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# Remote Zones Air Quality -Persistent Organic Pollutants: Sources, Sampling and Analysis

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# 1. Introduction

Concern about air quality has been rising since the Industrial Revolution and the so-called "Second Industrial Revolution" characterized by internal combustion engine, electrical technology and above all synthesis of new chemicals. Since then humankind has been facing the consequences of its thoughtless release of pollutants in atmosphere, consequences as reducing smog, acid rains and photochemical smog. Notwithstanding the seriousness of single episodes, these were local, or at most regional, phenomena. Nowadays, the variety of pollutants and the extent of pollution are greater than even in history, and air pollution problems are reaching up to global scale. In the last decades, it was established that manmade chemicals, such as polychlorinated biphenyls, chlorofluorocarbons and volatile chlorinated hydrocarbons, were present even in the remotest zones of the Earth, according to their volatility and half-life. This evidence stimulated the scientific community to monitor air quality of remote zones, areas considered a short time ago as uncontaminated.

This chapter deals with different sampling and analysis techniques for persistent organic pollutants (POPs) in the atmosphere of remote zones. Features, sources and environmental fate of POPs are presented in the first section. The second section focuses on logistic and experimental difficulties connected to surveys in remote zones. The third section focuses on recent developments and improvements concerning sampling and analytical methods for POPs in air. The most significant findings on the presence of POPs in remote zones are shown in the last section.

# 2. Persistent organic pollutants

Persistent organic pollutants (POPs) are carbon-based chemical compounds and mixtures that, to a varying degree, resist photolytic, biological and chemical degradation. POPs are characterised by low water solubility and high lipid solubility, leading to their bioaccumulation in fatty tissues. They are also semi-volatile, enabling them to be transported long distances in the atmosphere before deposition occurs.

The Agency for Toxic Substances and Disease Registry defined persistent organic pollutants as "organic substances that possess toxic properties, resist degradation, bio-accumulate and are transported, through air, water and migratory species, across international boundaries and deposited far from their place of release, where they accumulate in terrestrial and aquatic

ecosystems" (ATSDR, 1995; Syracuse Research Corporation, 2000). Where the term "substance" stands for "a single chemical species, or a number of chemical species which form a specific group by virtue of (a) having similar properties and being emitted together into the environment; or (b) forming a mixture normally marketed as a single article" (SCAR, 2009). POPs are chemicals that can be produced both intentionally and unintentionally. POPs can be chemicals currently or once used in agriculture, disease control, manufacturing, or industrial processes. To give an example as intentionally produced POPs, they can be cited PolyChlorinated Biphenyls (PCBs) and DichloroDiphenylTrichloroethane (DDT). PCBs have been used in several industrial applications (e.g., as dielectric fluids in transformers, capacitors, coolants, and as additives to paints and lubricants). DDT is a pesticide still used in malaria vector control in some countries. On the other hand, POPs can be chemicals unintentionally produced, generally as by-products. Polycyclic Aromatic Hydrocarbons (PAHs) and dioxins are POPs which result from industrial processes and incomplete combustion of organic matter (e.g., municipal and medical waste incineration and trash burning).

POPs can cause cancer, allergies and hypersensitivity, reproductive disorders, and disruption of the immune system; they can damage the central and peripheral nervous systems. Some POPs are endocrine disrupters: by altering the hormonal system, they can damage the reproductive and immune systems and have teratogenic effects (Stockholm Convention Secretariat, 2011). Some of these compounds can persist in the environment for periods of years. POPs are noted for their semi-volatility; such a physico-chemical characteristic that permits these compounds to occur both in the vapour phase and adsorbed on atmospheric particles. These properties of unusual persistence and semi-volatility, coupled with other characteristics, pre-dispose POPs to long environmental persistence and to long-range transport through the atmosphere, have resulted in POP ubiquity all over the world. The significant half-life and lipophilicity in human and animal fats of POPs allow them to biomagnify and bioconcentrate in organic tissue up to 70,000 fold and thereby potentially achieving toxicological relevant concentrations.

In virtue of their peculiar characteristics, POPs have been causing a growing concern to scientists and policy makers. Indeed, from 1990, several international initiatives were started aimed at reducing and/or possibly eliminating POP emissions and discharge, recognizing the need for global actions (such as international protocols and conventions) to protect and safeguard human health and the environment.

"The Stockholm Convention on Persistent Organic Pollutants" can illustrate the importance and the consideration of scientific community, concerning sources, behaviour, fate and effects of POPs. The Stockholm Convention is a global treaty realized and signed to date by 151 Nations and administered by the United Nations Environment Programme. The treaty was realized with the aim to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have adverse effects to human health or to the environment (Stockholm Convention Secretariat, 2011).

The Stockholm Convention, which was adopted in 2001 and entered into force in 2004, and its subsequent ratifications and amendments, requires Parties to take measures to eliminate or reduce the release of POPs into the environment. To date twenty-one chemicals have been recognized as POPs causing adverse effects on humans and the ecosystem. These 21 are listed in Table 1 and can be placed in three categories: pesticides, industrial chemicals and by-products.

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Initial POPs	Additional POPs (2009 amendment)
Aldrin	Chlordecone
Chlordane	Hexabromobiphenyl
DDT	Hexabromodiphenyl ether and
Dieldrin	Heptabromodiphenyl ether
Endrin	α-Hexachlorocyclohexane
Heptachlor	β-Hexachlorocyclohexane
Hexachlorobenzene	Lindane
Mirex	Pentachlorobenzene
Polychlorinated biphenyls	Perfluorooctane sulfonic acid, its salts and
Polychlorinated dibenzofuran	perfluorooctane sulfonyl fluoride
Polychlorinated dibenzo-p-dioxins	Tetrabromodiphenyl ether and
Toxaphene	pentabromodiphenyl ether

Table 1. Chemicals currently listed as POPs in the Stockholm Convention (Stockholm Convention Secretariat, 2011).

