the design of previous monitoring studies has not been adequate to provide a clear picture of the temporal and spatial variability of the full suite of PTSs in this assessment. Most importantly, the dominant interest from national research programmes in Antarctica is related to local environmental impact, rather than being directed at global monitoring. This leads to:

- Some classes of PTSs being excluded from the studies, because they are not likely to be produced by the operation or installation being assessed
- Dominance of data by local sources of contamination, even where these are trivial on a global scale
- Selection of sampling media, especially biota, which are difficult to interpret outside their local context, and which may sometimes be selected for their local significance but have little real value as pollution indicators
- Sometimes, but not always, a one-off or a 'before and after' sampling design which cannot be extended into a longer-term monitoring programme, or is unlikely to be so extended for practical reasons.

5.3.1.2 <u>Future monitoring programme</u>

The need for continued and globally-relevant monitoring of PTS levels in the region will not be met by an ad hoc assembly of varied measurement projects, as those reviewed in this report. A programme designed specifically to address the global exchange and fate of PTS would be required. However, such a monitoring programme does not need to be hugely complex in logistic terms.

5.3.1.3 Available national or multinational science programmes

It is clear that the type of study undertaken at present as part of most national research programmes in Antarctica and the Southern Ocean will not satisfy the requirements for a global monitoring programme. The multinational research network, of which SCAR is a core element, does not have any suitable coordinated project in place. Such a programme has been discussed in the past, but has never been implemented.

At present neither SCAR nor the national programmes are in a position to bear the burden of a global programme. However, the Antarctic research community does have a good record of multinational collaboration, and participation in global environmental projects. Any PTS monitoring programme would need to be based on existing logistic infrastructure, but the international community outside the Antarctic would need to bear the costs of the programme itself.

5.3.2 Requirements for a systematic monitoring programme

Although this report notes deficiencies in existing data, in the context of monitoring the global environment, the data contain much of the information needed to design an effective monitoring programme.

5.3.2.1 Can existing data be used to assign valid monitoring sites?

First, there are sufficient data on spatial variability of environmental levels of many key PTSs, together with trajectories for atmospheric transport, to select sites for the location of routine sample collection. Second, enough information is available about the location of local sources, and the extent of their contamination footprints, to establish monitoring sites away from possible contamination.

5.3.2.2 Can existing data be used to identify optimum sample media?

It is clear that the simple requirements of monitoring demand a routine assessment of those environmental media which will reflect best the input of PTS to the region. Concentrations in air appear to be the best measure of contemporary input to the region – atmospheric transport is the dominant mode of influx of PTSs to the region, and is also the one which responds most rapidly to changes in emission at source.

Expert advice is needed to assess the potential for deriving historical time series from so-called 'archive' samples such as sediment or snow-cores. Clearly, the period of interest spans around half a century, so that high-resolution, undisturbed samples are needed. So far as snow cores are concerned, the only sites which might provide the necessary temporal resolution will be in regions of high accumulation (i.e. high precipitation). Such cores have already been tested for some tracers of atmospheric environmental conditions, but their interpretation will require an understanding of how representative such areas would be.

Samples of biological material should also form a component of a monitoring programme, especially given the secondary issue that expanding fisheries in the region, for krill, fish and squid, may require specific monitoring if some PTSs accumulate in the food chain to levels which cause concern. As Section 3.3 demonstrates, there are considerable practical problems with selection of biotic samples which contribute meaningful data to a long-term monitoring programme. In particular, it should be certain that the large majority of the PTS load in a species is accumulated within the region, rather than during excursions into other regions. Ethical considerations will also play a part in determining the species and type of samples selected – the public spotlight on Antarctic science in many countries militates against killing of 'icon' animals such as seals for scientific purposes. Non-destructive sampling, such as removing oil from the preen gland (uropygial gland) (Van den Brink 1997) of birds or the collection of eggs, would be an acceptable alternative.

