GLOBAL MONITORING PLAN FOR PERSISTENT ORGANIC POLLUTANTS

UNDER THE STOCKHOLM CONVENTION ARTICLE 16 ON EFFECTIVENESS EVALUATION

FIRST REGIONAL MONITORING REPORT

LATIN AMERICA AND THE CARIBBEAN REGION



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PREFACE

Persistent organic pollutants (POPs) are a group of chemicals that are widely used in agricultural and industrial practices, as well as unintentionally released from many anthropogenic activities around the globe. POPs are characterized by *persistence* – the ability to resist degradation in various media (air, water, sediments, and organisms) for months and even decades; bioaccumulation - the ability to accumulate in living tissues at levels higher than those in the surrounding environment; and *potential for long range transport* – the potential to travel great distances from the source of release through various media (air, water, and migratory species). Specific health effects of POPs can include cancer, allergies and hypersensitivity, damage to the central and peripheral nervous systems, reproductive disorders, and disruption of the immune system. Some POPs are also considered to be endocrine disrupters, which, by altering the hormonal system, can damage the reproductive and immune systems of exposed individuals as well as their offspring. The ability of these toxic compounds to transport to isolated areas of the globe, such as the Arctic, and bioaccumulate in food webs has raised concerns for the health of humans and the environment, particularly for indigenous people that rely on traditional diets of aquatic mammals and fish. The transboundary movement of the compounds and the international scope of their manufacture, use and unintentional releases, and the long distances to impacted populations have led to the adoption of the Stockholm Convention on Persistent Organic Pollutants (the Convention) in May 2001 to "protect human health and the environment from persistent organic pollutants by reducing or eliminating releases to the environment". Substances presently being addressed under the Convention are aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, PCBs PCDDs/PCDFs and toxaphene. The Convention includes a procedure to add further substances to it.

The Convention calls for the reduction or elimination of releases of persistent organic pollutants, which should translate into reduced environment levels over time. Article 16 of the Stockholm Convention stipulates that the Conference of the Parties shall evaluate the effectiveness of the Convention four years after its date of entry into force. The effectiveness of the Convention shall be evaluated on the basis of available scientific, environmental, technical and economic information, including:

- Reports on monitoring of environmental levels
- National reports submitted pursuant to Article 15
- Non-compliance information provided pursuant to Article 17

An important component of effectiveness evaluation is the development of a global monitoring plan providing a harmonized organizational framework for the collection of comparable monitoring data or information on the presence of the persistent organic pollutants from all regions, in order to identify changes in levels over time, as well as to provide information on their regional and global environmental transport. The first report for the effectiveness evaluation will be presented at the fourth meeting of the Conference of the Parties in May 2009 and will serve as baseline for further evaluations.

The global monitoring plan is being implemented in all five United Nations Regions. This regional monitoring report is describing the findings in the GRULAC Region.

EXECUTIVE SUMMARY

Decision SC-3/19 established a regional organization group, composed of six members for each of the five United Nations Regions to facilitate implementation of the global monitoring plan, and invited Parties to nominate members to those groups with expertise in monitoring and data evaluation The main objectives of the regional organization groups (ROG) were to define and implement the regional strategy for information gathering, including capacity building and establishment of strategic partnerships in order to fill the identified data gaps, and to prepare the regional monitoring report as contribution to the first effectiveness evaluation report, to be presented to the Conference of the Parties at its fourth meeting in May 2009.

A regional organization group was established in the GRULAC region to deliver the current report describing the successes of meeting the objectives above.

For the development of the regional report, three meetings were carried out by the ROG (Mexico City, Mexico; Geneva, Switzerland and San José, Costa Rica). For collecting available information on core matrices and other media, questionnaires were sent to focal points in all the GRULAC countries. Data coming from monitoring programmes were obtained from the GAPS and WHO Human milk survey, and specific national surveillance studies.

This document is the first report on POPs monitoring in the core matrices in the GRULAC region it includes the first compilation and data evaluation within the 1998-2008 period proposed by the Stockholm Convention Secretariat.

Overview of the region

The Latin America and the Caribbean Region (GRULAC) includes 33 countries, comprising a surface area greater than 20 million square kilometres (ENCARTA, 2002), contains four subregions – Andean, Caribbean, Mesoamerica and Southern Cone – each having special features and rich biodiversity. Most of the countries are parties of the Stockholm Convention and some are signatories; however, only 10 out 33 countries have completed their national implementation plans (Argentina, Barbados, Bolivia, Chile, Ecuador, Mexico, Panama, Peru, Saint Lucia, Uruguay), including emission inventories for dioxins and furans, PCBs inventories and legacy persistent organic pollutant pesticides stockpiles. The region faces many problems related to pollution including persistent organic pollutants. The rich biodiversity, extreme climatic conditions, and notable differences in socio-economic development in the region require that monitoring efforts have large spatial resolution.