It must be recognized that relatively few substances possess the necessary properties to make them POPs. However, the number of substances that can have adverse effect on environment is higher.

Concerning this, in view of their knowledge contribution regarding the presence volatile chlorinated hydrocarbons (VCHCs) in the Antarctic environment, the authors believe that even substances as VCHCs should be considered as POPs and thus they should be regulated by international protocols and conventions. This even in consideration of massive industrial and commercial usage and release of VCHCs into the atmosphere, their ecotoxicity and above all in consideration of VCHC concentration levels retrieved in Antarctic waters and atmosphere, sometimes 1,000 folds higher than listed POPs (Zoccolillo et al., 2007; Zoccolillo et al., 2009).

Actually, the Stockholm Convention includes provisions for adding to the list further substances that exhibit the characteristics of POPs. At present, actions are promoted to identify further POP candidates and initiate international action on their control.

It is understood that such an international agreement has an effect limited to the substances listed and identified as POPs. In addition, the effect is limited even in consideration that, as long as materials and goods produced before the ban remain in use or are not definitively destroyed, they will represent an emission source of POPs.

Notwithstanding, in virtue of cited international conventions and protocols, many POPs are no longer produced and used in industrialized areas, a great number of developing nations have only fairly recently begun to restrict their production, use and release. Therefore, even in consideration of POP persistence, the evaluation of the occurrence of POPs in the environment is still an open question. Indeed, as a result of massive releases into the environment over the past decades, POPs are now widely distributed, including regions where POPs have never been used.

#### 2.1 Sources

The use of many POPs has declined or ceased in North America and Europe since the 1990s. On the other hand, in Asia, Africa and South America, where adequate environmental sensitivity and abatement measures for atmospheric pollutants are missing, the population increase and the subsequent growing energy demand, the burning of fossil fuels, the metal extraction, the intensive agriculture and the massive pesticide usage (for ensuring public health) lead to the introduction into the atmosphere of significant masses of persistent contaminants.

Thus, most of POPs are still in use or existing in many countries, but the actual quantity that specific countries may be currently using is unknown. There are not central registers of individual country use, although some organizations, like the FAO, United Nations Economic Commission for Europe, and the World Bank have begun to assemble aggregate use data (Ritteren et al., 1995).

POPs may enter the environment by several routes, e.g. by manufacture, use and disposal of specific chemical products and by-products and by the emissions from combustion and incineration processes. (It should be pointed out that while POPs as pesticides usually originate, according to specific applications, from agricultural or industrial use, POPs as PCBs are typically emitted from industrialised areas). In addition, it should be considered that materials and goods produced before the ban and containing POPs that are still in use or not definitively destroyed, represent an emission source of POPs even in countries where POPs are banned.

### 2.2 Environmental distribution

By definition, POPs are chemicals more persistent, mobile, and bio-available than other substances. These properties are conferred by POP molecular structure and, for halogenated POPs, they can be associated with the halogenation degree (e.g., DDT and PCBs). The physico-chemical properties of these compounds favour sufficiently high atmospheric concentrations.

According to the environmental partitioning of POPs, the physical properties of greatest importance are water solubility, vapour pressure, Henry's law constant, octanol-water partition coefficient, and the organic carbon-water partition coefficient; these properties are strongly dependent on environmental conditions such as temperature. Persistence in the environment is the other important property of a substance in terms of global transport. Persistence can be reduced by biotransformation, abiotic oxidation and hydrolysis, and photolysis. The relative importance of these processes depends on the rates at which they occur under natural environmental conditions (Rittern et al., 1995).

#### 2.3 Global diffusion

At ambient temperatures semi-volatile POPs can evaporate from water, soil and vegetation into the atmosphere; in addition if their use/application is dispersive, POPs as DDT and VCHCs can be directly emitted into the atmosphere. Once in atmosphere these substances are unaffected by breakdown reactions and are transported over long distances by winds before re-deposition that can occur via wet precipitation (rain or snow) and dry deposition. The chemicals travel through the atmosphere and the planet in several stages, with many volatilization/deposition cycles, according to the theory of global distillation and fractionation and cold condensation (Wania & Mackay, 1993; Wania et al., 1998). In such a way the most volatile compounds can redistribute globally. The process is quite complex, involving temporary deposition and re-volatilization and is influenced by weather conditions and chemical-physical properties of the compounds, such as Henry's constant, vapour pressure, octanol-water distribution coefficient and atmospheric half-life.

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Long-range atmospheric transport can move POPs away from source regions to remote and pristine locations such as Polar Regions. In Polar Regions POPs condense and the low temperatures reduce or block evaporation, producing relatively high environmental levels. The Polar Regions thus act as "cold traps" leading to an accumulation of chemicals in environmental matrices. That the dominant pathway for the transport of POPs to the Antarctic is the atmosphere, is indicated by comparable levels of POP contamination in seawater from north and south of the Antarctic Convergence, which separates sharply defined and distinct water masses (Montone et al., 2003).

The presence of POPs in remote zones as Antarctic and Arctic regions should not be underestimated. Remote zones are areas very vulnerable to contamination; ecosystems and food chains are simple, short, and consequently particularly fragile and take a long time to recover from damage. Even little chemical alteration in these pristine areas has the capability to cause global change phenomena. Therefore, a continuous atmospheric monitoring of POPs in remote zones should be made: to hold in check the level of chemical contamination, but even in order to help to explain the diffusion and distribution processes of environmentally important chemical compounds, and at the same time in order to evaluate any eventual concentration trends (e.g., resulting from a stricter application of environmental protection protocols).

# 3. Remote zones

Remote zones represent the preferential observatory for understanding the evolution of our Planet and global change processes. Unfortunately, there is no disguising the fact that researches in these areas can represent a challenge in scientific terms. In addition, geographic distance and wildness of sites implies heavy capital expenditure by research units and involvement of highly trained staff able to realize surveys even in case of unexpected difficulties.