Fish and squid taken by commercial fisheries would provide good material for monitoring, and samples are already collected under CCAMLR jurisdiction for collection of condition data used in regulating fisheries. As noted already, these samples may have intrinsic value in the future if PTSs accumulate in the marine food chain. Of the avian and mammalian top predators, endemic penguins seem to satisfy the criteria on the location of contamination better than flighted birds.

Terrestrial vegetation in the Antarctic has been used to monitor pollution (Bacci et al. 1986; Shears 1995) although typically for programmes related to local impacts. Terrestrial communities are poorly-developed and may be vulnerable to repeated sample collection. Rapid ecological change in some regions of the Antarctic, such as local climate-related changes in the Antarctic Peninsula region, may also compromise a long-term monitoring programme based on terrestrial plant samples.

5.3.2.3 Is there an adequate understanding of the transport of PTS into the region?

Atmospheric transport is the dominant mechanism for introduction of PTSs into the region. Concentrations of PTSs in air reaching sites within the region appear to be sensitive both to the temporal variation in the tracks of weather systems connecting the sampling site to the putative source (Kallenborn et al. 1998 – see also Figure 4-1), and to larger-scale geographic variability in source regions (Tanabe et al. 1983). This points to a likely relationship between temporal and spatial variability in the pattern of atmospheric circulation, especially storm tracks, which could be modelled. However, this could only be calibrated against existing or future data if source regions can be quantified adequately.

Oceanic transport is probably well-constrained on a large scale, but also subject to high mesoscale variability. It would be relatively simple, for instance, to calculate a reasonable estimate of the PTS load carried into the Antarctic Circumpolar Current by North Atlantic Deep Water, given a knowledge of PTS concentration and the transport rate. It would also be possible to identify where (and when) that water was last in contact with the

atmosphere or other inputs. Massive uncertainty comes in where mesoscale processes determine how that load is dispersed within the Southern Ocean. This, and the long-timescale for circulation and mixing, means that the concentration of PTS dissolved in seawater at a given site cannot be related to variability in a specific source in the way that appears possible, to whatever extent, for atmospheric input. In the sense of understanding PTS transport into the system, the ocean integrates on longer timescales than the atmosphere, but it may be that this integration can only be exploited with extensive sampling. The oceanographic use of novel tracers such as CFCs and bomb radionuclides provides a model for the sampling needed to determine PTS dispersal in the ocean.

So-called 'biotransport' is not a significant mechanism for PTS import to the region, but is significant in understanding the balance between autochthonous and allochthonous sources when interpreting the PTS loading of some mobile species such as birds. If this were thought to be a significant problem, good ecological information on key species is available to allow the re-interpretation of existing data.

5.3.2.4 <u>Is there an adequate understanding of environmental factors which give rise to local temporal and spatial variability in the levels of PTSs?</u>

There are several environmental factors which modulate the incoming PTS signal and which could in turn produce a false picture of global dynamics if they were not incorporated into sampling design. For instance, snow pack may accumulate PTS over winter, and then release much of this load in a few pulses during summer melting. Sea ice formation and melting are not only separated in time, they will also be separated spatially – meaning that PTS accumulation and release can occur in different places as well as at different times.

The first strategy should be to identify the most obvious of these processes and to design sampling programmes which yield data which are not compromised by local variability. This could be achieved both by selection of the type of sample, the period when the sampling is undertaken, and the time over which the sample integrates.

At a second level, further study could prove beneficial in providing an understanding of the dynamics of some of these local processes. This could aid in interpretation of existing data, and be used to refine sampling design in the future.

5.3.3 Can PTSs be prioritised for a future monitoring study?

Selection of PTSs for inclusion in a regional monitoring programme which is focused on global issues is a compromise between a number of factors. In assessing individual compounds, the following criteria have been used:

Concentrations of the compound should be of demonstrable environmental concern

- Concentration of the compound should be capable of being measured routinely with good accuracy and precision in a defined set of sample media
- The logistic and analytical infrastructure should be in place to collect and analyse samples for the compound
- Existing data for the compound should be sufficient to underpin a future time series
- It should be possible to isolate the extra-regional contribution to concentrations of the compound measured in the region, as opposed to locally-introduced contamination

Additional benefit derives from classes of compounds where specific composition gives information either on likely source, as is the case for HCH, or the history of the compound, as is done for metabolites and their parent compound e.g. DDE and DDT.