Contributing/collaborating programmes

The programmes contributing data to the present report were the Global Air Monitoring Passive Sampling (GAPS) and the United Nations Environment Programme-WHO human milk survey. Additional information was provided by the respective countries through the regional organization group members, including relevant data and scientific reports. Those were used to

provide information from media other than core media and assess long-range transport. Emphasis was given to quality data that were comparable.

The GAPS programme used polyurethane foam (PUF) passive samplers and hydrophobic polyaromatic resin (XAD) samplers, which have varying deployment times and temporal resolution. PUF samplers were used more often in the region; however, XAD samplers were deployed together with PUF samplers in some sites allowing for comparison between the two sampling systems. The analyses were conducted by Environment Canada. The PUF samplers were analyzed for polychlorinated biphenyls (PCBs) and some chlorinated pesticides, and XAD samplers for chlorinated pesticides only.

The other programme contributing data to the present report is the WHO-human milk survey, a global monitoring programme for persistent organic pollutants in human milk. These samples were analyzed by a WHO reference laboratory in Freiburg, Germany for dioxins, furans, PCB's and selected pesticides. No other persistent organic pollutants monitoring programmes were identified within the GRULAC region.

Main findings

Baseline levels of persistent organic pollutants in air

The data available for baseline concentrations in air media come from the GAPS programme (2005-2006) and involved 8 of the 33 countries from the Region: Argentina, Bolivia, Brazil, Chile, Colombia, Costa Rica, Cuba and Mexico. The programme did not provide sufficient information to statistically describe POPs contamination throughout region.

Concentrations of pesticides are greater in rural/agricultural areas. Many pesticides analyzed did not show values above the detection limits and there was much variability in the data. A seasonal variation of PCBs was identified in a report from Mexico using active air sampling; as the study lasted two years, it was possible to retrieve a temporal trend for some POPs.

The GAPS Programme does not include data on dioxins and furans. However, high levels of dioxins and furans were, reported in an air study in Sao Paulo, Brazil, one of the largest urban settings in the region. Argentina, Brazil, Chile and Mexico are developing nationally funded projects for air monitoring of persistent organic pollutants, but the data are not yet available.

Baseline levels of persistent organic pollutants in human milk/blood

Low levels of dioxins and furans in Brazilian human milk were detected in the third round of the WHO human milk survey with an average of 4.07 pg/g (as WHO toxic equivalents), and 1.78pg/g fat of dioxin-like PCBs, and 16.2 pg/g fat for marker PCBs. The levels were some of the lowest concentrations reported in this round. The fourth round is still in progress and a wider participation is expected from countries of the region; however, the representativeness of such data is too limited to provide a good regional overview.

A human maternal blood study administrated by the North American Commission for Environmental Cooperation, (2005-2006), provided limited data for Mexico. While the data were

insufficient to define a baseline for the entire region, indications suggested levels of POPs were within anticipated levels with a few anomalies for DDT. The study emphasized the need for a sustainable, coordinated regional human monitoring programme.

Levels of persistent organic pollutants in other media

Various countries of the region reported information relative to the presence of persistent organic pollutants in media other than the core media. Information relative to soil and sediment was supplied by Antigua & Barbuda. Information on human adipose tissue was reported by Mexico. Brazil reported several studies relative to persistent organic pollutants in human media. Barbados reported the routine monitoring of groundwater. These reports provided little information indicating the measures taken to ensure data quality, thus reducing their value as reference data.

Long-range transport

There is some evidence in the scientific literature regarding the occurrence of long-range transport within the region. However, the absence of long-term regional monitoring programmes on persistent organic pollutants does not allow the region to investigate this issue.

Data gaps

There are significant data gaps, in particular to establish temporal trends of persistent organic pollutants in the core media. There is a need to expand the existing monitoring network, which should begin with regional efforts to promote regionally managed monitoring programmes. Monitoring capabilities exist in at least four countries within the region. The region, however needs to create sound scientific monitoring programmes using local resources, as all the existing programmes are supported by external funding, which limits their long term support and sustainability. The commitment of countries to sustain monitoring programmes should be based on their national interest in reducing the risk of exposure to these substances and on their willingness to establish a regional structure able to support monitoring programmes on a long-term basis.

More research is needed to assess the risks of exposure to persistent organic pollutants through atmospheric transport within the region's boundaries. The most important information gap in the region is the absence of continuous monitoring programmes and subsequent atmospheric modelling capacity that are limiting factors to establishing temporal and spatial trends.