The remotest zone of the Earth is probably the Antarctic continent. Atlantic Pacific and Indian Oceans surround this continent; Antarctica is about 1000, 3800 and 2500 km from South America, Africa and Australia, respectively. Antarctica, on average, is the coldest, driest, and windiest continent, and has the highest average elevation of all the continents. Antarctica can be considered as a "frozen desert" with little precipitation; the South Pole itself receives less than 10 cm per year, on average. Temperatures reach a minimum of -80/-90 °C in the interior during winter and reach a maximum of 5/15 °C near the coast during summer. For a long time its climate, remoteness and physical geography discouraged exploration of the continent.

#### 3.1 Remote zones contamination

In virtue of Antarctic climatic and geographic features, remote zones contamination studies are referred above all to Antarctica; insomuch as, Antarctica was designated by United Nations Environment Programme (UNEP) as a region for the global assessment of persistent toxic substances.

As about 98% of the continent is permanently covered by ice, Antarctica, the remotest continent in the Southern Hemisphere, is usually perceived as a symbol of the last great wilderness untouched by human disturbance. Unfortunately, the Antarctic environment is no longer pristine, even Antarctica is affected by global anthropogenic activities notwithstanding the peculiar characteristics of this continent. Indeed, in Antarctica there is

no industrial activity or agriculture. Antarctica has a negligible non-native population, human presence is concerned largely with scientific investigations and related logistics operations (about 1,000 in winter to about 5,000 in the summer) (SCAR, 2009). Natural "barriers" such as oceanic and atmospheric circulation protect Antarctica from lower latitude water and air masses characterize Antarctica. Notwithstanding persistent organic pollutants were found in air, snow, mosses, lichens and marine organisms, showing that these contaminants are transported from other continents in the Southern Hemisphere (Bargagli, 2008). To give an example, pesticides have been neither produced or applied in Antarctica, but since 1960s several pesticides have been reported in biotic and abiotic matrices from Antarctica and the Southern Ocean (UNEP, 2002)

#### 3.2 POP sources in remote zones

The Antarctic region in characterised by the almost total absence of local pollution sources. Pollutants reach Antarctica almost exclusively by long-range transport processes. Source identification of POPs and input sources in the Antarctic area is a very important and complex task.

As POPs released to the environment have been shown to travel vast distances from their original source, they can reach remote zones. For instance, since in Antarctica there are no agriculture or insects, chemicals as organochlorine pesticides are not used, their presence in Antarctic ecosystem can be due almost exclusively to long-range atmospheric transport from areas where these substances are still used and produced.

The main sources of POPs in the Southern Hemisphere are urbanized areas characterized by intensive agriculture, and tropical and subtropical regions, in particular South America, where pesticides are largely used. Another source of POPs is e.g. PCBs used in older electrical devices that were deposited as landfill in some developing countries (Iwata et al., 1993). In addition, population growth and industrial development in several countries of the Southern Hemisphere are changing the global pattern of persistent anthropogenic contaminants and new classes of chemicals have already been detected in the Antarctic environment (Bargagli, 2008; Zoccolillo et al., 2009).

Locally, the greatest impact can be expected where research is carried out at long-term stations with a slight emission of some POPs. In addition, pelagic fisheries are an important operation in some parts of the region, and tourism is an increasingly important activity (SCAR, 2009). Unlike pesticides, some industrial POPs such as PCBs were used in Antarctica leading to contamination in neighbouring areas, e.g. at McMurdo Station (Ross Island) (Risebrough et al., 1990). The impact of scientific bases and related activities on the environment are more efficiently recorded by sediment analysis.

# 4. Air analysis of POPs

The sampling and the analysis of persistent organic pollutants in atmosphere remain a challenge, especially when the atmosphere of remote zone is considered, taking into account low POP atmospheric concentrations.

Undoubtedly, the most crucial step is the sampling step. The gathered sample has to be representative of the monitored atmosphere; the sample has to represent an aliquot of the monitored atmosphere with the same composition and characteristics. Furthermore, from sampling to analysis time no sample contamination (analyte addition), degradation (analyte transformation) or loss (analyte loss), have to occur. Thus, sampling devices have to be appropriate even according to storage and transport conditions.

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When a gas-phase component of the atmosphere has to be measured, two main approaches are operable during the sampling step: air sampling and analyte sampling. Air sampling consists in collecting an aliquot of atmosphere in special containers, the whole-air samplers, as plastic bags, glass vessels and stainless-steel containers. Analyte sampling consists in (passive or active) collecting only the gaseous analyte in a suitable "trap" avoiding air gathering. The approach's choice depends on several factors as chemical and physical characteristics of the air contaminant, its expected concentration, presence of interfering substances and ambient temperature and humidity. The selection of the sampling method depends also on analytical method detection limit: prior to sampling the minimum sample volume allowed by the analytical method has to be determined. Collection of the minimum volume is necessary to collect enough contaminant to meet the method's detection limit and thus measuring the expected concentration level. Therefore when the minimum volume exceeds e.g. 10 L, whole air sampling approach is unfeasible (the volume of whole air samplers is limited, in addition such an approach would be uneconomical) and thus analyte sampling approach has to be followed. This last is the case with semi-volatile compounds characterized by very low atmospheric levels, as PCBs.

Due to the low concentrations of POPs in atmosphere, an enrichment step is always required, i.e. a direct analysis of the air sample is unworkable. This step takes place just prior to analysis when a whole-air sample is collected, or at the same time of analyte sampling when the analyte is collected and then concentrated into the "trap".

The enrichment or trapping techniques can be based on three principles that "entrap" chemicals: absorption, adsorption and condensation. The analytes can be: a) collected into a solvent or on impregnated surfaces; b) collected onto adsorbents via passive or active sampling or onto fibres; c) condensed in cryotraps. The choice of the enrichment techniques strongly depends on the sample and on the contaminants to be collected.