Here, no judgement is made about the global importance of a particular group of compounds. If a single pesticide were shown to be of foremost global concern, it would receive high priority for inclusion in a future monitoring programme even if existing data are weak.

The following four categories divide the list of PTSs in this assessment into groups largely on the basis of existing data - in other words, those compounds for which there are already 'good' datasets form a more tractable basis for a global monitoring programme than those for which there are 'poor'.

Category 1. PTS compounds for which there are comprehensive regional data (baseline and/or time-series) for both environmental and biotic levels, and for which there are demonstrable concerns regarding local contamination

Polychlorinated biphenyls (PCBs) Polycyclic Aromatic Hydrocarbons (PAHs)

Category 2. PTS compounds for which there are comprehensive baseline and/or time-series data for regional environmental and biotic levels. Such compounds are of global concern, but may not be viewed as being of concern in a local context (such as issues addresed in environmental impact assessments)

Dichlorodiphenyltrichloroethane (DDT)

Hexachlorocyclohexanes (HCH)

Category 3. PTS compounds where existing regional data are adequate to provide a baseline for future monitoring, but where there are gaps in understanding of temporal, spatial and ecosystem variability *Chlordane*

Hexachlorobenzene (HCB)

Category 4. PTS compounds where existing data are too few to provide a confident estimate of current baseline concentrations in the environment or biota *Aldrin and Dieldrin*

Endrin Heptachlor Toxaphene (Polychlorobornanes and camphenes) Mirex Polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) Organomercury compounds

5.4 SUMMARY - REQUIREMENTS AND SCOPE FOR FURTHER ACTION

The region is unusual in its geography and ecosystems. PTS loadings are typically very low, no PTSs are manufactured or applied in the region, and local releases are small and of restricted spatial extent [Chapters 1,2].

There is wide variation in the data coverage for different PTSs. For some, such as DDT and HCH, there is a good temporal and geographic spread of samples from different environmental media and biota. These data allow statements to be made about the input of PTSs to the system, and their fate within it. At the other extreme, there are compounds or groups of compounds for which there are little or no data. Little of value can be said at present about these compounds in either a regional or a global context [Chapter 3].

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, and variation in measured airborne concentration appears to be explicable in terms of known variation in source distribution and transport trajectories. Oceanic transport is likely to be less important, and to integrate over a longer timescale [Chapter 4].

The current dataset has been evaluated, and a number of key features identified which qualify interpretation of the data. 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.

The region potentially offers sites to monitor the global occurrence and fate of PTSs, against a background that is close to being 'clean', and where local contamination is often well-documented. 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 focussed mainly on local impacts.

Existing data are often adequate to identify sites and sample media for a global monitoring programme. Development of models of transport, especially atmospheric transport, will benefit any monitoring programme and will enable better interpretation of some existing data.

Further work on the dynamics of some local processes, especially in connection with the interaction of PTSs with components of the cryosphere, 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 design for future monitoring

The use of snow cores as archive samples recording PTS input to the region needs to be assessed further. If comprehensive, temporally resolved analysis proves possible, these data would greatly enhance a future monitoring programme by providing a historical record dating back to the introduction of the various compounds considered in this report.

Existing environmental data comply with other evidence for long-term changes in global or hemispheric emission of PTSs. 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.