Capacity building needs

Capacity building in areas such as the design and implementation of monitoring programmes, the need for highly trained experts in the analysis of persistent organic pollutants together with aid for improving laboratory facilities, would help to establish a solid programme within the region. Building these capabilities and stimulating synergies seem to be the way to proceed to create a sustainable monitoring programme.

Future monitoring programmes

Future regional effectiveness evaluations could benefit from on-going programmes; however a stronger commitment is needed from the region to build capacity, both for monitoring and analysis. The existing ROG group could play a key role in coordinating actions to allow the development of monitoring programmes that contribute to a regional network; however, provision of financial support should be envisaged.

Future monitoring of human milk and blood samples should consider the relationships between both kinds of measurements to understand better the exposure of vulnerable groups as indicators to protect future generations, as stated in the Millennium Development Goals and the Stockholm Convention.

Conclusions and recommendations

The currently available monitoring data provide insufficient information about baseline persistent organic pollutant levels in ambient air and humans, to be used as reference to evaluate their changes as a function of time. For the regional monitoring programme to be effective, analytical capability for monitoring persistent organic pollutants, especially for environmental levels of contaminants such as dioxins and furans, will have to be enhanced. In addition, a common strategy, financial support and human resources will be required.

The Latin America and Caribbean region should formalize a coordinating structure to develop a Regional Action Plan (RAP). This would enable countries to evaluate options available and actions necessary to meet the requirements of the Stockholm Convention for persistent organic pollutant monitoring; develop a regional monitoring programme with indication of scope, limitations, costs and benefits; and identify requirements for capacity-building and access to external assistance.

It is imperative to forge synergies between countries. Interaction between Governments, academic institutions, industry and non-governmental organizations will be required, both at the national and regional levels, to build a successful strategy to face the challenge of monitoring persistent organic pollutants levels in the core media of the global monitoring plan.

ABBREVIATIONS AND ACRONYMS

BDL	Below Detection Limit
CDC	Centers for Disease Control (Atlanta, Georgia, USA)
CEC	Commission for Environmental Cooperation (Canada, USA, Mexico)
CENICA	Centro Nacional de Investigación y Capacitación Ambiental (National Centre for
	Environmental Research and Training)
CETAM	Centro de Tecnologías Ambientales (Chile)
COP	Conference of the Parties
CONAMA	Comisión Nacional del Medio Ambiente (Chile)
CONICYT	Comisión Nacional de Investigación Científica y Tecnológica (Chile)
CPCBs	Coplanar PCBs
CTQ	Centre de Toxicologie du Québec
CV	Coefficient of Variation
DCM	Dichloromethane
DDT	Dichlorodiphenyltrichloroethane
DHF	Dengue hemorrhagic fever
DLPCBs	Dioxin-like PCBs
ECLAC	Economic Commission for Latin America and the Caribbean
EDCs	Endocrine Disrupting Chemicals
GAPS	Global Atmospheric Passive Sampling
GC	Gas Chromatography
GDP	Gross Domestic Product
GEF	Global Environment Facility
GEMS	Global Environment Monitoring System
GMP	Global Monitoring Plan
GNP	Gross National Product
GRULAC	Group of Latin American and Caribbean Countries
HAPs	Hazardous Air Pollutants
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
HPLC	High Performance Liquid Chromatography
HRGC	High Resolution Gas Chromatography (capillary column)
HRMS	High Resolution Mass Spectrometry
ID	Identification
INSPMx	Instituto Nacional de Salud Pública, México
I-TEQ	International Toxicity Equivalent
kg	Kilogram
LAC	Latin America and the Caribbean
LAQ	Laboratorio de Química Ambiental
LAPPR	Laboratory Accreditation Program for Pesticide Residues
LRT	Long Range Transport
LRMS	Low Resolution Mass Spectrometry
Max	Maximum value
MDAMN	Mexican Dioxin Air Monitoring Network