Once decided the sampling method in accordance to needed sample type (instantaneous or time-integrated sample), sample number and above all expected chemical concentration and detection limit, the analytical question has to be faced. Compared to other chemicals and matrices, the analysis of POPs in atmosphere is time-consuming, complex, difficult, and expensive. Extremely sensitive, specific and efficient analytical procedures are required because the analysis must be performed for very low concentrations in the pg m<sup>-3</sup> and sub pg m<sup>-3</sup> range. Depending on the case, the pre-treatment step will consist in enrichment and desorption of the chemicals (in case of air sampling) or in extraction of the chemicals from the "traps" (in case of analyte sampling).

In consideration of chemical nature of chosen substances, analytical separation is generally carried out by high-resolution gas chromatography (GC). The detection can be realized by flame ionization detector (FID) or sometimes by electron capture detector (ECD), for electron-absorbing components such as halogenated compounds. However usually, detection and thus a certain identification of chemicals, is performed by high resolution mass spectrometer (MS) operated in electron impact ionization mode and in selected ion monitoring (SIM) mode

#### 4.1 POP sampling and analysis in the atmosphere of remote zones

Air quality studies in remote zones require above all specific sampling and analytical methods that consider extreme environmental conditions. Sampling and analytical methods and equipment have to be specifically planned and modified in order to overcome several hurdles. Sampling devices have to own specific features able to realize representative gatherings even at very low temperatures, made up in material resistant to transport under

adverse conditions and with relatively long-time storage capacity taking into account that several weeks might elapse between collection time and analysis. In addition, when sample collection has to be carried out at remote sites, the sampling equipment should be portable. On the other hand, analytical methods have to be at the cutting edge, as the low concentration levels of chemicals in the considered matrix; at times, a significant improvement concerning the current analytical methodology, in terms of precision and limits of detection can be required.

Whole-air samplings can be performed with a battery operated diaphragm pump and stainless steel canisters (Figure 1). As the pump is battery operated and oil-free, in situ samplings can be performed even in absence of electric current and no contamination of the air sample during the collection can occur. As the canisters are made in stainless steel with interior surface fully deactivated with SUMMA® electro polish technique, any adsorption, deposition and release phenomena are avoided. In addition, air can be collected in them under pressure, consequently a greater volume of sample is available for performing several analyses and, at the same time, any contamination from external environment is thus avoided and on-line analyses can be carried out without a lift pump. The sampling apparatus described is durable, quite light, easy to transport and allows long-term storage. The commercially available apparatus is inappropriate for the severe Antarctic temperatures. Therefore, it has to be suitably modified: a) covering the pump with insulating materials (expanded polyurethane foam and a woollen cap) and then connecting its air way-in to a stainless steel probe; b) realizing a self-warmed and insulated warming system to warm up the pump and compensate the battery charge loss during the sampling operations and to store the pump inside it during transport to the sampling site, to minimize temperature effects; c) replacing canister's original connections and valves with 316 stainless steel connections with metal-to-metal seals and 316 stainless steel diaphragm valves in order to guarantee canister's hermetic seals even at extremely low temperatures and during sudden changes of temperature. The sampling system can be easily cleaned with evacuation/helium filling operations prior to air collection. (Zoccolillo et al., 2009).

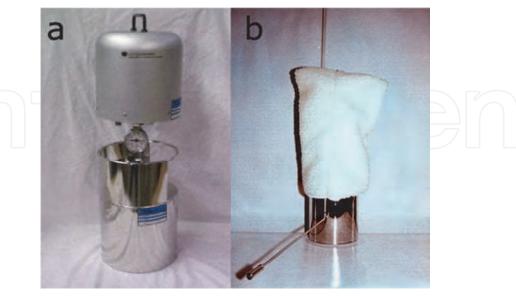


Fig. 1. Air sampling equipment: diaphragm pump and canister. Original apparatus (a) and modified apparatus in usage conditions for polar climate with woollen blanket and stainless steel probe (b) (Zoccolillo et al., 2010).

After whole-air sampling, a specific analytical methodology, characterized by high precision and accuracy and low limits of detection, has to be employed to quantify volatile organic compounds as VCHCs in air samples where the investigated substances can occur at pptv and sub-pptv levels. Volatile organic compounds can be analysed even in only slightly contaminated air samples, such as those from remote zones, with a specifically developed analytical technique based on a cryofocusing trap injector coupled to a gas chromatograph with mass spectrometric detection (CTI-GC-MS). The cryofocusing-trap-injector is the result of appropriate low cost modifications to an original purge-and-trap device to make it suitable for direct air analysis. Air samples, collected in stainless steel canisters, are introduced on-line directly into the CTI-GC-MS system; the volatiles contained in the air are cryo-concentrated into a cold trap at -120 °C and the entrapped volatiles are subsequently directly injected into the capillary column by means of rapid thermal desorption at 200 °C for the subsequent analysis of volatiles by GC-MS. Qualitative and quantitative analysis is performed by external standardization by means of certified gaseous standard mixture of the investigated VCHCs in synthetic air (Zoccolillo et al., 2010).

Active sampling of POPs from the atmosphere can be made with polyurethane foam plugs (PUF). Ambient air samples (from 1000 to 2500 m<sup>3</sup>), collected over a period of 4-5 days using a high-volume sampling system, pass through the PUF and the compounds in the gas phase are adsorbed on the PUF. To be more precise, air is pulled through a glass-fibre filter to remove particles and subsequently passes through the PUF sorbent plugs to extract vapour phase organic compounds from the filtered air. The complete system is housed in a clear-anodized aluminium outdoor shelter (Figure 2).



Fig. 2. Head of a PUF (polyurethane foam) sampler.