5.5 **RECOMMENDATIONS**

5.5.1 Existing data

Following further quality control, existing data need to be archived in a way in which they can be used effectively in a global assessment

Data on biotic loadings need to be assessed a brought to common bases in order to construct reliable pictures of spatial and temporal variability, and ecosystem effects

5.5.2 Local dynamics

Studies are needed to understand how PTSs are deposited in the region in snowfall, and how this relates to the atmospheric content of PTSs and to physical conditions

Studies are needed to understand the ways in which PTSs may be stored in parts of the abiotic environment, and how these stores may be subsequently mobilised (for instance by melting snow or sea ice)

Studies are needed to determine the forms in which PTSs are present in the marine environment, and to test hypotheses about their incorporation into the marine ecosystem

5.5.3 Long-range transport

Models of atmospheric transport should be developed to include region-specific dynamics, such as deposition in snowfall

Back trajectory analysis should be undertaken where possible for all existing studies of air and cryosphere (snow and ice) concentrations, in order to understand temporal and spatial variability in the context of likely sources

5.5.4 Global monitoring

Existing data should be used to identify potential sites for inclusion in a global monitoring network, and to define suitable samples for PTS analysis

Agency support should be sought for routine sample collection and analysis to contribute to future global monitoring of PTSs

5.5.5 Health issues

With increasing exploitation of marine resources in the Southern Ocean, potential hazards to human health from consumption of krill, squid, fish and marine mammals need to be identified

Where any potential hazard is identified, a suitable monitoring system should be established

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APPENDIX 1. GEOGRAPHIC LOCATIONS MENTIONED

(see Appendix 2 for the location of research stations)

Admiralty Bay (King George Island) Antarctic Peninsula Anvers Island Arrival Heights (Ross Island) Arthur Harbour (Anvers Island) Bird Island Bouvetøya Bransfield Strait Doumer Island Ellis Fjord Galindez Island (Argentine Islands) Gough Island Heard Island Hop Island Île St Paul and Île Amsterdam Îles Crozet Îles Kerguelen King George Island (South Shetland Islands) Macquarie Island McMurdo Sound Marion Island and Prince Edward Islands Paradise Bay (Paradise Harbour) Port Lockroy Ross Island Rothera Point (Alexander Island) Ross Sea Scotia Sea Signy Island (South Orkney Islands) South Georgia South Orkney Islands South Shetland Islands Terra Nova Bay	$62^{\circ}10'S, 56^{\circ}30'W$ see map, Appendix 2 $64^{\circ}35'S, 63^{\circ}30'W$ $77^{\circ}49'S, 166^{\circ}39'E$ $64^{\circ}46'S, 64^{\circ}05'W$ $54^{\circ}S, 38^{\circ}W$ $54^{\circ}S, 38^{\circ}W$ $63^{\circ}S, 59^{\circ}W$ $64^{\circ}51'S, 63^{\circ}34'W$ $68^{\circ}37'S, 78^{\circ}05'E$ $65^{\circ}16'S, 64^{\circ}16'W$ $40^{\circ}S, 10^{\circ}W$ $53^{\circ}30'S, 73^{\circ}30'E$ $66^{\circ}50'S, 77^{\circ}43'E$ $38^{\circ}S, 77^{\circ}30'E$ $46^{\circ}S, 51^{\circ}E$ $49^{\circ}S, 69^{\circ}E$ $62^{\circ}05'S, 58^{\circ}15'W$ $54^{\circ}30.S, 159^{\circ}E$ $77^{\circ}30'S, 165^{\circ}E$ $46.8^{\circ}S, 37.5^{\circ}E$ $64^{\circ}51'S, 62^{\circ}54'W$ $64^{\circ}49'S, 63^{\circ}30'W$ $77^{\circ}30'S, 168^{\circ}E$ $67^{\circ}34'S, 68^{\circ}08'W$ see map, Appendix 2 see map, Appendix 2 $60^{\circ}43'S, 45^{\circ}38'W$ $54^{\circ}20', 36^{\circ}40'W$ $60^{\circ}35'S, 45^{\circ}30'W$ $56^{\circ}S, 27^{\circ}W$ $62^{\circ}S, 58^{\circ}W$ $74^{\circ}50'S, 164^{\circ}30'E$
South Sandwich Islands	56°S, 27°W
	· · · · · · · · · · · · · · · · · · ·
5	
Vestfold Hills	68°33'S, 78°15'E
Weddell Sea	see map, Appendix 2
Winter Quarters Bay	77°51'S,166°37'E

References:

SCAR (1998) Composite gazeteer of Antarctica (South of latitude 60°S). Volume 2. Rome, Programma Nazionale di Ricerche in Antartida. 328 pp
UKHO (1997) The Antarctic Pilot. Fifth edition. Taunton, United Kingdom Hydrographic Office. 262 pp.