MDL	Minimum Detectable Level
MEA	Multilateral Environmental Agreements
Min	Minimum value
MSD	Mass Selective Detector
MS	Mass Spectrometry
N	Number of Samples
NAFTA	North American Free Trade Agreement
ND	Not Detected
ng	nanogram
NGOs	Non-Governmental Organisations
NHANES	National Health and Nutrition Examination Survey
NIPs	National Implementation Plans
OAS	Organization of American States
OCs	Organochlorines
OCPs	Organochlorine Pesticides
OECD	Organisation for Economic Co-operation and Development
РАНО	Pan American Health Organization
PAHs	Polycyclic Aromatic Hydrocarbons
PAS	Passive Air Samplers
PBDEs	Polybrominated Diphenyl Ethers
PCBs	Polychlorinated Biphenyls
PCDDs	Polychlorinated Dibenzo-p-dioxins
PCDFs	Polychlorinated Dibenzofurans
PeCDF	Pentachlorodibenzofuran
POPs	Persistent Organic Pollutants (includes the group of twelve as defined by the
	Stockholm Convention 2001)
ppt	parts per trillion
PUF	Polyurethane Foam
PVC	Polyvinylchloride
QA/QC	Quality Assurance and Quality Control
QFF	Quartz fibre filter
RAP	Regional Action Plan
ROG	Regional Organisation Group (of GRULAC)
SD	Standard Deviation
SICAP	Sistema Centroamericano de Áreas Protegidas (Central American System of
	Protected Areas)
TB	Tuberculosis
TCDD	Tetrachlorodibenzo-p-dioxin
TEQ	Toxicity Equivalents
TN	Trans-nonachlor
UN	United Nations
UNA	Universidad Nacional (Costa Rica)
UNEP	United Nations Environment Programme
USEPA	United States Environmental Protection Agency
UTFSM	Universidad Técnica Federico Santa María (Chile)
WHO	World Health Organization
XAD	Styrene/divinylbenzene-co-polymer resin

GLOSSARY OF TERMS

Activity	Any programme or other activity or project that generates data or information on the levels of POPs in the environment or in humans that can contribute to the effectiveness evaluation under Article 16 of
	the Stockholm Convention
Background Area	Area located far from identified point sources
Core matrices	These are the matrices identified by the Conference of the Parties to the Stockholm Convention at its second meeting as core for the first evaluation: $A =$ ambient air; $M =$ (human) mother's milk and / or $B =$ human blood
СТД	The characteristic travel distance –defined as the "half-distance" for
	a substance present in a mobile phase
I L-1	Instrumentation level 1 capable of analysing PCDD/PCDF and dioxin-like PCB at ultra-trace concentrations: must be a high-
I L-2	Instrumentation level 2 capable of analysing all POPs: (capillary column and a mass-selective detector)
I L-3	Instrumentation level 3 capable of analysing all POPs without PCDD/PCDF and dioxin like PCB (capillary column and an electron
I L-4	Instrumentation level 4 not capable to do congener-specific PCB analysis (no capillary column, no electron capture detector or mass
Intercomparisons	Participation in national and international intercalibration activities such as ring-tests, laboratory performance testing schemes, among others
LOD	Limit of detection. Definition: The lowest concentration at which a compound can be detected; it is defined as that corresponding to a size of the pairs.
LOQ	Limit of quantification. Definition: The lowest concentration that can quantitatively be determined is three times higher than LOD. Compounds found at levels between LOD and LOQ can be reported as present, or possibly as being present at an estimated concentration, but in the latter case the result has to be clearly
MDL	marked as being below LOQ. Method detection limit. The MDL considers the whole method including sampling, sample treatment and instrumental analysis. It is
PHASE I	Activities to support the Article 16 effectiveness evaluation that will be conducted by the Conference of the Parties at its fourth meeting, information collected between 2000 and 2007 (also termed as first evaluation).

1 INTRODUCTION

At its third meeting in May 2007, the Conference of the Parties adopted by decision SC-3/19 on effectiveness evaluation: the amended global monitoring plan for persistent organic pollutants (UNEP/POPS/COP.3/22/Rev.1, annex II) and the amended implementation plan for the global monitoring plan (UNEP/POPS/COP.3/23/Rev.1). Furthermore, it also adopted the Guidance on the Global Monitoring Plan for Persistent Organic Pollutants (UNEP, 2007), which was prepared by the technical working group, mandated by the Conference of the Parties in its decision SC-2/13. The guidance document provides the overall technical guidance for the implementation of the global monitoring plan in all United Nations Regions.

These decisions outlined a program to begin the evaluation of the effectiveness of the Convention through the use of regional monitoring reports that use existing national and international programs, in combination with strategic capacity building in regions where major data gaps have been identified, to provide information on the concentrations of the priority POPs.

Decision SC-3/19 established a regional organization group, comprised by six members for each of the five United Nations Regions, to facilitate implementation of the global monitoring plan, and invited Parties to nominate members to those groups with expertise in monitoring and data evaluation. The main objectives of the regional organization groups were to define and implement the regional strategy for information gathering, including capacity building and establishment of strategic partnerships in order to fill the identified data gaps, and to prepare the regional monitoring report as contribution to the first effectiveness evaluation report, to be presented to the Conference of the Parties at its fourth meeting in May 2009.

The regional monitoring report that summarizes the results of monitoring programs within their region to record baseline concentrations in the environment and in human milk or blood, against which temporal trends can be established, is a major output to be produced by the regional organization group.

