



United Nations Environment Programme Chemicals

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Eastern and Western South America REGIONAL REPORT

Regionally Based Assessment of Persistent

Substances

December 2002

Global Environment Facility

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UNITED NATIONS ENVIRONMENT PROGRAMME



CHEMICALS

Regionally Based Assessment of Persistent Toxic Substances

Argentina, Bolivia, Brazil, Chile, Ecuador, Paraguay, Peru, Uruguay

EASTERN AND WESTERN SOUTH AMERICA REGIONAL REPORT

DECEMBER 2002



GLOBAL ENVIRONMENT FACILITY

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Available from:

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

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PREFACE

This report is part of the work conducted under the Project Regionally Based Assessment of Persistent Toxic Substances, conducted by UNEP-Chemicals and contracted to EULA-Chile Center, University of Concepción, Chile and the Regional Team: Dr. Ricardo Barra – Regional Coordinator (University of Concepción, Chile) Dr. Juan Carlos Colombo (University of La Plata, Argentina), Dr. Wilson Jardim (University of Campinas, Brasil), Dr. Nadia Gamboa (Catholic University of Perú, Perú), and Dr Gabriela Eguren (University of La Republica, Uruguay).

Several people contributed to this report, including other colleagues from the eight countries belonging to our region, who actively participated in the technical workshops supporting with data and very useful opinions to make this report more representative of the actual situation related to Persistent Toxic Chemicals within the region.

We acknowledge that not all existing data regarding PTS substances is presented in this report, several governmental organizations kindly gave us access to data bases but others not. Therefore this report represents the analysis of available (i.e. accessible) data on PTS substances. To our knowledge this is a first effort to compile and analyze the information within the defined region Eastern and Western South America. Our thanks to UNEP-Chemicals and GEF for making this effort possible and we hope that new projects and research will be conducted using this document as a starting point.

Ricardo Barra, Juan Carlos Colombo, Nadia Gamboa, Gabriela Eguren, Wilson Jardim.

November, 2002.

EXECUTIVE SUMMARY

1. INTRODUCTION

This report represents the effort of data compilation on Persistent Toxic Substances (PTS) for the eastern and western South America region (Region XI). It is the first attempt to gather a comprehensive collection of data and analyse information covering eight countries: Argentina, Bolivia, Brazil, Chile, Ecuador, Paraguay, Peru and Uruguay. The region covers a wide diversity of ecosystems and climatic conditions with different patterns of use and disposal of chemicals both in agriculture and in industry.

The present UNEP assessment of PTS in South America is based on the data collected from different sources, international peer reviewed journals, governmental reports, contributions from individual researchers from the different countries belonging to the region and from questionnaires mainly filled in by the regional team.

2. MAIN FINDINGS OF THE REPORT

As in most other areas of the world, the South American region has been affected by PTS from different sources, including pesticides used for agricultural or sanitary reasons, industrial chemicals such as PCBs widely used within the region, and industrial by-products (dioxins and furans). Probably one of the most specific sources of PTS compounds may be the large amount of biomass combustion. The region still presents some areas of concerns (i.e. Hot spots).

Contamination associated with the use of DDT and aldrin, dieldrin, endrin (DRINs) is widely disseminated throughout the countries within the region. However geographical distribution of available information is not evenly spread throughout the Region. There is an obvious bias in the information collected towards data from contaminated areas.

2.1. Sources

The knowledge of contamination sources of the region is scarce, and when it does exist, is not normally readily available to the public. Also the amount of chlorinated pesticides used at a regional level before the banning of these products is not available, but some countries have information on imported pesticides. Several PTS were produced within Region XI (mainly in Brazil and Argentina), even after being forbidden and banned in Europe and North America. Consequently, the legacy of this industrial activity has been noted in several areas now considered as hot spots, or as 'heavily contaminated'.

Industrial chemicals and by-products are being assessed throughout the region. For instance, Uruguay released the first inventory of dioxins and furans and other countries have started PCB inventories.

Sources main issues

- The chlorinated pesticides continue as a problem because some of them are still in use within the region (e.g. lindane, endosulfan).
- The main source for polychlorinated biphenyls (PCBs) are oils contaminated in electrical equipments (in use or stored); however other uses cannot be discarded. The total amount of PCBs in the region are still unknown, but some countries have started national inventories. An estimated amount of 131000 tonnes have been reported but this should be treated as a preliminary figure since inventories are not yet complete.
- Practically all known sources of dioxins and furans described in the literature are present in the region. Unfortunately at this stage is only possible to make some emission estimates of dioxins and furans. The first regional workshop strongly recommended the use of the toolkit developed by UNEP, but it was suggested that emission factors should be evaluated before reliable estimations could be made. A total emission of 722 g TEQ/year to the atmosphere was estimated for the region using a correlation with CO₂ emissions. This estimate is lower than those of some industrialized countries (i.e. France).
- There is no conclusive evidence of the role of biomass burning (intentional or unintentional) a widely used practice throughout the region as an important source of dioxins/furans.
- From the priority point of view, a general consensus was obtained that there was an urgent need to evaluate sources of PCBs, dioxins and furans and PAHs within the region.

2.2. Contamination levels, trends and effects

Regional information about environmental concentrations are heterogeneous, strongly biased towards some compartments and with scarce evaluation of temporal or spatial trends.

Air levels

Very few data was retrieved for air samples. Some of these related to PAHs levels in atmospheric particulate from urban areas (Santiago de Chile, Sao Paulo, Buenos Aires, La Plata). PAHs represents a serious threat to human health in densely populated areas considering that more of the 75% of the total population within the region lives in urban settings. Reported levels are in same order of magnitude as highly industrialized cities. As mentioned before, PAHs are of concern because emission sources exist throughout the region; therefore more data should be gathered in large urban areas. There are no measurements of pesticides in air. The few data for dioxins, furans and PCBs indicate lower values than reported levels from the Northern Hemisphere .

Soil levels

The soil data refers mainly to chlorinated pesticides (Chile, Brazil) and in some cases PAHs. Some hot spots were reported from Brazil, mainly related to contaminated industrial sites where HCHs and aldrin were produced. In Chile, a national survey performed by INIA in the early 1990s reported low levels of chlorinated pesticides in agricultural soils, concluding that the banning of pesticides during the 1980s was effective. However a high frequency of detections in several parts of the country revealed that contamination was widespread. No further data have been produced.

Water and sediments levels

These exhibit a wide range of PTS values, strongly biased by high values from industrialized and urban areas such as Rio de La Plata (Argentina and Uruguay), Rio de Janeiro (Brazil) and Biobio River (Chile), which each have critical values far exceeding international regulations.

Biota levels

Biota represent a target for analysis of PTS, and in general concentrations in biota depend on their trophic level - higher concentrations are commonly found in top predators e.g. fish eating birds and marine mammals. A diverse data base exists for PTS levels in biota, chiefly represented by bivalve and fish data. Mussel Watch results indicate some critical areas in Argentina (Río de la Plata), Brazil (Recife) and Chile (Punta Arenas). Available fish data also support the higher degree of PTS contamination in urban-industrial centers. Another factor not considered is that migrating biota can be a important transport mechanism of PTS substances within the region but also outside the region

Foods levels

Most of this information is related to pesticide levels in foods, mainly dairy products, fish, meat, oils, chicken, vegetables, etc. DDTs, HCHs, DRINs, heptachlor, endosulfan are the most frequently detected pesticides. In general, data show a decreasing trend especially for DDT, in recent years. Few data for PCBs and dioxins and furans have been reported in food products.

Human levels

Reported levels of pesticides for occupational exposure are very high, however the database is relatively old sincethe data was produced more than ten years ago. It is expected than banning and regulations for pesticides during the recent years have resulted in reduced levels of these products in humans. Dietary human exposure through the food chain has been little explored. In spite of the alimentary habits for the people in this region, it is well known that dietary intake accounts for more than 90% total potential intake for dioxins and furans; the same situation is given for PCBs. Considering the potential exposure to these pollutants in the region, there is an urgent need to perform analysis and monitoring in foodstuffs. No data was gathered regarding human effects of PTS. There are an obvious concern and need to evaluate not only acute effects, already well described, but chronic effects for which little information exists..

2.3. Potential threats

- Recycling of stored PTS substances and Illegal use of PTS
- Release of PTS through accidents during production, transport, waste disposal, and storage, including existing dumps (e.g., leakage from landfill sites).
- Higher deposition of PTS substances from the atmosphere to cold, pristine and highland areas

- Occupational exposure and the intake through foods
- Legal gaps

2.4. Geographical areas of concern

Contaminants are widely, but not uniformly distributed around the region. Geographical variation in levels results from point sources of contamination, leading to local pollution where important industrial and urban settings are located (e.g. Rio de La Plata, Biobío River and cities of Sao Paulo and Rio de Janeiro). Unfortunately, data from some countries such as Paraguay and Bolivia, are very scarce pointing to the urgent need to promote monitoring activities within the region. Several important ecosystems within the region are not represented in the data base (e.g. Cordillera de los Andes, Amazonia, Patagonia, Highlands areas from Ecuador, Peru. Bolivia), therefore no conclusions can be obtained on the environmental levels in these large areas.

The South America region holds some areas of global importance such as the Amazon and the Pantanal, the largest wetland on Earth. In addition, the Sao Francisco, Paraguay-Parana-Rio de la Plata basin and the river basins draining to the Pacific Ocean, represent very important possible transporters of PTS.

2.5. Gaps in current understanding

The understanding of pathways of transport and deposition of PTS is poor, particularly the determination of contaminant focusing zones and understanding the processes of sequestration by sediments. There is also a need to increase the knowledge of local sources, levels and trends of PTS in this region. The information compiled by this report is biased by that generated in the principal cities of Brazil, Argentina and Chile and is not avalable in countries such as Paraguay, Bolivia and Ecuador.

Gaps exist in the understanding of emissions of PTS from slash and burning processes which are widely disseminated across the region. Knowledge about combined effects between climate change and contaminant pathways, including improvements of models for assessments is needed. Existing models on climate change and transport processes do not have the resolution and accuracy needed to fully assess environmental consequences of anthropogenic emissions into the region.

Current understanding of PTS inputs to coastal ecosystems via rivers is inadequate. It is necessary to remember that most of the population lives around coastal areas; therefore the levels of PTS in those areas should be a priority. Aquatic freshwater systems, dominated by large rivers represent the main intra- and inter-regional transport pathways, The use of natural and anthropogenic tracers to mimic contaminants and distinguish sources has been underutilized. There are no scientific studies concerning understanding the behaviour of PTS and their pathways in biota and humans via food in both the freshwater and marine environment.

It has also been recognized there is a lack of available ecotoxicological and toxicological information regarding PTS substances.

2.6 Recommendations for future activities

Compared to receptors, very little attention has been given to the identification and quantification of PTS sources. It is recommended to government environmental agencies the need for a more comprehensive program on source assessment. Toxicological and ecotoxicological assessment of PTS is another area of concern that needs more attention in the future. The understanding of the fate of PTS in remote areas is a strategic need for the region. Development of technology for adequate stockpiling and final destruction of PTS should be strengthened throughout the Region.

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. A regional coordinator assisted by a team of approximately 4 people controls each region. The co-ordinator 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 Information Collection And Data Base Structure

The task of data collection and compilation was carried out following the recommendations outlined in the project and developed during the Regional team meetings (Chile, April 2001; Peru, May 2002; Argentina, June 2002). After the initial steps of organization and project diffusion, the information collected was classified according to environmental media and reproduced on the appropriate questionnaires. Only data published in scientific papers or technical reports were considered. Owing to the relative paucity of information a compromise was taken between data quality and absence of information. This situation was particularly critical in less developed and remote areas.

Once filled and verified, the forms were completed and sent by Internet to UNEP Chemicals Geneva. The individual data extracted in each questionnaire grouped by environmental media were evaluated considering geographically distinct areas using the spatial resolution indicated in the Project maps by individual numeric codes. In this way, data were reduced to local area means for each environmental compartment; information from contrasted rivers/ecosystems was not averaged, i.e. more than one data for a same geographical code were included.

The region XI database has a total of 3694 questionnaires with a higher proportion of forms from Argentina, Brazil and Chile (Figure 1). The information correspond basically to chlorinated pesticides which have a >30 year-long monitoring tradition in some countries (i.e. Argentina, Brazil, Chile). Fewer reports were obtained for PCBs, PAHs and especially for dioxins and furans, which have been only recently measured in some areas of

the region. This trend is anticipated by the increasing analytical difficulties and more recent developments of PCBs and dioxin/furan techniques, whereas pesticides have been systematically determined. The PTS regional database is then strongly biased to chlorinated pesticides, and among them the most prevalent are HCH, DDTs, Heptachlors and Drins (Aldrin, Endrin and Dieldrin). The information is also skewed with respect to environmental compartments since animal, water, sediment, food and human data predominate. Proportionally, fewer reports were obtained for air, soil and vegetation. Another general data base pattern is the clear predominance of information from densely populated and industrialized areas (e.g. Buenos Aires, Santiago, Sao Paulo), reflecting the preoccupation with the most critical sites (hot spots). Remote and little impacted areas are thus under-represented due to the absence of systematic and extensive monitoring programs. The conclusions obtained should be thus interpreted in the context of these data limitations and possibly correspond to a worse case Regional scenario.



Figure 1.1 Number of questionnaires by country and compartment.

1.2.5 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 EASTERN AND WESTERN SOUTH AMERICA REGIONAL ASSESSMENT

The scope of this report is to deliver a first comprehensive analysis of the threats and danger of PTS substances to the human health and the environment in the Region XI. The South American region defined in the context of this project is composed by the following countries: Argentina, Bolivia, Brazil, Chile, Ecuador, Paraguay, Peru and Uruguay. Region XI supports a large number of people and global resources. Pollution issues within the region are very complex and to a great extent poorly understood. It is generally accepted, however, that PTS chemicals were widely used with different patterns and intensities in the region, but until now only few reports have been produced to evaluate the magnitude of the problem.

1.3.1 Existing Assessments

Currently, there have been little efforts to provide an integrated view of sources, levels and effects of PTS substances in the region. A precedent in this direction is the recent release by the Pan American Health Organization of a partial compilation of POPs studies in Latin America. (Torres *et al.*, 2001). To our knowledge there are no other regional assessment projects in progress in the region

1.3.2 Inter-Regional Links And Collaboration

Presently, there are no specific PTS networks or links in the region and the attempt to establish a regional team of experts provided by this project should be considered as a possible starting point. A precedent in this direction is the network of Pesticides and Alternatives for Latin America (RAPAL) that could be useful for strengthening a regional network. In addition, several multilateral cooperation structures from the MERCOSUR could be also useful for this purpose.

1.3.3 Omissions/Weakness

As indicated previously, there are no comprehensive PTS reports in the region. However, additional partial information probably exists, principally as rough data, notes and technical reports in governmental agencies. The weaknesses of the present report are chiefly associated with a lack of reliable information on source characterization, scarcity of PCDD/F environmental data, the effects on human health and ecosystems and transboundary modelling. Also, some difficulties were experienced in finding people and adequate information from some countries, where information regarding environmental levels and effects was not available. However, the regional network created by this project should help to overcome these difficulties.

1.4 GENERAL DEFINITIONS OF CHEMICALS

The initial 12 substances that have been selected under the Stockholm Convention include: aldrin, endrin, dieldrin, chlordane, DDT, toxaphene, mirex, heptachlor, hexachlorobenzene, PCBs, dioxins and furans. These substances have been assessed in this report. 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. The following chemicals have been selected by the regional team for assessment: HCH (lindane), endosulphan, pentachlorophenol, PAHs, and organo-mercury. A short definition of each of these substances is presented below.

1.4.1 Pesticides

1.4.1.1 <u>Aldrin</u>

<u>Chemical Name:</u> 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/L 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.

Persistence/Fate: 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 body weight. The acute oral LD_{50} in laboratory animals is in the range of 33 mg/kg body weight for guinea pigs to 320 mg/kg 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 LC_{50} values range from 1-200 µg/L for insects, and from 2.2-53 µg/L for fish. The maximum residue limits in food recommended by FAO/WHO varies from 0.006 mg/kg milk fat to 0.2 mg/kg meat fat. Water quality criteria between 0.1 to 180 µg/L have been published.

1.4.1.2 Dieldrin

<u>Chemical Name:</u> 1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydroexo-1,4-endo-5,8-dimethanonaphthalene ($C_{12}H_8Cl_6O$). <u>CAS Number:</u> 60-57-1

Properties: Solubility in water: 140 μ g/L 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 insects such as corn rootworms, wireworms and cat worms.

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

Toxicity: The acute toxicity for fish is high (LC₅₀ between 1.1 and 41 mg/L) and moderate for mammals (LD₅₀ in mouse and rat ranging from 40 to 70 mg/kg body weight). However, a daily administration of 0.6 mg/kg 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 milk fat and 0.2 mg/kg poultry fat. Water quality criteria between 0.1 to 18 μ g/L have been published.

1.4.1.3 <u>Endrin</u>

<u>Chemical Name</u>: 3,4,5,6,9,9-Hexachloro-1a,2,2a,3,6,6a,7,7a-octahydro-2,7:3,6-dimethanonaphth[2,3-b]oxirene ($C_{12}H_8Cl_6O$). <u>CAS Number</u>: 72-20-8

Properties: Solubility in water: 220-260 µg/L 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 50s 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 years 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/L. The acute toxicity is high in laboratory animals, with LD_{50} values of 3-43 mg/kg, and a dermal LD_{50} of 5-20 mg/kg in rats. Long-term toxicity in the rat has been studied over two years and a NOEL of 0.05 mg/kg bw/day was found.

1.4.1.4 Chlordane

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

Properties: Solubility in water: 56 μ g/L 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/L (pink shrimp) to 90 mg/L (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 body weight (19.1 mg/kg body weight for oxychlordane). The maximum residue limits for chlordane in food are, according to FAO/WHO between 0.002 mg/kg milk fat and 0.5 mg/kg poultry fat. Water quality criteria of 1.5 to 6 µg/L 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.

1.4.1.5 <u>Heptachlor</u>

<u>Chemical Name</u>: 1,4,5,6,7,8,8-Heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (C₁₀H₅Cl₇). <u>CAS Number</u>: 76-44-8

Properties: Sol. in water: 180 μ g/L at 25°C; vapour pressure: 0.3 x 10⁻⁵ mm Hg at 20°C; log K_{OW}: 4.4-5.5. **Production/Uses:** 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 years. Its high partition coefficient provides the necessary conditions for bioconcentrating in organisms. **Toxicity:** The acute toxicity of heptachlor to mammals is moderate (LD₅₀ values between 40 and 119 mg/kg have been published). The toxicity to aquatic organisms is higher and LC₅₀ values down to 0.11 μ g/L have been found for pink shrimp. Limited information is available on the effects in humans and studies are inconclusive regarding heptachlor and cancer. The maximum residue levels recommended by FAO/WHO are between 0.006 mg/kg milk fat and 0.2 mg/kg meat or poultry fat.

1.4.1.6 <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/L at 25°C; vapour pressure: 0.2 x 10⁻⁶ mm Hg at 20°C; log K_{OW}: 6.19 for *p*,*p*'-DDT, 5.5 for *p*,*p*'-DDD and 5.7 for *p*,*p*'-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% p, p'-DDT and 15% o, p'-DDT isomers.

Persistence/Fate: 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 50000 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/L for largemouth bass and 56 mg/L 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 body weight. DDT has been shown to have an estrogen-like activity, and possible carcinogenic activity in humans. The maximum residue level in food recommended by WHO/FAO range from 0.02 mg/kg milk fat to 5 mg/kg meat fat. Maximum permissible DDT residue levels in drinking water (WHO) is 1.0 µg/L.</u>

1.4.1.7 <u>Toxaphene</u>

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

Properties: Sol. in water: 550 μ g/L 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 days up to 12 years. It has been shown to bioconcentrate in aquatic organisms (BCF of 4247 in mosquito fish and 76000 in brook trout).

Toxicity: Toxaphene is highly toxic in fish, with 96-hour LC_{50} values in the range of 1.8 µg/L in rainbow trout to 22 µg/L in bluegill. Long term exposure to 0.5 µg/L reduced egg viability to zero. The acute oral toxicity is in the range of 49 mg/kg body weight in dogs to 365 mg/kg in guinea pigs. In long term studies NOEL in rats was 0.35 mg/kg bw/day, LD_{50} ranging from 60 to 293 mg/kg bw. 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/day for oral exposure.

1.4.1.8 <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/L 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. 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 2600 and 51400 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 Pa m³/mol).

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

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

Chemical Name: Hexachlorobenzene (C₆H₆). CAS Number: 118-74-1

Properties: Sol. in water: 50 μ g/L 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.

<u>Persistence/Fate</u>: 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/L. The acute toxicity of HCB is low with LD_{50} values of 3.5 mg/g for rats. Mild effects of the [rat] liver have been observed at a daily dose of 0.25 mg HCB/kg bw. HCB is known to cause liver disease in humans (porphyria cutanea tarda) and has been classified as a possible carcinogen to humans by IARC.

1.4.2 Industrial Compounds

1.4.2.1 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/L 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.

Persistence/Fate: 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, more than six years 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 more than ten years.

Toxicity: LC_{50} for the larval stages of rainbow trout is 0.32 µg/L with a NOEL of 0.01 µg/L. The acute toxicity of PCB in mammals is generally low and LD_{50} values in rat of 1 g/kg bw. 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.

1.4.2.2 Polychlorinated dibenzo-p-dioxins (PCDDs) and Polychlorinated dibenzofurans (PCDFs)

<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).

<u>Properties</u>: Solubility in water: in the range 0.43 - 0.0002 ng/L 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 agonist 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 fetus and neonatal infants.

Effects on the immune systems in the mouse have been found at doses of 10 ng/kg bw/day, while reproductive effects were seen in rhesus monkeys at 1-2 ng/kg bw/day. Biochemical effects have been seen in rats down to 0.1 ng/kg bw/day. In a re-evaluation of the TDI for dioxins, furans (and planar PCB), the WHO decided to 7

recommend a range of 1-4 TEQ pg/kg bw, although more recently the acceptable intake value has been set monthly at 1-70 TEQ pg/kg bw.

1.4.3 Regional Specific

1.4.3.1 <u>Hexachlorocyclohexanes (HCH)</u>

<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).

Properties: γ -HCH: sol. in water: 7 mg/L 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.

Persistence/Fate: 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 vapor pressures, particularly of the α -HCH isomer, determine their long-range transport in the atmosphere.

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

1.4.3.2 Endosulfan

<u>Chemical Name</u>: 6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide ($C_9H_6Cl_6O_3S$). <u>CAS Number</u>: 115-29-7.

Properties: Solubility in water: 320 μ g/L at 25°C; vapour pressure: 0.17 x 10⁻⁴ mm Hg at 25°C; log K_{OW}: 2.23-3.62.

Discovery/Uses: Endosulfan was first introduced in 1954. It is used as a contact and stomach insecticide and acaricide in a great number of food and non-food crops (e.g. tea, vegetables, fruits, tobacco, cotton) and it controls over 100 different insect pests. Endosulfan formulations are used in commercial agriculture and home gardening and for wood preservation. The technical product contains at least 94% of two pure isomers, α - and β -endosulfan.

Persistence/Fate: It is moderately persistent in the soil environment with a reported average field half-life of 50 days. The two isomers have different degradation times in soil (half-lives of 35 and 150 days for α - and β -isomers, respectively, in neutral conditions). It has a moderate capacity to adsorb to soils and it is not likely to leach to groundwater. In plants, endosulfan is rapidly broken down to the corresponding sulfate, on most fruits and vegetables, 50% of the parent residue is lost within 3 to 7 days.

Toxicity: Endosulfan is highly to moderately toxic to bird species (Mallards: oral LD_{50} 31 - 243 mg/kg) and it is very toxic to aquatic organisms (96-hour LC_{50} rainbow trout 1.5 µg/L). It has also shown high toxicity in rats (oral LD_{50} : 18 - 160 mg/kg, and dermal: 78 - 359 mg/kg). Female rats appear to be 4–5 times more sensitive to the lethal effects of technical-grade endosulfan than male rats. The α -isomer is considered to be more toxic than the β -isomer. There is a strong evidence of its potential for endocrine disruption.

1.4.3.3 <u>Pentachlorophenol (PCP)</u>

Chemical Name: Pentachlorophenol (C₆Cl₅OH). CAS Number: 87-86-5.

Properties: Solubility in water: 14 mg/L at 20°C; vapour pressure: 16 x 10⁻⁵ mm Hg at 20°C; log K_{ow}: 3.32 - 5.86.

Discovery/Uses: It is used as insecticide (termiticide), fungicide, non-selective contact herbicide (defoliant) and, particularly as wood preservative. It is also used in anti-fouling paints and other materials (e.g. textiles, inks, paints, disinfectants and cleaners) as inhibitor of fermentation. Technical PCP contains trace amounts of PCDDs and PCDFs

Persistence/Fate: The rate of photodecomposition increases with pH ($t_{1/2}$ 100 hr at pH 3.3 and 3.5 hr at pH 7.3). Complete decomposition in soil suspensions takes >72 days, other authors reports half-life in soils of 23-178 days. Although enriched through the food chain, it is rapidly eliminated after discontinuing the exposure ($t_{1/2}$ = 10-24 h for fish).

<u>**Toxicity</u>**: It has been proved to be acutely toxic to aquatic organisms and have certain effects on human health, at the time that exhibits off-flavour effects at very low concentrations. The 24-h LC₅₀ values for trout were reported as 0.2 mg/L, and chronic toxicity effects were observed at concentrations down to 3.2 μ g/L. Mammalian acute toxicity of PCP is moderate-high. LD₅₀ oral in rat ranging from 50 to 210 mg/kg bw have been reported. LC₅₀ ranged from 0.093 mg/L in rainbow trout (48 h) to 0.77-0.97 mg/L for guppy (96 h) and 0.47 mg/L for fathead minnow (48 h).</u>

1.4.3.4 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>:Various

<u>Properties</u>: Solubility in water: 0.00014 -2.1 mg/L at 25°C; vapour pressure: from 0.0015 x 10^{-9} to 0.0051 mmHg at 25°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 body weight respectively, whereas the higher PAHs exhibit higher toxicity and LD_{50} of benzo(a)anthracene in mice is 10mg/kg body weight. In *Daphnia pulex*, LC_{50} for naphthalene is 1.0 mg/L, for phenanthrene 0.1 mg/L and for benzo(a)pyrene is 0.005 mg/L. The critical effect of many PAHs in mammals is their carcinogenic potential. The metabolic action of these substances produce intermediates that bind covalently with cellular DNA. IARC has classified benz[a]anthracene, benzo[a]pyrene, and dibenzo[a,h]anthracene as probable carcinogenic to humans. Benzo[b]fluoranthene and indeno[1,2,3-c,d]pyrene were classified as possible carcinogens to humans.

1.4.3.5 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/L at 21°C (HgCH₃Cl) and 1.0 g/L 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).

<u>Production/Uses</u>: 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.

1.5 DEFINITION OF THE EASTERN AND WESTERN SOUTH AMERICA REGION

As indicated previously, countries covered by Region XI are Argentina, Brazil, Bolivia, Chile, Ecuador, Paraguay, Peru and Uruguay. The region limits are the Pacific Ocean to the west, Colombia, Venezuela and the Guyanas to the North, and the Atlantic Ocean to the East (Figure 1-2). With a total surface of 15.286.135 km², the region covers a wide latitudinal gradient from Ecuador down to the southern end of the continent at Patagonia. Therefore the climatic conditions vary widely from the tropics to the cold temperate and sub Antarctic areas in southern America. The most representative ecosystems within the region are: huge river

basins (*i.e.* Amazon, Río Paraguay-Paraná-Río de la Plata), the grasslands, the coastal areas and the highland areas (the Andes mountains).

Region XI total population is 284 million (average density 20 inhabitants/km²), is principally urban (75%) and unevenly distributed among the countries. The average population growth rate is 1.2% per year, being lowest in Uruguay (0.7%) and highest in Bolivia and Paraguay (up to 2.7%). The two most important languages spoken are Portuguese and Spanish. Brazil is by far the largest and most populated country (56 and 61% of total surface and population, respectively), followed by Argentina (20 and 13%), Peru, Bolivia Chile, Ecuador and Paraguay (Table 1.1).

Country	Surface, km ²	Population	Urban population, %
Argentina	2 766 890	37 384 816	89.6
Bolivia	1 098 580	8 152 620	64.6
Brazil	8 511 965	174 468 575	79.9
Chile	756 950	15 211 308	85.7
Ecuador	283 560	13 183 978	82.7
Paraguay	460 750	5 585 828	56.1
Peru	1 285 220	27 012 899	72.3
Uruguay	176 220	3 334 074	92.6
Total	15 286 135	284 334 098	

Table	1.1	Surface.	population	and urban	population	in Region XI
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Source (Recursos Mundiales, 2002)



Figure 1.2 The South American region (Source: Microsoft Encarta 1998)

1.6 PHYSICAL/GEOGRAPHICAL SETTING

1.6.1 Climatic And Geographical Description Of The Region

The huge latitudinal extension of the region (0° SL to 60° SL) and the contrasted geological setting produces a variety of climates from the tropics to the cold Patagonia (Figure 1-3) and landscape characteristics that can be grouped in the following areas:

1.-The Amazonian Basin is by far the most important hydrographic system covering a total surface of 6,1 million km², located in northern Brazil but also including parts of Ecuador, Peru and Bolivia. 2.- The Río de la Plata Basin, second most important both in extension and by its urban-industrial development, covers 3,1 million km² and principal rivers such as the Pilcomayo, Paraguay, Uruguay, Paraná and Iguazú. 3.- The grasslands of Brazil, Argentina, Paraguay, Uruguay and Southern Chile 4. -The highlands areas from Ecuador, Bolivia, Peru, Argentina and Chile 5.- The Andes' Mountains 6.- The coastal areas 7.- Desert and non inhabited areas 8.- Forestry areas (including exotic plantations) account for 47% of the total Region surface 9.- Agricultural crops and arable lands, accounts for 12.8% of total soil surface.



Figure 1.3 Region XI major climates

Detailed physical information on each country follows below.

Argentina

Argentina covers 2.766.890 km² in the Southern end of the region. Its large latitudinal extension (21°46' to 55°58', N-S: 3694 km) and the contrasted geological setting (from the Andes to the sea), produce a variety of climates (Subtropical, N; temperate, Center-East; Arid, NW-SE; cold, S) and landscape characteristics which are divided into 7 formal geographical regions. Major Argentinean rivers follow the general slope of the country from the Andes to the sea. The Río de la Plata Basin is by far the most important covering 3.100.000 km² in tropical and temperate regions of Paraguay, Brazil, Uruguay and Argentina principal rivers such as the Iguazú, Uruguay and Paraná, with a final discharge to the sea of ~20.000 m³/s . The other major systems are Patagonian rivers which cross the arid plateau, i.e. the Negro, Chubut and Santa Cruz.

Argentina's climate is predominantly mild and temperate in the center most populated area of the country; the northern reaches pose a tropical and subtropical climate, whereas the southern tip is submerged in Antarctic waters. Over this prevailing latitudinal gradient, the proximity of the ocean to the Andean mountains introduces marked climatic variations, from arid (NW hills, Patagonia) to humid and rainy (Iguazú, pampean plains,

deltaic environment in Buenos Aires Río de la Plata coastal area). Average temperature ranges between 17° and 29° in January and between 6 and 14°C in July around Buenos Aires.

Bolivia

Two large geographical areas, the altiplano and the lower lands characterize Bolivian territory. The most prominent feature of the Altiplano is the large lake at its northern end, Lake Titicaca. At 3810 meters above sea level, it is the highest navigable body of water in the world. With a surface area of 9064 square kilometers, it is South America's largest lake.

The land contains several salt flats, the dried remnants of ancient lakes. The largest of these is the Uyuni Saltpan, which covers over 9 000 square kilometers. Near the Argentine border, the floor of the Altiplano rises again, creating hills and volcanoes that span the gap between the eastern and western cordilleras of the Andes. The Bolivian territory is located in the subtropical area, but due to its altitudinal characteristics poses a wide climatic spectra. In highlands areas, the weather is cold and dry; in low lands weather is warmest, average temperatures ranges between 8°C in the highland area and in the oriental part of the country about 26°C.

Brazil

Brazil is one of the largest countries in the world, covering an area of approximately 8.5X10⁶ km². According to IBGE data (IBGE, 2001), Brazil has 5.561 cities, distributed in five geographical regions: (North, Northeast, Central west, Middle West, South, and Southeast). The relief of Brazil does not present formations of very high mountainous chains and prevailing altitudes are below 500 m. It is geographically divided into two great plateau areas and three plain areas.

Brazil, due to its continental dimensions, possesses a very wide climatic diversity, influenced by its geographical configuration, its significant coastal extension, its relief and the dynamics of the masses of air on its territory. The air masses, especially those that occur more directly in Brazil are, according to the Statistical Annual of Brazil (IBGE): the Equatorial air mass; the Tropical air mass; and the Polar Atlantic air mass. All these air masses provide the climatic differentiation in Brazil.

Thus, climates vary from very humid and hot climates, coming from the Equatorial air masses, as is the case for the great part of the Amazon area, to very strong semi-arid climates such as those in the hinterlands of northeastern Brazil.

Chile

Chile is one of the longest countries of the world (4630km), covering a long narrow strip of land (430 km wide) between the Andes and the Pacific Ocean. Total surface of the country covers 750 000 km².

The country is composed of three distinct and parallel natural regions—from east to west, the Andes, the central lowlands, and the Coast Ranges. The rivers of Chile are generally short and swift-flowing, rising in the well-watered Andean highlands and flowing generally west to the Pacific Ocean. The middle portion of the country, contains Chile's largest cities—Santiago, Valparaiso, and Concepción. A portion of extreme southern Chile lies in the rain shadow of the Andes and is covered by natural grasslands. This area also yields petroleum. The Andes are an orographic barrier with the western slopes and peaks receiving much precipitation.

Oceans moderate temperatures along the country. The northern part of the country is a desert and is characterized as one of the driest areas in the world. Rain rates increase to the south ranging from 300 mm in the capital city of Santiago de Chile to more than 5000 mm near the Magellan strait.