APPENDIX 2. LOCATION OF PERMANENT RESEARCH STATIONS

The term 'permanent' refers to year-round (overwinter) occupation. Other facilities are used intermittently, and research is also undertaken from field camps and by mobile field units. Stations are classified by nation, and are numbered clockwise from the Greenwich Meridian (see map). *Stations north of 60°S +Stations on King George Island

Argentina	China	
40 Belgrano II 77°52'29"S 34°37'37"W	27 +Great Wall 62°13'S 58°58'W	
36 Esperanza 63°23'42"S 56°59'46"W	10 Zhongshan 69°22'S 76°23'E	
32 +Jubany 62°14'16"S 58°39'52"W	France	
37 Marambio 64°14'42"S 56°39'25"W	7 *Alfred Faure, Iles Crozet	
38 Orcadas 60°44'20"S 44°44'17"W	46°25'48"S 51°51'40"E	
22 San Martin 68°07'47"S 67°06'12"W	17 Dumont d'Urville 66°39'46"S 140°00'05"E	
Australia	12 *Martin de Viviès, Ile Amsterdam	
16 Casey 66°17'00"S 110°31'11"E	37°49'48"S 77°34'12"E	
13 Davis 68°34'38"S 77°58'21"E	9 *Port aux Français, Iles Kerguelen	
18 *Macquarie Island 54°29'58"S 158°56'09"E	49°21'05"S 70°15'19"E	
8 Mawson 67°36'17"S 62°52'15"E	<i>Germany</i>	
Brazil	43 Neumayer 70°38'S 08°15'48"W	
34 +Comandante Ferraz 62°05'00"S 58°23'28"W	+5 Neumayer 70 505 00 15 +6 W	
Chile	India	
25 Capitan Arturo Prat 62°30'S 59°41'W	2 Maitri 70°45'57"S 11°44'09"E	
35 General Bernardo O'Higgins	Japan	
63°19'S 57°54'W	5 Syowa 69°00'25"S 39°35'01"E	
28 +Presidente Eduardo Frei	Korea	
62°12'S 58°58'W	31 +King Sejong 62°13'24"S 58°47'21"W	
26 +Escudero 62°11'57"S 58°58'35"W		

New Zealand

- 20 Scott Base 77°50'60"S 166°45'46"E**Poland** 33 +Arctowski 62°09'34"S 58°28'15"W **Russia** 29 +Bellingshausen 62°12'S 58°58'W 14 Mirny 66°33'S 93°01'E 6 Molodezhnaya 67°40'S 45°51'E 3 Novolazarevskaya 70°46'S 11°50'E 11 Progress 69°23'S 76°23'E 15 Vostok 78°28'S 106°48'E **South Africa**
- 42 *Gough Island 40°21'S 09°52'W
- 4 *Marion Island 46°52'34"S 37°51'32"E
- 44 SANAE IV 71°41'S 02°50'W

Ukraine

23 Vernadsky 65°14'43"S 64°15'24"W

United Kingdom

39 *Bird Island 54°00'31"S 38°03'08"W

- 41 Halley 75°34'54"S 26°32'28"W
- 21 Rothera 67°34'10"S 68°07'12"W

United States

- 1 Amundsen-Scott 89°59'51"S 139°16'23"E
- 19 McMurdo 77°50'53"S 166°40'06"E
- 24 Palmer 64°46'30"S 64°03'04"W