The role of the report is also to facilitate communication on contaminant issues between regions and assist in addressing gaps in the global program. The regional reports comprise an element of the reporting to the Conference of the Parties and they provide an important link between the field sampling programs and the evaluation of the effectiveness of the Stockholm Convention.

The persistent organic pollutants listed in Annexes A, B, and C of the Stockholm Convention share a number of physical and chemical properties that result in concerns for human health and the environment. Of particular importance is the toxicity of the compounds, and their ability to accumulate in the fat of humans and wildlife, as well as in soils and lakes sediments from where they may be re-emitted. Their accumulation in fat makes them resistant to clearance from the human body, except in the formation of milk, and are subsequently passed on to a nursing child. Among their physical properties, is their ability transport over long distances through air,

followed by condensation out of the same media due to the cold temperatures proper of the high latitudes and altitudes.

Determining the effectiveness of controls on POPs mandated by the Convention requires detailed information on the background environmental concentrations of priority POPs from programs that are statistically robust and can detect changes in contaminants over time. Hence the global monitoring plan must be able to provide a harmonized organizational framework to collect comparable information between the regions to help determine changes over time, but also spatial trends for chemical compounds.

A number of environmental media have been used to monitor trends through time and the Parties have recognized the role that many of these could play in a global monitoring program. National programs reporting the concentration of priority chemicals in mussels, fish tissue, bird eggs and sediments have all been used to establish trends through time, but these programs are often regional in nature and may not be widely applicable across the globe. Each of these media has specific advantages and disadvantages for trend detection and difficulties in terms of sample collection, storage and analysis. For a number of reasons, the Conference of the Parties has chosen three core matrices - air, human milk and / or human blood- for global monitoring, in that they provide information on the sources and transport of priority POPs and exposure levels of the human population. Data from regional programs using other media can be used to complement data from the core matrices to assist the establishment of trends using a weight of evidence approach. The first monitoring report, using data collected over the period 1998-2008, provides a critical baseline upon which concentrations in the core matrices will be studied over the long-term.

2 DESCRIPTION OF THE REGION

The region of Latin America and the Caribbean (GRULAC), covers a land area greater than 20 x 10^6 km² (ENCARTA 2002), composed by 33 countries stretching from Mexico in the north to Argentina and Chile in the South. On the West, it is bounded by the Pacific Ocean and on the East by the Atlantic Ocean and the Caribbean Sea. The land area covers 15% of the earth's surface. The overall population in the GRULAC Region is estimated at 562 million inhabitants, corresponding to 8.7% of the world total. The annual population growth rate has fallen – from 2.4% in 1972 to 1.3% in 2005 – Central America 2.1%; Mexico 1.0% (CONAPO, 2005); South America 1.4% and the Caribbean 1.0 % (CELADE - LAC Demographic Centre – 2002).

Life expectancy was 72.3 years in 2005. Over 77% of the population lives in urban areas: four cities have over 5 million inhabitants, 2 cities over 10 million, while Mexico City and Sao Paulo have over 15 million each. 43.4% of the people live in poverty, of which 18.8% belong to indigenous groups (ECLAC, 2003). Overall adult literacy rates averaged 88.6% in 2002 (UNDP 2001) but income distribution inequalities adversely affect access to schooling, attendance and performance levels. By the same token and little access to land underlie social instability and continuous political and financial turmoil. Economic growth was sluggish, after a period of steady growth throughout the 1990s.

Nonetheless, during the four year period (2003-2007) the most relevant increase in the GDP was recorded ever since the 70s. According to ECLAC, this trend continued during 2008, completing five growth years at 3% annual rate. These facts have helped to reduce poverty and unemployment. In some countries the inequalities have been reduced by 3.3% and indigence rates decreased to 2%.

The Latin America and Caribbean (GRULAC) region contains four subregions: the Andes, the Caribbean, Mesoamerica, and the Southern Cone, each with their own special characteristics and rich diversity. The topography ranges from tropical islands to mountain ranges and high plateaus, rainforests, deserts and plains. The climate varies widely; its diversity is reflected in the variety of ecosystems that include many of the world's biologically richest eco-regions, such as the tropical forests and several mega-biodiverse countries, as well as the urban environments, where 75 per cent of GRULAC citizens live.

Andean subregion: Bolivia, Colombia, Ecuador, Peru, and Venezuela

The Andean subregion characteristically comprises 4.7 million km² surface area, or 25% of Latin-America. The population in 2005 was 123.2 million and the subregional GNP reached \$US 255 billion, almost 14% of the Latin-American total. Nearly 20% of the GNP depends on the extraction and processing of natural resources. Forests cover 230 million hectares, or 35% of the GRULAC total, deforestation being a major challenge (GEO-LAC, 2003).