Ecuador

Ecuador has approximately 280000 square kilometers. The country is divided into three continental regions - the Costa, Sierra, and Oriente - and one insular region the Galapagos Islands. Costa, located between Pacific Ocean and Andes Mountains, consists of coastal lowlands and mountains. Sierra is composed of two major chains of Andes Mountains with an inter-mountain basin or plateau between the two chains. Cordillera Occidental contains Ecuador's highest peak at 6267m. Galápagos are islands of varied size located 1000 kilometers west off the Ecuadorian coast.

Ecuador weather is very diverse. Besides being located on the Equator, climate is also controlled by the wide variability in altitude. At the coastal area the weather is hot and humid, with an average temperature of 26°C. In the highlands, (sierra) temperatures range from 7° to 21 °C. Galapagos climate varies from tropical and desert-like at sea level to cold and wet at the highest point.

Paraguay

The two main natural regions in Paraguay are the Paraneña region - a mixture of plateaus, rolling hills, and valleys - and the Chaco region that is an immense piedmont plain. About 95 percent of Paraguay's population resides in the Paraneña region, which has all the significant orographic features and the more predictable climate. The Paraneña region can be generally described as consisting of an area of highlands in the east that slopes toward the Río Paraguay and becomes an area of lowlands, subject to floods, along the river. The Chaco is predominantly lowlands, also inclined toward the Río Paraguay, and is alternately flooded and parched

Paraguay's weather is subtropical with the highest amount of rain being 1120 mm in the capital City Asuncion to the Gran Chaco with 815 mm.

Peru

Peru is located in central, western South America bordering the Pacific Ocean, and is the third largest nation in South America and fourth in terms of population in Latin America. There are 84 of a total of 115 ecological zones of the world in Peru. Lima is the capital of the country and 29.2% of the population live there. Pre-Hispanic natural divisions are complex but in greater agreement with modern geographical principles. So Peru is divided in 8 natural regions: coastal plane, interandean valley, temperate region, high barren region and altiplano from 0 to 5000m and high Cordilleran, high forest and low forest regions ranging from 5000 to 80m respectively.

There are three important hydrographic basins: Pacific, Amazons and Titicaca Lake. The Pacific Basin has 52 rivers, 25 with permanent water. The Amazon River, the largest volume flow of any river in the world, rises from the conjunction of Ucayali and Marañon in Peru. Peru is a tropical country with great diversity of climate due to the high altitude and prevailing southwest winds by the cold Humboldt or Peruvian Current in the Pacific Ocean. In the coastal areas the temperature is usually moderate with an average value of 20°C during the entire year. Here, the annual precipitation is less than 30 mm per year. In the highlands, temperatures range from -7°C to 21°C. Maximum precipitation is (850 mm) over the city of Cusco and about 3,800 mm in tropical and warm areas in the northeast part of the country.

Uruguay

Uruguay is one of the smallest countries in South America covering almost 170.000 km². The country limits are Argentina to the West, Brazil to the North and Northeast, the Atlantic Ocean to the East, and the Río de la Plata to the South and Southwest. The landscape is defined by the dominance of subtropical prairies interspersed with forests, scrubs and wetlands. These prairies cover approximately 87% of the territory and are used fundamentally for cattle (bovine and ovine) (Achkar *et al.*, 1999).

The topography is slightly undulated, a mixture of plains crossed by long rivers and soft hills, with an altitude below 150m with the highest point barely reaching 500m. The country has over 200 km of coastline bordering the Atlantic ocean and the Río de la Plata.

According to the Köppen classification the predominant climate is *Cia* (warm and humid with no desert areas), with precipitation higher than 1,000 mm annually distributed throughout the year. Temperatures range from 22 to 32°C in summer and 10 to15°C in winter.

1.6.2 South American Freshwater Environments

Two of the most important freshwater ecosystems on earth are located in the Region, the Amazon River and the Rio de La Plata (Uruguay-Paraná Rivers). The mean annual flow rate of both rivers accounts for more than 80% of total freshwater resources within the region draining mainly to the Atlantic Ocean. Thus, the South American region is extremely rich in water resources as the Amazon, Orinoco, São Francisco, Paraná, Paraguay and Magdalena rivers carry more than 30 per cent of the world's continental surface water. Nevertheless, two-thirds of the region's territory is classified as arid or semi-arid. These areas include parts of northeastern Brazil, Argentina, Chile, Bolivia and Peru.

In spite of the large abundance of freshwater resources, water quality deterioration is rapidly increasing since most populated and industrialized centers are located along principal watercourses (i.e. São Paulo over the Tietê-Paraná, Buenos Aires along the La Plata River). In these highly impacted areas, industrial, agricultural and urban discharges introduce a heavy load of organic matter and toxic chemicals that strongly affect the quality of the rivers.

The principal cause of water pollution is the direct discharge of untreated domestic and industrial wastes to surface water bodies, which also contaminates adjacent groundwater aquifers. The main contributors are: growth in conventional sewerage systems that have not been accompanied by corresponding treatment facilities; intensification of agricultural land use close to metropolitan areas; changes in economic structure,

with increased emphasis on manufacture; concentrated run-off from paved areas in the growing cities; and the need for artificial regulation of stream flows.

During the past decade, environmental problems related to water have affected both urban and rural areas. In the arid and semi-arid areas, there has been increased competition for scarce water resources. Using polluted water for drinking and bathing spreads infectious diseases such as cholera, typhoid and gastroenteritis. Several countries have had recent outbreaks of these diseases, affecting, in particular, the urban poor.

1.6.3 South American Marine Environment

The marine and coastal systems of the region support a complex interaction of distinct ecosystems, with an enormous biodiversity, and are among the most productive in the world. Several of the world's largest and most productive estuaries are found in the region, such as the Amazon and Plata Rivers on the Atlantic coast, and the Guayaquil and Fonseca on the Pacific. The waters off Chile and Peru support one of the top five commercial fisheries and the world's fastest growing fishery is off the coast of Argentina and Uruguay (Esteves *et al.*, 2000).

During 1970-83 Peru's catch fell from 12 to 2 million tonnes due to the El Niño southern oscillation event but had increased to nearly 9 million tonnes by 1995 (IDB 1995). A large decrease is expected as a result of the 1997-98 El Niño, as it has been one of the most severe events ever recorded. The effects of fisheries on marine biodiversity and resource sustainability are also of major concern, since more than 80 per cent of the commercially exploitable stocks in the southwestern Atlantic and 40 per cent in the southeastern Pacific are either fully fished, over-fished or depleted (FAO 1997).

Mariculture is less important than in some other tropical regions. However, it is growing in countries such as Ecuador where a significant shrimp mariculture industry has developed, mostly in converted mangrove areas. Latin America produced 21.6 per cent of the world's farmed shrimp in 1995. Aquaculture in Chile is growing at more than 30 per cent a year, compared with 9.5 per cent worldwide. Activities are concentrated in salmon farming, induced by favorable export markets, and are generating some US\$450 million a year in export earnings. In 1997 salmon exports were more 145 000 tonnes and this trend is expected to continue (Servicio Nacional de Pesca Chile 2002).

Expanding ports and maritime trade are often accompanied by intensified transportation corridors in coastal ocean areas, as is happening off Argentina, Brazil, Ecuador and Uruguay.

1.6.4 Patterns Of Development/Settlement And Energy Consupmtion

Argentina

Argentina has diverse natural resources and economic activities. Mining is basically oriented to the extraction of oil, metallic and non-metallic minerals. Crude oil production amounts to 30 million m³. Natural gas exploitation is well developed and extended pipelines deliver the fuel from Patagonia and Bolivia to principal towns in Argentina, but also Chile and Brazil. Coal production, from Río Turbio, Santa Cruz, is also important (200000 tons/year).

Argentina's economy is based on the agricultural and livestock sector complemented by a fluctuating industrial activity. The per capita product attained US8.040 in the nineties and declined to < US8.3.362 with the 2002 currency devaluation and economic crisis.

Brazil

Brazil presents a gross domestic product (GDP) of the order of US\$ 788 billion (data from 1998), and it is among the ten largest economies of the world. The current Brazilian economy is based on agriculture, fisheries, and industrial production. Brazil possesses almost 20% of the water of the planet and 11.1% of the hydroelectric production of the world. The use of natural gas as source of energy is 38 million cubic meters a day.

Chile

Chile's economy is based on the export of minerals, which account for about half of the total value of exports. Copper is the nation's most valuable resource, and Chile is the world's largest producer of the mineral. Agriculture is the main occupation of about 15% of the population; it accounts for about 10% of the national wealth, and produces less than half of the domestic needs.

Hydroelectric plants provide an average of about 70% of Chile's electricity. Only an estimated 13% of hydroelectric potential is now utilized, but large viable sites are far from Santiago (40% of demand), requiring

large transmission line investments. Other energy sources comprise oil and coal, and lately natural gas coming from Argentina through pipelines.

Ecuador

Ecuador has a long history as a provider of natural resources including petroleum, fisheries, woods and hydroelectricity. The economic system is composed of agriculture-livestock (14% of GDP), industry (36% GDP) and services (50% GDP).

Paraguay

Paraguay's energy requirements are supplied by Itaipú (1.8%), Yaciretá (2.1%), and Acarai (42%) dams which also supply energy to Argentina and Brazil. Domestic gas utilization amount to 0.7 % whereas fossil fuels for industrial use reach 32%.

Peru

Peru's economy has long been dependent upon the export of raw materials. It is one of the world's leading fishing countries and has a wealth of mineral copper, lead, zinc, gold and silver extensively. Oil exploration in the eastern tropical forests and in the far north coast indicates substantial reserves. The hydroelectric potential of Peru is great, especially on the rivers flowing to the Amazon Basin. Almost 75% of the national electrical energy is produced from hydroelectric sources.

Uruguay

The agriculture, livestock and fishing produce, accounted for 9.9 % of total GDP. Sheep breeding for wool yielding is presently the main activity of the livestock sector, representing 35.7% of its total output, while cattle production meant 28.3%, and diary products 18.3%. Agricultural production is predominantly cereals, particularly wheat and rice, which account for half of Uruguay's cereal output. The fishing industry is of lesser importance since its output represented only 4% of the sector's total.

Energy consumption in Uruguay is oil (58%), gas (0.5%), electricity (19%) and wood (23%). The country imports oil and gas from various international sources. Electricity is produced primarily from hydroelectric sources.

Country	CO ₂ emissions, thousand tons	CO2 emissions per capita, kg
Argentina	129 852	3 687
Bolivia	10 102	1 330
Brazil	273 371	1 692
Chile	48 779	3 383
Ecuador	24 487	2 093
Paraguay	3 697	746
Peru	26 176	1 093
Uruguay	5 643	1 741

Table 1.2. Emissions of CO2 in the Region XI

Considering fossil, liquid and gas fuels, and cement production, 1996

Source: Recursos Mundiales, 2002

1.7 REFERENCES

Achkar, M., Cayssials, R. and Domínguez, A. 1999. *Desafios para Uruguay*. Editorial Nordan-Comunidad, Montevideo, Uruguay. (In Spanish).

Esteves, J.L., Ciocco, N.F., Colombo, J.C., Freije, M., Harris, G., Iribarne, O., Isla, I., Nabel, P., Pascual, M.S., Penchaszadeh, P.E., Rivas, A.L. y Santinelli, N. 2000. The Argentine Sea: The Southeast South American Shelf Marine Ecosystem. In: "Seas at the Millennium: An Environmental Evaluation" Volume I Regional Chapters 48: Europe, The Americas and West Africa. Ed. C. Sheppard, 749-771. Pergamon, Elsevier Science (Amsterdam). FAO 1997

IBGE, 2001 (brazil): Instituto Brasileiro de Geografia e Estatística, http://www.ibge.gov.br, consulted in July 2002.

Recursos Mundiales. 2002. PNUMA, PNUD, BM, IRN (en ingles WRI). Ecoespaña editorial. 2002

Servicio Nacional de Pesca (2002). http://www.sernapesca.cl/estadísticas. Consulted in July 2002

Torres JPM (2001) An Análisis of the Status of the Persistent Organic Pollutants (POPs) in Latin America and the Caribbean (1998-1999) A technical report for the Panamerican Health Organization, Health and Environment División and The United States Protection Agency, Office of International Activities. 156 pp.

2 SOURCE CHARACTERIZATION

2.1 BACKGROUND INFORMATION TO PTS SOURCES

Quantitative information on PTS primary or secondary sources, is very scarce and fragmentary for the region. In some countries there are available data for hot spots, namely contaminated soils, and stockpiles, whereas in others there is no information. Due to their long term use in the region, pesticide data are relatively more abundant. PCB information is fragmentary whereas dioxin and furan source data is practically non existent. PTS inventories are still in their early stage of development, i.e. PCB inventory work in Argentina, Chile and Uruguay begun in the year 2000.

2.2 DATA COLLECTION AND QUALITY CONTROL ISSUES

Receptor PTS evaluation (i.e. environmental levels) has a much stronger tradition than source evaluation in the region. Thus, in contrast to the environmental level forms, questionnaires for sources were not successfully implemented. Only some pesticide import data were filled out for some countries, but in general, available data did not allow segregation of individual PTS. In order to overcome this paucity of information several approaches were implemented to obtain a qualitative picture of the situation and estimate potential emissions: i.e. descriptions of most frequently imported, used or produced PTS, estimation by activity rates and emission factors (UNEP toolkit for dioxin and furans, EPA emission factors for PAHs) and Level I fugacity calculations.

Considering the lack of reliable quantitative source data for the region, the estimated values provided in this report should be taken with caution. In order to improve the quality of these estimates, more detailed information is needed.

2.3 PRODUCTION, USE AND EMISSION

2.3.1 Pesticides

Practically all chlorinated pesticides were widely used, produced or formulated in the region, in the mid 1950s-1960s. There was a declining trend in the 1980s-1990s due to legal restrictions on production and use. Currently only mirex is legally used in Uruguay. Other pesticides such as endosulfan and lindane are still in use in several countries in the region. The current legal status of each pesticide in all the countries of the region is presented in Table 5.4 of Chapter 5.

2.3.1.1 Aldrin, Dieldrin, Endrin

Cyclodiene organochlorines were first introduced in the region in the 1950s, and experienced rapid growth due to their lower costs and high efficacy. They have been formulated and later produced in some countries, (i.e.Argentina and Brazil). The Shell Company formulated aldrin and endrin from 1977 to 1990 in São Paulo State, Brazil. Despite this production, 294 tons of aldrin were imported in Brazil from 1989 to 1991 (MDIC, 2002). In Argentina, formulation of dieldrin in 1967 was 200 tons (conc. 5%) and 550 tons (conc.18%), compared to 100 tons (conc.4%) and 115 tons (40%conc.) for aldrin, and 300 tons (conc. 20%) for endrin (Alvarez, 1998). Presently, possible sources are stockpiles and severely contaminated areas. For instance, a contaminated site of 600 m² in the former site of the Shell Company in Paulinia (Sao Paulo, Brazil) had 1250 tons of contaminated soil and around 750 kg of aldrin, dieldrin and endrin (Drins). There is a possibility of environmental contamination of local people in the vicinity of this site. Chlorinated cyclodiene pesticides had widespread use throughout the region but are now officially forbidden in most countries. There are no emission measurements for the region.

2.3.1.2 Chlordane

Technical chlordane is a very complex mixture of more than 100 chlorinated compounds, with trans/cis chlordane and nonachlor as major constituents. Chlordane did not have widespread use within the region. Only in particular cases was it formulated and used, especially for ant control. Similar to aldrin, chlordane has been formulated in some countries with Argentina producing 220 tonnes in 1967. Within the region, no emission measurements have been reported.

2.3.1.3 <u>DDTs</u>

DDT was intensively and widely used in the region, principally in the early 1960s-1970s for anti-malaria programs in tropical and subtropical areas. It was produced as early as 1954 in Argentina (Alvarez, 1998). From 1962 to 1982, Brazil produced 73 481 tonnes of pure DDT. It also imported 31130 tonnes between 1962 and 1975 and between 1989 and 1991, 3200 tonnes were purchased (MDIC, 2002). DDT deserves special attention due to its possible reintroduction to the region in order to control widespread tropical and subtropical epidemic diseases such as dengue and malaria. Presently, a possible significant secondary DDT source is dicofol. This insecticide is used in the region and might contain DDT as an impurity. In the year 2000, Brazil imported 111 tonnes of dicofol and also produced 209 tons (IBAMA, 2002). Illegal trade could be another possible source for this PTS. No DDT emission measurements have been reported for the region.

2.3.1.4 <u>Heptachlor</u>

Heptachlor is a non-systemic insecticide used primarily against soil insects and termites. It is degraded in the environment to heptachlor epoxide that is of greater persistency and toxicity than the parent compound. In Brazil, heptachlor use has been authorised in agriculture, especially on sugar cane plantations. From 1996 to 2002, around 210 tonnes of this substance were imported by Brazil (MDIC,2002). Present estimated stock is around 165 tonnes. There are no emission measurements for the region.

2.3.1.5 <u>Hexachlorobenzene</u>

The main environmental input of hexachlorobenzene occurs as a by product in the industrial manufacturing of chlorinated solvents as well as some pesticides such as pentachlorophenol. There are well known highly contaminated sites and stockpiles of HCB in Brazil, e.g. Cubatão, that may be a significant environmental source (CETESB, 2001). In Cubatão, HCB was probably generated from perchloroethylene production and burning of other chlorinated residues. In 1965, Brazil imported 834 tons of HCB (MDIC, 2002). There are no emission measurements for the region.

2.3.1.6 <u>Mirex</u>

In Brazil, Uruguay and Argentina, mirex is popularly known as dodecachlor. It was principally used for ant control with restricted distribution within the region. Mirex has been forbidden in all the countries except Uruguay. There are no emission measurements for the region. Presently, there is a commercially available product in Brazil called Mirex-S, but the active ingredient is perfluoro sulphonamide, and not dodecachlor.

2.3.1.7 <u>Toxaphene</u>

Toxaphene is a complex mixture of chlorinated bornanes. There is no record of use for this substance in the region. Toxaphene has been officially forbidden in all countries. There are no emission measurements for the region.

2.3.2 Industrial Chemicals

2.3.2.1 Polychlorinated biphenyls

PCBs have been intensively used throughout the region, principally in electrical equipment (i.e. transformers). Residues of PCBs from commercial formulations (e.g. Aroclor 1242, 1254, 1260 and equivalent products) are ubiquitous in the environment. Detailed inventory information is still incomplete but there are some country estimates. In Brazil, there are conflicting data which indicate 250000-300000 tonnes for Askarel (PCB-contaminated oil) which implies a stock of 130 000 tonnes of PCBs (Costa, 2000). In Chile, PCB stocks have been estimated to be 700 tonnes, 46% of which are still in use (CONAMA, 2001). These data are comparable to stocks in Peru (1000 tonnes; González, personnal communication, 2002). In Paraguay, 70 tonnes of PCB containing oils are stored in open sites of the National Energy Administration (ANDE). In Uruguay electrical companies claimed stocks of 81 tons of PCB-containing oil with 25% still in use (DINAMA, 2000). Obsolete electrical equipment and used oil constitute relevant secondary sources of PCBs. An important effort to export PCB-containing material for destruction has been initiated in the region.

Due to their low water solubility, PCBs have a strong particulate-oriented behaviour, adsorb rapidly to suspended matter and are sequestered in bottom sediments. These residues constitute long term reservoirs and secondary sources. For example, in Río de la Plata coastal sediments from Buenos Aires, a preliminary Level I Fugacity exercise, indicated that sedimentary levels are in equilibrium with an estimated input of about 900 kg PCBs to the coastal area (Colombo, 2002 unpublished).

2.3.3 Unintended By-products

2.3.3.1 Dioxins and furans

PCDDs and PCDFs are ubiquitous trace residues in the environment resulting chiefly from combustion processes and chemical production. Air is an important receptor, but lack of precise measurements in the region does not allow a detailed analysis. A preliminary regional estimate was calculated considering the correlation between CO_2 emission from fossil fuels and the cement industries (World resources, 2000-2001) and TEQ emissions to air for some industrialized countries (UNEP, 1999) following the approach of Baker and Hites (2000). Figure 2.1 shows the regression obtained for UNEP countries and estimates from this region. The regression includes considerable error and does not fully explain the trend of the data (R^2 = 0.66). However, the country regression factors using the PCDD/F UNEP toolkit. Still, more detailed industrial information is considered vital for more precise evaluations (MVOTMA-DINAMA-UNEP, 2002). The agreement between these two estimates gives support to the conclusion drawn.

The total regional PCDD&F emission to air would be 722 g TEQ/year, with a markedly uneven distribution since only Brazil (45%) and Argentina (25%) account for 70%. In a decreasing trend follow Chile (11%), Peru (7%), Ecuador (6%), Bolivia (3%), Uruguay (2%) and Paraguay (1%). Region XI individual country emissions range in the intermediate/lowest range of reported values for North America, Asia and Europe. Considering that the individual country total to air ratio from the toolkit estimates are 1.6:2, the total (all media) regional PCDD/F emissions would be in the order of 1300 g TEQ/year. Toolkit calculations indicate that waste incineration, including hazardous and hospital wastes, is a major source (30-50%), comparable to biomass burning (20-40%). In spite of the agreement of these estimates, validation of emission factors for the region is considered essential. This should include different industrial technologies, but especially wildfires and biomass should be conducted in order to obtain empirical evidence for local emission factors.



Figure 2.1. CO₂-TEQ emission regression for UNEP 99 countries (red) and estimated TEQ emitted to air for Region XI countries (green and bar graph).

2.3.4 Other PTS Of Emerging Concern

2.3.4.1 <u>Lindane (γ-HCH)</u>

Gamma-HCH has been intensively used throughout the region, principally for agriculture applications. Its widespread detection in waters and organisms (see Chapter 3) reflect the importance of lindane sources in the region. This is supported by its early production and use in the area. Production in Argentina in 1956 was 20 tonnes (conc. 100%) and decreased to 5 tonnes (conc. 5%) and 30 tonnes (conc. 2.4%) in 1967 (Alvarez, 1998). Brazil produced 98 583 tonnes of total HCH from 1962 to 1985, and imported around 4200 tonnes of the mixture in the same period (MDIC, 2002). Brazil imported 490 tonnes of lindane from 1996 to 2002 (MDIC, 2002) and the present available stock has been estimated in between 21 to 40 tonnes A stockpile of 7 tonnes of HCH (conc. 50%) has been stored since 1975 in Uruguay (Doll, 2002, personal communication). Lindane is currently used for louse control and as a wood preservative in some countries. There are no emission measurements for the region.

2.3.4.2 Endosulfan

Endosulfan (Thiodan) is of high concern due to its widespread use in the region. It is one of the sole chlorinated pesticides allowed for agricultural use, and it has been imported since the early 1970s in considerable amounts. In Argentina, endosulfan imports from 1992-94 amounted to 641 tonnes principally 92-96% active ingredient (Gallo Mendoza, 1995), while Uruguay imported for the period 1973-2001 approximately 204 tonnes (Ministerio de Ganaderia, Agricultura y pesca, Uruguay, 2002). Brazil produced and imported endosulfan 1554 and 3446 tonnes, respectively in 2000). Recent available data show that the importation in the early nineties was less with only 2,495 tonnes being imported between 1989 and 1996 (MDIC, 2002).

2.3.4.3 <u>Pentachlorophenol</u>

Pentachlorophenol is a low cost, broad-spectrum pesticide that has been widely used in the region, principally as wood preservative (termite and fungi combat). Current pentachlorophenol application is restricted to wood preservation and agricultural use is generally forbidden. Chile imported until 1999 approximately 700 tonnes of PCP-Na per year (Camara de Comercio de Santiago, 2001). In 1965 Brazil imported 474 tonnes of pentachlorophenol. Between 1970 and 1972 the Brazilian consumption was, on average, 469 tonnes/year. The estimated current stock of PCP in Brazil is around 80 tonnes. There are no emission measurements for the region.

2.3.4.4 Polycyclic aromatic hydrocarbons (PAHs)

PAHs with 3-5 benzene rings are ubiquitous in the environment. These unintended by-products are principally derived from natural and anthropogenic combustion sources. Due to their low water solubility, PAHs are concentrated in bottom sediments and biota where they exert well characterized toxic effects (i.e. carcinogenic, mutagenic). There are no PAHs emission measurements for the region. However, the extensive forest resources and their intensive use (intentional and unintentional biomass burning) makes PAHs one of the high priority PTS for the region. Petrogenic PAH sources are also significant, mainly related to petroleum exploitation, refining and transport. The estimates of PAH emissions calculated with EPA 7-PAHs and 16-PAHs emission factors within the project indicate a total emission of 111-500 tonnes polycyclic organic matter/year for Argentina, principally derived from wildfires (49%), residential wood combustion (31%) and coke production (8%). In Brazil, emissions were estimated at 467-6607 tonnes/year, with wood combustion accounting for at least 90% of these values.

2.3.4.5 Organic mercury and tin

There are very few available data for organometallic compound sources, especially for organic tin. Biomethylation in reducing environments is the main process for organic mercury generation whereas antifouling paints are the principal source for organic tin. The Amazon basin is a possible organic mercury hot spot, not only due to the intensive use of mercury in gold mining, but also due to high levels of naturally occurring mercury. Very recent data on organic tin in Mar del Plata, Argentina, indicated high levels in sediments that were associated to an elevated imposex incidence in marine molluscs (Sbarbatti de Nudelman, 2002, personal communication). Recently, limited data on organic mercury in water and sediment were generated from the Rio Negro and in biological samples from the riparian population of the Rio Tapajós in the Amazon basin (Fadini and Jardim, 2001). There are no emission measurements of organic mercury and tin for the region.

2.4 HOT SPOTS

There are very few officially recognized contaminated sites, mostly in heavily populated industrial areas, i.e. Sao Paulo (Brazil), Buenos Aires (Argentina), Santiago and Concepción (Chile). However, these official numbers grossly underestimate the real situation due to the existence of illegal or non-reported contaminated sites throughout the region. In Argentina, several legal pesticide stocks exist, e.g. the Servicio Nacional de Sanidad y Calidad Agroalimentaria (SENASA) have declared stocks of Dieldrin (~ 6 tonnes in La Rioja state) and gamma-HCH (1200L in Cordoba). In the City of Buenos Aires, about 6-30 tonnes of HCH and thallium have been stored for years (Vilar de Sarácha, 1997), although recent estimates indicate that this stock would not exceed 10 tonnes. Twenty tonnes of organophosphorous and chlorinated pesticides were inadequately disposed in El Cuy, Río Negro state but were remediated in 1998. An obsolete PTS stockpile of 6 tonnes of residual DDTs from ancient anti-malaria programs was deposited in the northwest of Argentina. The most important known illegal disposal of more than 30 tonnes of HCHs and other organochlorines (chiefly DDT) took place in the small town of La Argentina in Santiago del Estero Province. In Brazil, the environmental agency of the state of Sao Paulo published a list of 255 hot spots, of which 162 are contaminated by hydrocarbons

(CETESB). Three other well known contaminated sites with chlorinated compounds exist in Paulinia, São Paulo, Cubatão, Sao Paulo (miscellaneous chlorinated compound) and Cidade dos Meninos, Río de Janeiro (HCH). In Chile, the official disposal of about 100 tonnes of oils containing PCBs has been reported in the Antofagasta region (CONAMA, 2001).

2.5 DATA GAPS

Source information is far from complete for the region. Full quantitative measurements are unavailable and inventory information is fragmentary. Some official information on sources is not available for public access.

2.6 SUMMARY OF MOST SIGNIFICANT REGIONAL SOURCES

In spite of the fact that detailed source information is fragmentary, in terms of relative importance, PCBs appear as one of the most relevant PTS for the region. PCB sources are mostly confined to heavily industrialized and urbanized areas with high energy demand and some disposal sites.

PAHs are also priority PTS; in contrast with the more restricted distribution pattern of PCBs, their generation is widespread throughout the region, both in industrialized areas through energy generation and transport, but also in remote sites due to biomass burning.

Dioxin and Furans do not appear to be in the same priority ranking as PCBs and PAHs as evaluated by potential emission calculations. However, quantitative data are limited, and inventories are still not complete (the first inventories were developed by Uruguay) due to lack of detailed information of some industrial processes.

Chlorinated pesticides (e.g. cyclodienes, DDT) have been intensively used in the region in the past. As a consequence, several official stockpiles and disposal sites exist awaiting final treatment or remediation. Most of these sites are more than twenty years old and there is a risk of emission if affordable cleaning technologies are not available. Illegal trade and disposal of chlorinated pesticides is another relevant aspect related to sources. Lindane and endosulfan are two potentially relevant PTS of emerging concern due to their widespread use in the region. Pentachlorophenol and its salts also have to be considered even though their use and distribution are more limited within the region.

2.7 SOURCES OF REGIONAL PRIORITY

Source priorities were evaluated both in the first technical workshop on sources and environmental levels in Campinas, Brazil (March 2002) and finally at the regional priority setting meeting held in Viña del Mar, Chile in August 2002. In both meetings a general consensus was attained in terms of PTS source priorities:

- PCBs = PAHs > dioxins&furans > DDTs = endosulfan = lindane = PCP > other pesticides and industrial chemicals.
- Therefore, according to these results PAHs emissions, especially considering biomass combustion and PCBs inventories are priority issues. Dioxins and furan sources should be evaluated and measured under different conditions; the importance of biomass burning as relevant PCDD/F source should be confirmed.
- Certain pesticides including DDT, endosulfan, lindane and PCP demand consideration toward precisely locating and quantifying the principal existing stocks.

2.8 REFERENCES

- Alvarez, N. 1998. Productos fitosanitarios. Su evolución en Argentina. Cámara Argentina de Sanidad Agropecuaria y Fertilizantes (CASAFE).
- Baker, J.I. and Hites, R.A. 2000. Is combustion the major source of polychlorinated dibenzo-p-dioxins and Dibenzofurans to the environment? A mass balance investigation. Environmental Science and Technology, 34: 2879-2886.
- Cámara de Comercio de Santiago (2001): Servicio de Comercio Exterior, Boletines Estadísticos de Comercio Exterior del Banco Central.

CETESB (Companhia de Tecnologia e Saneamento Basico de Sao Paulo). www.cetesb.sp.gov.br accessed in June 2002.

- CONAMA (Comisión Nacional de Medio Ambiente), 2001. PCBs en Chile. Diagnóstico Nacional de Contaminantes Orgánicos Persistentes. Documento de Trabajo Nº 2. 79 p.
- Costa, C. (2000). Dias contados para o Ascarel, Brasil Energia, 240, 89-91.
- DINAMA (Dirección Nacional de Medio Ambiente) 2000. Proceeding UNEP Chemical Workshop on the Management of Polychlorinated Biphenyl, Dioxins and Furans. UNEP Chemicals, Montevideo, Uruguay, 19-22 Septiembre. 399 p.
- Fadini, P.S.; Jardim, W.F. (2001). Is the Negro River basin (Amazon) impacted by naturally occurring mercury? Sci. Total Environ., 275, 71-82.
- Gallo Mendoza, G. 1995. Los agroquímicos, la sanidad animal y vegetal y la salud de la población humana: reflexiones en el marco del desarrollo social y ambientalmente sostenible. Fuente de los datos: Instituto Argentino de Sanidad y Calidad Vegetal (IASCAV)-Secretaría de Agricultura Ganadería y Pesca.
- MDIC (Ministério do Desenvolvimento da Indústria e Comércio). http://aliceweb.mdic.gov.br, acceded in August 2002.
- MGAP (Ministerio de Ganadería Agricultura y Pesca). www.mgap.gov.uy accessed in June 2002.
- MVOTMA-DINAMA-UNEP, 2002. Inventario Nacional de liberaciones de dioxinas y furanos, Uruguay 2000. Ministerio de Vivienda, Ordenamiento Territorial y Medio Ambiente-Dirección Nacional de Medio Ambiente-UNEP, 54 p
- Sbarbatti de Nudelman, N. 2002. Personal communication.
- UNEP, 1999. Dioxin and Furan Inventories, National and Regional Emissions of PCDD/PCDF. United Nations Environment Programme, UNEP Chemicals.
- Vilar de Saráchaga, D. 1997. Perfil nacional para la gestión de sustancias químicas. Foro Intergubernamental de Seguridad Química. United Nations Institute for Training and Research (UNITAR).
- World Ressources 2000-2001: People and Ecosystems: The Fraying Web of Life United Nations Development Program, United Nations Environment Program, World Bank, World Resources Institute. Elsevier Science, 2000.

3 ENVIRONMENTAL LEVELS, TOXICOLOGICAL AND ECOTOXICOLOGICAL CHARACTERISATION

Owing to the scarcity of ecotoxicological data for the region, most of this section is related to environmental levels and spatial patterns. The information is generally aggregated in densely populated areas along the extensive hydrographic basins of major rivers of the region such as the Amazon, Paraná and Río de la Plata. Thus the database is strongly biased towards freshwater environments. In spite of the large development of coastal marine areas along the Atlantic and Pacific Oceans, they have received proportionally less attention. Another general regional trend for environmental PTS information is the uneven contribution among countries that reflects the different patterns of economic and technical development.

3.1 LEVELS AND TRENDS

3.1.1 PTS In Air

There are no regional routine programs on PTS monitoring in air. Available data represent a few geographical areas within the region. This contrasts with other environmental media, and reflects the lower attention given to air monitoring. The low representation of these measurements should be stressed given the well recognized high variability of air masses which cross the Region. Table 3.1. presents PTS data available for air.

Table 3.1	PTS ra	anges in	Air.
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	PTS Concentration (ng/m ³) – PCDD/F (pg-TEQ/m ³)						
	PCBs	HCHs	CHLs	DDTs	HPTs	PCDD/F	PAHs
Sample							
Particulate (Range)	1 – 3	1-1.5	1-1.5	1-1.5	1-1.5	3-394	0.342-294
Stack stream							1,000
Deposition (Range)*	5.9-1,344	4.0				13,986- 18,000	0.55-1.319

* deposition expressed in $ng/m^2/d$.