Uruguay

30 +Artigas 62°11'04"S 58°54'09"W

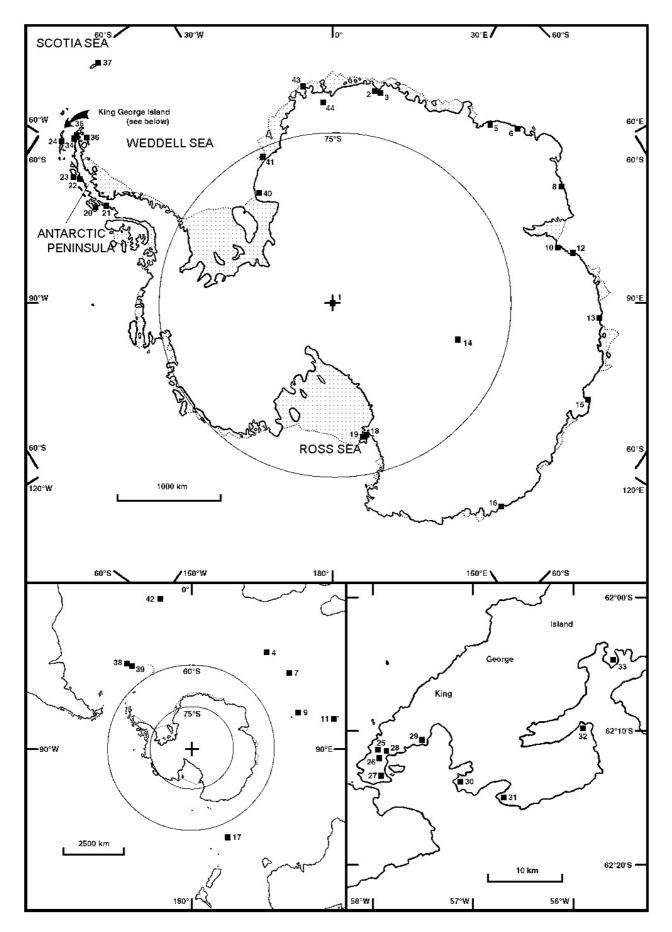


Figure A2-1. Location of permanent research stations in Antarctica (winter 2001). (Map courtesy of SCAR)

APPENDIX 3. SCIENTIFIC NAMES OF ANIMALS

Invertebrates

Antarctic krill Antarctic limpet Antarctic scallop Antarctic soft-shell clam Antarctic Yoldia

Fish

Blackfin icefish Mackerel icefish Icefish Humped rockcod Emerald rockcod

Birds

Adélie penguin Antarctic skua Blue-eyed shag (cormorant) Cape petrel Emperor penguin Gentoo penguin Giant petrel Rockhopper penguin Royal penguin Southern fulmar South polar skua Storm petrels Wilson's storm petrel Wandering albatross

Mammals

Crabeater seal Leopard seal Southern elephant seal Southern fur seal Weddell seal

References:

Euphausia superba Nacella concinna Adamussium colbecki Laternula elliptica Yoldia eightsii

Chaenocephalus aceratus Chamsocephalus gunnari Chionodraco hamatus Gobionotothen gibberifrons Pagothenia bernachi

Pygoscelis adéliae Catharacta lönnbergi Phalacrocorax atriceps Daption capensis Aptenodytes forsteri Pygoscelis papua Macronectes giganteus Eudyptes cristatus Eudyptes chrysolophus Fulmarus glacialoides Catharacta maccormicki Oceanites spp Oceanites oceanicus Diomedea exulans

Lobodon carcinophagus Hydrurga leptonyx Mirounga leonina Arctocephalus gazellae Leptonychotes weddellii

Fischer W, Hureau J-C (editors) (1985a) FAO species identification sheets for fishery purposes. Southern Ocean (Fishing areas 48, 58 and 88). Volume 1. Rome, Food and Agriculture Organization. 1-232 **Fischer W, Hureau J-C (editors) (1985b)** FAO species identification sheets for fishery purposes. Southern Ocean (Fishing areas 48, 58 and 88). Volume 2. Rome, Food and Agriculture Organization. 233-471

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Phone : +41 22 917 1234 Fax : +41 22 797 3460 E-mail: chemicals@unep.ch http://www.chem.unep.ch

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