For POP determination, the PUF is Soxhelt-extracted with organic solvents for several hours. After concentration and clean-up, the extracts are analysed by gas chromatography-mass spectrometry (GC-MS) (Gambaro et al., 2005; Kallenborn et al., 1998) or by gas chromatography-electron capture detection (GC-ECD) (Montone et al., 2003). In order to minimize the interfering substances contamination and to provide acceptable blanks, prior the sampling the PUF plugs have to be cleaned by a long Soxhlet extraction, then the cleaned PUF plugs are dried in a dessicator, packed in glass flasks and sealed in plastic bags until sampling (Montone et al., 2003). PUF plugs are convenient to handle and economical, but can exhibit breakthrough of semivolatile and volatile compounds (Camel & Caude, 1995).

Passive sampling of POPs from the atmosphere can be made with semipermeable membrane devices (SPMDs). These samplers are constituted by a thin film of triolein lipid enclosed in lay-flat, low-density polyethylene membrane (Figure 3). The polymer consists of transport corridors of less than 10 Å in diameter; these pores allow for the selective diffusion of hydrophobic organic chemicals, which are then sequestered in the lipid phase. SPMDs have to be deployed in appropriate screen to protect them from direct wet-deposition and sunlight (Figure 3).



Fig. 3. a) Semipermeable membrane device (SPMD); b) SPMDs deployed inside a stainless steel container.

For POP determination, SPMDs are dialysed with the appropriate solvent and the extract, after clean up, is analysed by GC-MS (Ockenden et al., 2001a). SPMDs are deployed over weeks/months/years in the chosen site. Deployment time of the SPMD is analyte-dependent; in addition, it depends on instrument limit of detection, SPMD blank level, uptake rates and typical atmospheric concentration of the POP. The capacity of the SPMD depends on the quantity of lipid in the sampler and uptake rates by SPMDs depend on permeability of the membrane. Uptake rates are influenced by ambient temperature and wind speed; performance reference compounds can be used to "correct" for site-specific differences in uptake rates. SPMDs are easily contaminated, thus SPMD field blanks have to be taken to the field in sealed containers but not exposed, in order to evaluate the degree of contamination. Despite cited drawbacks, SPMDs are ideal samplers for studies into spatial differences in concentrations and profiles of POPs in the atmosphere, to identify sites where further investigations are required and for producing time-integrated data (Ockenden et al., 2001a).

#### 4.2 Quality control

Quality control of the analytical procedure for POP determination in samples from remote zones is a very critical step in consideration of low atmospheric POP levels and the time lag between sampling and analysis. The risk of contamination is higher in particular for Antarctic air samples due to the much longer transport and storage time.

Suitable analytical quality control and quality assurance programs have to be run in the sampling site and in the laboratory, during sample gathering and analysis in order to guarantee data reliability.

With the purpose of assuring the overall quality and validity of experimental data, a systematic and detailed sampling strategy and blank choice have to be carried out. In order to prevent any contamination during sampling operations, clean room protocols should be attended. All the samplings should be performed downwind and away from local contamination sources, e.g. scientific stations. The operators should wear special clean room clothing and polyethylene gloves even during sampling, over their warm clothing. Immediately after the gathering, an opportune storage procedure (different according to the sampling method and sampling device) is applied in order to maintain unaltered the sample characteristics. The laboratories where the analysis will be performed, should be "Class 100 clean room", as classified by ISO Standard 14644-1. The chemicals used for sample treatment have to be ultra-clean reagents. The laboratories.

Improvement of the storage containers to suppress the risk of contamination during storage should be realized prior to actual sampling. For instance, in order to evaluate the storage capability of a canister at very low temperatures and in case of sudden temperature changes, the canisters can be maintained at -20 °C (or at lower temperature if feasible) for a lapse of time comparable to Antarctic expedition duration and brought back to room temperature during the storage. Canister content, e.g. air with the lowest levels of organic contaminants, can be analysed immediately after the collection and after a variable storage time. No significant deviations of the composition during the storage should be noticed, at the investigated concentration level (Zoccolillo et al., 2009).

The risk of sample contamination has always to be investigated by taking field blanks. At least one field blank should be processed with each sampling episode. As an example, a field blank for POP sampling with PUF consists of a sample cartridge containing PUF and filter (spiked with a standard solution) shipped to the field, installed on the sampler and passively exposed at the sampling area. It is then sealed and returned to the laboratory for extraction, cleanup, and analysis, such as an actual sample.

A part from field blanks, procedural blanks have to be evaluated by analysing different types of blank samples, according to sampling and analytical procedures, e.g. laboratory method blanks and solvent blanks.

Finally, the samples processed have to give highly reproducible results by using traceable standards. Unfortunately, gas standard reference materials, with similar composition of remote zone atmosphere, are lacking.

# 5. Levels of POPs in remote zones air

While measurements of POPs in the Northern Hemisphere are quite well documented, Southern Hemisphere measurements, and particularly POP measurements are still sparse and relatively limited. There is a limited atmospheric database on POPs in remote areas. Data about air levels of POPs are very sparse and originate mainly from cruises close to the Antarctic continent and from a few sampling campaigns on the continent itself.

The studies concerning the atmospheric content of POPs in Antarctica mostly focused PCBs, organo-chlorine pesticides as hexachlorocyclohexanes and dioxins and emerging pollutants such as VCHCs and PAHs, that were determined in atmospheric samples collected at different Antarctic sites. The studies carried out by several research groups all over the world, focused on long-range transport processes, latitudinal distribution of POPs, concentration temporal tends, scientific expedition impact and on future emerging pollutants.

#### 5.1 Long-range transport studies

Measurements of POPs in the atmosphere of remote zones can be useful to estimate the contribution of long-range atmospheric transport to the input of different classes of POPs in the southern hemisphere. The results obtained by several research groups are consistent with the hypothesis of global fractionation and long-range transport.