3.1.1.1 <u>PCBs</u>

Few measurements of PCBs in air have been undertaken in the region. Recent PCB reports for Santiago de Chile indicated values from 1.04 to 1.75 ng/m³, comparable to other urban areas of the world (CENMA-CONAMA 2002). Levels of PCBs in air particles smaller than 2.5 μ m in diameter (PM_{2.5}) in Temuco-Chile ranged from 0.67 ng/m³ to 1.7 ng/m³, while in Santiago reported levels ranged 1.15 to 2.7 ng/m³ (Mandalakis and Stephanou, 2002). Unexpectedly, observed differences between these two cities where not high, in spite of differences in population density, indicating that the atmosphere in these two Chilean cities is fairly polluted with PCBs even when compared with other urbanized areas of the world.

Data for other urban areas in Argentina (La Plata city) indicate low PCB values ranging from 1-3 ng/m^3 , whereas chlorinated pesticides levels were in the low 1-2 ng/m^3 range (Colombo, 1993, unpublished).

In the southeast Atlantic Ocean, data presented by Ockenden *et al* (2001) reveals several congeners of PCBs in Islas Malvinas (Falkland Islands). Levels of PCBs 28,52,101,153/132 and 138, ranged from 0.13 to 3.1 pg/m^3 with higher concentrations of less chlorinated congeners. Air concentrations over the sea reached more than 100 pg/m³ for PCB 28 and only 0.67 pg/m³ for PCB 138. In addition, a temporal trend of increasing air levels in summer periods was also reported with variable concentrations according to the sampling station. Average total PCBs levels sum 5.1 pg/m³. This illustrates either local sources or the impact of transport by air or water to remote environments throughout the southern hemisphere.

In Brazil, PCB concentration in air samples as well as total deposition were carried out in Araraquara (São Paulo State), São Paulo city, and Cubatão (São Paulo State). Air concentrations ranged from 2-6.5 ng/m³ (ambient) and deposition between 0.9-1.3 ng/m²/d (Zancul *et al.*, 1999). Further details are provided in the case study box at the end of this chapter.

3.1.1.2 Dioxins and Furans

There are very few measurements of PCDD/F levels in air within the region. Limited data are reported for Brazil and an interesting study performed by Lohmann *et al*, 2001 along a transect from Lancaster U.K. to the southern Atlantic Ocean reported data from coastal and offshore areas in Argentina, Brazil, and Uruguay. Measured concentrations were very low (compared to measured values from the Northern hemisphere). The sole exception was Montevideo (Uruguay) which presents an anomalous very high value of 4000 fg/m³ of Cl₄-Cl₈ PCDD/F, equivalent to 40 fg TEQ /m³. Further work is needed to identify the principal sources in this area.

In general, reported ambient air concentrations are comparable to those found in remote areas, in fact in Islas Malvinas (Falkland islands) PCDD levels where 330 fg/m³ for Cl_4 - Cl_8 congeners, very similar to remote areas in the Irish coast. Data reported for Brazil (Krauss, 2000; Zancul *et al.*, 1999) also indicate low PCDD/F concentrations (Table 3.2).

Location	pg I-TEQ/ m²/d	fg I-TEQ/ m ³
Cubatão, SP	8 - 72	38-48
Sao Paulo	32 - 78	86-169
Araraquara	0.2 - 17	16-267
Cantagalo, RJ	0.6 - 2.5	28
Santa Cruz, RJ	149 - 262	994
Barra Mansa, RJ	4.2 - 39	18-839
Volta redonda, RJ	1.8 -3.2	3
Belford Roxo, RJ	51 - 54	
Manaus, AM	0.2 - 8.7	

 Table 3.2
 Air PCDD/F concentrations in Brazil

The other countries within the region (Argentina, Ecuador, Bolivia, Chile, Paraguay, Peru) do not report data on PCCD/Fs in air. It is interesting to note that most data presented represent only isolated information obtained from the scientific literature. As a general conclusion it appears that trace levels of PCDD/Fs are detectable in air samples; environmental levels are very low and comparison of data is difficult because they represent only a few samples.

3.1.1.3 <u>PAHs</u>

In contrast to other PTS, PAHs have been more frequently analysed in air samples within the region. Argentina reported 4 data corresponding to PAHs in particulate matter in the southern Patagonia. Particulate PAH concentrations in air from Puerto Madryn averaged 6 ng/m³ whereas in the local industrial park, site of the biggest country aluminum plant, it reached 1000 ng/m³ (Ares and Zavatti, 1993). Benzo(a)Pyrene predominated in stack stream samples but decreased markedly in air samples, which was attributed to its faster decay relative to Benzo (ghi) Perylene and especially to the more abundant Benzo(k) Fluoranthene. In La Plata city (Buenos Aires) the total particulate PAHs ranged from 3 to 30 ng/m³ and the highest concentrations corresponded to fall and winter due to reduction of photochemical activity during cold months (Catoggio *et al.*, 1989). Pyrene, Phenanthrene, Benzo(a)Pyrene and Benzo(a)Anthracene predominated denoting the importance of pyrogenic sources. Benzo(a)pyrene levels ranged from 0.09 to 2.3 ng/m³. Highest levels of semi-volatile aliphatic hydrocarbons and lead confirmed the importance of mobile sources in this urban area during the day (Colombo *et al.*, 1999; Bilos *et al.*, 2001).

PAHs were measured in air samples in Santiago de Chile by Adonis *et al* (2000). These data represent the only published temporal trend of PAHs in air particulate matter (PM10). Reported values are higher than other values for urban areas in the region. Concentrations ranged from 43-294 ng/m³. Higher values were detected in 1992 (Adonis et al., 2000), with a net decline of PAHs in recent years. Benzo (a) pyrene levels averaged 9.2 and 4.9 ng/m³ for 1995 and 1996 respectively. Other carcinogenic PAHs detected included Benzo(k) fluoranthene (23.5-4.3 ng/m³ for 1992), and Dibenzo (a,h) anthracene (54.5, 49.4, and 4.5 ng/m³ for 1992, 1994

and 1996, respectively). The authors suggest that besides the reduction of air PAHs levels, values are still high and a potential risk for human health.

There are few measurements of air (10 data set) PAH levels in Brazil. Air concentration and total (wet and dry) deposition were determined in Salvador (Bahia State), Amazon State, Araraquara (São Paulo State), São Paulo city, and Cubatão (São Paulo State). Higher values were detected in the industrial area of Cubatão (55 ng/m³); in São Paulo city the concentrations ranged from 3 to 15 ng/m³ compared 0.003 up to 1.5 ng/m³ in other regions (Vasconcellos (1996); Vasconcelos et al. (1998); Zancul *et al.*, 1999; Beretta (2000); Franco (2001); Vasconcellos et al., in press).

In Brazil, the results obtained for PAHs in the atmosphere of Araraquara (an agricultural area heavily devoted to sugar cane plantation and combustion) indicated unexpected low values of these compounds. This behavior was explained assuming that most of the fire in these plantations occurred as smoldering (i.e. low temperature), which is not the most favorable condition for the formation of PAHs. Also, the segregation of PAHs from other pyrogenic sources was not carried out, which omplicates the interpretation. The major PAHs found were Benzo[b]fluoranthene and Benzo[k]fluorantene (Franco, 2001).

The results illustrated in Table 3.1, show the value for gaseous phase for winter of 1994 and summer of 1995, when 25 samples were analyzed for total PAHs. The results for benzo(a)anthracene ranged from 15 to 732 pg/m³. The occurrence of substantial levels of certain PAH congeners and methyl-PAH derivates in airborne particles collected in the Amazonian forest in August and September 1993 is suggestive of emissions from extensive forest fires in that area. Indeed, a similar pattern of PAH was detected on particles emitted by biomass combustion carried out under field and controlled conditions. The PAH distribution recorded in the rainforest was rather different from that observed in urban (São Paulo State, Brazil and Rome, Italy) and suburban samples (Montelibretti, Italy) as the airborne particulates were coming from both forest combustion as well as from motor vehicle emission. The levels of total PAH in the Amazonian forest were surprisingly high when compared with those commonly found in suburban, agricultural and forest areas of Europe and North America.

A study carried out in a rural community in the winter of 1991, in the southern part of Brazil, investigated the impact of wood burning stoves on indoor air quality. Concentrations of PAHs, NO₂, and suspended particulate matter (SPM) were monitored in houses using wood stoves, and the results were compared with concentrations obtained in houses equipped with gas stoves. As expected, higher (p<0.01) concentration of PAHs, and much higher (p=0.07) concentrations of SPM existed when using wood stoves. In contrast, NO₂ concentrations were slightly higher in houses with gas stoves. These parameters were minimally affected by smoking, outdoor air pollution, or other emissions from indoor combustion products. Results appear to support the hypothesis that domestic wood burning stoves are risk factors for some upper digestive and respiratory tract cancers in Brazil (Hamada *et al.*, 1992).

3.1.1.4 <u>Data gaps</u>

Obviously there are large data gaps in the region regarding PCBs and dioxins in air. Systematic and intensive monitoring programs are needed to understand the environmental fate of these PTS within the region, especially the highly toxic PCDD/F congeners. Only few pesticide data in air were retrieved, and thus it is very difficult to evaluate their fate and impact in the region.

3.1.1.5 <u>Recommendations for monitoring</u>

As biomass burning is one of the most important energy sources in the region, it is recommended that PAHs levels in air should be monitored both in densely populated areas and in remote sites within the region. Another suitable candidate for air monitoring are PCBs, particularly in the most populated cities. Sampling air in remote areas is also needed in order to evaluate the potential of long range transport of these pollutants within the region. Higher PTS levels may be found in highland areas, therefore it would be interesting to monitor air levels also in those highly populated areas such as Quito, La Paz, etc.

The use of bioindicators (moss and lichens) has been proposed as good surrogates and tracers of tropospheric PTS levels. On the other hand, the use of semipermeable sampling devices (SPMDs) has been also indicated as potentially good tools for air monitoring (Ockenden et al, 1998).

3.1.2 PTS In Soils

Soils are natural sinks for persistent and lipophilic compounds, which strongly adsorb to the organic carbon and remain relatively immobile in this reservoir (Mackay, 2001). Thus, soil is a typical 'long-memory' accumulating matrix. Therefore, PTS inputs received in the past will persist with very little clearance and long half-lives. Soils receive inputs of environmental pollutants via different pathways, including direct pesticide
application, atmospheric deposition, application of sewage sludge or composts, spills, erosion from nearby contaminated areas and contaminated water irrigation. Once PTS contamination is detected in soils, a historic evaluation has to be performed to determine which was the predominant input pathway (sometimes pattern analysis might provide further evidence). In general, it is difficult to determine when soil contamination occurred. The concentrations in soil tends to reflect the baseline contamination of a region. Therefore, urban areas exhibit higher concentrations than rural, at least for those PTS produced by industrial activities, but obviously higher levels of Pesticide PTS are expected in soils treated historically with these substances.

3.1.2.1 <u>Regional Activities/Monitoring</u>

No routine monitoring activities have been performed to obtain a clear picture of PTS levels in soils of the region. Most soil data obtained refer to urban, contaminated areas. Very few studies cover a large spatial area. Chile carried out a national survey at the end of the eighties to evaluate pesticide levels (i.e. DDTs) and heavy metals in soils.

Little information has been obtained from several countries, so the data base is limited and probably does not reflect the actual situation within the whole Region. Table 3.3 show the concentration of PTS in soil samples from Chile and Brazil.

	Table 3.3 PTS ranges and average values in Soils													
	PTS (ug/kg dw) – PCDD/F (ng I-TEQ/kg)													
	HCHs DDTs HPTs ALD DIEL END HCB ENDS PCDD/F PAHs													
Range	2-109,290	2-7,868,000	2,79-2,145,000	2,8-24,280	4-11,838	1,7-15,897		20-180	0.001-1.607	50-1,000				
Mean	18,270	1,124,040	715,002	7,322	1,983	5,300	6,480	100	0.027					
SD	44,591	2,973,807	1,238,414	11,548	4,409	9,177		113		0				

14000 12000 Aldrin 10000 Dieldri Endrin 8000 6000 НСН НСВ Conc/ µg/kg (dry weight) 4000 PCB 2000 CHLs HPTs Dioxin Furan 0.04 EndS PAH 0,03 0.02 0,01 0.00 + Rio de Janeiro RJ Duque de Caxias RJ Uberlândiar MG Canoas/RS Cubatão/Sp Araraquara/Sp

Figure 3.1 Levels of PTS in soils from Brazil (µg/kg, dry weight)

Soil levels of dioxin and furans have been recently provided by Krauss (2001) indicating very high levels in several locations, particularly in a former HCH production plant (Table 3.4).

Table 3.4 Soil levels of dioxin and furans in Brazil. Range in ng I-TEQ /kg.

SP:	Sao	Paulo.	RJ:	Rio de	Janeiro.	AM:	Amazonia.	MG:Minas	Gerais.
· · ·	Suo	i uuio,	110.	itio ue	sumono,		r mazonia,	o.ioimas	ourais.

Location	Range ng I-TEQ /kg
Cubatao SP	11-34
Araraquara SP	0.1-1.2
Manaus AM	0.05-0.4
Formiga MG	1.4-654
Industrial Areas RJ	1.1-654
Recreation Areas RJ	0.03-1.8
Duque de Caxias RJ	13,900

Soils from the Amazon basin contained 0.02-0.4 ng I-TEQ/kg PCDDs and PCDFs, and 0.1-7.7 g/kg of PCBs. The low PCDD/PCDF concentrations were explained by the absence and lack of dioxin formation during forest burning, or a lack of humic acids in soils preventing the adsorption of dioxins. This behavior also reinforces the hypothesis that dioxins measured during biomass burning may be due to volatilization and not due to in situ formation (Krauss *et al.*, 1995). The work of Torres *et al.* (2002) described the presence of DDT residues in areas located in the southern Amazon region in Brazil. Considering that since 1985 the use of DDT in the agriculture was forbidden, the presence of this compound in higher levels than its main metabolites suggests that current contamination is derived from the more recent use of this pesticide or another active principle contaminated with DDT.

Braga *et al.* (2000) found higher values of dioxin in soil samples in collected from a supposed remediated area from Cidade dos Meninos (Rio de Janeiro State, Brazil), a well known PTS hot spot due to stockpiles left from a pesticide industry operated by the Ministry of Health and now deactivated.

The level of PCDD/F, PCB, and PAH in 21 Brazilian municipal solid waste (MSW) samples of different degrees of maturation have been evaluated. The study showed that most PCDD/F concentrations are above the levels acceptable by German standards (17 ng L-TE/kg), especially for samples from metropolitan areas. These results are, however, similar to those found for Germany. For PCB, the average concentration for the sum of the six congeners (28, 52, 101, 138, 153, and 180) was about 3 times lower when compared to German samples, all of them below the value indicated by the legislation (0.2 mg/kg) (Grossi *et al.*, 1998).

In 18 topsoils samples from Uberlândia (Minas Gerais, Brazil), the concentration of PAHs was in the range of 7-390 g/ kg, whereas the concentration of PCB varied in the range 0.05-1.25 g/kg. These results are comparable to or are below background concentrations normally found in temperate soils (Wilcke *et al.*, 1999).

Chile performed a national survey in the agricultural areas in the country during the late eighties. A summary of the reported values follows below. The overall conclusion of this study indicated low levels of Chlorinated pesticides in surface soils in different agricultural areas in Chile; despite detection frequency was relatively high.



Figure 3.2 PTS concentrations (ng/g dw) in soils from Chile.

3.1.2.2 National Monitoring Programmes

To our best knowledge, no routine monitoring activities focused on soil contamination by PTS were performed during recent years in the region. Brazil is implementing a national monitoring program of mercury in soils and other environmental matrices for the Amazonian and Pantanal regions, but no other PTS are considered in this first phase.

3.1.2.3 Hot Spots In The Region

It is widely accepted that probably several PTS stockpiles are relevant sources for soils, but few data have been gathered up to now. Just recently, some institutions in Chile, and the IBAMA in Brazil are starting a project looking for contaminated sites with PCP and other chemicals. It is expected that soon, additional data on contaminated soils will be reported as these programmes are implemented.

Area	HCHs	DDTs	HPTs	ALD	DIEL	END	HCB	END	Dioxin	PAHs	Reference
Rio de Janeiro,	0.3										Oliveira et al.,
Rio de Janeiro,									0.014		Braga <i>et al.</i> , 2000
P I Paulínia, SP				243	118	159					Jardim <i>et al</i> (2000)
Canoas, RS	109	787	215	5	2		6				CETESB (1997)

Table 3.5 Values obtained for PTS in soil in some Hot Spots in Brazil. Concentration (mg/kg)

In the study performed by Oliveira *et al.* (1996), the authors demonstrated that the risk of contamination was restricted to the population close to the contaminated area, and to the consumption of food and other products produced in Duque de Caxias (Rio de Janeiro State, Brazil). In this region, a Lindane plant belonging to the Ministry of Health, operated for many years, and when it was closed down, in 1955, many tons of pesticides were left unattended in the area. An extremely high level of surface soil contamination (order of hundreds of mg/kg) was found in the area up to 100 m away from the old plant.

The high values in soils obtained for PTS in Canoas (RS) were associated with a pesticide industry. In Paulínia (São Paulo State) Shell Chemical manufactured pesticides from 1975 to 1993, and contaminating the soil with aldrin, endrin and dieldrin.

Another well known case of PTS (D&F) hot spot in Brazil refers to the Solvay Company, in Santo André, São Paulo State. In the CETESB (2000) report, it was shown that lime samples had concentrations of dioxin and furan in range of 0.1-31138 ng/kg TEQ for samples collected in August and December of 1998. In March 1998, high levels of dioxin were found in the milk produced in the German state of Baden-Wurttemberg, leading to its removal from the market. tracing the origin of this contamination led to cattle feed that was tainted with high levels of dioxins. Six components of the feed were analyzed separately and the citrus pulp pellets from Brazil were identified as the source. A broker, Carbotex Ind. & Com. de Cal Ltda, had marketed the lime produced by Solvay in Santo André, since 1986.

Rhodia (Cubatão city, São Paulo State) manufactured chemicals used for wood treatment, such as pentachlorophenol, sodium pentachlorophenate, as well as tetrachloroethylene and carbon tetrachloride. The principal chemical waste compounds from the manufacture of these chemicals were HCB, hexachloroethene and hexachlorobutadiene. In 1984, it was reported that the company had 11 illegal waste dumps around the area.

3.1.2.4 Data Gaps

Spatial data gaps are evident, so contamination of soils have not been documented adequately within the region. There is an obvious need for a larger data base of PTS in soils, especially considering the direct link between soil quality and agriculture-food production. Another important aspect related to hot spots is the reluctance of Governmental agencies to provide data and to accept the existence of such contaminated areas. In this context, the recent publication of risk areas (contaminated soil) in the State of Säo Paulo by the Environmental Agency (www.cetesb.sp.gov) is highlighted.

3.1.2.5 <u>Recommendations for Monitoring</u>

A regional monitoring program for soils within the region is an obvious need. This should be oriented to identify and classify hot spots and historical background contamination. This will permit the establishment of relationships between sources and receptors, as well as quantifying the potential for PTS recycling.

3.1.3 PTS In Freshwater Environments

3.1.3.1 PTS in Waters

As indicated previously, the majority of information on levels comes from major rivers of the region. Table 3.6 presents PTS regional ranges and averages for waters. The data base is not completely representative for the whole area since it contains information mostly from Argentina and Brazil (c.a. 95%) and to a lesser extent, Uruguay, Ecuador and Chile. There is a lack of information from the other countries. Most data correspond to chlorinated pesticides (> 90%) and PAHs (8%), with few reports of PCBs (1%) and organic mercury (< 1%, and in Brazil only). A recent report from CETESB from an environmental survey in the Santos bay (São Paulo State) is the only published study for PCDD/Fs in water (see box at the end of this chapter). All the 25 samples analysed were below the detection limit. Overall, several high pesticide levels for freshwaters in the region suggest a complex situation, but the low representativity of the data impose a cautious interpretation. Usually, only suspected contaminated ecosystems are monitored and large-scale regional water monitoring programs have never been undertaken. In addition, very frequent non detectable levels were not included in the data base, i.e. Table 3.6 mean values overestimate the regional picture due to the strong influence of contaminated sites.

	Table 3-6	PTS	ranges	and	averages	in	waters.	Brac	keted	values	inclu	ıde	critical	cases.
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				PTS (n									
	PCBs	HCHs	CHLs	DDTs	HPTs	ALD	DIEL	ENDR	НСВ	ENDS	MIR	PAHs	Org. Hg
Range	7-39	3-790 (7300)	0.6-400 (7500)	0.6-6510	0.9-1060	1-3710	0.8-5000	2-230	1-14160	1-1900	0.3	1.9-41	
Mean	17	146 (622)	104 (703)	1267	206	74 (187)	42 (447)	100	418 (1384)	343		16	
SD	14	191 (1572)	124 (1978)	1920	274	79 (647)	50 (1200)	61	422 (3280)	529		12	

PCBs have only been reported for the Uruguay River, Paraiba River (Rio de Janeiro), Río de la Plata (Argentina), and the Biobío River in Chile. In the Uruguay river, concentrations (7 ng/l; DINAMA-SOHMA, SHN, 1998) are above the recommended Argentinean limit of 1 ng/l. USEPA recommend a guideline value of 14 ng/l. In the Río de la Plata, PCB levels in contaminated sediments close to Buenos Aires are even higher than this more permissive guideline (see Río de la Plata case study Annex III). In the Biobío River, PCB concentrations are also higher than recommended guidelines (22 ng/l; Gavilan *et al.*, 2001), comparable to those registered in the other environments. In Brazil, Telles (2001) showed that concentrations of PCBs and organochlorine compounds in surface water samples collected in the State of Pernambuco were below the detection limit. Another important survey carried out in Brazil by UFSCar/UNICAMP/CETESB (Qualised Project) showed non-detectable levels of PCBs in the water column and interstitial waters in the Tiete River.

Pesticide levels are quite variable (0.6-14160 ng/l) reflecting distinct ecosystem conditions, from less impacted environments to severely polluted streams located in densely populated and industrialized areas close to Buenos Aires and Sao Paulo. Heptachlor, HCHs, Aldrin and DDTs are the most frequently reported pesticides in water accounting for more than 60% of the total database.

As expected, according to its higher water solubility, Lindane and its isomers are frequently detected in high levels (grand mean = 622 ± 1572 ng/l). The information chiefly reflects Argentinian data (47 over 56 cases) which present high HCH concentrations (0.3-7 µg/l) in the Reconquista river, Buenos Aires (Topalián *et al.*, 1996; Rovedatti *et al.*, 2001), but also in some Northern and Central areas (San Luis, La Pampa, Corrientes, Entre Ríos, Sta. Fe; García Fernandez *et al.*, 1979; Caviedes Vidal, 1998), exceeding by 3-400 times the Canadian guidelines (10 ng/l). Excluding these critical sites, the general mean decreases drastically to 146±191 ng/l, but is still higher than guidelines. In the Río de la Plata, concentrations as high as 520 ng/l have been reported in the vicinity of the Buenos Aires sewer (see case study). HCH data from important Argentinean rivers in the North (Paraná, Uruguay, Río de la Plata) or south of the country (Río Negro, Río Limay) are consistently higher than 10 ng/l suggesting that these compounds are of concern throughout the country. The

relatively high pesticide levels in the Río Negro, Patagonia, reflect the intense agricultural activity in this valley (vegetables and fruits) and related pesticide use, e.g. organophosphorous, Dicofol, Endosulfan, Endrin and Heptachlor (Natale et al., 1988). In the Guayas ecosystem in Ecuador values as high as 15 μ g/l of lindane have been detected, but in general values range from 1.6 to 890 ng/l. (Resabala *et al*, 2002).

Heptachlor and Aldrin data are more widely distributed within the region, have lower general means than HCHs (206±274 and 187±647 ng/l, respectively), but are still higher than guideline values (3.8-4 ng/l, Canadian-USEPA). Dieldrin shows a worse situation, specially in Brazil which has a larger set of Dieldrin reports (12 over 19 cases), including the highest levels. The general Dieldrin average (447±1200 ng/l) is almost an order of magnitude higher than USEPA guideline (56 ng/l). The general mean of Aldrin and Dieldrin are shifted by a few contaminated sites in Brazil (3710 and 1000-5000 ng/l, respectively; CETESB, 1997; Chagas et al., 1999) and Argentina (Dieldrin: 1429 ng/l; Caviedes-Vidal, 1998). Excluding these outliers the averages decrease 3-10 times (42-74 ng/l) closer to guidelines. A study from Ecuador reports Heptachlor concentrations ranging from 0.1 to 500 ng/l in river waters (Resabala et al., 2002).

DDTs is also frequently reported with very high concentrations, i.e. the general mean $(1267\pm1920 \text{ ng/l})$ s double that of the more soluble HCHs. Reports from northern freshwater environments in Argentina and Brazil indicate very high levels (1000-6000 ng/l), more than 3 orders of magnitude above the USEPA guideline (1 ng/l), suggesting higher inputs possibly related to subtropical agricultural exploitations and vector control. However, this variability probably includes methodological uncertainties, especially in older works, since water analysis of highly hydrophobic compounds such as DDTs is recognized as more difficult. As observed for HCH, excluding the critical samples, the DDT average decreases to a few tens of ng/l, but still remain 1-2 orders higher than guidelines. Also a report from Ecuador reports high concentrations of DDTs in surface waters, ranging from 0.01 to 50 µg/l of DDTs, however the authors state that the data quality must be taken with caution.(Resabala et al., 2002).

HCB concentrations present the highest regional average, similar to DDTs, but with a larger variation in levels $(1384\pm3280 \text{ ng/l})$, which are within accepted guidelines (USEPA: 3680 ng/l). This average is raised by Brazilian data which has the largest HCB data set (25 over 31 cases) with the highest concentrations (6000-14160 ng/l; Celeste *et al.*, 1987; CETESB, 1997). A report from Ecuador reports concentrations ranging from 9 to 14 ng/l in surface waters at the Guayas Ecosystem (Resabala *et al.*, 2002).

PAH concentrations in waters are relatively high (average: $16\pm12 \mu g/l$) but the data base is not homogeneous. Lower concentrations (1.8-12 $\mu g/l$) have been determined by GC-FID in the Uruguay and Rio de la Plata rivers (see Annex III), whereas the highest levels (8-41 $\mu g/l$) correspond to fluorimetric determinations in coastal marine Patagonian waters impacted by crude oil extraction activities (Esteves and Commendatore, 1993). The Canadian water quality guidelines for 11 individual PAHs range from 0.012 to 5.8 $\mu g/l$ (mean= 1.7±2.1 $\mu g/l$; sum= 18.2 $\mu g/l$).

The presence of organic mercury in the water column of Amazonian rivers has been recently investigated by Bisinoti (2002) and Roulet *et al.* (2000). The results show values in the same order of magnitude that the ones normally found in other areas of the globe.

There was only one sample over 6,000 analyzed in the routine program (annual) maintained by SABESP (Water Company in the State of São Paulo) in which the PCP was detected in drinking water served in the Metropolitan Region of São Paulo (Sabesp, 2002).

3.1.3.2 PTS in Sediments

Table 3.7 presents PTS ranges and averages for sediments. In this case, the data base (n= 214) presents a more uniform contribution from the different countries: Argentina (45%), Brazil (31%), Chile (14%), Peru (10%) and Uruguay (5%). Individual PTS information is also more equilibrated, but chlorinated pesticide data still dominate (61%) followed by PAHs (23%), PCBs (10%). PCDD/F (6%) including two reports for Peruvian coastal sediments (Whelan et al., 1983) and 10 from the Brazilian CETESB (2001) for an environmental survey in the Santos bay (São Paulo State) that also include organic mercury in sediments from the Amazon region. Overall, as observed for waters, sediment data indicate a complex situation in densely populated areas affected by urban-industrial inputs which present high PTS levels, e.g. HCH, DDTs, PCBs, whereas sediment levels of PAHs are very high in areas of crude oil extraction and petrochemical activities.

Table 3.7. PTS	ranges and	averages in	sediments.	Bracketed	values	include	critical	cases.
	0	0						

	PTS (ug/kg dw) - PCDD/F ugTEQ/g													
	PCBs	HCHs	CHLs	DDTs	HPTs	ALD	DIEL	ENDR	нсв	ENDS	MIR	PCDD/F	PAHs	Org. Hg
Range	0.8-23 (580)	0.1-15 (57100)	0.2-15	0.1-48 (85800)	0.1-17 (2700)	0.02-4	0.2-5 (24000)	0.2-2 (22200)	0.1-22 (26400)	0.5-49 (23500)	0.03	0.04-5.12	0.1-286000	0.1
Mean	9.1 (58)	3.2 (4395)	4.2	9.7 (4009)	3.9 (211)	1.4	1.0 (1847)	0.8 (3701)	6 (4473)	9.4 (14008)			29520	
SD	7.7 (149)	4.4 (15836)	5.7	14 (18274)	5.4 (748)	1.5	1.3 (6656)	0.6 (9063)	13 (10762)	20 (37037)			63492	

The most frequently reported PTS in sediments are DDTs, HCHs, PCBs and Heptachlors accounting for 46% of the total database. The concentrations show a large variability, basically introduced by some highly contaminated sites in Argentina and principally Brazil (hot spots), which present 4-5 orders of magnitude higher levels (Machado *et al.*, 1996; Costa *et al.*, 1997; Tavares *et al.*, 1999; Torres *et al.*, 2002).

Some data from Ecuador reports high levels of Chlordane ranging 142-669 µg/kg dw in sediments from Taura Guayas river (Resabala et al., 2002), whereas DDTs and HCHs present lower values 6-16 µg/kg, respectively.

In Chile, Barra *et al* (2001) reported low levels of DDTs in a dated sediment core from an urban site in Central Chile, historic deposition pattern reached high values during the 1972-1978 period reaching 1,309 ng/m²/yr and steeply declined in recent years after DDT banning during the 80's. However, actual deposition rates of lindane were relatively high (188 ng/m²/yr), reflecting the recent use of this pesticide.

Torres *et al.* (2002) analyzed sediment samples from Paraíba do Sul-Guandu system. This river is the only source of potable water for more than 10 million in the metropolitan area of Rio de Janeiro. PCBs were detected in a few collected surface sediments at low levels. The average concentration of Σ DDT was around 225 ng/g, whereas HCB was detected in trace concentrations. Sediment collected near the city of Volta Redonda (Rio de Janeiro State) showed PAHs levels around 40 times higher than the average value for the basin, indicating the presence of an important source in this city.

Overall, PCB concentrations in sediments are relatively high, but the database is strongly biased by contaminated sites in Argentina, the Río Santiago (998 μ g/kg; Colombo et al., 1990) and Brazil (580 μ g/kg; Lamparelli *et al.*, 1996). Excluding these sites, the general PCB mean decreases from 58±149 to 9.1±7.7 μ g/kg, lower than the Canadian guideline for protection of aquatic life (34.1 μ g/kg). However, polluted sediments from the Río de la Plata estuary often exceed this value (see Annex III).

Essentially the same pattern registered for PCBs of some very critical sites and more homogeneous residual concentrations is observed for chlorinated pesticides. Thus, the grand mean averages consistently exceed all sediment guidelines. Excluding these more critical sites (bracketed values in table 3.7), the general averages decrease 2-3 orders of magnitude but still remain generally higher than Canadian freshwater guidelines for protection of aquatic life, i.e. Heptachlor (3.9 ± 5.4 Vs a reference value of 0.6 µg/kg); DDTs (9.7 ± 14 Vs 6.15 µg/kg); HCHs (3.2 ± 4.4 Vs 0.94 µg/kg); Chlordanes (4.2 ± 5.7 Vs 4.5 µg/kg).

Most PAHs reports correspond to harbors and ports in heavily impacted areas and thus present a huge variability (0.1-286000 μ g/kg). PAHs grand mean value is very high (29520±63492 μ g/kg) exceeding by several orders of magnitude Canadian guidelines for individual PAHs (5.9-111 μ g/kg for 13 PAHs; sum= 468 μ g/kg). Most affected areas correspond to the intensive traffic in the Paraná, Uruguay and Río de la Plata rivers, specially close to heavily populated areas such as Buenos Aires and Montevideo, the Argentine Patagonian coastal area, where crude oil extraction and transport are very active, and the Tiete river and surrounding environments close to Sao Paulo in Brazil.

Patagonian total fluorimetric PAHs concentrations ($29500\pm59300 \mu g/kg$) are very high considering that these are mostly coarse sediments (0.1-58% fines) with low organic contents (0.4-3.6%). However, the CG-FID evaluation of the aliphatic composition of these samples indicated a clear petrogenic signature in most contaminated sites from the San Jorge Gulf, severely affected by oil production and transport activities (Commendatore *et al.*, 2000). PAH concentrations in the Río de la Plata estuary are generally lower but show some critical values in bays, harbors and ports (see Annex III).

3.1.4 PTS In Animals

As expected, available data on PTS in Region XI for both aquatic and terrestrial animals are relatively scarce when compared to other regions of the globe. Aquatic organisms are by far the most studied organisms, and among them, bivalves and fish. Terrestrial organism data are almost completely centered on birds, with some Brazilian data available for bovines and insects. As observed for other environmental receptors, the regional distribution of data is uneven, heavily centered in coastal environments, mainly in the Atlantic coast. Data availability reflects both the capacity of each region to maintain a routine environmental monitoring program as well as the environmental monitoring carried out by universities and research centers, which are by far the two most active data generators in South America. The data presented for aquatic and terrestrial organisms are solely from Argentina, Brazil, Chile, and Peru, and most of them are centered in freshwater and estuarine ecosystem in the Paraná-Río de la Plata, principally affected by PCBs, and the Amazon basin, where organic mercury seems to be the most important contaminant in the forest area.

3.1.4.1 <u>Aquatic Organisms</u>

3.1.4.1.1 Shellfish

Considering the South American coastal environment as a whole, the most comprehensive program of monitoring PTS in coastal organisms is the Mussel Watch (Farrington and Tripp, 1995). Baseline PCB concentrations range from 200-700 μ g/kg lipids in unpolluted sites; 1000-3000 μ g/kg in samples from moderately contaminated sites, and 4000-13000 μ g/kg lipids in most affected bivalves. Sampling sites showing high PTS levels in the region includes Recife, Brazil (Figure 3.3, BRRE), Río de la Plata (ARRPi m, see Annex III), and Punta Arenas, in Chile (CHPA).