The Caribbean subregion (Antigua & Barbuda, Bahamas, Barbados, Cuba, Dominica, Dominican Republic, Grenada, Guyana*, Haiti, Jamaica, Saint Kitts and Nevis, Saint Lucia, St. Vincent and the Grenadines, Suriname*, Trinidad and Tobago)* (These countries were included in the Caribbean subregion).

The Caribbean subregion is mainly a chain of islands surrounding the Caribbean Sea, organized into 27 territories, including sovereign states and colonies of European nations. The Caribbean islands of the region, widely vary in size; namely, from 91 km² (Anguilla) to 110 860 km² (Cuba). Important variations in socio-economic conditions, cultures and political systems are found in this subregion, for example, Cuba accounts for over one-third of the population (approx.11 million) and almost half the land area. There is a wide diversity of habitats, including coral reefs, sea-grass beds, mangroves, wetlands and rocky shores. Tourism contributes 30-50% of GDP – receives over 6% of the world tourism. Designing suitable environmental protection policies is a major challenge (GEO-LAC, 2003).

Mesoamerican subregion: Belize, Costa Rica, El Salvador, Guatemala, Honduras, Nicaragua, Mexico and Panama

The Mesoamerican surface area is 2.5 million km^2 – the land bridges North and South America. 30% of the subregion is covered by the Mesoamerican Biological Corridor – comprising the Central American System of Protected Areas (SICAP, from its Spanish initials), neighboring buffer zones and multiple use areas. Mesoamerica covers a wide geographical diversity – the 100km-long Mesoamerican Barrier Reef System, extensive mountain chains, an 8,000 kilometer-long coastline, and extensive mangroves. Over 20 % of the population lives from coastal marine activities. Deforestation is a major challenge due to logging, agricultural and range expansion, and domestic fuel requirements in over 60% of the homes in rural areas (GEO-LAC, 2003).

The Southern Cone: Chile, Uruguay, Paraguay, Argentina and Brazil

The southern cone subregion comprises a surface area of 12.6 million km^2 , which was home to 250 million people in 2005. It bears a wide variety of landscapes – forests (629 million hectares), prairies, steppes, shrubs, wetlands, and desert. The countries cited have the lowest population density and the highest urbanization rates in GRULAC. Large percentages of urban dwellers are present – over 89.3% in Argentina; 80% in Brazil and 93% in Uruguay. This is the fourth largest economic group in the world after the EU, NAFTA and Japan – a total GDP of US \$ 1100 billion. Urban environment management and deforestation are the major challenges (GEO-LAC, 2003).

Most Relevant Environmental Problems

The GRULAC region has the world's largest reserves of arable land – but unplanned urban expansion, erosion, non-sustainable land use, loss of nutrients, chemical pollution, overgrazing and deforestation have caused degradation of what once was productive agricultural land – over 300 million hectares – representing 16% of the whole world. Land degradation is a major environmental issue in this subregion. The problem is more severe in Mesoamerica, where 26 % of the territory has been affected, whereas in the Southern cone subregion only 14 % has suffered

so (UNEP 2004). An estimation shows that only in the Southern cone subregion, 682 000 km² have nutrients loss, with about 450 000 km² affected in a moderate or severe degree. Fertility is decreasing in north-eastern Brazil and northern Argentina, while other critical areas are found in Mexico, Colombia, Bolivia and Paraguay. Only 12.4 % of the subregion's agricultural land has no fertility limitations. In 2002, the subregion consumed approximately 5 million tons of nitrogen fertilizers, equivalent to 5.9 % of the global consumption, of which 68 % was consumed by Argentina, Brazil and Mexico alone. The impact of pesticide's use on the environment is being addressed as a priority by the scientific community. Developing countries account for 30% of the global pesticide consumer market and among them, Brazil is the largest individual consumer market, accounting for half of all Latin American pesticide consumption (Peres *et al.* 2007).

The 40% of the population lives in areas having only 10% of the region's water resources. The quality of the surface and groundwater has deteriorated. Pollution of aquifers is extensive and saline intrusion affects coastal areas. Freshwater availability in Latin America and the Caribbean is much higher than the world average. The region contains 30 % of the world's renewable water and three hydrographical regions that cover 25 % of the region. Freshwater resources are unevenly distributed. Brazil alone has nearly 40 % of this resource. On the opposite, almost 6 % of the region's land is desert, and, in some places, such as the Chihuahua or Atacama deserts, there is scarce precipitation. Over the last 30 years, there has been a significant decrease in both surface and groundwater quality in the region due to increasing use in agricultural and domestic untreated wastewater (GEO-4 2007). The growing water demand and pollution, especially in and around the urban areas, has progressively diminished water availability and quality. For the first time in the last 30 years, water availability has become a limiting factor for socioeconomic development of some Latin America and the Caribbean areas, particularly in the Caribbean (ECLAC 2002).