The possibility of atmospheric long-range transport episodes from South America to Signy Island was pointed out by Kallenborn in 1998 which measured POPs such as polychlorinated biphenyls and pesticides in ambient air at Signy Island (Antarctica), a sub-Antarctic sampling station, over a period of 17 weeks in the austral summer of 1994. Mean concentrations for single polychlorinated biphenyls (0.02-17 pg m<sup>-3</sup>), for chlordanes (0.04-0.8 pg m<sup>-3</sup>), DDT compounds (0.07-0.40 pg m<sup>-3</sup>) and γ-hexachlorocyclohexane (22 pg m<sup>-3</sup>), were comparable to those in Arctic air (Kallenborn et al., 1998). Previous studies realized in by Tanabe et al. (1983), Weber & Montone (1990) and Larsson et al. (1992) provided further evidence of atmospheric transport of PCBs and organo-chlorine pesticides in the Antarctic environment. Tanabe et al. (1983) measured PCBs and chlorinated hydrocarbon pesticides such as DDTs and hexachlorocyclohexanes (HCHs) in air sampled in proximity of the Japanese research stations in Antarctica and adjacent oceans during December 1980 to March 1982. The atmospheric concentrations of chlorinated hydrocarbons seemed to decrease in the transport process from northern lands to Antarctica, but the compositions of PCBs, DDT compounds and HCH isomers were relatively uniform throughout this process. Regional and seasonal variations were found in aerial concentrations of these pollutants at Syowa Station and adjacent seas in Antarctica. Larsson et al. (1992), monitored PCBs, p,p'-DDT, p,p'-DDE and y-HCH in the lower atmosphere of Ross Island, in Antarctica for 2 yr. Geometrical means were 15.2 pg m<sup>-3</sup> for PCBs, 2.0 pg m<sup>-3</sup> for p,p'-DDT, 1.0 pg m<sup>-3</sup> for p,p'-DDE and 25.8 pg m<sup>-3</sup> for γ-HCH. Atmospheric levels of γ-HCH were positively correlated with temperature, and a significant difference was found between spring-summer and summer-winter concentrations. No season related differences were found for the other chlorinated hydrocarbons, possibly owing to their lower vapour pressure and the cold climate. Periods with increased atmospheric levels of PCBs and DDT compounds were recorded. Chlorinated pesticides in air were measured from the Greenpeace ship Gondwana between New Zealand and Ross Island, January-March, 1990. Geometric mean concentrations:  $\alpha$  and  $\gamma$ -HCHs 4.0 and 3.8 pg m<sup>-3</sup>, hexachlorobenzene 60 pg m<sup>-3</sup>, heptachlor epoxide 0.52 pg m<sup>-3</sup>, chlordanes and nonachlors 1.8 pg m<sup>-3</sup>, p,p'-DDE and p,p'-DDT 0.81 pg m<sup>-3</sup> (Bidleman et al., 1993). Concentrations of DDTs in Antarctic air were similar to those in the Arctic. A trend of decreasing pesticide concentration at higher latitudes was noted. Further evidence of atmospheric transport of PCBs in the Antarctic environment was provided by Fuoco et al. (1996) whose studies of Antarctic lake sediment found high contributions of atmospheric particulate matter and concluded that it is the primary vehicle of transport and diffusion of PCB in the environment. Montone et al. (2005) determined the atmosphere content of a large number of organo-chlorine compounds (HCB, HCHs, pp'-DDE, pp'-DDD, pp'-DDT and 11 PCB) in a survey performer in November of 1995 in the open ocean between 23°S and 62°S. Air mass back trajectories were used to assess the origin of the air masses that arrived at the sampling point at low altitude. Organo-chlorine levels in the atmosphere ranged from not detected (<0.6) to 25.3 pg m<sup>-3</sup> for HCB (with a mean concentration of 15 pg m<sup>-3</sup>), 3.9–32.5 pg m<sup>-3</sup> for  $\Sigma$ HCHs ( $\alpha$ -HCH +  $\gamma$ -HCH) (with a mean concentration of 8.8 pg m<sup>-3</sup> for Lindane), 3.7- 102.6 pg m<sup>-3</sup> for PDDTs (pp'-DDT + pp'-DDD + pp'- DDE) and 46.2 up to 985.0 pg m<sup>-3</sup> for PCBs (Montone et al., 2005). Choi et al. (2008)

deployed passive air samplers for one year at the Korean polar research stations at Ny-Alesund, Norway (2005-2006) and King George Island, Antarctica (2004-2005) to assess levels and patterns of polychlorinated biphenyls (PCBs) and organo-chlorine pesticides in polar regions. The observed backward trajectories suggested that long-range transport from source regions in Northern Europe and Russia and the southern tip of South America, respectively affect the Arctic and Antarctic areas. The results were consistent with the hypothesis of global fractionation and long-range transport. The authors also observed relatively high levels of PCB-11, averaging 60 pg m<sup>-3</sup>, suggesting an unusual source of PCB-11 to the Southern Hemisphere. The average level of  $\Sigma_{205}$ PCB (excluding three mono-CBs and PCB-11) was five times higher in the Arctic (95 pg m<sup>-3</sup> range) than in the Antarctic (19 pg m<sup>-3</sup>). The difference of concentration in terms of  $\Sigma_{205}$  PCBs reflects the hemispheric distribution of global PCB emissions. Levels of  $\Sigma_9$ PCB at Ny-Ålesund were similar to those reported for other Arctic sites, while levels at King George Island were lower than at other sites on the Antarctic Peninsula but 1 order of magnitude higher than background levels measured at a more remote Antarctic site. Light homologues were predominant in all samples, consistent with the hypothesis of global fractionation and predictions of long-range transport potential (Choi et al., 2008).

#### 5.2 Latitudinal distribution studies

To establish POP background air concentrations in oceanic regions and to assess their latitudinal distribution, POP data concentration can be collected during cruises such as the Atlantic cruise from the United Kingdom to Halley, Antarctica (Lohmann et al., 2004).