Figure 3.3 Mussel Watch data for South America. From the left in N to S direction on the Atlantic (Aruba, Venezuela: VE, Brazil: BR, Uruguay: UR, Argentina: AR) and from S to N on the Pacific (Chile: CH, Peru: PE, Ecuador: EC, Colombia: CO).

Among PTS shown in Figure 3.3, PCBs predominate, followed by DDTs and Chlordanes. Considering all the results obtained for aquatic organisms presented in this report, PCB data are available only in more recent works, whereas when old data are considered (> 10 years old), DDT, HCH, DRINS and HCB are the most common PTS. For PAHs, the same trend is observed, where mainly recent data were gathered. In the Río de la Plata, PCBs, chlorinated pesticides and PCDD/F showed a consistent spatial pattern of highest levels around Buenos Aires and size-increasing trend in Asiatic Clams utilized as sentinel organisms (see Annex III). A recent study from CETESB from an environmental survey in the Santos bay (São Paulo State) constitutes another of the very few existing PCDD/F data reported for biota in the region (CETESB).

For PCBs, comparison of values presented is difficult, since some data are not normalized by the lipid content. In this context, when considering all the data available for bivalves, PCB measurable concentration average 20 ng/g in almost all data gathered, reaching values above 200 ng/g in the work of Farrington & Tripp (1995) only. This is an interesting result, and according to Lopes *et al* (1992), these high values may reflect a seasonal variation in PTS content in bivalves. Fresh weight concentrations in these bivalves are one order of magnitude lower than the guideline for PCBs (0.15-0.2 compared to 2,000 ng/g), and concentration patterns tend to follow both the industrial and population development observed in the Pacific and Atlantic coastal areas.



Figure 3.4 General trend of PCBs in bivalves (*Perumytilus purpuratus*, *Alacomya ater* and *Choromytilus chorus*) from 5 coastal sites in Chile

Another PTS that deserves attention in bivalves is DDT and PAHs. For DDT, average values are around 10 times lower than the ones observed for PCBs, well below the proposed guideline value (5,000 ug/kg), and follow a similar pattern observed for this class of compounds. PAH data are available for a limited number of samples, including the already mentioned Mussel Watch Program



Figure 3.5 PAHs data from the Mussel Watch PTS Program in South America (Farrington and Tripp, 1995). Acronyms as in Figure 3.3.

Data shown for PAHs (Figure 3.5) are consistent with the pattern observed for PCBs. In less polluted areas, background levels in bivalves are below 10 mg/kg lipids, ranging from 10-50 mg/kg in moderately polluted samples, and above 200 mg/kg in some impacted sites such as Punta Arenas (Chile); Recife (Brazil); Concepción (Chile) and Bahía Camarones, Río de la Plata and Bahía Blanca (Argentina). Elevated concentrations in some of these sites can be associated with offshore oil production and petrochemical activities (Argentine Patagonia and Brazil). A similar pattern was observed in the Santos coastal area (São Paulo State) where bivalves collected in 26 points in the area under influence of a petrochemical complex show values as high as 860 ng/g (mainly naphthalene), as presented in the CETESB report (2001).

Within the frame of the international Mussel Watch Program (Sericano *et al*, 1995), levels of several congeners of PCBs were analyzed in five samples collected within the wide latitudinal gradient of Chilean coast, and the results are shown in figure 3-6. As mentioned, the results show very low levels, increasing as one moves to the southern part of the country.

3.1.4.1.2 Fish

The data base used to assess the present stage of fish contamination by PTS is composed of a set of reports from Argentina (188); Brazil (377), and Chile (11), and the majority of these results are normalized by the lipid content. A summary of the results considering this normalization is presented in Table 3-8. In a similar trend observed for the results obtained in bivalves, PTS contents in fish shows a tremendous variability due to environmental characteristics as well as organ-related components. PCBs are the major organochlorine residue, follow by DDTs and HCHs.

Table 3.8. PTS ranges in fish muscle tissue (µg/kg of lipids). All values corrected for lipid contents

PCBs	HCHs	CHLs	DDTs	HPTs	D&F	PAHs	Methyl-Hg*
30- 47550	11- 1927	15-112025	88-27125	10-24067	0.17-0.39	4381-38314	20 - 2000

* values expressed as fresh weight

Fish from the Río de la Plata presented the highest PTS levels; principally PCBs and PCDD/F, compared with samples collected upstream along 1500 km on the Paraná and Iguazú rivers (see Annex III). In contrast to the Argentinean results, Focardi *et al* (1996) determined PCBs levels in fish muscle sampled at the Biobío River (central region of Chile), and observed upstream values around 530 ng/g of lipid (n= 45), an order of magnitude higher than those of marine fish. The basin is characterized by pulp and paper mills, petrochemicals, forestry and diversified agriculture. The value of 1842 ± 1005 (n=6) found for *M. cephalus* sampled in the river mouth may reflect the additional influence of the heavy local industrial activity.

In Brazil, the vast majority data on chlorinated compounds refers to the Tietê River (São Paulo State), and for mercury in the Amazonian area. In the study conducted by Caldas (1999), DDT, lindane, dieldrin and heptachlor in lake species were below the maximum permitted by the Codex Alimentarius. In respect to the Amazon basin, the major detected PTS seems to be methyl mercury, reaching levels that are above the maximum recommended daily intake by the WHO in predators (Barbosa *et al*, 1997), mainly in the samples from the Negro River area. The mercury contamination was once attributed solely to gold mining activities, but recent studies show that natural contamination is also important in that area.

A very comprehensive survey in the Santos-Cubatão area (Brazil) was recently carried out by the São Paulo State Agency (CETESB), selecting 26 sampling points, including water (n=26), sediments (n=71) and biota (n=2242). The results indicate that PCBs are by far the most abundant persistent toxic compound, being detected in 96% of the organisms, with 14% above the human criteria for daily consumption. PAHs rank as the second more important contaminant, being detected in 76% of all organisms, but none were above the acceptable levels for consumption. As expected, the most abundant dioxin found in 11 biota samples was the octachlorine (OCDD), detected in 10 samples. TEQ values in the area varied between 0.6 -1.7 pg/g for crabs, 0.003 for bivalves (*Perna perna*) and 3.45 pg/g for *Cassostrea sp.*, and between <0.0001 to 0.16 pg/g for fish (*Mugil curema*). These values are in general low when compared to similar organisms analyzed in Argentinian (Clams) and the northern hemisphere. The main findings of this project are presented in the box at the end of this chapter.

3.1.4.1.3 Other aquatic organisms

Other organisms that have been analyzed for PTS in the region are crabs (*Cyrtograpsus angulatus*), dolphins (*Pontoporia blainvillei*) and porpoises (*Phocoena spinipinnis*) from the Atlantic Argentine coast and continental shelf (Menone et al., 2001; Borrel et al., 1994; Corcuera et al., 2002). As expected, according to their different feeding habits and trophic status, dolphins and porpoises collected along the Buenos Aires Atlantic coast present ~1 order of magnitude higher lipid concentrations in blubber samples. PCBs show the highest levels (averages: 296, 1980 and 3300 µg/kg lipid in crabs, dolphins and porpoises, respectively), closely followed by DDTs (170, 1670 and 4320 µg/kg lipid). Cetacean values are comparable to those of moderately contaminated bivalves from the Mussel Watch (Figure 3.4) but much lower than those of polluted clams and fish from the Río de la Plata.

Samples from *Callinectes sapidus* (omnivorous) collected in the Santos bay area (Brazil) showed that octachloro dioxin to be the most important congener in these animals (around 30 pg/g wet weight), followed by the heptachloro congener (around 8 pg/g), whereas for furans, the 7-chlorine congener was the most abundant. Total TEQ values average 1.5 pg/g wet weight.

There are some available results for chlorinated compounds in crustacean and gastropods in the Valdivia area, Chile, (Palma-Fleming *et al*, 1998) showing that DDTs and DRINs are the PTS with higher concentration, but with low levels compared to other regions in the globe, ranging from 0.8 up to 5 ng/g wet weight. Very few available data from organisms (n= 10) collected in the Peruvian coast showed DDT levels ranging from 1 up to

10 ng/g (n=5), PCBs residues in the range of 0.12 to 17.8 (n=3), and DRINs as the most common PTS, all in the concentrations similar to the ones found in non-impacted areas.

3.1.4.1.4 Birds

Bird eggs from common gulls were analyzed by Muñoz and Becker (1999) in order to correlate PCBs levels to their different throphic status and anthropogenic influence in different colonies sampled along the Chilean coast (Table 3-9). PCBs levels were higher by a factor of two in central Chile compared to eggs collected in southern Chile, reflecting the impact of anthropogenic sources. Nevertheless, average data for 6 PCB congeners indicate that levels are at least one order of magnitude lower than those reported for gull's eggs in the northern hemisphere (Muñoz and Becker, 1999).

РСВ	Algarrobo	Concepción	Maiquillahue	Doña. Sebastiana	Isla Magdalena
Congener	(n = 10)	(n = 20)	(n = 7)	(n = 8)	(n = 10)
28	4,1 ± 2.7	3.5 ± 0.7	3.5 <u>+</u> 0.3	3.0 ± 0.2	2.8 <u>+</u> 0.4
52	3.5 ± 1.4	3.5 ± 0.7	4.1 <u>+</u> 0.8	3.4 ± 0.4	2.8 ± 0.3
101	6.6 ± 2.1	6.3 ± 1.9	7.8 <u>+</u> 1.8	5.4 <u>+</u> 0.9	6.7 <u>+</u> 1.5
118	9.8 ± 5.7	9.2 ± 3.6	4.9 <u>+</u> 0.9	4.5 <u>+</u> 0.9	4.9 + 2.2
138	17.1 ± 11.9	14.4 <u>+</u> 6.0	7.2 <u>+</u> 1.0	5.2 <u>+</u> 2.0	8.5 <u>+</u> 4.6
153	35.8 ± 24.0	27.6 <u>+</u> 11.8	13.4 <u>+</u> 2.4	9.5 <u>+</u> 4.4	17.2 <u>+</u> 10.7
180	20.2 ± 17.9	16.3 <u>+</u> 6.9	7.0 <u>+</u> 1.3	5.0 <u>+</u> 2.0	11.0 ± 9.6
PCB6Cong	87.3 ± 56.4	71.6 <u>+</u> 25.4	43.1 ± 6.1	31.4 + 9.6	49.0 <u>+</u> 24.7

Table 3.9 Levels of PCBs (ng/g fresh weight) in eggs of *Larus dominicanus* (common gull) from 5 localities in Chile (Muñoz and Becker, 1999).

Focardi *et al.* (1996) analyzed tissue residues of PCBs and other chlorinated pesticides in muscle and liver samples of three species of birds collected in the Biobío river basin (central Chile) in an attempt to evaluate a possible pollution gradient from the Andes (Santa Bárbara) to the sea (380 km). Levels of PCBs were higher in the most urbanized area (Concepción) with an important industrial activity. The similar compositional pattern observed for PCB congeners in both areas indicates a common source for this PTS.

Table 3.10 Total PCBs (ng/g of lipid) in bird muscles in two sites in the Biobio river basin, Central Chile. Bold numbers show a single sample value (Focardi et al., 1996).

Sampling Point	Species	n	$PCBs \pm sd$
(VIII Region Central Chile			ng/g lipid basis
Santa Bárbara Biobio	L. dominicanus	4	1894 ± 870
Santa Bárbara Biobio	L. serranus	4	1734 ± 1284
Santa Bárbara Biobio	P. olivaceus	1	1250
Concepción.Biobio	L. dominicanus	6	3047 ± 1870
Concepción Biobio	P. tagus	1	962
Concepción Biobio	P. olivaceus	6	4398 ± 2750

3.1.5 PTS In Human Food

Owing to their persistent and bioaccumulative properties, PTS are transferred through terrestrial and aquatic food chains and ultimately accumulate in top predators and humans. As omnivorous man occupies a top position in terrestrial and aquatic food chains thus favouring the biomagnification of PTS.

All regional data collected through questionnaires indicate a clear concern in controlling PTS levels in foods, especially milk products, grains, vegetables and oils (e.g. soya, cotton, corn, fish, sperm and peanut). Besides, it is also important to recognize that results reported in older papers must be considered with caution due to the changes in analytical techniques in the last two decades.

PCDD/F, PCBs and PAHs are scarcely reported for food items in the region. Most frequently reported PTS are DDTs and HCBs, (five countries) HCHs, mainly Lindane, and Aldrin (four countries), followed by Heptachlors, Dieldrin and Endrin (three countries), Chlordanes, and Endosulfan (two countries) and PCBs, Mirex and Toxaphene (one country) (Figure 3.6). Chile and Argentina are the countries with more reports

whereas Paraguay, Bolivia and Ecuador do not present any information. Overall, HCH and DDTs usually represent the highest concentrations in food items in the region, with a decreasing trend in recent years, probably associated to the restrictions in the use of these pesticides for agricultural purposes.



PAR ECU BOL URU PER BRA CHI ARG

Figure 3.6 PTS food data by country in Region XI

3.1.5.1 Argentina

The most frequently reported PTS in food in Argentina are HCHs and DDTs, followed by Heptachlors, Chlordanes, Aldrin and Endosulfan (Table 3-11). In dairy products the most abundant residues are DDTs and HCHs, especially in older reports (Higa, 1978). Considering all data, the concentrations decrease in the order DDT (mean: $246\pm371 \ \mu g/kg$ lipids) > HCH (mean $134\pm132 \ \mu g/kg$) > Aldrin ($56\pm77 \ \mu g/kg$) ~ Heptachlor (mean $49\pm18 \ \mu g/kg$) > Dieldrin ($30\pm21 \ \mu g/kg$). Maitre *et al.* (1994) report the highest levels, particularly for DDT, in milk samples in Santa Fe. The high detection frequency and relative abundance of HCHs and DDTs (also meat and vegetables) supports the results from other environmental compartments confirming their widespread distribution. More recent data (Lenardon *et al.*, 1994; Maitre *et al.*, 1994; Villaamil *et al.*, 1999a; Villaamil, 2000) show lower concentrations, well below action levels (HCH: 12-51 Vs. action level of 200-300 $\mu g/kg$; DDT: 12-24 and up to 990 Vs. 1250 $\mu g/kg$), probably reflecting pesticide restrictions in the '80 and '90 (Figure 3.8).

In animal flesh, the concentrations are very low and homogeneous, and consistently below action levels (Figure 3.8). Heptachlor present the highest concentrations, followed by DDTs and HCHs. According to a recent study based on usual consumption rates in Buenos Aires, the daily pesticide intake does not exceed the reference ADI from WHO/FAO; Heptachlor is the most critical pesticide approaching the ADI (Villaamil *et al.*, 2000). A recent work in infant milk samples confirmed the higher risk associated to Heptachlor which exceeded actual ADI, *i.e.* the risk is increased by the high milk intake and low body weight of infants (Villaamil *et al.*, 2002, personal communication).

PTS data for vegetables present a large variability, specially associated to some higher values measured in broccoli. In effect, the highest concentrations correspond to Endrin and Aldrin in broccoli, 218–226 μ g/kg (Table 3.11). Other chlorinated pesticides concentrations are more homogeneous with one or two orders of magnitude lower concentrations: HCHs 11 ± 8 μ g/kg, Chlordanes 9 ± 19 μ g/kg, DDTs 20 ± 25 μ g/kg, Heptachlors 6 ± 7 μ g/kg and Endosulfan 4 ± 5 μ g/kg (Villaamil *et al.*, 1999b).

Data from the National Plan for Residue Control in Food (SENASA-CREHA) indicated a few percentage of organochlorinated excesses in meat (0.05% for beef and 1.5% for sheep) in 1995, and a decreasing trend of positive detections for animal and vegetable products in more recent years. Data from the same CREHA Plan for bovine meat in 1997 indicated several detections of chlorinated pesticides in the low level range on a lipid basis, (*i.e.* n=269 for < 0.05 mg/kg; n=67 for 0.05–0.1 mg/kg; and n=24 for 0.11–0.2 mg/kg). Thirty eight over

37400 samples (0.1%) exceeded the action level of 0.2 mg/kg for chlorinated pesticides, whereas PCBs were below detection in all the samples.

					-				-		-
FOOD	HCH	CHL	DDT	HPT	ALD	DIEL	END R	HCB	ENDS	MIR	REFERENCE
milk ⁽¹⁾	360		200			40					Higa, 1978; Astolfi & Higa, 1978
cheese (1)	190		110			50					Higa, 1978; Astolfi & Higa, 1978
butter ⁽¹⁾	160		140			30					Higa, 1978; Astolfi & Higa, 1978
butter ⁽¹⁾	29		24	64	110						Lenardón et al., 1994
milk ⁽¹⁾	51	23	990	55				7	17		Maitre et al., 1994
dairy (1)	12	1.7	11.6	29	1.02	1.26	0.43	0.85	0.8		Villaamil et al., 2002
infant milk (2)	6		52			2					Astolfi & Landoni, 1980
infant milk $^{\rm (3)}$	0.65	0.12	0.29	0.64	0.4			0.14	0.16		Rodriguez Girault et al., 2001
beef ⁽²⁾	280					49					Higa, 1978; Astolfi & Higa, 1978
beef ⁽¹⁾	1.7	0.15	2.28	16.61	0.59	0.64		1.03	0.61	2.65	Villaamil et al., 2002
pork ⁽¹⁾	0.59	1.62	3.04					0.33			Villaamil et al., 2002
chicken ⁽¹⁾	5.84	0.11	5.67	2.82	1.19	0.69	0.08		0.67		Villaamil et al., 2002
fish ⁽¹⁾	1.63	1.23	8.18	16.85		1.04	7.7	3.5	0.83		Villaamil et al., 2002
corn ⁽³⁾	10										Higa, 1978; Astolfi & Higa, 1978
wheat ⁽³⁾	610										Higa, 1978; Astolfi & Higa, 1978
cereals ⁽³⁾	0.05		5.2			0.27	2.21		0.02	0.09	Villaamil et al., 1999
fruits ⁽²⁾	0.26	0.1	0.08	0.28	0.03	0.03					Villaamil et al., 2002
grape ⁽²⁾			10								Higa, 1978; Astolfi & Higa, 1978
peach ⁽²⁾			10								Higa, 1978; Astolfi & Higa, 1978
Tomato ⁽²⁾			26								Higa, 1978; Astolfi & Higa, 1978
green pepper ⁽²⁾			41								Higa, 1978; Astolfi & Higa, 1978
lettuce ⁽²⁾	8	0.5	1	8	2				2		Gonzalez et al., 2001
broccoli ⁽²⁾	9	43	65	18	226		218		12		Gonzalez et al., 2001
red onion ⁽²⁾	25	2	3.5	2.5	38				2.5		Gonzalez et al., 2001
swiss chard ⁽²⁾	3.7	0.5	1.6	1.3	0.9				0.4		Gonzalez et al., 2001
vegetables ⁽²⁾	10	0.53	0.39	1.33	3.93	0.13	0.07	0.09	1.42	0.2	Villaamil et al., 1999

Table 3.11. PTS (µg/kg) in food for human consumption in Argentina.

1: lipids; 2: fresh weight; 3: dry weight



Figure 3.7 PTS in dairy products and animal flesh in Argentina. Note the decreasing trend (1978-1994-2000) and action levels (FDA-FAO) for dairy products. Meat levels are very low compared to action levels (2000-5000 µg/kg lipid).

3.1.5.2 Bolivia

Data for PTS in Bolivia are scarce. However, it was possible to obtain information about the Aldrin content in some vegetables from a personal communication at the Second Regional Technical Worshop. (Santiváñez, 2002, personal communication; Table 3.12).

FOOD	ALD	REFERENCE
tomato	201.4	Pérez, 1996
carrot	1319.1	Pérez, 1996

Table 3.12 PTS (µk/kg) in food for human consumption in Bolivia.

3.1.5.3 <u>Brazil</u>

Values for PTS in food for human consumption in Brazil are summarised in Table 3.13, where a very high value of HCBs in soya samples, 2045 µg/kg is observed (Lara *et al.*, 1999).

The State of Paraná Health Agency performed a monitoring of agrochemical residues in food during 5 years (1987-1992), in which 523 samples of vegetables were analyzed. From these, 155 samples had concentration above the legislation (Sandoná *et al.*, 1993). During 1982-198, CETESB was responsible for a PTS monitoring in fruits, vegetables, rice, soya, wheat and other seeds in Porto Alegre (Rio Grande do Sul State). None of the samples showed values above the ones allowed by the legislation (Cetesb, 1982, 1983, 1985, 1986).

FOOD	DDT	HCB							ENDS	REFERENCE
Bitter egg- plant							80			Ungaro et al, 1980
Escarola	20									Ungaro et al, 1980
Kale	4									Ungaro et al, 1980
Cucumber							80			Ungaro et al, 1980
Sweet Pepper	50									Ungaro et al, 1980
Tomatoe	320									Ungaro et al, 1980
Fig	50									Ungaro et al, 1980
Guava	30									Ungaro et al, 1980
Melon	250									Ungaro et al, 1980
Strawberr	130					30	10			Ungaro et al, 1980
Peach	740									Ungaro et al, 1980
Sugar-cane			0.045	0.05	0.045			445		Zancul et alii, 1999
Manioc			9							Instituto Adolfo Lutz, 1994.
Inhame			1.5							Instituto Adolfo Lutz, 1994.
Olive oil								0.9		Pupin et all, 2001
Lime				0.007	0.007					Carvalhaes et al, 1999
Tomato									280	Araújo et al., 1999
cotton oil		240								Lara et al., 1999
Peanut oil		130								Lara et al., 1999
corn oil		430								Lara et al., 1999
soya oil		2045								Lara et al., 1999
Parsley		22								Lara et al., 1999
Bulb		120								Lara et al., 1999
Tomato		8								Lara et al., 1999
Cabbage		12								Lara et al., 1999
Bean	250	38								Lara et al., 1999
Lettuce		15								Lara et al., 1999

Table 3.13 PTS (µk/kg), in food for human consumption in Brazil.

FOOD	DDT	HCB	ENDS	REFERENCE
Potato		1		Lara et al., 1999
Carrot		9		Lara et al., 1999
feedstock for poultry (juvenile female)		18		Lara et al., 1999
feedstock for poultry (hen egg)		50		Lara et al., 1999
feedstock for poultry (adult)		12		Lara et al., 1999

3.1.5.4 <u>Chile</u>

Probably the most complete database of PTS substances in Chile is that related to food levels. National Institute of Health (ISP) has been collecting, for at least 7 years, samples of butter, milk, powder milk, and cheese in different regions of the country. The most interesting result is shown in Figure 3.9, where the trends in total DDT concentrations clearly show a decrease during a 10 years period (1983 - 1993), following the banning of DDT in 1984; nevertheless levels were always below risk values (i.e. 1.25 ppm for total DDT). Other chlorinated pesticides also detected showed different temporal patterns. However, the results reflected perhaps the analytical limitations because levels were one or two orders of magnitude lower than reported DDT values.



Figure 3.8 DDTs in butter samples from southern Chile during 1983-1993.

Table 3.14 summarizes PTS data in human food for Chile (ISP). Frequently reported compounds in foodstuffs were HCHs, DDTs, Dieldrin and Heptachlor. Higher concentrations were found for total DDT in milk samples, with an average of 290 µg/kg, followed by Lindane, Dieldrin and Heptachlor with average concentrations of 131, 130 and 120 µg/kg respectively. DDT presented highest concentrations in cheese and butter, with average values of 370 and 300 µg/kg respectively. Within these three milk products, and considering all available data, concentrations range in decreasing order: DDT (395 ± 156 µg/kg) > Lindane (104 ± 294 µg/kg) > Dieldrin (111 ± 28 µg/kg) > Endrin (31 ± 11 µg/kg) > Heptachlor (97 ± 28 µg/kg) > HCB (43 ± 53 µg/kg).

DDT concentrations in meats were the highest (423 μ g/kg), followed by Dieldrin (236 μ g/kg), Heptachlor (238 μ g/kg), Chlordane (149 μ g/kg) and Lindane (136 μ g/kg). In other foods such as wheat flour, concentrations are relatively low and quite homogenous. Aldrin (1.4 μ g/kg) presented the highest concentration followed by Lindane (1.3 μ g/kg), Dieldrin (1.2 μ g/kg), DDE (0.9 μ g/kg) and Chlordane (0.6 μ g/kg).

The most complete database on organochlorinated compounds, between 1983–1989 to 1993, in the country (ISP) shows that levels of DDT, Lindane and Heptachlor decrease in this period, coincidentally with the prohibition of the use of these compounds (with the exception of Lindane forbidden for agricultural purposes in 1998). However a contrasting trend was observed with Dieldrin, whose levels are increasing. This probably includes analytical inconsistencies due to the confounding elution pattern of DDE and Dieldrin; DDE levels are actually increasing whereas DDT values are going down.

An interesting result coincident with other data gathered in the southern part of the country was that highest levels of chlorinated pesticides in milk in the Magellan Region (XII), for butter in the Biobio Region (Central Chile) and for cheese in Temuco - Osorno (Southern Chile). These probably reflect local uses of these pesticide products. Data can be compared by sampling site, central and southern regions presented highest average concentrations of chlorinated pesticides in food, e.g. 317 and 263 μ g/kg, respectively. The Codex Alimentarius establishes 0.06 μ g/kg as maximum limit of Lindane and 20 μ g/kg for DDT. Several measured values in foodstuff are higher than international recommended values.

CODE	FOOD	НСН	CHL	DDT	HPT	ALD	DIEL	END R	HCB	REFERENCE
361C	Milk ⁽¹⁾	133		225	60		50			Min. Salud 1983-1993, INIA, 1989
361C	butter ⁽¹⁾	42		145	695		33			Min. Salud 1983-1993, INIA, 1989
361C	fat ⁽¹⁾	82		423			132			Min. Salud 1983-1993, INIA, 1989
361C	cheese (1)	89		299	190		149			Min. Salud 1983-1993, INIA, 1989
361C	meat ⁽¹⁾	136	149	423	238	107	263			Min. Salud 1983-1993, INIA, 1989
361C	wheat flour ⁽¹⁾	1	1	1		1	1			Min. Salud 1983-1993, INIA, 1989
361C	eggs ⁽¹⁾	4	5							Min. Salud 1983-1993, INIA, 1989
361B	milk ⁽¹⁾	56		128	231		155			Min. Salud 1983-1993, INIA, 1989
361B	butter (1)	56		134	535		24			Min. Salud 1983-1993, INIA, 1989
361B	fat ⁽¹⁾	55		267	142		226	1		Min. Salud 1983-1993, INIA, 1989
361B	cheese (1)	302		9	212		117			Min. Salud 1983-1993, INIA, 1989
351A	milk ⁽¹⁾	103		250	177		276			Min. Salud 1983-1993, INIA, 1989
351A	butter ⁽¹⁾	31		721	906		251			Min. Salud 1983-1993, INIA, 1989
351A	fat ⁽¹⁾	104		621	164		431	145		Min. Salud 1983-1993, INIA, 1989
351A	cheese (1)	65		253	56					Min. Salud 1983-1993, INIA, 1989
3519	milk ⁽¹⁾	52		423	375		30	227		Min. Salud 1983-1993, INIA, 1989
3519	butter (1)	72		213	342		347			Min. Salud 1983-1993, INIA, 1989
3519	fat ⁽¹⁾	162		1757	109		495	5	157	Min. Salud 1983-1993, INIA, 1989
3519	cheese (1)	65		629	14		79			Min. Salud 1983-1993, INIA, 1989
3518	milk ⁽¹⁾	71		291	332		35			Min. Salud 1983-1993, INIA, 1989
3518	butter (1)	165		268	321		25		6	Min. Salud 1983-1993, INIA, 1989
3518	fat ⁽¹⁾	99		1104	163		75	7	4	Min. Salud 1983-1993, INIA, 1989
3518	cheese (1)	113		591	4		785			Min. Salud 1983-1993, INIA, 1989
3516	milk ⁽¹⁾	119		218						Min. Salud 1983-1993, INIA, 1989
3516	fat ⁽¹⁾	17		99	29		7			Min. Salud 1983-1993, INIA, 1989
3512	milk ⁽¹⁾	381		486			245			Min. Salud 1983-1993, INIA, 1989
3512	fat (1)	66		89			19			Min. Salud 1983-1993, INIA, 1989

Table 3.14 PTS (µk/kg) in food for human consumption in Chile.

1: lipids

3.1.5.5 <u>Ecuador</u>

Very few data was gathered in Ecuador, but analysis of information indicates that levels of PTS in foods are low with the exception of DDTs, whose values are in the range of ppm values,

				*	
Pesticide\Site	Litoral	Interandina	Amazonía	Litoral	Interandina
	n=20 Range	n=20 Range	n=20 Range	n=37 Range	n=61 Range
HCHs	0.02-0.24	0.022-0.070	0.056-0.015	0.32-0.8	0.14 - 0.92
HEPTs	0.0012-0.0027	0.0024-0.0078	0.0026-0.0023	0.10-027	0.11-2.3
Aldrin	0.0025	0.0094	0.0027-0.0067	0.07-0.27	0.13 - 5.10
ENDOs	0.08-0.11	0.15-0.835	0.051-0.21	ne	ne
Dieldrín	0.0014-0.0029	nd	nd	0.71-8.31	0.17-1.82
Endrín	0.7224	nd	nd	0.11-12	2.32 - 5.78
DDTs	5-48.12	2.65 - 18.40	5.03-6.99	0.15-059	0.12 -0.5
Mirex	ne	ne	ne	0.1-022	0.11-021

Table 3.15 PTS (µg/kg ww) in food for human consumption in Ecuador.

ne = non studied; nd = non detected

3.1.5.6 Paraguay

There were no data available for this country.

3.1.5.7 <u>Peru</u>

Table 3.15 shows the data for PTS levels in foods detected in Peru. Most of these data resulted from the research of foreigner scientists taking samples in Peru and analysing them in laboratories with high confidence and performance (Ballschmitter, 1990; INDA, 1987). Chemical analysis were made in butters and oils from fish, sperm, soya-cotton and corn, and potatoes. Data collected by questionnaires for PTS in foods in Peru represent 24% of all questionnaires; 51% of them correspond to PTS levels in butter, 27% for soya-cotton oils, 8.7% for fish oil, 7.8% for sperm oil and 3.9% for corn oil. Two additional data were obtained for potato which is an important food item for Peruvians (Cabrera, 1993).

Butter samples were collected (INDA, 1987) in two areas, the Northern coastal area and the central region of the country. DDTs levels in butter ranged from 89 μ g/kg (Centre) to 202 ± 76 μ g/kg (Northern coastal area), and were also detected in oils; levels are 42 ± 31 μ g/kg and 153 ± 101 μ g/kg for fish oil and sperm oil respectively in Ica City (Ballschmitter, 1990). For soya – cotton oil samples, levels are 49 ± 32 μ g/kg for the Callao and Lima areas, and 121.3 μ g/kg for corn oil in Lima (INDA, 1987).

HCHs, mainly Lindane, were detected in butter and fish, sperm, corn and soya-cotton oils. Combining all the data, Lindane concentrations rise to $48 \pm 53 \ \mu\text{g/kg}$ with a maximum 166 $\mu\text{g/kg}$. For soya-cotton oil, also the combined data result in Lindane average concentration of $11 \pm 7 \ \mu\text{g/kg}$. Levels of HCHs in fish oil, sperm oil and corn oil are $3.5 \pm 3.4 \ \mu\text{g/kg}$, $1.5 \ \mu\text{g/kg}$ and $44 \ \mu\text{g/kg}$ respectively (INDA, 1987).

Samples of *Solanum tuberosum* were analysed by Cabrera (1983), who detected Aldrin in concentrations of about 279 \pm 25 µg/kg. FAO/WHO Food Standards Programme refers EMRL (Environmental Maximum Residue Level) value of 100 µg/kg for root and tuber vegetables. Unfortunately, these data were the only two obtained and the analyses were made in laboratories in a local university with low confidence levels of performance. It is important to consider that Peruvians consume daily an amount of root vegetables in addition to corn and grains, i.e., products exposed to inputs of organochlorine compounds used as pesticides despite the restrictions about these substances. Butter samples were also analysed for Aldrin, resulting in average concentration of 264 \pm 294 µg/kg with a maximum 1058 µg/kg (INDA, 1987). Aldrin analysis in corn oil and soya-cotton resulted in 152.2 µg/kg and 50 \pm 45 µg/kg respectively. The analytical procedures used with low detection limits and high deviations in instrumental baselines for the old reports explain the large standard deviations in these results and others. Although the laboratories involved in the INDA research specifically have a great level confidence, it is recommended that these limitations are considered.

Heptachlors were detected in soya-cotton oil samples with average concentration of $190\pm 319 \ \mu$ g/kg with a maximum 1205 μ g/kg (Ballschmitter, 1990) and 169 μ g/kg for corn oil. FAO/WHO Food Standards Programme indicates EMRL as 500 μ g/kg for crude soya bean oil and 20 μ g/kg for refined soya bean oil. Analysis for HCB was performed for fish oil and sperm oil with 3 μ g/kg and 4 μ g/kg respectively. PCB were present in both oils in 368 μ g/kg and 752 μ g/kg. PCB was detected in 368 μ g/kg in fish oil and 752 μ g/kg in sperm oil. Finally, Toxaphene was analysed in fish oil and sperm oil resulting in 20 μ g/kg and 72 μ g/kg respectively (INDA, 1987). All concentrations levels are given on lipid basis.

CODE	FOOD	РСВ	нсн	DDT	HPT	ALD	HCB	тох	REFERENCE
3229	butter		85	201.7		71.8			INDA, 1987
3325	fish oil	368	3.47	42.3			3	20	Ballschmitter, 1990
3325	sperm oil	752	1.5	153.3			4	72	Ballschmitter, 1990
3326	soya-cotton oil		12.27	61.5	7.5	54.8			INDA, 1987
3326	corn oil		43.7	121.3	169	152.2			INDA, 1987
3326	potato					279			Cabrera, 1993
3327	soya-cotton oil		9	45.5		36.5			INDA, 1987
3426	butter		25	89	204.4	346.9 (4)			INDA, 1987

Table 3.16 PTS (μ k/kg) in human food in Peru.