With 25% of the world's forests, GRULAC accounted for over 40% of the natural forest loss over the last 30 years and has some of the world's most endangered forest habitats and fastest rates of deforestation. However, protected areas actually cover 11 % of the land (GEO-4 2007). New protection efforts have been made; these include the creation of the Mesoamerican Biological Corridor from southern Mexico to Panama. The Brazilian Amazon annual deforestation rates are falling and the strategies to diminish deforestation include repression through licensing procedures, monitoring, and fines. As a result of integrated prevention and control programs, annual deforestation in the Amazon decreased from some 26 100 km² in 2004, to 13 100 km² in 2006 (INPE, 2006). Policy reform is also needed to address the root causes of deforestation, including the role of clearing in establishing land claims (Fearnside, 2005). Paraguay, which until 2004 had one of the world's largest forest loss rates, has diminished them in its eastern regions: the so-called "Zero Deforestation Law" passed in 2004 by the Paraguayan Congress has helped to reduce the deforestation rate by 85 % (WWF 2006).

Biodiversity is threatened by habitat loss, land degradation, land use change, deforestation, and marine pollution. From 178 eco-regions, 31 are in a critical state and 30% of Caribbean coral reefs are considered at risk (GEO LAC, 2003).

Land-based pollution, over-exploitation of fisheries, habitat conversion (including by tourism), and the oil and gas industry pose the major environmental threats. 60% of the population lives

within 100 km of the coast – the quality of coastal ecosystems has been modified by coastal urban development. 34 of the 51 local production systems in the Central Caribbean are threatened by over-exploitation of commercially valuable species (GEO LAC, 2003).

Poor air quality has been a problem in the region, especially in larger urban areas such as Mexico City, Santiago de Chile, Sao Paulo, and Bogota. Air pollution is blamed for 2.3 million annual cases of chronic respiratory diseases in infants and 100,000 cases of chronic bronchitis in adults. Urban growth – population growth and rural-urban migration have caused an urban population explosion from 163.9 million in 1970 to 399.2 million in 2001 (UNDP, 2001. UN Population Division). The problems of urban areas include inadequate water supply and sanitation, insufficient waste management, poor air quality, health problems, violence, and other social problems, environmental pollution, and the increasing vulnerability to natural hazards.

Health issues

Infant mortality in the region has declined dramatically over the past decade, largely due to the success of proven low-cost technologies and approaches to improving child health. Mortality rates in children less than 1 year old declined from 47.2 per 1,000 live births in 1990 to 29.6 in 2008. Malnutrition continues to be a major concern, particularly in Central America, where stunting among children under age 5 is still very high. (USAID, 2007) Stunting is a sign of nutritional deficiencies that result in irreversible physical and mental limitations, leaving these children with a burden they will carry into adult life.

Infectious diseases, including tuberculosis (TB) and malaria, are also important health concerns for the GRULAC region; some progress has been attained in the past decade by increasing case detection and improving treatment outcomes. Reported malaria cases in the GRULAC region exceeded 800,000 in 2003, with more than 75 percent occurring in the Amazon Basin countries of Brazil, Colombia, and Peru. Dengue and dengue hemorrhagic fever (DHF) pose another serious public health threat in the GRULAC region. Brazil, Colombia, and the Central America subregion account for the majority of cases. In 2002 and 2003, the reported cases of dengue and DHF in these countries nearly totalled 1.4 million (USAID, 2007).

Other infectious diseases with public health impact in the GRULAC region include Chagas disease, and leishmaniasis. Chagas, a debilitating and fatal disease of smooth muscle tissue that is spread through the bite of the Chagas beetle, is endemic in 18 Latin American countries. Leishmaniasis occurs in South America, primarily in Brazil, Bolivia, and Peru. Transmitted by the bite of the infected female phlebotomine sandfly, the leishmaniases are a globally widespread group of parasitic diseases. The common form causes nonfatal, disfiguring lesions, but epidemics of a rarer form can cause thousands of deaths (USAID, 2007).

In spite of the existence of several studies related to chemical exposure and health effects, there is no a complete diagnosis in the region oriented to evaluate these relationships in the population in general.