With the purpose of give evidence of POP transport from the northern hemisphere to the southern and to reconstruct their trends in concentrations, Lakaschus and co-workers collected POP data during two cruises across the Atlantic Ocean between the Arctic Ocean (Ny-Alesund/Svalbard, 79°N; 12°E) and the Antarctic Continent (Neumayer Station/Ekstroem Ice Shelf, 70d°S; 8.2°W) in 1999/2000 (Lakaschus et al., 2002). Hexachlorocyclohexanes (HCHs) were determined simultaneously in air and seawater. The concentrations of  $\alpha$ -HCH and  $\gamma$ -HCH in air and surface waters of the Arctic exceeded those in Antarctica by 1-2 orders of magnitude. Between Cape Town and Neumayer Station the average gaseous concentrations of α-HCH and γ-HCH were 1.1 pg m<sup>-3</sup> and 1.4 pg m<sup>-3</sup> and decreased further to 0.36  $\pm$  0.03 pg m<sup>-3</sup> and 0.15  $\pm$  0.04 pg m<sup>-3</sup> on the Ekstroem Ice Shelf at Neumayer Station. By comparison of results obtained from archived samples taken (by the same research group) in 1987/1997 and those from 1999, a systematic decrease of α-HCH was observed at all sampling locations (Lakaschus et al., 2002). Booij and co-workers collected POP data during a cruise from the island of Texel (The Netherlands) to Walvis Bay (Namibia) and Cape Town (South Africa). Aerosol and surface water samples were collected and different classes of organic pollutants were determined (Booij et al., 2007). The content of PCBs, hexachlorobenzene (HCB), 1,1-dichloro-2,2-bis(4-chlorophenyl)ethene (4,4'-DDE), and polyaromatic hydrocarbons (PAHs) were determined. The air concentrations of HCB ranged from 56 to 145 pg m<sup>-3</sup>, a value typical for background levels for air (4–140 pg m<sup>-3</sup>) (Barber et al., 2005). Atmospheric 4,4'-DDE concentrations ranged from 0.1 to 0.9 pg m<sup>-3</sup> and were smaller than the values of observed by Iwata et al. (1993) in the same area during one cruise carried out in April 1990 (1.3-6.3 pg m<sup>-3</sup>). During the same cruise, the atmospheric content of polycyclic aromatic hydrocarbons (PAHs) and of one emerging class of pollutants (polychlorinated naphthalenes, PCNs) were determined. The highest PAH concentrations occurred in the European samples, and in samples close to West Africa and South Africa.

Consistently low PAH concentrations were measured in the southern hemisphere open ocean samples (190-680 pg m<sup>-3</sup>). Concentrations showed a diurnal cycle, the day/night ratios of phenanthrene, 1-methylphenanthrene and fluoranthene were typically ~1.5-2.5:1. The highest PCN concentrations occurred in the European samples, but high values were also detected off the West African coast, and in the sample taken closest to South Africa (Jaward et al., 2004).

#### 5.3 Temporal trend studies

Studies regarding atmospheric temporal trends of POPs as organo-chlorine pesticides can be carried out by measuring the atmospheric content of HCB, heptachlor,  $\alpha$ - and  $\gamma$ -HCH, heptachlor epoxide.

Dickhut et al. (2005) determined hexachlorobenzene (HCB), heptachlor, α- and γ- HCH and heptachlor epoxide in air, seawater, sea ice, and snow. Samples were collected during the austral winter (September-October 2001) and summer (January-February 2002) along a transect in the Western Antarctic Peninsula. By comparison with previous studies they concluded HCB and HCH levels decreased over the last twenty years,  $\Sigma$ HCH showed a halflife of 3 years in Antarctic air. On the other hand, heptachlor epoxide levels did not show such a reduction, possibly due to its continued use in the southern hemisphere. They detected peak heptachlor atmospheric concentrations in coincidence with air masses moving into the region from lower latitudes. Levels of y-HCH were 1.2-200 times higher in annual sea ice and snow compared to  $\alpha$ -HCH, likely due to greater atmospheric input of  $\gamma$ -HCH. Based on the ratio of  $\alpha/\gamma$ -HCH <1 in Antarctic air, sea ice and snow they concluded that there is a predominance of influx of y-HCH versus technical HCH to the regional environment. In addition, they also observed that the  $\alpha/\gamma$ -HCH in seawater was >1, likely due to more rapid microbial degradation of  $\gamma$ - versus  $\alpha$ -HCH. Also this study concluded that the water/air fugacity ratios for HCHs demonstrate continued atmospheric influx of HCHs to coastal Antarctic seas, particularly during late summer (Dickhut et al., 2005). The spatial distribution of a-HCH and the net direction of air/water gas exchange were determined between November 1997 and February 1998 by Jantunen et al. (2004). Air and water samples were collected during a cruise between South Atlantic Ocean (South Africa) and Antarctica SANAE Base (70°S, 3°E). The α-HCH concentrations in air and surface water resulted much lower than in Arctic regions, consistent with the historically lower usage of technical HCH in the Southern Hemisphere. The water/air fugacity ratios of α-HCH were lower than or equal to 1.0, indicating steady state or net deposition conditions. The results of one analysis of the enantiomeric fractionation showed that the a-HCH in water was enantioselectively metabolized and that the two isomers  $[(-)\alpha$ -HCH and  $(+)\alpha$ -HCH] in the air boundary layer reflected those in surface water, showing the bidirectional nature of gas exchange (Jantunen et al., 2004).

#### 5.4 Scientific expedition and station impact studies

Unlike pesticides, only some industrial POPs such as PCBs were used in Antarctica (Risebrough et al., 1990). Therefore, scientific expedition and bases can be a source of POPs. In order to study the impact of scientific expeditions and bases, areas neighbouring stations and zones where occurred scientific operations, can be monitored. A concentration gradient was observed with distance from the main buildings of scientific bases in the Antarctic, which strongly indicated the influence of local sources (Choi et al., 2008).