Figure 3.9 HCHs (a) and DDTs (b) levels in butters and oils in Peru

3.1.5.8 <u>Uruguay</u>

The information obtained for residues in food is very scarce and correspond to some agricultural products for export (meat, rice and wheat). During 1983-84, the CIVET Laboratory analysed stored wheat and detected only in five samples residues of HCB (highest value of 0.1 ppb) and Endrin (highest value of 0.02 ppb). In the same period, the Uruguayan Technological Laboratory analysed 62 samples of rice for export and none of them showed detectable residues of HCB, HCH, heptachlor, dieldrin, endrin and pp' DDE (detection limit 5ppb). Between 1978-87, 34856 samples of meat were analysed for HCH, HCB and Endrin. The results showed a very low percentage of samples (< 1%) exceeding action levels and a decreasing trend along to the period (Boroukhovitch, 1999).

3.2 PTS IN HUMANS

The environmental persistence, resistance to degradation, lipophilic character, and toxicity of PTS poses a serious risk to human health, since these substances have the potential to biomagnificate through food chains. PTS may be incorporated and accumulated in the adipose tissues leading to body burdens that pose potential risks and adverse health effects. Once ingested, PTS are sequestered in body lipids, where they equilibrate at roughly similar levels on a fat-weight basis between adipose tissue, serum, and breast milk.



From the early 1980s rose the concerns within Region XI in relation to the levels of PTS in different human tissues. Several governmental report and surveys of occupationally exposure and limited numbers of scientific papers were produced during 1980-90. Approximately a total of 450 questionnaires were sent with data of chlorinated pesticides followed by PCBs and very scarce information on organometallic compounds (Figure 3.10).

The Region has important differences in relation to the information obtained, both in qualitative and quantitative terms. Argentina, Brazil, Chile and Uruguay have a long history of human tissue sampling with standardized protocols for analysing many PTS, while in Peru fewer analyses of human samples were reported.

3.2.1 Chlorinated Pesticides

Chlorinated pesticides were more often reported (76% of the total data) and discriminated by individual pesticides the most frequently detected were DDTs, HCHs, HCBs and Drins (Aldrin, Dieldrin and Endrin).On the other hand, the matrix most often monitored were breast milk and blood with scarce reports in adipose tissues and urine.

Some chlorinated pesticide data in humans show high levels, with some critical cases for DDT in breast milk and blood, and for Dieldrin in blood. Breast milk was the matrix that presented the highest variability for all compounds studied following by blood. This factor together with differences in statistical management, make comparisons between the data difficult.

SAMPLE	DDT	HCHs	HCB	Dieldrín
Breast milk	n=76	n=35	n=34	n=31
Range	9.0-230 (9 x 10 ³)	5.0-150 (3,910)	8-205	3-48
Mean	69.6 (1,109)	86.5 (620.3)	77	30.3
Blood	n=48	n=41	n=39	n=29
Range	0.4-97 (17 x 10 ⁴)	1.1-50 (308)	3-42	0.7-20.4 (3 x 10 ⁵)
Mean	25.0 (12,135)	15.0 (39.4)	24.2	6.94 (25042.9)
Fatty tissue	n=5	n=4	n=4	n=3
Range		0.3 -19 (790)	0.4-13 (146)	0.04-0.04 (70)
Mean		6.5 (202.4)	4.6 (39.9)	0.04 (23.36)
Urine	n=4	n=2		
Range	11.3 - 34.9	14.4 - 46.3		
Mean	21.9	30.4		

Table 3.17 PTS ranges and averages in Humans ($\mu g/kg$ or $\mu g/L$)

Bracketed values include critical cases.

As a general pattern, it is evident that the countries of Region XI differ in terms of uniformity of the database for the different PTS in humans. Three groups may be discerned: (a) countries with a broader data base (more compounds), e.g. Argentina and Uruguay, (b) countries which have focused on a few compounds, e.g. Chile and Brazil and Ecuador and (c) a third group with no information on human PTS level, e.g., Bolivia, Paraguay.

The exposure pathways for chlorinated pesticides are very similar throughout the Region and in general terms the occupational and accidental exposures are the principal factors, with some cases of environmental exposure and via food intake.

3.2.2 PCBs

The data of PCBs in the Region are very scarce and correspond to levels in breast milk and adipose tissue, reported by Chile (Table 3.18). A total of 540 samples of human milk were analyzed; 18.3% were positive for PCBs with levels ranging from 0.09 mg/kg to 84.93 mg/kg in a lipid basis (Tamayo *et al.*, 1994). On the other hand, a mean level of 54 ng/g fresh weight in samples of fatty tissue from persons living in an industrialized area was also reported with corresponding PCB TEQs values of 1.09 pg/g w.weight (Mariottini *et al.*, 2000).

These levels are almost an order of magnitude lower than values reported for relatively non industrialized areas in Italy (400 ng/g lipids).

Location	Sample	Mean	Source
Concepción	Adipose tissue	54	Mariottini et al., 2000, 2002
Valdivia	Milk	5,820	Tamayo et al., 1994
Valdivia	Milk	10,090	Tamayo et al., 1994

Table 3.18 PCBs in Human (µg/kg)

3.3 ECOTOXICOLOGICAL EFFECTS

Ecotoxicological studies on the effects of PTS in biota are scarce in the region. Recent developments in this area include the study of biochemical responses, e.g. Cytochrome P450, CYP1A, Ethoxy Resorufin O-O-Deethylase activity (EROD), gluthathione-S-transferase, in bivalves and fish from contaminated rivers and coastal areas such as the Río de la Plata, Argentina (Suárez *et al.*, 200; Peri *et al.*, 2001 and 2002), Billings reservoir, Santa Catarina and Río de Janeiro coast, Brazil (Bainy *et al.*, 1996; 1999; 2000; Ventura et al., 2002), and the Biobío River in Chile (Sanchez-Hernandez *et al.*, 1998; Barra *et al.*, 2001). These works confirm the induction of the detoxifying systems of bivalves and fishes from sites affected by heavy PTS loads including especially PCBs and PAHs.

3.4 CONCLUSIONS

In general, PTS data in aquatic and terrestrial organisms available for Region XI are scarce, lacking both temporal and spatial continuity. Major institutions involved in environmental monitoring are Universities, followed by Environmental Agencies, which are still in an early development stage in many countries within the area.

The majority of the countries within the Region lack routine monitoring programs and most of the available data were generated by individual monitoring studies rather than comprehensive programs. Studies are concentrated in densely populated areas within principal hydrographic basins. For this reason, the database concerning environmental levels reflect a strong bias towards freshwater ecosystems.

The environmental compartments most studied are aquatic animals, followed by sediments, water and humans, with fewer data for air and soil. According to the published data, the majority correspond to chlorinated pesticides and PAHs, with few reports covering other compounds. In general, environmental levels of pesticides have decreased in recent decades, especially in foods, mainly due to the legal restriction or banning in the countries of the Region. However, other PTS show clear patterns of contamination in sediments, water and biota, in densely populated and industrialized areas.

Toxicological and ecotoxicological effects have not been assessed in the region, with some few exceptions. A strong call for assessment of effects was made at the second technical meeting in Lima.

A common scenario observed in Argentina, Brazil and Chile is the existence of some effective routine monitoring programs generating a great deal of reliable data, but unfortunately this is not available to the public. For instance, the Adolfo Lutz Institute, in São Paulo, runs a routine monitoring not only in biological samples (blood, urine, etc), but also in many different types of food, generating more than 5,000 results per year. The Argentine sanitary service has essentially the same data restriction politics. According to the published data on biota, PTS demanding major concern are PCBs followed by PAHs.

3.5 SUMMARY

Most of this section is related to environmental levels and spatial patterns principally from densely populated areas along major rivers such as the Amazon, Paraná and Río de la Plata. The database is thus strongly biased towards freshwater environments in detriment of coastal marine areas which have received proportionally less

attention. Another general regional trend for environmental PTS information is the uneven contribution among countries which reflects the different patterns of economic, technical and scientific development.

3.5.1 Air

PTS monitoring in air is little developed in the region. There are no regional routine programs and the available data represent a few geographical areas within the region. PCB levels in air from some urban area in Argentina, Brazil and Chile are low to moderate (0.7-6.5 ng/m³), but considerably higher than those reported for the remote Islas Malvinas (5 pg/m³). The scarce measurements of PCDD/F in air within the region also indicate very low levels offshore along the Southern Atlantic Ocean with some anomalous high values (40 fg TEQ /m³) in industrialized bays. Brazils PCDD/F data confirm the low to moderate PCDD/F levels (3-839 fg TEQ /m³). In contrast to other PTS, PAHs have been more frequently analysed in air samples within the region. Urban PAH levels reflect the predominant input from mobile sources (transit and transportation) and range from a lower 3-55 ng/m³ in Argentina and Brazil to higher 43-294 ng/m³ in most affected Santiago (Chile), which presents a gradual decline over time. Biomass combustion is an important energy ressource in the region and a major PAH source in remote areas.

3.5.2 Soils

PTS monitoring in soils is also limited within the region. There are no regional programs and most data refer to agricultural areas in Chile and urban, contaminated areas (hot spots) from Brazil. Chlorinated pesticides in some Brazilean hot spot sites ranged from 0.3 to 787 mg/kg. Soil levels of PCDD/F also indicate very high levels (0.03-654 to 13.900-31.138 ng TEQ/kg) in several Brazilean locations, particularly in a former HCH production plant, compared to very low values in the Amazon basin (0.02-0.4 ng I-TEQ/kg), suggesting little PCDD/F formation during forest burning. PTS levels in Brazilian municipal solid waste were low, below the legislation limits whereas soil PAHs (7-390 ug/kg) and PCBs levels (0.05-1.25 ug/kg) are below background concentrations. Chilean soil data from agricultural areas indicate generally low levels of chlorinated pesticides in spite of a relatively high detection frequency.

3.5.3 Waters

Most information comes from major rivers including chlorinated pesticides, PAHs and few reports of PCBs and PCDD/F. Overall, several high pesticide data for freshwaters in the region suggest a complex situation, but the low representativity of the data impose a cautious interpretation. Usually only suspected contaminated ecosystems are monitored and large-scale regional water monitoring programs have never been undertaken. The few PCB reports indicate generally low to moderate levels (7-22 ng/l), higher than recommended guidelines in urbanized estuaries and rivers such as the Río de la Plata (Argentina) and Biobio (Chile). Pesticide levels show high variability (0.6-14160 ng/l) reflecting distinct ecosystem conditions, from less impacted environments to severely polluted streams located in densely populated areas close to Buenos Aires and Sao Paulo. Heptachlor, HCHs, Aldrin and DDTs are the most frequently reported pesticides in water accounting for more than 60% of the total database.

PAHs concentrations in waters are relatively high (average: $16\pm12 \ \mu g/l$) but the data base is not homogeneous. It includes lower concentrations (1.8-12 $\mu g/l$) determined in the Uruguay and Rio de la Plata rivers, and highest values (8-41 $\mu g/l$) from coastal marine Patagonian waters impacted by crude oil extraction activities.

3.5.4 Sediments

Regional PTS information for sediments is also dominated by chlorinated pesticides but present a more balanced contribution of PAHs and PCBs with few reports for PCDD/F. Overall, as observed for waters, sediment data indicate a complex situation in densely populated areas affected by urban-industrial inputs which present high PTS levels. The most frequently reported PTS are DDTs, HCHs, PCBs and Heptachlors. The concentrations show a large variability, basically introduced by some highly contaminated sites in Argentina and principally Brazil (hot spots) with 4-5 orders of magnitude higher levels. The general PCB average is low (9.1 \pm 7.7 µg/kg), below Canadian freshwater guidelines, but heavily contaminated sites from present much higher levels (580-998 µg/kg). Essentially the same pattern with some very critical sites and more homogeneous residual concentrations is observed for chlorinated pesticides. The general averages are higher than Canadian guidelines, i.e. Heptachlor (3.9 \pm 5.4 Vs a reference value of 0.6 µg/kg); DDTs (9.7 \pm 14 Vs 6.15 µg/kg); HCHs (3.2 \pm 4.4 Vs 0.94 µg/kg); Chlordanes (4.2 \pm 5.7 Vs 4.5 µg/kg). Most PAHs reports correspond to harbors and ports in heavily impacted areas and thus present a huge variability (0.1-286000 µg/kg). Most affected areas are related to the intensive ship traffic in the Paraná, Uruguay and Río de la Plata rivers, specially close to heavily populated areas such as Buenos Aires and Montevideo, the Argentine Patagonian coastal area,

where crude oil extraction and transport are very active, and the Tiete river and surrounding environments close to Sao Paulo in Brazil.

3.5.5 Animals

As expected, aquatic organisms are by far the most studied organisms in the region, and among them principally bivalves and fish. Terrestrial organism data are centered on birds and a few bovines and insect data. As observed for other environmental receptors, the regional distribution of data is uneven, heavily centered in coastal environments and in some countries (Argentina, Brazil, Chile, and Peru). Most of them correspond to freshwater and estuarine ecosystems in the Paraná-Río de la Plata, principally affected by PCBs, and the Amazon basin, affected by organic mercury. The most comprehensive PTS monitoring program in the South America coastal environment is the Mussel Watch. Among the PTS studied, PCBs predominate, followed by DDTs and Chlordanes. Baseline PCB concentrations range from 200-700 µg/kg lipids in unpolluted sites; 1000-3000 µg/kg in moderately contaminated sites, and 4000-13000 µg/kg lipids in most affected bivalves from the Río de la Plata (Argentine side), Recife (Brazil), and Punta Arenas (Chile). DDT averages in bivalves are an order of magnitude lower than those of PCBs, bellow the 5 ppm guideline, and follow a similar spatial pattern. PAH also follow this pattern, with background levels below 10 mg/kg lipids, 10-50 mg/kg in moderately polluted bivalves, and above 200 mg/kg in sites impacted by offshore oil production and petrochemical activities, i.e. Punta Arenas (Chile); Recife (Brazil); Concepción (Chile) and Bahía Camarones, Río de la Plata and Bahía Blanca (Argentina).

In spite of being normalized by lipid contents, PTS levels in fish shows a tremendous variability which has environmental, size and organ-related components. PCBs are the major organochlorine residue (30-47550 μ g/kg of lipids, fresh weight) followed by DDTs (88-27125 μ g/kg of lipids) and chlordanes, heptachlor and HCHs. Fish from the Buenos Aires area of the Río de la Plata present the highest PTS levels; principally PCBs (3.8±2.0 mg/kg, higher than the 2 ppm guideline) and PCDD/F, compared with samples collected upstream along 1500 km on the Paraná and Iguazú rivers. An opposite pattern, higher in upper freshwater fish and lower in marine organisms is described for Biobio river fish. In Brazil, the majority of PTS fish data refers chlorinated pesticides in the Tietê River (São Paulo State), and mercury in the Amazonian area. A comprehensive survey in the Santos-Cubatão area (Brazil) indicated that PCBs are by far the most abundant PTS detected in 96% of the organisms, 14% above consumption guidelines, followed by PAHs detected in 76% of the organisms, but none above the acceptable levels for consumption.

Other organisms that have been analyzed for PTS in the region are crabs (*Cyrtograpsus angulatus*), dolphins (*Pontoporia blainvillei*) and porpoises (*Phocoena spinipinnis*) from the Atlantic Argentine coast and continental shelf. PCBs show the highest levels (averages: 296, 1980 and 3300 µg/kg lipid in crabs, dolphins and porpoises, respectively), closely followed by DDTs (170, 1670 and 4320 µg/kg lipid). PCDD/F analyzed in *Callinectes sapidus* (omnivorous) collected in the Santos bay area (Brazil) showed total TEQ values of 1.5 pg/g wet weight with the predominance of octachloro dioxins, followed by heptachloro congeners. PTS data in crustaceans and gastropods from the Valdivia area (Chile) show generally low levels, basically of DDTs and DRINs (0.8-5 ng/g wet weight), while very few data from organisms collected in the Peruvian coast show low DDT (1-10 ng/g), and PCBs levels (0.12-17.8 ng/g).

3.6 REFERENCES

- Adonis, M and Gil, L. 2000. Polyclic aromatic hydrocarbon levels and mutagenicity of inhalable particulate matter in Santiago, Chile. Inhalation Toxicology, 12: 1173-1183.
- Ares, J. and Zavatti, J. 1993. Comparative analysis of emissions and diffusion of air PAHs at a coastal arid site (Patagonia, Argentina). Bulletin Environmental Contamination and Toxicology, 50: 333-339.
- Astolfi, E. And Higa de Landoni, J. 1978. Residus des pesticides chlore dans le lait. Facultad de Medicina, Universidad del Salvador, Buenos Aires, Argentina.
- Astolfi, E., Gotelli, C. and Higa, J. 1984. Organochlorinated pesticide residues in human milk 13 years monitoring (1971-1984). Hommage Prof. R. Truhaut, 35-9. Fac. Pharm. Univ. Paris, France.
- Ballschmitter, K. and Zell, M. 1980. Baseline studies of the global pollution. I. Occurrence of organohalogens in pristine European and Antarctic aquatic environments. Intern. J. Environ. Anal. Chem. 8, 15-35
- Barra, R., Cisternas M., Urrutia R., Pozo K., Pacheco P., Parra O. and S Focardi 2001.First Report on Chlorinated Pesticide Deposition in a sediment core from a small lake in Central Chile. Chemosphere 45,749-757.
- Barra, R., Sanchez-Hernandez, JC., Orrego LR., O.Parra and JF Gavilan 2001. Bioavailability of PAHs in the Biobio River (Chile): MFO activity and biliary fluorescence in juvenile Onchorhynchus mykiss 45,439-444.

- Bainy, A.C.D., Saito, E., Carvalho, P.S.M. and Junqueira, V.B.C. 1996. Oxidative stress in gill, erythrocytes, liver and kidney of Nile tilapia (Oreochromis niloticus) from a polluted site. Aquatic Toxicology, 34: 151-162.
- Bainy, A.C.D., Woodin, B.R. and Stegeman, J.J. 1999. Elevated levels of multiple cytochrome P450 forms in tilapia from Billings Reservoir-Sao Paulo, Brazil. Aquatic Toxicology, 44: 289-305.
- Bainy, A.C.D., Almeida, E.A., Muller, I.C., Ventura, E.C. and Medeiros, I.D. 2000. Biochemical responses in farmed mussel Perna perna transplanted to contaminated sites on Santa Catarina Island, SC, Brazil. Marine Environmental Research, 50: 411-416.
- Beretta, M. 2000 Adequação de protocolo analítico para hidrocarbonetos petrogênicos na atmosfera do recôncavo baiano; Tese de doutorado em Química Analítica, Instituto de Química, UFBA, p.139-140 Salvador.
- Bilos, C., Colombo, J.C., Skorupka, C. y Rodriguez Presa, M. J. 2001. Sources, distribution and variability of airborne trace metals in La Plata City area, Argentina. Environmental Pollution, 111: 149-158.
- Bisinoti, M. C. (2002) "Produção de Hgorgânico em sedimentos tropicais a partir do Hg0: experimentos em microcosmos". Dissertação de mestrado, Instituto de Química, Universidade Estadual de Campinas, Campinas SP.
- Borrell, A., Pastor, T., Aguilar, A., Corcuera, J., and Monzón, F. 1994. Contaminación por DDT y PCBs en Pontoporia Blainvillei de aguas Argentinas. Variación con la edad y el sexo. Anais do 2ª Encontro sobre Coordenação de Manejo e Pesquisa da Franciscana Florianópolis, SC. EF /2/DT11.
- Boroukhovitch, 1999. Current State of Chlorine Containing Pesticides in Uruguay. http://irptc.unep.ch/pops/POPs_Inc/proceedings/Iguazu/URUGUAYE.html
- Braga, A. M. C. B.; Krauss, T. 2000 PCDD/F-concetrations in soil and cows' milk from a hexachlorocyclohexane contaminated area in Rio de Janeiro Brazil. Organohalogen Compd., 46, p. 354-357.
- Cabrera, E. 1993. Determinación semicuantitativa de residuos de plaguicidas organoclorados (Aldrin) y carbamatos (Carbaryl) en Solanum Tuberosum: papa. Tesis. Universidad Nacional Mayor de San Marcos. Lima.
- Caviedes Vidal, E. 1998. Project Report Fisiología Ecológica de las Aves de San Luis. Línea Ecotoxicología: Búsqueda de bioindicadores de xenobióticos organoclorados en la Región centro-oeste.
- Cattogio, J.A., Succar, S.D. and Roca, A.E. 1989. Polynuclear aromatic hydrocarbon content of particulate matter suspended in the atmosphere of La Plata, Argentina. The Science of the Total Environment, 79: 43-58.
- Celeste, M. F. And Cáceres, O. 1987 Resíduos de Pesticidas clorados em águas do reservatório Lobo (Broa) e seus tributários. Ciência Cultura, 39, p. 66-70.
- Cetesb- Companhia de tecnologia de saneamento ambiental, programa de controle de poluição. sistema estuarino de santos e são vicente, agosto de 2001, disponível em cd e impresso.
- Cetesb (1997) Avaliação Preliminar De Área Contaminada Por Organoclorados (Depósitos De Agrotóxicos Do Município De Canoas (Rs) Fepam Cooperação Técnica Brasil-Alemanha. Outubro De 1997. Coordenação Inter-Projetos (Cip) Gtz/Fepam/Feema/Cetesb.
- CETESB (2000) Informação técnica no. 010/00/EEAS.
- CETESB (1986) Relatório Parcial do Projeto de pesquisa: "Def-global II: resíduos de defensivos agrícolas em frutas, hortaliças, arroz, trigo, soja e grãos importados" referente a grãos importados do convenio CIENTEC/FINEP No. 54.84.0260.00. Porto Alegre, RS.
- CETESB (1983) Relatório Parcial do Projeto de pesquisa: "Def-global II: resíduos de defensivos agrícolas em frutas, hortaliças, arroz, trigo, soja e grãos importados" referente a arroz do convênio CIENTEC/FINEP No. 54.84.0260.00. Porto Alegre, RS.
- CETESB (1982) Relatório Parcial do Projeto de pesquisa: "Def-global II: resíduos de defensivos agrícolas em frutas, hortaliças, arroz, trigo, soja e grãos importados" referente a trigo do convênio CIENTEC/FINEP No.54.84.0260.00. Porto Alegre, RS.
- CETESB (1985) Relatório Parcial do Projeto de pesquisa: "Def-global II: resíduos de defensivos agrícolas em frutas, hortaliças, arroz, trigo, soja e grãos importados" referente a arroz do convênio CIENTEC/FINEP No. 54.84.0260.00. Porto Alegre, RS.
- CETESB (1985) Relatório Parcial do Projeto de pesquisa: "Def-global II: resíduos de defensivos agrícolas em frutas, hortaliças, arroz, trigo, soja e grãos importados" referente a pêssego indústria do convenio CIENTEC/FINEP No. 54.84.0260.00. Porto Alegre, RS.
- Chagas, C. M.; Lopes, M. E. R. Q.; Neves, A. A.; De Queiroz, J. H.; De Oliveira, T. T. And Nagen, T. J. 1999 Determinação de compostos organoclorados presentes em rios da região de Viçosa, MG. Química Nova, 22, p. 506-508.
- Commendatore, M.G., Esteves, J.L., Colombo, J.C. 2000. Hidrocarbon in Coastal Sediments of Patagonia, Argentina: Levels and Probable Sources. Marine Pollution Bulletin 40 (11), 989-998.

- Colombo, J.C., Khalil, M.F., Arnac, M., Horth, A., and Catoggio, J.A. 1990. Distribution of Chlorinated Pesticides and Individual Polichlorinated Biphenyls in Biotic and Abiotic Compartiments of the Rio de La Plata. Environmental Science & Technology 24 (4): 498-505.
- Colombo, J.C., Landoni, P. and Bilos, C. 1999. Sources, distribution and variability of airborne particles and hydrocarbons in La Plata area, Argentina. Environmental Pollution, 104: 305-314.
- Corcuera, J., Monzón, F., Aguilar, A., Borrell, A., and Raga, A.J. Life History Data, Organochlorine Pollutants and Parasites from Eigth Burmeister's Popoises, Phocoena spinipinnis, Caught In Nothern Argentine Waters. Rep. Int. Whal. Comm. Special Issue on Phocoenids (in press).
- Costa, M. A De C. 1997 Estudo dos níveis ambientais de DDT em fauna e sedimentos na região da Baía de Todos os Santos: Dissertação de Mestrado em Química Analítica Instituto de Química, UFBA, p.65, Salvador.
- DINAMA-SOHMA-SHN. 1998. Informe técnico. Impacto de Zonas Costeras. Módulo Salto-Concordia. Comisión Administradora del río Uruguay. Subcomisión de Contaminación.
- Esteves, J.L., and Commendatore, M. 1993. Total Aromatic Hydrocarbons in Water and Sediments In coastal zone of Patagonia, Argentina. Marine Pollution Bulletin, 26 (6): 341-342.
- Farrington, F.W., and Tripp, B.W. 1995. NOAA Technical Memorandun NOS ORCA 95. International Mussel Watch Project. Initial Implementation Phase. Final Report.
- Focardi, S., C. Fossi, C. Leonzio, S. Corsolini & O. Parra. 1996. Persistent organochlorine residues in fish and water birds from the Biobio River, Chile . (Dipartimento di Biologia Ambientale, Siena, 53100, Italy). Environ. Monit. Assess., 43(1), 73-92.
- Franco, A. 2001 Determinação de hidrocarbonetos poucos voláteis no material particulado da atmosfera de Araraquara. Instituto de Química, UNESP, Araraquara.
- Frías, G. 1990. Contaminación de leche materna por insecticidas organoclorados en el Valle de Mala. Tesis. Universidad Peruana Cayetano Heredia. Lima.
- García Fernandez, J.C., Marzi, A., Casabella, A., Roses, O., Guatelli, M. and Villaamil, E. 1979. Plaguicidas organoclorados en aguas de los ríos Paraná y Uruguay. Ecotoxicología, 1: 51-78.
- Gavilan, J. F., R. Barra, M. C. Fossi, S. Casini, G. Salinas, O. Parra & S.Focardi. 2001. Biochemical Biomarkers in Fish from Different River Systems Reflect Exposure to a Variety of Anthropogenic Stressors. Bull. Environ. Contam. Toxicol., 66(4), 476-483.
- Gonzalez, M., Miglioranza, K.S.B., Gerpe, M.S., Menone, M.L., Lanfranchi, A.L., Aizpún de Moreno, J.E., and Moreno, V.J. 2001. Acumulación de plaguicidas organoclorados (POC's) en vegetales comestibles cultivados en una huerta orgánica. IV Reunión Anual de SETAC Latinoamérica. Buenos Aires. Argentina. SQ6.
- Gonzalez, S. 1990. "Fuentes de Contaminación con Residuos de Plaguicidas Organoclorados y Metales Pesados en Sectores Agrícolas, Regiones IV a XI". INIA la Platina. Ministerio de Agricultura. 266 pag.
- Grossi, G.; Lichtig, J.; Krauss, P. 1998 Pcdd/F, PCB and PAH content of Brazilian compost. Chemosphere, 37, p. 2153-2160.
- Hamada, G. S.; Kowalski, L. P.; Murata, Y.; Matsushita, H.; Matshuki, H. 1992 Wood stove effects on indoor air quality in Brazilian homes: carcinogens, suspended particulate matter, and nitrogen dioxide analysis. Tokai J. Exp. Clin. Med., 17, p. 145-153.
- Higa de Landoni, J. 1978. Contaminación por Plaguicidas Clorados en la canasta familiar Argentina. Repercusión Biológica. Facultad de Medicina. Universidad del Salvador, Buenos Aires.
- INDA: Instituto Nacional de Desarrollo Agroindustrial. 1987. Evaluación preliminar del grado de contaminación química en algunos alimentos. Lima.
- Jardim, W. F.; Almeida, F. V. And Ghiselli, G. 2000 Disponibilidade técnica e estudos econômicos do uso de reagente Fenton na descontaminação de solos impregnados com Aldrin e seus derivados Relatório técnico apresentado a Shell.
- krauss, p. 2000 United Nations Environment Programme. Chemicals Proceedings Unep Chemicals Workshop on The Management Of Polychlorinated Biphenyls (Pcbs) And Dioxins/Furans. Montevideo, Uruguay. 19-22 September.
- Krauss, P.; Mahanke, K.; Freire, L. 1995 Determination of PCDD/F and PCB in forest soil from Brazil. Organohalogen Compd., 24 (Dioxin 95, 15th International Symposium on Chlorinated Dioxins and Related Compounds, p. 357-361.
- Lamparelli, M. C.; Kuhlmann, M. L.; Carvalho, M. C.; Salvador, M. E. P.; Souza, R. C.; Botelho, M. J. C.; Costa, M. P.; Martins, M. C.; Carvalho, P. M.; Araújo, R. P. A; Buratini, S. V.; Zanardi, E.; Sato, M. I. Z.; Roubicek, D. A; Valent, G. U.; Rodrigues, P. F.; Hachich, E. M.; Bari, M. D.; Curcio, R. L. S.; Júnior, A P. T.; Lorenzetti, M. L.; Truzzi, A C.; Pereira, D. N. And Boldrini, C. V. 1996 (out/92 a out/93) Avaliação do complexo Billings: Comunidades aquáticas, água e sedimento. Relatório técnico da Companhia de Saneamento Ambiental (CETESB) DAH.

- Lenardon, A., Maitre de Hevia, M., and Enrique de Carbone, S. 1994. Organochlorine Pesticides in Argentinian butter. Science of the Total Environment 144: 273-277.
- Lohmann, R; Ockenden W.A.; Shears, J,and K..C Jones (2001) Atmospheric distribution of Polychlorinated dibenzo-pdioxins, dibenzofurans (PCDD/Fs), and Non-ortho biphenyls (PCBs) along a North- South Atlantic transect, Environ.Sci.Technol 35,4046-4053.
- Lopes, J. L. C.; Casanoca, I. C.; Figueiredo, M. C. G.; Nather, F. C. and Avelar, W. E. P. (1992) Anodontites trapesialis: A biological monitor of organochlorine pesticides Arch. Environ. Contam. Toxicol.. 23(3): 351-354.
- Lara, W. H.; Barreto, H. H. C. and Takahashi, M. Y. 1999 Resíduos de pesticidas clorados em frutas e verduras Revista do Instituto Adolfo Lutz.
- Lenardon, A., Maitre de Hevia, M., and Enrique de Carbone, S. 1994. Organochlorine Pesticides in Argentinian butter. Science of the Total Environment 144: 273-277.
- Machado, J. C. V. 1996. Estudo Do Grau De Contaminação Por Hidrocarbonetos Nos Sediemntos Da Baía De Todos Os Santos. Dissertação De Mestrado Em Química Analítica, Instituto De Química, Ufba, Salvador, 124p.
- Mackay, D 2001. Multimedia Environmental Models: The Fugacity Approach. Lewis Publishers, USA.
- Maitre, M.I. de la Sierra, P., Lenardon, A., Enrique, S. and Marino, F. 1994. Pesticide residue levels in Argentinian pasteurized milk. The Science of the Total Environment, 155: 105-108.
- Mariottini, M., S. Aurigi & S. Focardi. 2000. Congener profile and toxicity assessment of polychlorinated biphenyls in human adipose tissue of Italians and Chileans. (Dipartimento di Biologia Ambientale, Universita degli Studi di Siena, Siena, 53100, Italy). Microchem. J., 67(1-3), 63-71.
- Mariottini, M., C. Guerranti., S. Aurigi., I.Corsi & S. Focardi. 2002. Pesticides and Polychlorinated Biphenyl Residues in Human Adipose Tissue. Bull.Environ Contam Toxicol 68, 72-78.
- Martínez, C. y Jacinto, M. 1997. Niveles de plaguicidas organoclorados y PCBs en el ecosistema marino costero peruano. Inf. Inst. Mar Perú. N° 126, 46-54
- Mandalakis M and E.G.Stehpanou 2002.Polychlorinated byphenils associated with fine particles (PM 2.5) in the urban environment of Chile: Concentration Levels and Sampling volatilization losses . Environ Toxicol Chem 21(11):2270-2275.
- Menone, M.L., Aizpún de Moreno, J.E., Moreno, A.L., Lanfranchi, T.L., Metcalfe, T.L., and Metcalfe C.D. 2001. Organochlorine Pesticides and PCBs in a Southern Atlantic Coastal Lagoon Watershed, Argentina. Archives of Environmental Contamination Toxicology 40: 355-362.
- Ministry of Health. Institute Public Health of Chile. Subdepartamento Bromatología. Inform processed on analysis of Organochlorine pesticides in foods, years 1983-1993.
- Muñoz, J. & P. H. Becker. 1999. The kelp gull as bioindicator of environmental chemicals in the Magellan region. A comparison with other coastal sites in Chile.. Sci. Mar., 63 (Suppl. 1), 495-502.
- Natale, O.E., Gomez, C.E., and Pechen de D'Angelo, A.M. 1988. Waterborne Pesticides in The Negro River Basin (Argentina). Hazardous Waste: Detection. Control. Treatment. Edited by Elsevier Science Publishers B.V., Amsterdam.
- Ockenden W., Lohmann R., Shears J and K.C. Jones 2001. The significance of PCBs in the atmosphere of the southern hemisphere. Environ Sci and Poll Res 8, 189-194.
- Ockenden W., Sweetman A., Prest H., Steinnes E.and K.C. Jones 1998. Toward an understanding of the global atmospheric distribution of Persistent Organic Pollutants: The use of semipermeable membrane devices as time integrated passive samplers. Environ Sci Technol 32, 2795-2803.
- Oliveira, R. M.; Brilhante, O. M. 1996 Hexachlorocyclohexane contamiantion in na urban area of Rio de Janeiro, Brazil. Environ. Int., 22, p. 289-294.
- OPS: Organización Panamericana de la Salud. 1998. Situación actual del DDT y de los plaguicidas organoclorados en el Perú. Lima.
- Palma-Fleming, H, O. Espinoza, E. Gutierrez & M. Pino. 1998. Organochlorine pesticides in sediment of the Valdivia river estuary in Chile. (Universidad Austral de Chile, Facultad de Ciencias, Instituto de Quimica, Valdivia, 567, Chile). Bol. Soc. Chil. Quim., 43(4), 435-445.
- Peri, S.I., Suárez, G., Speranza, E.D. and Colombo, J.C., 2001. Cuantificación de citocromo P450 en sábalos y almejas del Río de la Plata. 4ta Reunión Anual de SETAC Latinoamérica, Buenos Aires 22-25 de Octubre.
- Peri, S.I., Suárez, G., Lombardi, P., Arias, F. and Colombo, J.C., 2002. Biomarcadores en Sábalos del Río de la Plata. XXII Jornadas Interdisciplinarias de Toxicología, ATA, B. Aires 18-19 de Septiembre, p. 88.
- Resabala C., Lourdes-Maya M and M. Montaño 2002. Sustancias Tóxicas Persistentes en el Ecuador. Evaluación preliminar. Documento no publicado 13 pp.

- Rodriguez Girault, M.E., Alvarez, G., Ridolfi, A., Rovenna, A., Mirson, D., Villaamil, E., Lopez, C.M., and Roses, O. 2001. Plaguicidas organoclorados en leches infantiles. XII Congreso Argentino de Toxicología, VA-8, p. 30. Rosario, Argentina.
- Romero, R and Munoz, V. 2001. Caracterización de bifenilos policlorados (PCBs) en atmosfera urbana de la región metropolitana de Chile. Informe final. Cenma-Conama. 26 pp.
- Roulet, M.; Lucotte, M.; Guimarães, J. R. D.; Rheault, I 2000 Methylmercury in water, seston, and epiphyton of an amazon river and its floodplain, Tapajós River, Brazil. The Science Of The Total Environment, 261, p. 43-59.
- Rovedatti, M.G., Castañe, P.M., Topalian, M.L., and Salibian, A. 2001. Monitoring of Organochlorine and Organophosphorus Pesticides in the water of the Reconquista River (Buenos Aires, Argentina). Water Research 35: 3457-3461.
- Sanchez-Hernandez, J. C., M. C. Fossi, C. Leonzio, S. Focardi, R. Barra, J. F. Gavilan and O. Parra. 1998. Use of biochemical biomarkers as a screening tool to focus the chemical monitoring of organic pollutants in the Biobio river basin Chile.. Chemosphere, 37(4), 699-710.
- Sandona M. S., Zappia S., Regina V 1993. Toxic agrochemical residues in food results of five years of monitoring performed by the Health Department of Parana. Pesticidas, 3, 49-95, 1993.
- SABESP (2002) Relatório de substâncias tóxicas persistentes monitoradas semestralmente pela SABESP no período de 2000 a 2002, São Paulo.
- Sericano Jl., Wade T., Jackson T., Brooks J., Tripp B., Farrington J., Mee L., Readman J., Villeneuve J.P. and Goldberg E 1995. Trace organic contamination in the Americas: an overview of the US National Status and Trends and the International Mussel Watch Programms. Mar Poll Bull 31,214-225.
- Suárez, G., Peri, S.I., Cappelletti, N. And Colombo, J.C, 2000. Actividad de la EROD en la glándula digestiva de la Almeja Asiática. XX Jornadas Interdisciplinarias de Toxicología, Buenos Aires 18-20 de Septiembre, p 72.
- Tamayo C., R., M. N. Matus, S. C. Montes and V. R. Cristi. 1994. Polychlorinated biphenyls (PCBs) determination in human milk samples collected in three provinces of the tenth region of Chile 1990 Rev. Med. Chile 122 (7), 746-53.
- Tavares, T. M.; Bereta, M.; Costa, M. C. 1999 Ratio of DDT/DDE in the All Saints Bay, Brazil and its use in environmental management Chemosphere 38(06), p. 1446.
- Telles, D. L. 2001 Inseticidas organoclorados e bifenilos policlorados (PCBs) na região estuarina de Itamartacá/PE: Aspectos analíticos e ambientais Tese de Doutorado Recife-PE.
- Topalián, M.L., Castañé, P.M. and Rovedatti, M.G. 1996. Dos años de monitoreo regular de plaguicidas en el agua del Río Reconquista. X Congreso Argentino de Toxicología, 34, p. 35. Buenos Aires, Argentina.
- Torres, J. P. M.; Malm, O; Vieira, E. D. R.; Japenga, J.; Koopmans, G. F. 2002 Organic micropollutants on river sediments from Rio de Janeiro state, Southeast Brazil. Cadernos de Saúde Pública, Rio de Janeiro, 18 (2): 277-488.
- Torres, J. P. M.; Pfeiffer, W. C.; Markowitz, S.; Pause, R.; Malm, O and Japenga, J. 2002 Dichlorodiphenyltrichloroethane in soil, river, sediment and fish in the Amazon in Brazil Environmental Research, 88 (2), p. 134-139.
- Vasconcellos, P. C. 1996 Um estudo dobre a caracterização de hidrocarbonetos policíclicos aromáticos e seus derivados, e hidrocarbonetos alifáticos saturados em material particulado atmosférico proveniente de sítios urbanos, suburbanos e florestais. Tese de doutorado, Instituto de Química, Universidade Estadual de São Paulo.
- Vasconcellos, P. C., Carvalho, R. F. L.; Zacarias, D. In Press Atmospheric Environment.
- Vasconcelos, P. C.; Artaxo, P. E.; Ciccioli, P.; Brancaleoni, E.; Frattoni, M. 1998 Determinação dos hidrocarbonetos saturados e policíclicos aromáticos presentes no material particulado da atmosfera amazônica. Quim. Nova, 21, p. 385-393.
- Ventura, E.C., Gaelzer, L.R., Zanette, J., Marques, M.R.F. and Bainy, A.C.D. 2002. Biochemical indicators of contaminant exposure in spotted pigfish (Orthopristis ruber) caught at three bays of Rio de Janeiro coast. Marine Environmental Research, 54: 775-779.
- Velásquez, H. y Gomero, L. 2001. Evaluación de nivel de dioxinas en cenizas de incineradores y rellenos sanitarios de desechos urbanos de la Provincia de Lima. RAAA/RAPAL. Octubre 2000 – Marzo 2001.
- Villaamil, E.C., Ridolfi, A., Ravenna, A., Pongelli, V., Roses, O. 1999a. Investigación de residuos de plaguicidas organoclorados en alimentos no grasos de consumo habitual en Buenos Aires. XI Congreso Argentino de Toxicología, AN16, p. 83. Buenos Aires, Argentina.
- Villaamil, E.C., Ridolfi, A., Ravenna, A., Paonessa, A., Roses, O. 1999b. Investigación de residuos de plaguicidas organoclorados en alimentos grasos de consumo habitual en Buenos Aires. XI Congreso Argentino de Toxicología, Buenos Aires, Argentina.
- Villaamil, E.C. 2000. Residuos de plaguicidas organoclorados en alimentos de consumo habitual en la ciudad de Buenos Aires. Tesis Doctoral, Toxicología y Química Legal, FFyB, UBA.

- Wilcke, W.; Lilienfein, J.; Do Carmo, L.; Bayreuth, B. 1999 Contamination of highly weathered urban soils in Uberlandia. J. Plant. Nutr. Soil. Sci., 162, p. 539-548.
- Whelan, J. and Hunt, J. 1983. Volatile C1-C8 organic compounds in sediments from the Peru upwelling region. Org. Geochem. 5, 13-28

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PTS in Air and total deposition in areas with heavy biomass burning

Title: Comprehensive study to evaluate PTS compounds emitted from sugar cane plantation in Araraquara, São Paulo State, Brazil.

Reference: CETESB 2002

Objective/Historical: Evaluate the emission of PCB, PAH and dioxins/furans due to biomass burning (sugar cane) in the Araraquara region (chosen as a model-area due to the predominance of this type of agriculture). PTS were analyzed in the air, soil, and leaf samples, as well as total deposition of air particulates. Results were compared to the ones obtained in heavily populated areas (São Paulo) and heavily industrialized area (Cubatão).

Sites (name; location):	Total deposition samples: Araraquara (12 from urban and
Araraquara city / São Paulo State /	rural areas); São Paulo (8); Cubatão (12)
Brazil;	Air samples: Araraquara (5 from burning areas and 7 in
São Paulo city / São Paulo State /	urban areas); São Paulo (2); Cubatão (2)
Brazil;	
Cubatão city / São Paulo State / Brazil	



Objectives: Evaluate the environmental contamination in the estuarine area of Santos and São Vicente (São Paulo State), through a comprehensive study of water, sediments and aquatic organisms, and correlate with the known sources of pollution (petrochemical complex). This assessment provide technical parameters to guide the prevention, control and management of environmental conflicts that appear between the estuary preservation interest and the industrial, port, tourist and fishing activities.

Historical: The region contains the largest port in Latin America, the second industrial complex in the country (Cubatão city), the proximity with the metropolitan region of São Paulo city and many facilities of transport and energy that led to the implantation (since the 50's) of a diversity of base industries (metallurgic, petrochemicals, fertilizer) inside a wide net of estuarine channels and mangrove system. The disposal coming from industrial activities and sewage from the port of Santos and cities in the region, led to a serious environmental degradation, reflected in the social welfare and public human health. The inappropriate disposal of solid residues (industrial and domestic), the frequent oil leakage and the presence of other toxic substances in the water flux also contribute to the degradation scenario.

In 1984, an intense program of pollution control (in air, water and soil) was launched in Cubatão industrial area, with investments close to US\$ 800 millions, that led to the implementation of effluent treatment plants in every factory in the region and reduced the load of pollutants to the aquatic system. From that time, a progressive recovery of the aquatic ecosystems was observed, with enhancement of diversity of birds, aquatic organisms and intensification of the fishing activity.

A former report (1988) showed that the region remains impacted by high concentration of metals and organochlorinated compounds in water, sediments and aquatic organisms (fishes and crabs). During the 90's the control system was improved, leading to recycling of effluents, assessment and treatment of underground water contaminated by hydrocarbon and organochlorinated compounds.



Results: The concentration of PTS in aqueous samples was below the detection limits in almost all sampling points. The only compound detected in water was Endosulfan B, occurring in 4 samples, in concentration above the CONAMA levels (1-2.6 μ g/L).

- BHC results in biota showed much lower values when comparing to the study performed in 1992. In the present study BHC was detected above the detection limit (10 ug.kg⁻¹) in only one organism. For DDTs, Drins and all other chlorinated pesticides were bellow detection limits (10 ug.kg⁻¹) in 100% of the organisms.

- For PCB in biota the scenario was different. Nine different species were sampled and analyzed (crabs, shrimps, oysters, and fishes) and several showed levels above the limit proposed by USEPA (14 ug.kg⁻¹), considering the ingestion of 12 meals/month (227 g each meal). Oysters reached values of 17 ug.kg⁻¹, clams reached 42 ug.kg⁻¹, while fish reached 23 ug.kg⁻¹.

- PAH in biota varies widely. Among the 16 compounds, the concentration in different organisms varied from 0.01-5000 ug.kg⁻¹. Benzo(a)pyrene was detected above the limit for human consumption in oysters and clams, but in general, all other organisms presented values bellow detection limits (10 ug.kg⁻¹), with the exception for Naphthalene, the most toxic PAH.

- For dioxins and furans, once more the organisms with the highest levels were oysters and clams. Most of samples from these two organisms showed values above the criteria proposed by USEPA (0.15 ppt TEQ) and larger oysters showed values exceeding 1.2 ppt TEQ, a limit that characterizes no consumption in any case. Some crabs also showed values above 1.2 ppt TEQ, what may pose some health threats, since these organisms are often consumed by the population.

Comments: The results compared with historical data allowed the identification of main sources of those compounds to the aquatic system. For organic compounds the potential sources are: landfills leachate, water and sewage treatment plants, raw sewage discharge in the water bodies.

Conclusions: The analysis of water samples indicates a reduction in the concentration levels for soluble hexachlorobenzene and BHC, comparing with the 1990 study. The analytical limitations associated to current detection limits for water samples, does not allow a detailed evaluation for slightly soluble pollutants, suggesting that the aqueous compartment is not suitable for evaluating the contamination from these compounds. Biota shows to be the compartment with the highest accumulation index for dioxins/furans and PCBs of all other compartment sampled.

PTS in Sediments

Title: Sediment Quality Criteria in the Tietê River System – QUALISED

Reference: http://lqa.iqm.unicamp.br/links/qualised

Objectives: QUALISED project is the first attempt in Brazil to generate a sediment quality criteria for the protection of aquatic fauna. The project main goal is to generate a data bank on chemical and biological factors (structure of communities, nutrients, metals; hydrophobic organic compounds and toxicity tests) for sediments and interstitial waters in order to support a sediment quality guidelines. In this project, sediments with different degrees of contaminants from five reservoirs located in the Tietê River watershed from São Paulo State, Brazil were sampled between January/2000 to November/2001. Among the PTS, PAHs and PCBs were the main target, but chlorinated pesticides were also investigated in a screening study.



Results: An spatial gradient of PAH and PCB concentration was observed from the Metropolitan area of São Paulo city, where the most degraded water bodies are located, to central-lower parts of the basin, considered to be more preserved. The highest concentration of total PAH was observed for Billings Reservoir (21 ug/g dry sediment). The extracts were also tested for mutagenicity using S. typhimurium strains TA98, TA100, YG1041, and YG 1042 with and without metabolic activation (S9 mixture). Positive responses were found only in the two most contaminated reservoirs for T98 and TA100, with S9 confirming the presence of mutagenic PAH in the samples collected in Billings and Rasgão reservoirs with potencies ranging from 100 to 1000 revertants/g.

4 ASSESSMENT OF MAJOR PATHWAYS OF CONTAMINANTS TRANSPORT

4.1 INTRODUCTION

As PTS are semi-volatile and have low water solubility, their transport can occur either in the atmosphere or the aquatic environment. Due to their low vapour pressure and high Kow and Koc values, PTS tend to partition mainly into organic carbon and lipid containing media, such as soil, sediment, biota or aerosols. However, their volatility is often high enough to allow for long-range transport in a way that has been described as the "grasshopper effect" (Wania and Mackay 1993, 1996). This means that the chemical is trapped in an organic phase without being degraded, and depending on the development of an equilibrium imbalance, it is then released back into the atmosphere or water, where it can travel short distances before being trapped again. The procedure continues until the chemical is ultimately degraded. This "grasshopper effect" allows persistent chemicals of low vapour pressure to be transported long distances to areas where they have never been used, which is obviously of concern. Migrating fish and birds could also contribute to the regional transport of PTS.

Regardless of in which medium a chemical is being transported, what ultimately determines a chemical's potential for long-range transport and thus transboundary movement are its partitioning properties in combination with the nature of the environmental media where the transport occurs. Therefore, in order to achieve an adequate description of a chemical's movement, it is crucial to create a picture, that accurately describes the possible transport pathways that a chemical substance can use. This is a difficult task, since the complexity of the environment cannot be underestimated. As a first approach the environment can however be divided into basic units, or compartments, which might include air with aerosols, water with water particles, soil, sediment and vegetation, or other significant media. The aim is then to achieve a description of transport pathways an example of how a generic environment can be described and the direction of possible transport processes that a chemical might undertake in that environment.



Figure 4.1 Compartments and transport processes of a chemical in the environment.

4.1.1 Region Specific Features

The South American region shares very interesting features in order to analyse transboundary pollution analysis. However, this issue has not been subject to particular research within the region. Both atmospheric circulation affected by the Atlantic winds in the eastern part and by Pacific winds in the western part could be important transporters of PTS in the atmosphere. Cold subtropical highlands and southern sub-regions may favour the atmospheric deposition of PTS within those areas. The Andes Cordillera may be a suitable candidate for the analysis of their role as a "natural trap" or barrier for PTS substances transported by the atmosphere. Other potential transboundary pathway of movement should be major rivers draining huge hydrographic basins in the region such as the Amazon and Río de la Plata. These systems cover enormous surfaces (3-6 million km² each) and include the main urban/industrial areas in the region (i.e. Sao Paulo, Buenos Aires). Consequently, contaminated sediments and biota act as steady reservoirs of PTS that can be easily transported downstream to coastal areas, and even upstream through large freshwater fish migrations (i.e. the Sábalo, *Prochilodus platensis*).

On the other hand oceanic circulation could serve as an exporting pathway of PTS discharged by terrestrial ecosystems (Figure 4.2). Two major systems of marine current circulation operate in the region: a dynamic system of upstream cold water movement in the Pacific Ocean called the Humboldt or Perú-Chile current system. In the Atlantic Ocean, the warm Brazilian current flowing southward meets the upward flowing cold Malvinas current resulting in a migrating front which meets Río de la Plata freshwater, with its nutrient-rich discharges, resulting in a very productive coastal zone.



Figure 4.2 Major ocean circulation systems in the region (Source: Microsoft Encarta 98).

4.2 OVERVIEW OF MODELLING PROGRAMMES AND FUTURE PROJECTS

4.2.1 Introduction

Traditionally modelling efforts have not been oriented to the prediction of transboundary modelling in the region. There are some models of oceanic water circulation, air movement, but these models are not coupled with contaminant transport. It is acknowledged that exellent capabilities for modelling exist within the region, but it is necessary to motivate this kind of research.

A chemical substance, either natural or xenobiotic, discharged in whatever environmental compartment (air, water, soil) follows a specific biogeochemical cycle that determines its transport and distribution. This distribution depends not only on diffusion and transport patterns within the single compartment, but also on partition processes among the various compartments. Moreover within each compartment the chemical is subject to degradation. Although it must be considered that degradation processes are very limited for PTS substances since they have very long half-lives

A scheme of the main mechanisms regulating distribution and fate of a chemical in the environment is shown in Figure 4.3.



Figure 4.3 Simplified mechanisms regulating the fate of chemicals in the environment

It is obvious that the biogeochemical cycle of a chemical and its environmental fate depend on the characteristics of the various compartments and on other environmental parameters. On the other hand, fixing

the environmental conditions, environmental distribution and fate of a chemical substance depend on its properties. In particular, at least in ideal conditions of equilibrium, steady state and well mixing, distribution among the various compartments is regulated by some physico-chemical properties of the chemical substance, representing essentially partition coefficients among the different phases.

It follows that a few molecular parameters regulate environmental partitioning of organic substances and, as a preliminary step, a rough evaluation can be based on single molecular properties. For example, it is evident that a very soluble substance will partition mainly in water, whereas a very volatile one will go principally in air. Moreover it must be remembered that many environmental factors will highly affect molecular parameters. Temperature influences vapour pressure and water solubility more than other parameters like Kow. A more important role can be played by pH in the case of dissociating, ionisable or redox sensitive compounds.

In summary, environmental distribution of chemical substances is the result of a sum of partition and mass transport processes depending on environmental and molecular factors strictly related toe another. For persistence, it depends on several transformation processes typical of different environmental compartments, as shown in Figure 4.3.

It is now increasingly accepted that successful management of chemicals in the environment requires quantitative information on major sources, environmental concentrations, transport pathways and routes of exposure to human and wildlife. Essential to this are risk assessments determined by the proximity of concentration levels or body residues to those at which effects are observed. This quantitative information concerning chemical fate cannot be assembled from monitoring data alone, and is best managed in multimedia mass balance models. As a result, environmental fate models are widely used to predict contaminant fate and behaviour profiles and are useful tools in the risk assessment process. The reliability of such models, however, is paramount if they are to be used successfully. There has also been considerable interest in developing screening models to cope with a range of geographical scales. Until recently much of the research carried out into the fate and behaviour and the likely effects of contaminants in the environment was on a local scale. This usually involved an assessment of the impact of a single point source on the local vicinity. However, as a result of the measurements of contaminants in remote areas e.g. the Arctic or Antarctic, there has been increasing interest in the atmospheric transport of contaminants on a regional and global scale. Indeed remote areas such as the Andes Cordillera may become sinks for semi-volatile contaminants as they are preferentially deposited in cold climates where degradation processes are extremely slow. It is therefore clear that for successful management of contaminants an understanding of their long-range transport must be understood. Development of predictive models requires an understanding of the release of a contaminant (both quantity and emission route), its migration pathway through a multi-media environment, the dynamics of inter-compartmental exchange (e.g. clearance rates) and its ultimate fate. As the end use of such models is to protect human or wildlife then these models need to be linked to food-chain models that can be used to predict exposure.

4.2.2 Steady State Models: Partition Analysis and Related Models.

To predict environmental distribution and fate of chemical substances, Baughman and Lassiter (1978) introduced the concept of an evaluative model, with the aim of developing a quantitative approach for the evaluation of exposure. According to these authors, evaluative models "incorporate the dynamics of no specific environment but are based on the properties of stylised environment of hypothetical pollutants for which we specify (rather than measure) inputs". In the ensuing years, many publications appeared on the same subjects (Haque, 1980; Hutzinger, 1980; Neely and Blau, 1985).

In general, models related to the original approach proposed by Baughman and Lassiter are extremely simple and easy to handle. They require only a few input data and are based on partition properties of the chemical, i.e. partition coefficients are the main input data needed

Several models based on partition analysis were developed at different levels of complexity, from simple standard screening models to more complex site-specific approaches, with differing predictable capability. Among the various methods based on the partition analysis, one of the most widely used is the fugacity approach proposed by Mackay and co-workers (Mackay, 1979; Mackay, 2001).

Fugacity is an old concept of physical chemistry (Lewis, 1901) introduced at the beginning of this century as a criterion for equilibrium between phases. Accordingly to Clark et al.(1988): "fugacity is analogous to chemical potential as it pertains to the tendency of a chemical to escape from a phase (e.g., from water). It is expressed in units of pressure (Pascal) and is essentially a partial pressure exerted by the chemical in each medium. If a chemical attains concentrations in various media that are in equilibrium, its fugacity is equal in these media".

All four levels of the original fugacity model can be applied, with a very reduced computer support, in its standard form to a theoretical unit of world and adopted as a useful screening method. For those purposes, the

fugacity model was suggested by the OECD (1981) and in Europe by some national official organisations (Lange, 1991) as a procedure for the hazard evaluation of chemical substances. Moreover, the extreme versatility of the fugacity model allows its application in a site-specific form, substituting the standard unit of world with the characteristics of a real environment. Obviously in this case, additional input data are the properties of the experimental system such as volumes of environmental compartments, meteorological and climatic characteristics, soil and sediment characteristics, and hydraulic balance and other advection parameters. More details about the various aspects of the fugacity models and of other models related to the general fugacity concept can be found in the original papers or in a comprehensive overview of the fugacity approach (Mackay, 2001).

An example of application of this approach to understand the process governing the fate of PCBs in La Plata river estuary was presented by Colombo (2002) at the first technical regional workshop in Campinas, Brazil. Overall, the results indicated that calibrating a Fugacity I model for the coastal area of the Río de la Plata with a PCB input of 220 kg adequately reproduced the concentrations in abiotic phases, whereas levels in biota were consistently sub-estimated, probably reflecting the effect of trophic biomagnification in fish and clams. Considering the equilibrium concentrations and the transport/sedimentation dynamics of the system, a total PCB discharge of 900 kg was estimated, which would be chiefly retained in fine coastal sediments.

4.3 EXPERIMENTAL EVIDENCE FOR LONG-RANGE TRANSPORT (LRT)

As previously discussed, atmospheric and multimedia transport models are useful tools for estimating the potential of a chemical to be transported long distances, but it is important to demonstrate that effectively the region have been subjected to LRT, remote areas sampling and movement through rivers. Also, biota should be analysed as experimental evidence of transport both inter and intra-regionally.

However, in order to provide experimental evidence, measurements should be performed. Reliable experimental data that support model predictions for a number of PTS can encourage a wider use of models for other substances as well. Lack of experimental data however, makes it impossible to validate or evaluate model predictions. Recent measurements of PTS have been carried out in areas far from any potential point sources of the chemical. PTS have been detected in background and remote areas in this study (Barra *et al.,* 2002a).

Detection of a substance at remote locations where it has never been used provides valuable evidence for longrange transport by natural and/or anthropogenic pathways. However, detection of a pollutant in a remote area is not enough evidence of transport (Mackay et al, 2001). In order to obtain experimental evidence for LRT potential of PTS in the region, more extensive investigations are required. Such research should include sampling along latitudinal or altitudinal gradients in one or more environmental media with the aim to provide information on changes in concentrations when moving away from identified point source areas. Altitudinal and latitudinal gradients in the Andes Cordillera could be very helpful in understanding if the "cold trap effect" is actually occurring in the region. If concentrations decline quickly, then LRT is unlikely to occur, but if a shallow slope of the concentration curve is obtained, then LRT might be an issue.

Airborne concentrations of PCBs and dioxins/furans were measured by air samplers along a latitudinal transect from the south of the UK to the Southern Atlantic region. Results indicate that PCBs and PCDD/Fs are detectable in air and water samples in several remote areas including the Antarctic. This suggests that probably LRT processes are operating, even though at a lower scale ascompared to the Northern Hemisphere (Lohmann *et al.*, 2001). Similarly, the spatial variation of PCB concentrations in mytillids along the Chilean coast indicates that the relative concentrations of more volatile PCBs (tri-and tetrachlorinated) increased with latitude (Barra *et al.*, 2002).

At the first and second regional workshops, (Campinas and Lima, 2002) the development of regional projects was proposed with the aim of evaluating process of LRT within the region. These projects propose to sample fish to evaluate PTS levels in major river basins (Fish Watch project), and to analyse environmental levels of selected PTS in remote cold areas (Andes Trap project). In addition to recent observations (Grimalt *et al.*, 2001), highlands areas could trap selectively PTS substances from the atmosphere. therefore, a more complete understanding of deposition process from the air compartment in highland areas where a large number of people are living, is in urgent need (Kidd *et al.*, 1998).

 Table 4.1 Long-range transport of selected substances (PTS in italics not assessed).

Substance	Measurements	Main transport	References
Aldrin	no	Water	
Chlordane	yes	air, water	Brorström-Lundén, regular monitoring
DDTs	yes	air, water	Calamari, 1991, Muir et al., 1995
Dieldrin	yes	Water	Muir et al., 1995?
Endrin	yes	Water	
Heptachlor		Air	
НСВ	yes	Air	Calamari, 1991, Simonich & Hites, 1995
Mirex			
Toxaphene	yes	air, water	
PCBs	yes	Air	Iwata et al., 1993, Muir et al., 1996; Simonich
Dioxins	yes	air	
Furans	yes	air,water	
HCHs	yes	air	Iwata et al., 1993; Simonich & Hites, 1995
РСР	?	air, water	
PAHs	yes	water	
Org. Mercury Compunds	?		
Org. lead comp.	no		
Endosulphan	no	water	
Atrazine	no	water	
Chlordecone			

4.4 CONCLUSIONS

Studies on the Long Range Transport (LRT) at regional level are practically nonexistent in the Region. Traditionally modelling efforts have not been oriented to the prediction of transboundary modelling but directed at oceanic water circulation and air movement, These models are not coupled with contaminant transport but it is acknowledged that exellent capabilities for this extension of the current knowledge base exist within the region.

Several PTS including PCBs, Dioxins, Furans and other chlorinated compounds have been detected in remote areas (Andes Mountains and South Atlantic ocean), demonstrating the relevance of atmospheric and ocean transport. Taking into consideration the abundance and extensive area covered of freshwater ecosystem, LTR through this medium is very likely to occur. The transport and spread of PTS to remote areas is certainly possible within the Region, but there are very few experimental data to evaluate the importance of this mechanism to the present scenario of PTS assessment in the region.

4.5 **REFERENCES**

- Baughman G.L., Lassiter R.R. (1978): Prediction of Environmental Pollutant Concentration, in Cairns J.Jr., Dickson K.L., Maki A.W. (Eds) Estimating the Hazard of Chemical Substances to Aquatic Life. ASTM STP 657, Philadelphia, 35-54.
- Barra R., Suarez, C., Quiroz R., Popp, P., Cisterna M. (2002). Saltmarsh sedimentary records for assessing Persistent Toxic Substances Pollution in a Remote Area in Chile. Organohalogen compounds 57,285-288.
- Barra, R., Quiroz, R., Mendoza, G., Urrutia, R., Pozo, K., Focardi, S. 2002. Polychlorinated biphenyls in Perumytilus purpuratus (Lamarck 1819) along the Chilean coast reflects latitudinal concentration gradients. Organohalogen compounds. Vol. 58,481-484.
- Calamari, D.; Bacci, E.; Focardi, S.; Gaggi, C.; Morosini, M. and M. Vighi (1991). Role of plant biomass in the global environmental partitioning of chlorinated hydrocarbons. Environ. Sci. Technol. 25:1489-1495.
- Clark T., Clark K., Paterson S., Mackay D., Norstrom R.J. (1988): Wildlife Monitoring, Modelling and Fugacity. Environ. Sci. Technol. 22, 120-127.
- Grimalt, J. O., Fernandez, P., Beride, L, Vilanova, R. M., Catalan, J., Psenner, R., Hofer, R., Appleby, P. G., Rosseland, B. O., Lien, L., Massabuau, J. C., Battarbee, R. W. (2001): Selective Trapping of Organochlorine Compounds in Mountain Lakes of Temperate Areas. Environ. Sci. Technol. 35, 2690-2697.
- Haque R. (ed.) (1980): Dynamics, Exposure and Hazard Assessment of Toxic Chemicals. Ann Arbor Science Publisher Inc.-Collingwood, Michigan.
- Hutzinger O. (Ed.) (1980): The Handbook of Environmental Chemistry. Reaction and Processes, vol. 2, Part 8, Springer-Verlag, Berlin.

- Iwata, H.; S. Tanabe; N. Sakai and R. Tatsukawa (1993). Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of the ocean on their global transport and fate. Environ. Sci. Technol 27,1080-1098.
- Kidd, K, Hecky R, Latorre, R.,Baker J, Barra, R., Muir DGC, Swackhamer D and F. Wania (1998) Interrelationships among climatic variation, climate change and persistent organic pollutant cycling in the Americas. NWRI Contribution Nº 98-128.
- Lange A.W. (1991): The Experience of a National Competent Authority in Hazard Assessment from the Data Provided by Industry and Its Relates to Ecotoxicology. In: Chambers P.L. and Chambers C.M. (eds.): Registering New Chemicals in Europe. JAPAGA, Ashford, Ireland.
- Lewis G.N. (1901): The Law of Physico-chemical Change. Proc. Amer. Acad. Sci., 37, 49-56.
- Mackay D. (2001): Multimedia Environmental Models, The Fugacity Approach. 2nd ed.Lewis Publishers, Chelsea, MI.
- Lohmann, R; Ockenden W.A.; Shears, J,and K..C Jones (2001)Atmospheric distribution of Polychlorinated dibenzo-pdioxins, dibenzofurans (PCDD/Fs), and Non-ortho biphenyls (PCBs) along a North- South Atlantic transect, Environ.Sci.Technol 35,4046-4053.
- Mackay D. (1979): Finding Fugacity Feasible. Environ. Sci. Technol.13, 1218-1223.
- Mackay D, McCarty LS. And MacLeod M (2001). On the validity of classifying chemicals for persistence, bioaccumulation, toxicity and potential for long range transport. Environ Toxicol Chem, 20, 1491-1498.
- Muir, D. Grift, N. Lockhart, W. Wilkilson, P. Billeck, B. and Brunskill, G., 1995. Spatial trends and historical profiles of organochlorine pesticides in Artic lake sediments. Sci. Tot. Environ. 160/161, 447-457.
- Muir DGC., Omelchenko A., Grift N., Savoie D., Lockhart W., Wilkinson P. and Brunskill G. (1996) Spatial Trends and historical deposition patterns of Polychlorinated biphenyls in canadian midlatitude and artic lake sediments. Environ Sci Technol 30,3609-3617.
- Neely W.B., Blau G.E. (eds.) (1985): Environmental Exposure from Chemicals. Vol. 1. CRC Press Inc., Boca Raton, FL.
- OECD (1991): Workshop on the Application of Simple Models for Environmental Exposure Assessment, Berlin, 11-13 September 1991.
- Simonich, S. L., Hites, R. A. (1995): Global distribution of persistent organochlorine compounds. Science 265, 1851-1854.
- Wania, F, Mackay, D. (1996): Tracking the distribution of persistent organic pollutants. Environ. Sci. Technol., 30, 390A-396A.
- Wania, F, Mackay, D. (1993): Global fractionation and cold condensation of low volatility organo-chlorine compounds in polar regions. Ambio, 22, 10-18.
5 PRELIMINARY ASSESSMENT OF THE REGIONAL CAPACITY AND NEEDS TO MANAGE PTS

5.1 INTRODUCTION

During the regional priority setting meeting held in Viña del Mar, representatives from the different countries expressed their views on the national capacity for the management of PTS related problems, including Legal status of PTS, handling, monitoring and waste management issues. All these aspects are discussed in this chapter.

The management authorities are generally the Agriculture, Health Ministry, Environmental Agency, Foreign Affair and Commerce authorities or Industrial representatives dedicated to environmental issues. They are therefore responsible for regulating importation, selling, distribution and final disposal of wastes of PTS substances within the country. At a regional level, some national institutions are responsible for the enforcement of pesticides, but industrial chemicals and by-products are generally less well regulated, probably in part due to the deficit in specialized laboratories measuring environmental PTS levels, recognised as a major drawback within the region.

Other characteristics that can be mentioned within this context, relate to the lack of national monitoring programs on PTS substances. Many monitoring activities are developed by universities and, with the exception of some particular cases, very few by state or government agencies. Therefore, sustained monitoring programs are needed to perform national and regional diagnostics, with emphasis in those countries where information is very scarce.

It is interesting to note that in general all countries have some regulation for pesticides PTS and lately PCBs, dioxins and furans, however no monitoring/enforcement capabilities do actually exist in several countries in order to effectively accomplish these regulations.

5.2 EXISTING REGULATIONS AND MANAGEMENT STRUCTURES

5.2.1 Argentina PTS Regulation And Management

Chlorinated pesticides have been intensively produced, formulated and used in Argentina in the past, since 1945-50, e.g. synthesis of HCH in 1947, production of DDT in 1954, introduction of cyclodiene organochlorines in 1955 and more recent formulation of Chlordane (Alvarez, 1998).