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#### 5.5 Recent studies

Recent studies carried out in Antarctica, increased the limited atmospheric database on POPs in remote areas by reporting POP concentrations during the austral summer and hypothesizing their possible sources.

Montone et al. (2003) reported atmospheric levels of PCBs near the Brazilian Antarctic Research Station, at King George Island, during a sampling survey undertaken in the austral summer of 1995-1996. Single PCB congeners ranged from below detection limit to 33.2 pg m<sup>-3</sup>. The lower chlorinated congeners (PCB-101 and below) predominated in the air samples and represented 66.7% of the total PCB concentrations. Atmospheric levels of PCBs were correlated with meteorological conditions (as well as to the general synoptic atmospheric circulation of the region) and the higher levels were associated with the passage of the frontal system coming from South America over the Drake Passage causing a local increase in air temperature and surface winds from northwest, north and northeast (Montone et al., 2003). Gambaro et al. (2005) monitored the air near Italian Antarctic Research Station. Gas-phase concentration of individual PCB congeners in the air of Terra Nova Bay ranged from below detection limit 0.25 pg m<sup>-3</sup>. The gas-phase  $\Sigma$ PCB concentrations ranged from 0.61 to 1.78 pg m<sup>-3</sup> with a mean concentration of 1.06 pg m<sup>-3</sup>. Over 90% of the total PCB content was due to congener with one to four chlorine atoms and only about 10% with five to seven chlorines, whereas higher chlorinated PCBs were below detection limits. In agreement with other studies, the results emphasized that the PCB profile was dominated by tri-CB and tetra-CB with relatively high contributions from mono-CB and di-CB (Gambaro et al., 2005). In addition, investigations on POP distribution in Antarctica were made by Ockenden at al. (2001b) which monitored the air for PCBs at two sites in the southern hemisphere, one over land and the other over water. They found that the highest concentrations were observed when temperatures were greater and the air concentrations were higher over water than over land. POP concentrations were found to be higher in air samples from the Antarctic Peninsula and sub-Antarctic islands than in those from continental sites (Bargagli, 2005).

#### 5.6 Future emerging pollutants

According to substances not yet listed in the Stockholm Convention (see § 2), concern is growing on manmade chemicals that for their physical-chemical properties can reach remote zones, potentially explicating their ecotoxic effect on fragile ecosystems.

Zoccolillo et al. (2009) measured some volatile chlorinated hydrocarbons in the proximity of the Italian Antarctic Research Station (Mario Zucchelli Station), at Edmonson Point, Thethys Bay and Talos Dome. The VCHCs investigated were present in all samples in concentrations varying from tens to hundreds of ng m<sup>-3</sup>. Surprisingly, it emerged that the Italian air gathered in rural areas had a comparable level of chemicals, whereas POPs as PCBs show a substantial difference in concentration between temperate and remote zones; in addition, VCHC concentration levels were 1,000 fold higher that other POPs. These results can be considered evidence that other organic compounds may represent future emerging pollutants in Polar Regions and suggest that future monitoring and regulating actions should be undertaken. Other contaminants like polybrominated dyphenil ethers (PBDEs), perfluorooctanesulfonic acid (PFOS) and endosulfan, not yet included in the POPs list but being considered for inclusion in the Stockholm Convention, have already been taken into consideration in a few studies carried out in Antarctica. On the other hand, some organochlorine compounds (mirex, dieldrin, and chlordane) included in the Stockholm Convention have been recently investigated, but data are still very limited.

Although the presence of useful research studies and data in recent literature, a coordinated action is still lacking. An international coordinated project should be promoted on key targets in order to cover actual gaps such as temporal trends of contaminants, processes controlling distribution and transport of POPs in polar environments, including mass transfer at the environmental interfaces (air-water, air-snow, air-biota), and monitoring of future emerging pollutants in polar regions (SCAR, 2009).

# 6. Conclusion

The Stockholm Convention in 2001 banned manufacture and new use of 21 POPs. Unfortunately, such action has a limited effect, because the number of substances that can have adverse effect on environment is higher, insomuch as many new chemicals are under consideration for listing under the Stockholm Convention. In addition, as long as materials and goods produced before the Stockholm Convention ban remain in use or are not definitively destroyed, they will represent an emission source of POPs.

In this scenario, the scientific community has to keep on studying the environmental sources, behaviour and impact of POPs, especially in remote zones due to vulnerability of Polar Regions to organic contaminants that originate from lower latitudes. At present, not many research groups reported on POP atmospheric levels in remote zones, probably due to the difficulty connected with such a determination in terms of sampling and analytical techniques. Despite reported POP atmospheric concentrations seem to be below those documented to have biological effects, it is impossible to directly transfer toxicological data and models developed in temperate climate on polar biological systems. Polar living beings are endemic species with a long evolutionary story in bio-geographical isolation, more vulnerable to the adverse effects of persistent contaminants. The length of the food chains enhances the biomagnifications of POPs, potentially threatening the health of wildlife. Therefore, it is to be hoped a continuous monitoring of POPs, and other manmade chemicals that behave similar to POPs, in the atmosphere remote zones with the suitable sampling and analytical techniques, in order to better understand their transport pathways and environmental fate, and to monitor their presence and their concentration trends in fragile ecosystems.

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Human beings need to breathe oxygen diluted in certain quantity of inert gas for living. In the atmosphere, there is a gas mixture of, mainly, oxygen and nitrogen, in appropriate proportions. However, the air also contains other gases, vapours and aerosols that humans incorporate when breathing and whose composition and concentration vary spatially. Some of these are physiologically inert. Air pollution has become a problem of major concern in the last few decades as it has caused negative effects on human health, nature and properties. This book presents the results of research studies carried out by international researchers in seventeen chapters which can be grouped into two main sections: a) air quality monitoring and b) air quality assessment and management, and serves as a source of material for all those involved in the field, whether as a student, scientific researcher, industrialist, consultant, or government agency with responsibility in this area.

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