Practically all chlorinated pesticides have been officially forbidden in Argentina for different uses and applications since 1969 (HCH, Endrin, Dieldrin, Heptachlor, Chlordane, excepted for ant combat; Law 18073/69, Decree 2678/69), 1973 (HCB and DDT; Law 20418/73), 1980 (Dieldrin; Law 22289/80), 1990 (Aldrin, DDT, Endrin and Heptachlor; Decree 2121/90), 1998 (Chlordane, Resolution 513/98; Lindane for sanitary use, Resolution 7292/98), 1999 (Mirex, Resolution 627/99), 2000 (Toxaphene, Metoxychlor, Resolution 750/00, and HCB). Endosulfan is the sole chlorinated pesticide actually in use. Dicofol (e.g. Kelthane or Agrofol), is also used for cotton and citric cultures and gardening, rising the possibility of a significant input of DDT that should not exceed 0.1% as DICOFOL impurity according to local guidelines. The regulation for other PTS include the prohibition of PCP in 2000 (Resolution 750/00), and PCBs, Polybrominated Biphenyls and Terphenyls in 2001 and 2002 (Resolutions 209/01, 437/01 and 249/02). A National Plan for Environmentally Sound Minimization and Disposal of PCBs and Contaminated Material has been also advanced by the Sustainable Development and Environmental Policy Secretariat (Estocolmo 2001). The management of hazardous substances including the topics of generation, handling, transport, treatment and disposition, is regulated through the National Law 24.051 (1992) that includes accepted guidelines for several substances (including PTS) in air, waters and soils according to different uses and quality criteria. A recent report of banned and restricted chemicals, including obsolete PTS, has been published by the Health and Defense Ministries through the Working Group on Obsolete Chemicals for the National Plan for the Management of Chemicals and the Chemical Risk Program adopted by resolution 527/2000 (Ministerio de Defensa, http://www.mindef.gov.ar/, accessed in August 2002).

In spite of the relatively complete legal body for PTS substances in Argentina, repeated contradictions are observed between practices and existing Laws. This is basically associated to the general countries organization and control problems exacerbated by the recurrent economic crisis. Additional contributing factors are the lack of harmonization between provincial and national regulations and a deficient integration of Laws and Decrees.

Argentina's academic Institutions provide the basic expertise and know-how on Chemistry, Environment, Laws and related fields, contributing Professionals to both Provincial and National Government Agencies and Ministries and the private sector. Several National services related to agriculture and food control have relatively complete laboratories and a long pesticide-monitoring tradition in foodstuffs, e.g. National Service of Agricultural Quality (SENASA), the Central Market Lab, but unfortunately very often with severe limitations for public access to the data. Other Government laboratories with advanced instrumentation are the National Institute of Industrial Technology (INTI), the Army Chemical Laboratory, the Toxicological Laboratory of the Buenos Aires Justice Ministry, the Center of Water Technology (INA), the Customs Laboratory, and the Hydrographic Service. Many private laboratories are also well equipped for environmental analysis and are often contracted for specific product analysis.

On the other hand, National Universities and research Institutions together with some provincial homologues are principal environmental data generators through specific research projects, most commonly dedicated to selected ecosystems (e.g. coastal areas, lakes and rivers such as the Paraná and Río de la Plata). Projects and studies are typically oriented to a monitoring strategy of PTS distribution in different environmental matrices.

The ecotoxicological-effect approach is comparatively less developed, principally as tests and laboratory experiences. The scientific activity is thus concentrated in the most important urban centers with large Institutions such as the Universities of Buenos Aires, Córdoba, La Plata, Rosario, and some regional centers and Universities with a more specialized orientation, e.g. Marine Sciences in Mar del Plata, Bahía Blanca and Puerto Madryn, and Chubut. The resulting pattern is an uneven country distribution of scientific-technical capacities that are particularly deficient in some northern Provinces such as Santiago del Estero, Chaco, Jujuy, Catamarca and Misiones. Thus, Government-University harmonized projects and long-lasting national monitoring programs are not frequent, although the human resources and basic equipment are currently available in some parts of the country, with the most important exception being a state-of the-art PCDD/F laboratory. However, the scientific-technical capacities of Argentinean Research Institutions are rapidly deteriorating as a consequence of the economic crisis.

5.2.2 Bolivia PTS Regulation and Management

Regulation of PTS substances started in 1972, where the DS 10283 was promulgated, chlorinated pesticides were restricted for use in agriculture. In 2002, through the law 2061 pesticides were totally banned. Still no regulations exist for PCBs, dioxins and furans as well as for organic tin and mercury.

5.2.3 Brazil PTS Regulations and Management

Historically, a landmark in the environmental legislation worldwide is linked to two major events: the Stockholm Convention (in 1972) and the Earth Summit (Rio Conference), in 1992. In Brazil, it was not until the Constitution of 1988 that the word "environment" was first used. However, even before the promulgation of the Constitution, the Earth Act (30/11/64), the Forest Code (15/09/65), the Fishing Code and the Mining Code (28/02/67) acted as starting points for all the legal aspects related to environmental protection. The Federal Law 6938 (31/08/81) established the National Policy for the Environment, fixing its principals, objectives and instruments.

As already mentioned, according to the Constitution of 1988, each State of the Federal Republic is responsible for environmental monitoring and compliance, whereas the Union acts in a more generic way. Nonetheless, the Potable Water Act (Portaria 36, recently replaced by Portaria 1469) regulates at a national level, besides many other parameters, the following PTS: Benzo[a]pyrene, Alachlor, Aldrin + Dieldrin, Chlordane (all isomers), DDT (all isomers and congeners), Endosulfan, Endrin, Heptachlor (including epoxy), Hexachlorobenzene, Lindane, and PCP.

The Water Classification Act (CONAMA 20) are applied throughout the country, and the following PTS are regulated among many other parameters: Benzo[a]pyrene, Aldrin, Chlordane (all isomers), DDT (all isomers and congeners), Endosulfan, Endrin, Heptachlor (including epoxy), Hexachlorobenzene, Lindane, and PCP.

The same occurs with pesticides whose license use and discharge are managed under Federal Level, under the responsibility of both the IBAMA (Ministry of the Environment) and the Ministry of Agriculture.

Major aspects related to pesticides in Brazil relies on the Federal Law 7802 (11/07/89), where several aspects such as production, research, containers, transport, handling, marketing, use, imports and final disposal, among others are specified. Also, according to this law, the duty for controlling the use, production, consumption, selling and stocking are responsibility of each State of the Union.

The prohibition of using chlorinated pesticides (Aldrin, BHC, Toxaphene, DDT, Dodecachlor, Endrin, Heptachlor, Lindane, Endosulfan, Metoxichlor, Nonachlor, PCP, Dicofol and Chlorobenzilate) in the agropecuary in Brazil was signed in 1985, according to the Portaria 329 (02/09/1985), Ministry of Agriculture, but allowed restricted use (Article 1) to some of these compounds as wood preservative, or when applied under the responsibility of public institution in the benefits of the public health.. This legal aspect may be acting as a gate for an expressive production of some PTS, whose stock presently available in Brazil is shown in Table 5.1.

PTS	Amount Available (tonne)
Sodium Pentachlorophenate	78 (10)
Lindane	20 (38)
Heptacloro	162 (2.5)

(Amount available as active principle; formulated products in brackets)

5.2.3.1 <u>Monitoring Capacities</u>

Environmental monitoring in Brazil is carried out by State Agencies, but data generation varies widely since the capacity varies tremendously within the country. Whereas in some areas (Southern and Southeast region), environmental monitoring is carried out on a routine basis, in some areas of the country there is virtually no data on air, water and soil values for not only PTS, even for other common pollutants such as SO_2 and Particulate Matter. More recently, an increase in the participation of both public and private Universities in carrying out environmental monitoring has been observed, mainly due to scarcity of funds provided by the Government. This trend has to be looked upon carefully, because most of these activities have been carried out as a routine (merely technical) work, unlinked to any research project.

Besides some active State Environmental Agencies, many private laboratories, including the determination of Dioxins and Furans, also carry out PTS monitoring. Other public institutions such as EMBRAPA (Ministry of Agriculture), Instituto Adolfo Lutz, Instituto Biológico, INCQS (Ministry of Health), also carry out monitoring but results, unfortunately, are not available to the public.

5.2.3.2 <u>Situation</u>

There are very few data on inadequate storage and stockpiles of chlorinated pesticides, specially for expired PTS. According to IBAMA, a recent programme was launched to identify these inadequate stockpiling of PTS throughtout the country.

5.2.3.3 <u>Waste Management</u>

As already mentioned, Federal Law 7802 (11/07/89) regulates, containers, transport, handling, and final disposal, of pesticides in use. Also, the triple washing followed by the partial destruction of the container before sending it to the collection center is widespread along the country.

5.2.4 Chile PTS Regulation and Management

The legal regulation of pesticides in Chile begins with Law No. 15,703 of 1964 and Decree No. 567, which empower the Ministry of Agriculture, through the Division of Agriculture and Fishing and the Department of Agricultural Defense, to regulate the manufacture, formulation, distribution, and application of pesticides, which include PTS pesticides. In 1980 Decree-Law No. 3,557 for Agricultural Protection repeals previous legislation and empowers the Agricultural and Livestock Service (SAG). On the other hand, the Ministry of Health, through Exempt Resolution No. 1,450 of 13 December 1983, sets the maximum tolerances for pesticide residues in food for domestic consumption. In accordance with the Sanitary Code this Ministry has the power to authorize the manufacture and importation of toxic or hazardous substances for sanitary and domestic use.

In Chile the importation, manufacture, sale, distribution and use of the following compounds have been prohibited: DDT since 1984; aldrin since 1988; and chlordane, dieldrin, endrin, and heptachlor since 1987. PCBs have been regulated since 1982 where a prohibition of refilling transformators with oils cntaining PCBs was set up. Regarding Dioxins and Furans a recent regulation establishes maximum emission levels.

In Chile no manufacture of Pesticides or industrial by products such as HCB or PCBs have been performed, but the use status of these PTS substances are : PCBs, HCH Endosulfan are still used. There is no exportation of

any PTS substances, but PCBs have been exported for elimination purposes under the Basel Convention protocols.

5.2.4.1 Monitoring Capacities:

In Chile there are public (state owned and private laboratories that have the necessary analytical techniques and trained personnel for the analysis and quantification of PTS (mainly pesticides and PCBs). There are no regular monitoring programs specifically designed for PTS, but eventually existing monitoring programs such as the Biobio river water quality program or the air monitoring program existing in Santiago will analyse some PTS compounds (PAHs). Other programs collect information but on an irregular basis. NO programs looking at biota levels or effects exist (aquatic, terrestrial are or have been implemented so far in Chile). The ecotoxicological-effect approach is comparatively less developed; some research groups at the universities of Concepción and Chile have been working on these issues. Scientific activity is thus concentrated in the most important urban centers with large Institutions such as the Universities of Chile, Católica, Concepción, Austral de Chile etc. and some regional centers and Universities with a more specialized orientation, e.g. National center for the Environment (CENMA-U de Chile, EULA U de Concepción). The resulting pattern is an uneven country distribution of scientific-technical capacities that are particularly deficient in the northern region and the extreme south.

5.2.4.2 <u>Situation</u>

There are no antecedents in relation with storage or stockpiles of chlorinated pesticides. It is supposed that they are not used any longer in Chile. Some stokpiles of PCBs are located in the northern part of the country (mining areas) in the Antofagasta and Atacama regions.

5.2.4.3 <u>Waste Management</u>

There is a regulation for managing dangerous residues that are enforced by the Ministry of Health, this regulation is still in development, on the other hand no technologies are available in the country for eliminate this toxic compounds, however there are several research efforts towards the development of clean technologies adaptable to the Chilean situation.

5.2.5 Ecuador PTS Regulation and Management

Aldrín, Dieldrin, BHC, Campechlor, Amitrole, mercuric compounds, DDTs, lindane, Heptachlor and Mirex were banned on July 1985

PCBs and PCP were officially banned on May 2001, however without legal instruments to carried out this decision.

Dicofol is registered in Ecuador under the commercial name MITIGAN and is used as acaricide, total importation were 2384 kg in 2000 and 2059 kg in 2001. The Endosulfan registered under the commercial name of Parmarol Endolfan, Flavylan, Galgofan, Thiodan, Thionex, Thionil y Methofan, a total imported amount is 56590 Kg and only in 2002 3850 Kg were imported. Lindane has not been imported in the country after banning

5.2.6 Paraguay PTS Regulation and Management

A complete set of regulatory rules from international conventions until resolutions at ministry level, are in course in Paraguay. Chlorinated pesticides corresponding to PTS were banned in 1992 and 1993 (Resolución 87/92 and 447/93 including the following pesticides: Aldrin, Dieldrín, Endrín, Heptachloro, Chlordane, Metoxicloro, Canfecloro, DDT, Lindane and in addition Pentaclorofenol. (Resolución 448/93).

5.2.6.1 Monitoring capacities:

Monitoring capacities are very limited, with the exception of a state owned laboratory with limited facilities. There are no ongoing monitoring programs of PTS in any environmental media or in human tissues. Probably Paraguay is one of the countries where information is not available or non-existent.

5.2.6.2 Situation

There are few reports regarding storage of chemicals in the Asuncion harbor, however there are uncertainties about their content, no information exists about storage of PTS substances in the country.

5.2.6.3 <u>Waste management</u>

Even though regulatory bodies exist, there is a consensus from government officers that the regulatory body is not efficient in the following aspects of storage, transport, use and management and final disposal. It is not known if banned pesticides are disposed of in an environmental friendly way.

5.2.7 Peru PTS Regulation and Management

The Ministry of Agriculture in Peru has regulated the use of pesticides by restricting or forbidding their use in the country. These legal actions began in 1991 with the total forbidden of the use of Aldrin, Endrin, Dieldrin, HCH, Heptachlor, Toxaphene and DDT as well as their derivatives by Supreme Decree 037-91-AG in 1991. Some years later, in 1999, the Chief Resolution 036-99-AG-SENASA banned in the same way as before HCB, PCP and Chlordane as well as their derivatives. In the year 2000, Chief Resolution 043-2000-AG-SENASA and Chief Resolution 060-2000-AG-SENASA banned the registration, importation, formulation, distribution, sell and use of commercial formulations and technical materials of pesticides for agricultural uses in base of Lindane and Mirex respectively.

5.2.7.1 Monitoring capacities

The monitoring capacities are very limited and performed by very few local universities. The exception is CEPIS-OPS laboratory which is equipped for these chemical analysis but access is limited for economic reasons.

5.2.7.2 <u>Situation</u>

Some stockpiles of DDT might be stored in the Northeastern part of the country. However, there is scarce information about the fate of the stockpiles of PCBs or other PTS in the country.

5.2.7.3 <u>Waste management</u>

There is no regulation for managing dangerous residues and a review is in progress by the Water Law which considers monitoring PCBs. Recently, a Technical Group composed by Ministries of Agriculture and Health represented by SENASA and DIGESA, respectively, and political, social and academic representatives has been formed in order to evaluate and recommend actions about dangerous residues according to Stockholm, Basel and Rotterdam Conventions.

5.2.8 Uruguay PTS Regulations and Management

In 1968, the Uruguayan Government decree 367/68 empowered at the Livestock and Agriculture Ministry (MGAP) to regulate, the use, banning or restrict of pesticides in livestock and plant cultures. In the same year (resolution 6/6/1968), the use of aldrin, dieldrin, endrin, chlordane, heptachlor, gamma isomer of HCH, DDT and endosulfan was restricted, only for ant control in focussed treatments. Other resolution (decree 149/977 dated, March/977, December/977) banned the use of Chlorinated insecticides in grasslands and grain treatment destined for human and/or animal consumption and/or industrialization; and banned hexachlorociclohexane importation, manufacture, formulation and sale for agricultural and veterinary uses.

In 1988 the registration and sale authorization of endrin was revoked for all agronomic uses, except parakeet control (*Myiopsitta monachus*, *Aves Psittaciformes*), but it must be used with authorisation from Plant Protection Directorate.

5.2.8.1 Monitoring capacities

Several organizations have facilities for performing PTS analysis mainly pesticides and PAHs such as Ministries, local universities, and some private laboratories. However there are no regular monitoring programs for PTS. Only agricultural exporting goods are controlled for pesticides residues, but the public access to this information is limited. Toxicological and ecotoxicological assessments have a limited development and only have been performed at the University.

5.2.8.2 Situation

The only information in relationship with stockpiles of PTS correspond to 70 tons of HCH stored in poor conditions and c.a. 60 tons of PCBs. Both stockpiles are under the supervision of Ministry of Health and National electrical company (UTE), respectively.

5.2.8.3 Waste Management

There is a regulation for managing dangerous residues that are enforced by DINAMA and MGAP, this regulation is still in development On the other hand no technologies are available in the country for eliminating toxic substances. Currently thecountry export through the BaselConvention.

Table 5.2 Current legal status within the eight countries of persistent toxic substances covered in this report (Source :Data from the RPSM Viña del Mar. Chile 2002)

	Argentina1	Bolivia2	Brasil3	Chile4	Ecuador	Paraguay	Perú	Uruguay
Aldrin	Banned 1990	Banned 2002	Restricted use (1985)	Banned 1987.	Banned 1985	Banned 1993	Banned 1991	Restricted 1968, Banned 1998
Endrin	Banned 1990	Banned 2002	Restricted use (1985)	Banned 1987	Banned 1985	Banned 1993	Banned 1991	Restricted 1968, Banned 1998
Dieldrin	Banned 1980	Banned 2002	NI	Banned 1987.	Banned 1985	Banned 1993	Banned 1991	Restricted 1968, Banned 1998
Chlordane	Banned 1998		Restricted use (1985)	Banned 1996.	Banned 1985	Banned 1993	Banned 1999	Restricted 1968, Banned 1997
Heptachlor	Banned 1992		Restricted use (1985)		Banned 1985	Banned 1993	Banned 1991	Restricted 1968, Banned 1998
DDT	Banned 1990	Banned 1996	Restricted use (1985)	Banned 1994.	Banned 1985	Banned 1993*	Banned 1991	Restricted 1968, Banned 1977
НСВ	Banned 2000	Banned 2002	Restricted use (1985)	Never registered as a pesticide. Banned in 2002	Banned 1985	Banned 1993	Banned 1999	Never registered
γ-HCH (lindane)	Banned 1998	In use	Restricted use (1985)	Restricted use Banned for agricultural use in 1998, but still used for sanitary reasons	Banned 2001	Banned	Banned 2000	Restricted 1968, Banned 1997
Mirex	Banned 1999	Banned	Restricted use (1985)	Never registered as a pesticide. Banned in 2002	Banned 1985	Banned 1993	Banned 2000	In use
Toxaphene	Banned 2000	Banned 2002	Restricted use (1985)	Never registered as a pesticide. Banned 1998.	Banned 1985	Banned 1993	Banned 1991	Never registered
Endosulfan	In use	In use	Restricted use (1985)	In use	In use	In use	NI	Restricted 1968
TBT	NI	In use	NI	NI	NI	NI	NI	In use
РСВ	Banned 2001	NI	Restricted use (1985)	Banned in 1982	Banned in 2001	NI	NI	NI
РСР	Banned 2000	In use	Restricted use (1985)	Suspended in 1999	Restricted 1985/Banned 2001	NI	Banned 1999	NI

 $^{1}NI = no information.$

2 Law 2061 (2002) Administrative resolution 0055, banning the use, import of chlorinated pesticides. Even though they are forbidden there is some evidences of use* DDT was forbidden according the Law, but it was used by the Ministry of health in campaigns against the Dengue fever (years 1999-20

5.2.9 Regional Assessment

As mentioned in earlier chapters of this regional report, some countries have capabilities to perform PTS monitoring and research activities. However, one must take into account that some countries (Bolivia, Ecuador, and Paraguay) need international support to improve their national capabilities. This international support can provide the methodologies and tools for managing PTS related problems. In relation to PTS management, some countries are developing dechlorination and oxidative technologies suitable for in situ or ex situ treatment of PCBs as well as other contaminants. Therefore, within the region there are some national capacities for PTS treatment and remediation that could be supported in order to favor the interregional cooperation.

The number of environmental oriented consulting companies active in both air and wastewater treatment, as well as soil decontamination is growing steadily in some countries in the region. Regionally there is concern in relation to the management of stockpiled pesticides and chemical products. There is practically no information regarding the location of some of these or in other cases this is considered confidential information. IBAMA in Brazil, has just launched a program trying to identify major sites where old pesticides are stored.

Another complex regional problem is the non-harmonized regulatory status of pesticides and PCBs in the different countries. Some countries banned all uses of PTS including export and import activities while others do not. There is therefore an open window for illegal transport of pollutants within the region, which is aggravated by the recurrent economic problems. This represents a serious challenge for Region XI countries which would have to move to more strict regulations in order to accomplish the Stockholm convention regulations. Also another important aspect related to the use, import and disposal of pesticides comes from the Mercosur, what is the first attempt to standardize procedures (1995) involving a group of different countries in South America.

The Stockholm Convention on Persistent Organic Pollutants was adopted at the December 2000 meeting of the intergovernmental negotiating committee for an international legally binding instrument for implementing international action on certain persistent organic pollutants in Johannesburg. The objective of this Convention is to protect human health and the environment from persistent organic pollutants. The selected list of POPs is of direct relevance to the UNEP assessment of PTS. The Convention was opened for ratification signatures on 23 May 2001. All the countries of the XI region signed up to the convention, but none of them has yet ratified it.

5.3 STATUS OF ENFORCEMENT

The status of enforcement in the different countries is quite similar, since PTS are not a priority issue in terms of environmental or public health problems. Generally, enforcement activities are reduced to the routine measurement of some pesticide products in foodstuffs and in some environmental matrices. It was widely recognized that such monitoring programs were more active during the eighties, as in general, levels in foodstuffs were below national regulations so no actions were taken.

Industrial products such as PCBs and some by products like dioxins and furans are not routinely monitored, but some regulations are in progress in the region. PCBs are still permitted in some countries while in others it is forbidden for electrical uses.

5.4 ALTERNATIVES OR MEASURES FOR REDUCTION

The more effective means of reducing the PTS concentration in environmental receptors is to reduce their source. As long as the offer of any banned product occurs in the international market, there will be a chance that this product could be used. So, firstly there should be efforts to totally inhibit the production of these compounds. Secondly, the overuse of pesticides is a routine procedure in most developing countries, normally encouraged by the producers, and this should also be approached by educational programs, an issue that is virtually ignored by most countries. Not all countries have the enforcement capacities for making the regulations effective, paricularly with respect to alternatives to chlorinated pesticides.

The development of adapted technologies for treatment and elimination of stocks of PCBs and some pesticides will make it possible to eliminate stored or in use stocks of certain PTS.

5.5 TECHNOLOGY TRANSFER

Intraregional cooperation both in regulatory and technical issues is needed. There are two Basel convention networks in the region (Argentina and Uruguay), that are developing a series of activities for improving the regional capacities in treatment and elimination of PTS. Other countries i.e. Brazil have the technological development for helping neighbours countries to eliminate in a environmentally friendly way the wastes of pesticides and PCBs and it is recognised that the region needs to advance with more of these initiatives.

5.5.1 Identification of Barriers

One of the barriers that are recognized for a better management of PTS issues within the region is the absence of a coherent regulatory framework for these substances. Some countries have never used some pesticides and in some cases (i.e. with PCBs) countries have no regulations at all. This lack of legislation enables the easy

transport of substances. There are limited restrictions to prohibit the movement of chemicals from one country to another.

The second identified barrier is that enforcement capacities within individual countries of the region are limited. This is because in terms of national priorities, the control of toxic chemicals is not at the top of their list of priority actions. The lack of resources and capacity building in the less developed countries in the region is a key issue to overcome difficulties in implementing the Stockholm Convention at a national and regional level. Borders are large and this natural fact impedes the adequate control of entry of pesticides or other chemicals bewteen countries.

The third identified barrier relates to the absence of regional cooperation programs related to PTS issues. We acknowledge that certain experts participating in the technical workshops are willing to exchange their experiences with less developed countries and this should be encouraged and promoted.

The fourth barrier we identified is the difficulty of harmonizing control procedures for avoiding the re-use and illegal circulation of PTS. Coordinating actions in pursuit of National implementation plans involves highly coordinated actions for managing PTS. The requirements of the convention will probably be the stimulus for coordinating actions at a national level. The technological development for eliminating PTS substances is very limited. Some efforts must be directed in this direction principally aimed at stimulating and promoting the creation of appropriate technologies which can be adapted to the region.

5.6 IDENTIFICATION OF NEEDS

Some of the needs identified by the regional Team are listed below:

- To agree regulations avoiding illegal transport of PTS across the region borders
- To increase the exchange of experts within the region
- To eliminate known stocks of PTS (PCBs and Pesticides)
- To develop appropriate technologies for eliminating PTS
- To incentive monitoring programs within the region
- To Improve analytical capabilities within the region
- To incentive training and capacity building at regional level

5.7 CONCLUSIONS

Monitoring capacity in the Region is heterogeneous at both the National and Regional levels. For example, very limited capacity for PTS monitring was identified in Bolivia, Equador and Paraguay. There are no recognised national monitoring programs and much of the available data relates to specific project work which makes time trend evaluations difficult to determine. For comparative purposes, standardization (or, at least, increased data compatibility) of research and assessment methodologies and reporting requirements is needed throughout the Region. This would both facilitate the compilation of reliable regional state of the environment assessments, and facilitate cross-country comparisons of information.

The regulatory status of the Region is also diverse with a wide variety of legislation for PTS management and wide variations in the degree of compliance. It is recognised that countries facing low levels of organisational capacity and weak economies have serious difficulties in increasing environmental protection and fulfilling international commitments. In this respect, banned products could still be illegally imported in some of these countries, many of which have extensive, difficult to police borders.

The control and management of PTS at national levels is dispersed among various authorities depending on the PTS type. Pesticides are usually regulated by the corresponding Agricultural Ministries, Industrial PTS are very poorly monitored and managed, the levels of PTS in biota are either the responsibility of the Environmental or

Agricultural (Veterinary) Ministries. Finally, PTS control and regulation in foodstuff is usually the responsibility of the corresponding Health Authorities.

As a Regional priority, the identification and remediation and stockpiled waste PTS compounds is considered important as current information is difficult to obtain and often incomplete.

The data clearly indicate that most of the countries do not have yet sufficient resources for an adequate implementation of international standards. In this context, regional co-operation should be strengthened for the development of national plans for the management of PTS. Regional co-operation may successfully stimulate the production and dissemination of technical and scientific knowledge, and also expand and sustain regional environmental assessment capacities. Such assessment work will be instrumental as a basis for prioritizing issues and formulating joint policies.

6 FINAL RESULTS AND RECOMMENDATIONS

6.1 IDENTIFICATION OF PRIORITIES

6.1.1 Sources Characterisation

The identification and quantification of PTS sources and releases to the environment are poorly developed in the Region. Most of the results presented in this report refers to critical areas (hot spots), and to a lesser extent, to stockpiles, acting as major environmental sources for the most common PTS. Industrial emissions and other point sources, including the unintended ones, are largely ignored, and there are no records available to estimate the real threats they may pose to humans and to the environment. However, at a regional level biomass burning has been identified as a major regional issue as an unintended source of PTS, including PAHs. The emissions of these compounds were estimated using emission factors (USEPA) and the value obtained ranged from 500-7,000 tonnes/year. Even more critical is the assessment of compounds recently classified as potential PTS such as flame retardants, nonvlphenols, tributhyltin, atrazine, for which there are no data available. Emissions of Dioxins and Furans to the atmosphere were estimated using both the UNEP toolkit as well as CO₂ emissions. The value obtained for the whole region is relatively low (~700 g TEQ/year), comparable to those reported for many single European countries such as France, Belgium and UK. This regional estimate must be validated with experimental data. In relation to PCBs the main sources are inadequate use, disposal and maintenance of the available stock. In an increasing priority rank, PCBs were considered as the most important PTS issue for the region. The discharge of untreated effluents throughout the whole region is recognized as a major input pathway of PTS to the environment.

6.1.2 Environmental Levels, Toxicological And Ecotoxicological Characterization

The majority of the countries within the Region lack routine monitoring programs and most of the available data were generated by induced monitoring rather than comprehensive programs in densely populated areas, along principal hydrographic basins. For this reason, the database concerning environmental levels reflect a strong bias towards freshwater ecosystems and the current status and trends of a vast areas of the region are not available.

The environmental compartments most studied are aquatic animals, followed by sediments, water and humans, with fewer data for air and soil. According to the published data the majority correspond to chlorinated pesticides and PAHs, with few reports of PCBs and organic mercury. In general, environmental levels of pesticides have been decreasing in recent years, especially in foods, mainly due to legal restrictions or banning in the countries of the Region. However, other PTS show clear patterns of contamination in sediments, water and biota, particularly in densely populated and industrialized areas.

Prioritization of chemicals within the region resulted in high scores for PCBs and PAHs, followed by Dioxins and furans and several pesticides. The main concerns related to these chemicals relates to their wide use and elevated levels found in some environmental compartments within the region.

Regarding toxicological and ecotoxicological effects, they have not been assessed in the region, with some few exceptions. Concern was raised about effects of some PTS substances and attention should be focussed on human chronic effects in those situations where exposure is elevated. In relationship to environmental effects and responses, despite the attention to environmental levels in biota few studies have been carried out regarding effects of such exposure. A strong call for assessing effects was made at the second technical meeting in Lima.

6.1.3 Assessment Of Major Pathways Of Contaminants Transport

Studies on the Long Range Transport (LRT) at a regional level are practically nonexistent; very few have been carried out in some countries of the Region. Several PTS such as PCBs, Dioxins, Furans and other chlorinated compounds have been detected in remote areas (Andes Mountains and South Atlantic ocean), highlighting the potentail of atmospheric and ocean transport. Taking into consideration the abundance and extensive area covered of freshwater ecosystems, LTR through this medium is very likely to occur, although there is no experimental data to support he fact that large rivers within the region could be major pathways of transport. In conclusion, the Region presents all the necessary conditions to allow the transport and the spreading of PTS to remote areas, but there are very few experimental data to evaluate the real contribution and the importance of this mechanism to the present scenario of PTS assessment in the region.

6.1.4 Regional Capacity and Need to Manage PTS

Monitoring capacity in the Region is heterogeneous at both the National and Regional levels. There are no recognised national monitoring programs and much of the available data relates to specific project work which makes time trend evaluations difficult to determine. The regulatory status of the Region is also diverse with a wide variety of legislation for PTS management and wide variations in the degree of compliance. It is recognised that countries facing low levels of organisational capacity and weak economies have serious difficulties in increasing environmental protection and fulfilling international commitments. In this respect, banned products could still be illegally imported in some of these countries, many of which have extensive, difficult to police borders.

Analytical capabilities are well developed in some countries within the region, often associated with private institutions, governmental laboratories and Universities. Pesticide analysis is relatively well developed, however as PCBs, PAHs are considered priorities, countries should promote the development of such analytical methodologies in order to assess the actual status of pollution with these PTS in their countries.

As a Regional priority, the identification and remediation and stockpiled waste PTS compounds is considered important as current information is difficult to obtain and often incomplete.

Most of the countries do not have yet sufficient resources for an adequate implementation of international standards for PTS control and management. In this context, regional co-operation should be strengthened for the development of national plans for the management of PTS.

6.2 RECOMMENDATION FOR FUTURE ACTIVITIES

6.2.1 Sources Characterisation

Procedures for source apportionment of contaminants and improved quantification of emissions need to be further developed to better identify the magnitude and relative contribution over time from natural and anthropogenic sources. Practically no work has been done on source characterization of PTS in the region. Biomass combustion could be an important source of PTS and should be evaluated. Dissemination of information gathered by public institutions should be made accessible to citizens and interested parties.

6.2.1 Environmental Levels, Toxicological And Ecotoxicological Characterisation

Cooperation among the countries should be strengthened in order to improve the analytical capabilities and to implement a Quality Control /Quality Assurance System. These programs should include inter-laboratory comparison, storage and archiving of samples, handling, reporting and analysis of data. More advanced countries must share their experience, mistakes and lessons learned from PTS studies.

There is a need to reinforce the national monitoring programs, create a network at a regional level and promote awareness of these issues within government and the general public, principally in those countries where no data exist.

There is a need to develop at a Regional level, a common monitoring program based on evaluative model applications and systematic sampling campaigns in both remote and contaminated areas. It is essential to establish baseline spatial and temporal trends. For example, 'Fish Watch' project proposed by this report (in addition to the Mussel Watch) will be a unique opportunity to have comparable data sets. The use of retrospective techniques (soil, sediment and ice-core studies, analysis of specimen bank samples) and the development of epidemiological studies should be promoted because the history of pollution and their effects on human and ecosystem health are poorly understood. In this way, methodologies for evaluating long term effects in human and ecosystems health due to exposure to PTS could be developed. These will fill very important dat gaps because throughout the Region, studies on these topics do not exist. These actions should be directed to reinforce the monitoring networks existing at the national level, transferring such expertise through cooperation programs to those countries with less experience. Support from international organizations is needed to create and sustain such a Regional network for long term research in ecotoxicology of PTS substances.

6.2.2 Major Pathways Of Contaminant Transport

The South American region holds one of the most important reservoirs of freshwater throughout the world. Many large important densely populated cities are served by these rivers and lakes, and these act as important pathways of transboundary transport. The potential for movement of contaminants via this pathway should be addressed.

PTS pollution in remote areas within the region with different climatic and ecosystem conditions, should also be also be addressed and quantified. Spatial analysis of PTS along gradients of environmental conditions (i.e. climatic, latitudinal, altitudinal) could help to understand the relative importance of different transport pathways.

Development of multimedia mass balance models to predict the environmental fate and transport of PTS substances within the region should be developed and applied.

6.2.3 Regional Capacity And Needs To Manage PTS

The region should take all necessary steps to ensure their domestic responsibilities and adequate arrangements are in place to reduce contaminant inputs, recycling and outputs within the frame of the Stockholm convention but also of other international regulating bodies (Basel convention). If these responsibilities and arrangements are not properly addressed, actions recommended to reduce environmental levels and the associated human and ecosystem risks, will not be effective.

In this context, clean up of contaminated sites (hot spots) should be given high priority in order to minimize the negative environmental effects of this potential PTS source.

Finally, regional co-operation should be strengthened for the development of national plans for the management of PTS. Integration of physical and biological models with environmental measurements and information on sources and pathways should be strengthened to aid the design and implementation of effective monitoring, research projects and chemical management, including remediation. Regional co-operation may successfully stimulate the production and dissemination of technical and scientific knowledge, and also expand and sustain regional environmental assessment capacities. Such assessment work will be instrumental as a basis for prioritizing issues and formulating joint policies.

ANNEX I: LIST OF ABBREVIATIONS

The following abbreviations may be found in this Regional Report without definition. ANDE: National Energy Administration **BCF: Bioconcentration Factor** CENMA: National center for the Environment CEPIS-OPS: Centro Panamericano de Ingenieria Sanitaria y Ambiental-Organización Panamericana de la Salud. CETESB: Companhia de Tecnologia e Saneamento Basico de Sao Paulo CONAMA: Comisión Nacional del Medio Ambiente (National Comisión on the Environment) DDT: Dichlorodiphenyltrichloroethane DINAMA: Dirección Nacional de Medio Ambiente EMRL : Environmental Maximum Residue Level EPA: United States Environmental Protection Agency FAO: Food and Agriculture Organization FAO/WHO: Food Standards Programme refers GDP: gross domestic product **GEF:** Global Environment Facility HCH: Hexachlorocyclohexanes HCB: Hexachlorobenzene IARC: International Agency for Cancer Research **IBAMA** Brazilian Environmental Protection Agency INA: Center of Water Technology INC: Intergovernmental Negotiating Committee ISP: National Institute of Health (Chile) INTI: National Institute of Industrial Technology Kow. Octanol Water Partitioning coefficient Koc Octanol Carbon Partitining coeficcient LRT Long Range Transport LATU. Laboratorio Tecnológico del Uruguay LC₅₀ Lethal Cooncentration 50 MGAP: Livestock and Agriculture Ministry MDIC: Ministério do Desenvolvimento da Indústria e Comércio NGOs Non Gobernemental Organizations NOEL Non observed effect Level PCP: Pentachlorophenol PCDDs: Polychlorinated dibenzo-p-dioxins PCDF: Polychlorinated dibenzofuransUNEP POPs: Persistent organic pollutants PTS: Persistent Toxic Substances PCBs: Polychlorinated biphenyls

PAHs: Polycyclic Aromatic Hydrocarbons RAPAL: Pesticides and Alternatives for Latin America SENASA: Servicio Nacional de Sanidad y Calidad Agroalimentaria (National Service of Agricultural Quality) SAG: Agricultural and Livestock Service (Chile) TEQ Toxicity equivalent UTE : National electrical company (Uruguay) USEPA US Environmental Protection Agency UNECE United Nations UNICAMP University of Campinas Brazil WHO World Health Organization UNPD: United Nations Program Development Program

ANNEX II: LIST OF PARTICIPANTS

Leiva Devia INTI. Subregional Basilea ARGENTINA <u>luniere@inti.gov.ar</u>

Adriana Corres Secretaría de Ambiente y Desarrollo Sustentable. Dirección Nacional de Gestión Ambiental ARGENTINA <u>acorres@medioambiente.gov.ar</u>

Issaly Pablo sergio Secretaría ambiente y desarrollo sustentable ARGENTINA <u>pissalj@medioambiente.gov.ar</u>

Appleyard Jorge Tomás Ministerio de Relaciones Exteriores. Dirección General de Asuntos Medioambientales ARGENTINA <u>axj@nrecic.gov.ar</u>

Dra Edda Villamil Lepori Cátedra de Toxicología y Qca Legal Facultad de farmacia y Bioquímica Universidad de Buenos Aires ARGENTINA <u>evillaam@ffyb.uba.ar</u>

Dr. Juan Carlos Colombo Universidad de la Plata Laboratorio de Química Ambiental La Plata ARGENTINA <u>laqab@arnet.com.ar</u>

Dr. Jose Luis Esteves Conicet Puerto Madryn ARGENTINA <u>esteves@cenpat.edu.ar</u>

Tania SantivañezUniversidad de Nuetra Señora de la PazBOLIVIATsantiva@ceibo.entelnet.bo

Maria Galarza Coca Ministerio de desarrollo sostenible y planificación. Viceministerio del medio ambiente, recursos naturales y desarrollo forestal BOLIVIA mgalarza coca@hotmail.com Guido Condardo aguilar Ministerio de salud y previsión social. La paz BOLIVIA casoage@ceibo.entelnet.bo Maria Galarza Ministerio de Desarrollo Sostenible v Planificación BOLIVIA mgalarza coca@hotmail.com Guido Condarco

Instituto Nacional de Salud Ocupacional La Paz BOLIVIA <u>casoaga@ceibo.entelnet.bo</u>

Jeannette Estrada Belmonte Dirección General de Salud Ambiental La Paz BOLIVIA <u>estrjean@yahoo.com</u>

Tania Santiváñez Universidad Nuestra Señora de la Paz BOLIVIA <u>tsantiva@ceibo.entelnet.bo</u>

Tania Santiváñez Universidad Nuestra Señora de la Paz BOLIVIA <u>tsantiva@ceibo.entelnet.bo</u>

Prof. Dr. Wilson Jardim Universidad de Campinas Campinas BRAZIL <u>wfjardim@iqm.unicamp.br</u> Mirtes Suda ABIQUIM BRAZIL <u>mirtes@abiquim.org.br</u>

Marcia Bissinoti University of Campinas Campinas BRAZIL <u>bisinoti@iqm.unicamp.br</u>

Nilda A.C.G. de Fernicola CETESBI, Sao Paulo BRAZIL <u>nilda@cetesb.sp.gov.br</u>

Heloisa de Toledo Instituto Adolfo Lutz SP. BRAZIL <u>hetoledo@hotmail.com</u>

Fernanda Vasconcelos University of Campinas Campinas BRAZIL <u>falmeida@iqm.uniamp.br</u>

Antonio Carneiro Barbosa IBAMA, Brasilia BRAZIL <u>bantonio@sede.ibama.gov.br</u>

Joao Paulo Machado Torres Universidad Federal do Rio de Janeiro BRAZIL jptorres@biof.ufrj.br

Siomara Regina Jacobucci Environmental Health UNICAMP, Campinas BRAZIL <u>siomaraj@fcm.unicamp.br</u>

Dr. Angelo Trapé Area de Saude Ambiental FCM Campinas BRAZIL <u>aztrape@fcm.unicamp.br</u> Cacilda Jiunko Aiba CETES B Sao Paulo BRAZIL <u>cacildaj@cetesb.ap.gov.br</u>

Ricardo Barra University of Concepción Concepción CHILE <u>ricbarra@udec.cl</u>

Gonzalo Mendoza University of Concepción Concepción CHILE <u>rmendoza@udec.cl</u>

Bárbara Inzunza University of Concepción Concepción CHILE binzunza@udec.cl

Roberto Quiroz University of Concepción Concepción CHILE <u>robquiro@udec.cl</u>

Claudia Suarez University of Concepción Concepción CHILE <u>clsuarez@udec.cl</u>

Dr.Claudio Zaror Chemical Engineering Department University of Concepción CHILE <u>czaror@diq.udec.cl</u>

Dr. Rodrigo Romero Private Consultant Santiago CHILE <u>rromerom@entelchile.net</u>

Pamela Santibañ	ez Valverde		
Ministry of Healt	h	Carola Resabala	L
Santiago		ICQ-ESPOL	
CHILE	Spamela@netchile.cl	Guayaquil	
		ECUADOR	cresabol@goliaf.espol.edu.ec
Felipe Leiva Sala	izar		
National Comisio	on on the Environment (CONAMA)	María de Lourde	es Maya
Santiago		SGAC	
CHILE	Fleiva@conama.cl	Guayaquil.	
		ECUADOR	mariadelourdes@hotmail.com
Mariano Galdam	ez		
National Comisio	on on the Environment (CONAMA)	Eduardo Espin	
Santiago		Ministerio ambi	ente ecuador.
CHILE	mgaldames@conama.cl	Subsecretaria ca	lidad ambiental
		Quito	
Claudia Paratori		ECUADOR	eespin@ambiente.gov.ec
National Comisio	on on the Environment (CONAMA)		
Santiago		Carola Resabala	L
CHILE	cparatori@conama.cl	ESPOL	
		Guayaquil	
Iván Triviño		ECUADOR	cresabal@goliat.espol.edu.ec
Instituto de Saluc	l Pública de Chile		
Santiago		Dra Beatriz Var	gas
CHILE	itrivino@ISPCH.cl	Instituto Nacion	al de Higiene
		Quito	
Dra Lucia Molin	a	ECUADOR	inh@andinanet.net
Depto Salud Ocu	pacional		
Instituto de Saluc	l Pública	Gloria León	
Santiago		SEAM, Asunció	on
CHILE	lmolina@ispch.cl	PARAGUAY	gloriabeatrizleon@yahoo.es
Dr. Andrei Tchei	nitchin	Guillermo Ase I	Pineda
ICBM		SEAM.CONAM	1
Facultad de Med	icina	PARAGUAY	camells06@yahoo.es
Universidad de C	Chile		
Santiago		Dr. Nadia Gamb	Doa
CHILE	atcherni@machi.med.uchile.cl	PUCP	
		Lima	
Isabel Guerrero		PERÚ	ngamboa@pucp.edu.pe
Depto Laboratori	os del Ambiente		
Instituto de Saluc	l Pública		
Santiago, CHILE	iguerrero@ispch.cl		

		Dra Cristina Alonzo)			
Cesar Cervantes Galvez		Departamento de Salud Ambiental				
Consejo Nacion	nal del Ambiente. CONAM	Y Seguridad Quími	ca			
PERÚ <u>ccervantes@conam.gob.pe</u>		Ministerio de Salud	Pública			
		Montevideo				
Elsa carbonell	torres	URUGUAY	aloncris@adinet.com.uy			
SENASA						
PERU	ecarbonell@senasa.gob.com	Gabriela Eguren				
		University of La Re	publica			
Ana María Gor	nzález del Valle	Montevideo				
DIGESA		URUGUAY	geguren@fcien.edu.uy			
Lima,						
PERU	agonzale@digesa.sld.pe	Marcelo Bonilla				
		MGAP/DGSA				
Dra. Carmen C	astañaga	URUGUAY	amboni@adinet.com.uy			
DIGESA-MIN	SA					
Lima		Silvia Aguinaga				
PERU	cgastana@digesa.sld.pe	Ministerio de vivier ambiente	nda, ordenamiento territorial y medio			
Dr Heidelore F	iedler	URUGUAY	saguinaga@adinet.com.uy			
UNEP Chemica	als					
Geneva		Isabel Dol				
SWITZERLAN	ND <u>hfiedler@unep.ch</u>	Ministerio de salud	pública			
		URUGUAY	isabeldol@msp.gub.uy			

DATA CONTRIBUTORS AND ASSISTANTS

The Regional Team acknowledge the help and enthusiasm of the following people

Argentina	
Lic. Constanza Bisogno	Peru
Lic. Andrea Barreda	Ing Delia Romero
Lic. Natalia Cappelletti	Lic Karina Ayala
Ing. Patricia Landoni	Ecuador
Lic. Carolina Migoya	Carola Resabala
Brazil	Maria de Lourdes Maya
Fernanda Vasconcelos de Almeida	Mariano Montaño
Marcia Cristina Bisinoti	Uruguay
João Paulo Machado Torres	Lucía Boccardi,
Chile	Leonidas Carrasco,
Gonzalo Mendoza	Esteban Charbonier,
Bárbara Inzunza	Franco Teixeira de Melo

ANNEX III: RANKING OF PRIORITIES

Chemical	Arg	Bol	Bra	Ch	EC	Par	Peru	Uru	Region
Dieldrin, Aldrin & Endrin	1/1	1/1	1/2	1/1	1/1	0/1	1/1	0/1	1/1
Chlordane	1/1	1/1	1/1	1/1	1/2	0/1	1/1	0/0	1/1
Heptachlor	1/2	1/1	1/1	1/1	1/1	0/1	1/1	0/0	1/1
DDT	2/1	1/1	2/1	1/1	2/1	1/2	1/1	0/1	1/1
Toxaphene	1/2	1/1	0/2	0/1	1/2	0/1	1/1	0/0	1/1
Mirex	1/1	1/1	0/1	0/1	1/2	0/1	1/1	1/1	1/1
НСВ	1/1	1/1	1/1	1/1	1/2	0/1	1/1	0/0	1/1
PCBs	2/2	1/1	2/1	2/2	2/2	2/2	1/1	2/2	2/2
Dioxins & Furans	1/2	1/1	1/2	1/2	2/2	2/2	1/1	2/2	1/2
НСН	2/1	1/1	1/1	1/1	2/1	1/2	1/1	1/2	1/1
Endosulfan	1/1	1/1	1/1	1/1	2/1	1/1	1/1	1/1	1/1
РСР	1/1	1/1	1/2	1/2	2/2	1/1	1/1	2/2	1/2
PAHs	2/1	1/1	2/1	2/2	2/2	2/2	1/1	2/2	2/2
Org. Tin Compds.	1/2	1/1		1/1	1/2	1/2	1/1	1/1	1/1
Org. Mercury Compds.	1/2	1/1		1/1	1/1	1/1	1/1	0/2	1/1

REGIONAL SUMMARY OF PRIORITIES (Source: Viña del Mar RPSM, August 2002, Chile)

First number for Sources

0: No concern

1:Local Concern

2: Regional Concern

Second number for Data Gaps

0: Information available

1: Little information available

2: No available information

It is important to note that this is absolutely qualitative rank and their construction was widely discussed in the technical workshops and priority setting meetings. According to this chemicals of priorities for the region XI are: PCBs and PAHs, followed by Dioxins and Furans and pesticides Endosulfan, PCP and DDTs.

A) Scoring for Sources and environmental levels, Campinas Meeting, Brazil

SCORING FOR PRIORITISING PTS FOR SOURCES AND ENVIRONMENTAL LEVELS

Table 1. Scoring for Prioritising PTS for Sources

Chemical	Sources ^a	Data Gaps ^b	Comments
Aldrin	1	2	It is not made and is forbidden in all countries within the region. Amounts used are unknown
Chlordane	1	2	
DDT	2	2	Some use for health reasons, illegal circulation of the products within the region. Other pesticides could act as new sources (i.e. dicofol) but this is unknown
Dieldrin	1	2	
Endrin	1	2	
Heptachlor	1	2	
HCB*	2	2	Associated to emissions of plastic burning , there were mentioned correlations with dioxin emission (please add references)
Mirex	0	2	It is not used in most of the countries within the region
Toxaphene	0	2	Not recorded use within the region
PCBs	2	1	Disperse use within the region, scarce information about amounts, however countries are advancing in national inventories.
Dioxins*	2	2	All described sources exist within the region, one importan difference with other regions could be the biomass burning that should be an important source
Furans*	2	2	Idem
НСН	1	1	Still used in several countries, agricultural uses are restricted, but it is unknown HCH uses.
РСР	2	2	Saw wood
PAHs	2	1	Combustión widely distributed within the region
Endosulphan	1	1	Still used, but few data on amounts

*Assuming that combustion process is important and that emission factors used are correct

a: The number expresses the concern for sources (2:Regional concern 1: Local concern 0: No concern)

b: The number expresses the relative depth of data gaps (2: No data 1: Some data: 0 Enough data)

B) Scoring for Environmental Levels

Chemical	Environmental Levels ^a	Data gaps ^b
Dieldrin and Aldrin	1	1
Endrin	1	1
Chlordane	1	1
Heptachlor	1	1
DDT	1	0
Toxaphene	0	2
Mirex	0	1
Hexachlorobenzene	1	1
PCBs	2	1
Dioxins and Furans	1	2
НСН	1	0
Endosulfan	1	1
РСР	1	1
PAHs	2	1
Org. Mercury Compds.	1	1
Org. Tin Compds	0	2

a: The number expresses the concern for environmental levels (2:Regional concern 1: Local concern 0: No concern)

b: The number expresses the relative depth of data gaps (2: No data 1: Some data: 0 Enough data)

C) Scoring for effects

Compound	Effects/human levels Concern/data gaps
PCBs	2/2
Dioxins	1/2
Furans	1/2
РСР	1/2
Aldrin	1/2
Endrin	1/2
Dieldrin	1/2
Heptachlor	1/1
НСН	1/1

DDT	2/1
Endosulfan	1/2
НСВ	1/1
Toxaphene	-
Chlordane	-
PAHs	2/2
Organo tin	1/1
Hg-Organic	1/1

a: the first term express the concern (2:Regional concern 1: Local concern 0: No concern)b: the term express the data gaps (2: No data 1: Some data: 0 Enough info) -: no info

ANNEX IV: CASE STUDY: PTS IN THE RIO DE LA PLATA ESTUARY

System characteristics

The Río de la Plata is a funnel-shaped coastal-plain estuary 300 km long, 30 to 220 km wide and 0.5-25 m deep with a total surface area of 30.000 km². Its drains more than 3 millions km² in tropical and temperate rainy areas of Brazil, Argentina, Paraguay, Bolivia and Uruguay and transports 500-880 km³ fresh water and 90 millions tons of suspended solids per year. In spite of the huge dimensions and dilution capacity of the estuary, the large urban-industrial zone developed in the first 100 km of the Argentinean coast produced a severe impact in the coastal area. Large amounts of polluted waters and toxic materials are discharged daily to the estuary via small tributaries, which act as open sewers, or directly as untreated effluents. This heavy load is clearly reflected by the abundance of PTS in waters, sediments and biota.



Figure 1 Hydrographic basin and detailed view of the Río de la Plata. Note the high solid charge (source: American Association for the Advancement of Science).

PTS in waters

The discharge of effluents and polluted tributaries (e.g. Reconquista, Riachuelo, Río Santiago) result in high PTS levels on the Argentine coast. PCB concentrations in upper RLP coastal waters range from non-detected to 6-40 ng/l, often exceeding the 14 ng/l USEPA guideline. Decreasing patterns are observed from polluted rivers to offshore stations, e.g. 20-56 to 1.6-9 ng/l of PCBs (Colombo *et al.*, 1990). High PCB levels are also

registered at Buenos Aires sewer, 50 ng/l total (dissolved + particulate; Colombo, 2001a). Chlorinated pesticides also show high levels along the coast, i.e. gHCH: 20-61 to 0.9 ng/l offshore; DDTs: 5-9 to 2 ng/l (Colombo et al., 1990). Polluted effluents show extreme PTS values, i.e. 520 to 4900 ng/l of gHCH in the Buenos Aires sewer area and Reconquista river, respectively (Janiot *et al.*, 1991; Rovedatti *et al.*, 2001). Reported HCH concentrations are lower on the Uruguayan side, (3-45 ng/l), but also show an urban pattern of highest levels close to Colonia (Moyano, 1992). The coastal contamination pattern is also reflected by hydrocarbons which are introduced by effluents, sewers, ship transit and chronic and accidental oil spills (Colombo, 2000a).

PTS in sediments

The finer nature (clay-silt) and close proximity to major sources, makes Argentine RLP sediments important PTS reservoirs (Colombo et al., 1990, 1995, 2001a). Average PCB concentrations in the top 2.5 cm decrease from Buenos Aires-La Plata area ($12\pm17 \ \mu g/kg$) to the southern sector ($2.7\pm5 \ \mu g/kg$) and with distance to the coast ($2.0\pm2.1 \ \mu g/kg$; Figure 2). Muddy Samborombon sediments are the ultimate deposit of turbidity maximum transported PTS. These PCB averages are lower than Canadian sediment quality guidelines ($34.1\mu g/kg$). However, higher levels have been registered in polluted tributaries and in sewage and industrially affected RLP sediments (20-90 to 998-1085 $\mu g/kg$; Colombo et al., 1990; AA-AGOSBA-ILPLA-SHN, 1997).



Recent data from three sampling campaigns (Colombo, 2002 unpublished) of beach and coastal sediments along the Argentine coast confirms the higher PTS levels in sandy-silts affected by sewage and industrial effluents close to Buenos Aires and decreasing seaward values (i.e. PCBs 15 ± 21 to $1.1\pm1.1 \ \mu g/kg$; chlordane 1.1 ± 1.2 to $0.1\pm0.2 \ \mu g/kg$ and DDTs 1.4 ± 1.3 to $0.1\pm0.1 \ \mu g/kg$ dry weight). PAHs also decrease more than 1 order of magnitude seaward (Figure 2). As observed for PCBs, maximum chlordane (4-1917 $\mu g/kg$), DDTs (4-263 $\mu g/kg$) and HCH levels (0.4-27 $\mu g/kg$) have been registered in polluted tributaries (AA-AGOSBA-ILPLA-SHN, 1997).

Figure 2 PTS in Río de la Plata coastal sediments. Stations are San Isidro: SI, Reserva Ecológica: RE, Dominico: DO, Bernal: BN, Quilmes: QU, Sewer: SW, Berazategui: BG, Hudson: HU, Punta Lara: PL, P.Blanco: PB, La Balandra: LB, Magdalena: MG, Punta Indio: PI, Punta Piedras: PP, Punta Rasa: PR. Sites at 2.5 km from the coast in black.

PAH concentrations in Río de la Plata sediments show high variability; i.e. 50-1500 μ g/kg in offshore sediments affected by ship transit and petrochemical inputs to 2500-555000 μ g/kg in heavily affected harbors areas and ports such as Buenos Aires, La Plata and Montevideo (Colombo *et al.*, 1989; Moyano *et al.*, 1993; Muniz *et al.*, 2002). The quantification of methylated and unsubstituted PAH indicated pyrogenic inputs predominating in offshore stations, petrogenic sources in ports, harbors and coastal areas, and detrital or diagenetically derived Perylene, in low-contaminated reducing sediments (Colombo *et al.*, 1989).

PTS in biota

The most conspicuous organisms in the upper freshwater RLP are bivalves (clams) and bottom dwelling fish which are generally fatty and thus efficient PTS accumulators.

In agreement with sediment patterns, Asiatic Clams (*Corbicula fluminea*), utilized as sentinel organism showed an order of magnitude decrease of PCBs in the seaward direction (Colombo et al., 1990, 1995, 1997; Figure 3). Fresh weight PCB levels were below the 2 mg/kg action level for human consumption $(0.3\pm0.1 \text{ to } 0.04\pm0.05 \text{ mg/kg})$. However, on a regional scale, these are one of the most contaminated bivalves in South America (see Chapter 3). PCB composition in clams showed a marked abundance of PCBs with 4-6 chlorines (Aroclor 1254) with reduced abundance of \geq 7 Cl congeners. In decreasing abundance followed chlordane, DDTs and HCHs.



Figure 3 PCB concentrations in clams from the Argentinean coast. Acronyms as in figure 2.

A study of the long-term accumulation of PCBs and PCDD/F in clams of increasing size, indicated steady-state or depuration for tri-tetra PCBs with $logk_{ow} < 6$, and preferential uptake of penta-hexa PCBs (Figure 4). The selective bioaccumulation of tetra/hexa PCDDs and planar PCBs 77 and 126, and mono-ortho substituted 118, explained 95% of the TEQ increase from 10 to 35 mm clams, i.e. 7.1-13 pg/g ww for a 4-year growth period (Colombo et al., 1997).



Figure 4 Variation of PCBs and PCDD/F in Asiatic Clams of increasing size (4-year growth).

Owing to their feeding specialization as sedimentary-organic matter consumers, PTS bioaccumulation is more pronounced in the Sábalo (*Prochilodus lineatus*). The study of Sabalos collected along 1500 km on the Paraná river and the Rio de la Plata (Colombo et al., 1990, 2000, 2001b) showed consistent spatial patterns with those of clams and sediments (Figure 5). Fresh weight PCB concentrations are highest in the Río de la Plata close to Buenos Aires sewer and industrial area, and decrease in the Upper Paraná and Iguazú. The highest value (mean= 3.8±2.0 mg/kg, n=17) exceeds the 2 ppm consumption guideline. Low PCB levels in supermarket fish indicate that they come from the upper Paraná. Seaward in the Samborombon Bay, White Croakers still show prevailing PCB residues, but with significantly lower levels, i.e. 0.02-0.4 mg/kg ww (Lanfranchi et al., 1998).

PCB traces in RLP fish were dominated by congeners with 4-7 chlorines, similar to an Aroclor 1254-1260 3:2 mixture. Dioxin based toxicity equivalents in contaminated Sabalos ranged from 39 to 50 pg/g fresh weight and allowable consumption rates calculated from EPA dose factors and PCB cancer slope factors were as low as 0.5-1 g fish/day for a 70 kg person. A clear hazard ranking was indicated by tissue levels and the compound individual toxicities: PCBs > PCDD/F > chlordane > heptachlor epoxide > DDTs >> lindane (Colombo *et al.*, 2000b).



Figure 5 PTS in fish collected along the Paraná, Río de la Plata and markets (H1,2,3). Paraná stations are Iguazu: IG; Ituzaingo: IT; Corrientes: CO; Empedrado: EM; Goya: GO; Esquina: ES; La Paz: PZ; Paraná: PA; Rosario: RO; San Nicolás: SN, Tigre: TI. Río de la Plata acronyms as in figure 2 plus Buenos Aires: BA and Pearson: PE. The error bar is for PCBs. The 2 ppm guideline is indicated in red.

The comparison of PCBs/DDTs ratios in RLP sediments, clams and fish with Samborombon White Croaker (Lanfranchi et al. 1998) and values from Argentine shelf cetaceans (chapter 3), illustrate the decreasing terrestrial influence of Río de la Plata PCB inputs (Figure 6). Ratios decrease an order of magnitude from RLP (12-18) to cetaceans (1.2-1.4), indicating more equilibrated background industrial and agricultural inputs in these coastal-pelagic species.



Figure 6 PCBs/DDTs ratios in RLP sediments and biota compared with pelagic cetaceans.

Level 1 Fugacity model for PCBs in the Río de la Plata

In order to estimate the amounts of PCBs discharged in the Río de la Plata accounting for the observed PCB concentrations, a Level I Fugacity model exercise was performed (see Chapter 4). The model predicts the equilibrium concentrations in the environmental compartments based on the chemical properties (e.g. water solubility, octanol-water partition coefficient, vapor pressure or Henry law constant) and the environmental characteristics, namely volume and density of the phases and organic contents of suspended particles and sediments and lipids of biota.

The coastal area of the Río de la Plata modeled comprise two sectors with an average depth of 3 m, the most contaminated area from Buenos Aires to La Plata city (BALP: 3 km offshore x 70 km = 210 km^2) and south to La Plata to Punta Piedras (LPPP: 3 km offshore x 100 km = 300 km^2). PCB inputs were considered to occur through direct effluent discharges to the coast (soil partition excluded). To estimate the potential discharge, PCB inputs were varied to reproduce the concentrations observed in sediments which are the major reservoir and whose levels are well characterized. Table 1 presents the parameters and results of the model.

Table 1 Parameters and results of a Level 1 Fugacity model for Río de la Plata coasta	l area.
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Physico- Chemical		Phase	Density	Volume (m ³)		% OM-% Lipid		Observed PCB Conc (ng/m ³ -l-g)		Calculated Conc (ng/m ³ -l-g)		%Total
Properties Aroclor 1254		Properties	g/cm ³	BALP	LPPP	BALP	LPPP	BALP	LPPP	BALP	LPPP	
MW (g/mol)	327	Air	0.00119	2.1E+11	3E+11	-	-	1-3	1-3	2.8	0.7	0.3-0.4
S (mol/m3)	1.22E-04	Water	1.0	6.3E+08	9E+08	-	-	2±2	0.8±0.5	0.6	0.2	0.2
H (Pa.m3/mol)	12.2	SPM	2.4	24150	104625	17	16	99±88	30±35	158	36	5.5-15
Log Kow:	6.60	Sediments	2.4	5250000	7500000	2	2	12±17	2.5±5.0	12	2.7	84-93
		Fish	1.2	525	750	60	13	6050±2940	620±340	1355	72	0.1-0.5
								Equilibrium i	nput (kg)	165	58	

Overall, the results indicate that PCB levels in abiotic coastal phases, which contain > 95% of the total load, are in equilibrium with an input of 220 kg PCB. Levels in biota are consistently sub-estimated, possibly reflecting the effect of trophic biomagnification of PCBs in detritivorous fish. The equilibrium inputs calculated correspond to the net amount retained in the system, i.e. transport processes are not included in this Level 1 model. Thus the total amount discharged must be larger to account for the particle-bound PCB transport throughout the estuary. Sediment levels in the 3-8 km offshore area (mean: 2.0 ± 2.1 ng/g) and Samborombon Bay (6.7 ± 9.8 ng/g) suggest an additional PCB stock of 145 and 500 kg, respectively. Thus, according to these estimates, RLP coastal sediments contain about 900 kg PCBs, plus an unknown amount retained on the Uruguayan side and a residual exported to Brazil and Argentina continental shelf.

Concluding remarks

In spite of the huge dimensions and carrying capacity of the Río de la Plata, the extended discharges of crude urban and industrial effluents produced a serious impact on the coastal area. Muddy sediments from the Argentine shore are the ultimate sink of this high load of organic matter and associated PTS. In accord with the system characteristic of high solid abundance, detritivorous organisms are dominant and diversified. Clams and specially iliophagous (mud consumers) fish are efficient PTS accumulators and a critical contamination pathways for humans. Calculated allowable consumption rates in this fish were as low as 0.5-1 g/day with PCBs as the most hazardous PTS followed by PCDD/F, chlordane, heptachlor epoxide, DDTs and lindane. A continued effort is required to assess the potential effects of PTS on the human population and on the rich biological resources of the estuary and adjacent continental shelf.

REFERENCES

- AA-AGOSBA-ILPLA-SHN, 1997. Calidad de Aguas de la Franja Costera Sur del Río de la Plata. (San Fernando-Magdalena). 157 p.
- CARP-SIHN-SOHMA, 1989. Estudio para la evaluación de la contaminación en el Río de la Plata. Informe de avance, 422 p.
- Colombo, J.C., Pelletier, E., Brochu, C., and Khalil, M. 1989. Determination of hydrocarbon sources using nalkane and poliaromatic hydrocarbon distribution index. Case study: Rio de La Plata Estuary, Argentina. Environmental Science & Technology **23**: 888-894.
- Colombo, J.C., Khalil, M.F., Arnac, M., Horth, A., and Catoggio, J.A. 1990. Distribution of chlorinated pesticides and individual polychlorinated biphenyls in biotic and abiotic compartments of the Rio de La Plata. Environmental Science & Technology **24**: 498-505.
- Colombo, J.C., Bilos, C., Campanaro, M., Rodríguez Presa, M.J., and Catoggio, J.A. 1995. Biaccumulation of polychlorinated biphenyls by the Asiatic Clam Corbicula fluminea: its use as sentinel organism in the Rio de la Plata Estuary, Argentina. Environmental Science & Technology 29: 914-927.
- Colombo, J.C., Brochu, C., Bilos, C., Landoni, P. and Moore, S. 1997. Long-term accumulation of individual PCBs, dioxins, furans and trace metals in Asiatic Clams from the Río de la Plata Estuary, Argentina. Environmental Science & Technology, **31** : 3551-3557.

- Colombo, J.C. 2000a. Biogeochemical assessment of the 1999 Río de la Plata oil spill. 7th Latin-American Congress on Organic Geochemistry. Brasil, 22-26 de Octubre, p. 257-259.
- Colombo, J.C., Bilos, C., Remes Lenicov, M., Colautti, D., Landoni, P. and Brochu, C. 2000b. Detritivorous fish contamination in the Río de la Plata estuary. A critical accumulation pathway in the cycle of anthropogenic compounds. Canadian Journal of Fisheries & Aquatic Sciences, **57**: 1139-1150.
- Colombo, J.C. 2001a. Aspectos biogeoquímicos del impacto del emisario cloacal en el ecosistema costero del Río de la Plata. Technical Report. Municipalidad de Berazategui, 29 p.
- Colombo, J.C., Migoya, M.C., Landoni, P. and Barreda, A., 2001b. COPs en Argentina: perspectiva ambiental indicada por Sábalos del Paraná y Río de la Plata. 4ta Reunión Anual de SETAC Latinoamérica, Buenos Aires 22-25 de Octubre.
- Esteves, J.L., Ciocco, N.F., Colombo, J.C., Freije, M., Harris, G., Iribarne, O., Isla, I., Nabel, P., Pascual, M.S., Penchaszadeh, P.E., Rivas, A.L. y Santinelli, N. 2000. The Argentine Sea: The Southeast South American Shelf Marine Ecosystem, "Seas at the Millennium: An Environmental Evaluation" Volume I, Chapter 48. Europe, The Americas and West Africa. Ed. C. Sheppard, 749-771. Pergamon, Elsevier Science (Amsterdam).
- Janiot, L.J., Orlando, A.M., and Roses, E. 1991. Niveles de Plaguicidas Clorados en el Río de La Plata. Acta Farmacéutica Bonaerense 10: 15-23.
- Lanfranchi, A.L., Moreno, J.E.A., Moreno, V., Metcalfe, T., and Menone, M.L. 1998. Distribution of organochlorine compounds in tissues of Croaker (Micopogonias furnieri) from Samborombón Bay, Argentina. Environmental Science 6: 055-067.
- Moyano, M. 1992. Residuos de pesticides en ríos y mares. In: Plaguicidas agrícolas y su impacto ambiental. Ed. Fundación P. Vazquez y Vega, p 53-62.
- Moyano, M., Moresco, H., Blanco, J., Rosadilla, M. And Caballero, A. 1993. Baseline studies of coastal pollution by heavy metals, oil and PAH in Montevideo. Marine Pollution Bulletin, 26: 461-464.
- Muniz, P., Venturini, N. and Martinez, A. 2002. Physico-chemical characteristics and pollutants of the benthic environment in the Montevideo coastal zone, Uruguay. Marine Pollution Bulletin 44: 962-968.
- Rovedatti, M.G., Castañe, P.M., Topalian, M.L., and Salibian, A. 2001. Monitoring of Organochlorine and Organophosphorus Pesticides in the water of the Reconquista River (Buenos Aires, Argentina). Water Research 35: 3457-3461.

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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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