Governance

In Latin America and the Caribbean were marked by the continuation or persistence of environmental problems in part associated with overpopulation in large cities and poverty. The 90's decade also saw a number of positive changes. These included a greater participation by citizens in decision making, the development of public and private networks defending the environment and the promotion of environmental education. In Latin America and the Caribbean environmental governance is a complicated issue; since the environment has not yet been granted the high-priority status it requires (Gabaldón and Rodríguez 2002). Regional participation in global multilateral environmental agreements (MEAs) is generally high and governmental institutions formally devoted to environmental matters were created in most countries over the last 15 years. However, the profile and budgets of environmental institutions are often lower than those of other ministries or departments, which have so far failed to mainstream environmental criteria. Despite these difficulties, governmental, academic and social institutions increasingly ensure that environmental issues are taken into account (Guimaraes and Bárcena, 2002). Over 90 per cent of the countries in Latin America and the Caribbean have signed MEAs, such as, the Montreal and the Kyoto protocols and the Basel Convention. MEAs related to biological diversity and desertification had even higher levels of participation. By contrast, participation in MEAs (signatories), such as the Cartagena Protocol, and the Rotterdam and Stockholm conventions, was considerably lower, at 76, 45 and 64 per cent, respectively. Ensuring compliance with MEAs continues to be a major challenge, as enforcement depends on national (and sometimes sub-regional) action in which governmental capacities are critical (Geo-4, 2007). The Wider Caribbean (the Cartagena Convention) and its protocols are important multilateral regional agreements and action plans for the future.

Several countries of the region also belong to the Antarctic Treaty (Argentina, Brazil, Chile, Peru, Ecuador, Uruguay), and many of them perform research activities within the Antarctic region, but there are no publications available related to POPs research. The countries of the GRULAC region have been working in many coordinated efforts, addressing regional problems during several years. However, even when these efforts have been very effective in the international forums, still these are not enough for building sustainable POPs programs with a proper regional structure.

Under the article 15 of the Stockholm Convention, countries must report total quantities of POPs listed in the annex A, B and C. Only 4 countries have submitted their national report pursuant to Article 15 of the said Convention, Argentina, Brazil, Chile and Mexico (available in internet at <u>www.pops.int</u>. August 2008).

The GRULAC region has nominated 4 regional centres of the Stockholm Convention (Brazil, Mexico, Panama and Uruguay), which may play an important role to support a regional monitoring program.

POPs related issues in the region

Most of the GRULAC countries are parties of the Stockholm Convention (25 parties and 8 signatories). Some of them (Argentina, Barbados, Bolivia, Chile, Ecuador, Mexico, Panama,

Peru, Saint Lucia, Uruguay) have concluded their National Implementation Plans. Information regarding sources and inventories of POPs are reported in these NIPs.

The predominant regional POPs sources in the Mesoamerica and the Caribbean regions are agriculture, energy, industry, waste management. Many of the POPs pesticides have been applied in the region in agriculture or vector control. Also, PCBs have been used in many electrical devices including capacitors and transformers. Further, inadequate incineration of domestic, industrial and agricultural waste and land-clearing fires are potential sources of PCDDs, PCDFs. In many countries in the region, incinerators are widely used for hospital wastes. Disposal of obsolete stocks of banned pesticides and other POPs poses a problem.

In the countries of the Andean and Southern Cone subregions, the knowledge of POPs contamination sources is scarce; POPs pesticides are readily forbidden but the total amount of chlorinated pesticides used at a subregional level before the banning of these products is not available. Some POPs pesticides were even produced within the region; consequently, the legacy of this industrial activity has been noted in several areas now considered as hot spots, or as 'heavily contaminated'. The main source for polychlorinated biphenyls (PCBs) are contaminated oils in electrical equipment (in use or stored); however other uses cannot be discarded. The existing dioxins and furans inventories in the region reveal that uncontrolled biomass combustion is one of their major release sources, and that they are, responsible for up to 70% of the total releases. Incinerators for hospital wastes are widely used in many countries of the region. Disposal of obsolete stocks of banned pesticides and other POPs poses a problem.

Independent estimations using both CO_2 emissions and the GDP, indicate a total release of dioxins to the air that reaches a 3000 – 5000 g TEQ/Year for the entire region (Barra et al. 2005, 2007).

Human exposure to POPs has been documented in many countries within the region, but the data are still incomplete to allow an in depth evaluation. However it is expected that the general population could be exposed through different environmental media and food.

Regional evidence of POPs in air, marine, freshwater and terrestrial ecosystems, foods, and human biological samples is scattered across time periods, locations, and methods, with scarce evaluation of temporal or spatial trends. Therefore, it is difficult to attempt creating an overall picture because of incomparability between surveys and lack of monitoring and surveillance programs. Chlorinated pesticides and PCBs have been detected in atmospheric, marine, freshwater, groundwater, sediment, soil, food and biota samples, including human blood and milk.

It is expected that pesticides banning and regulations enforcement during 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% of the total potential intake for dioxins and furans (Domingo and Bocio, 2007); the same situation is given for PCBs.

3 ORGANIZATION OF REGIONAL IMPLEMENTATION

3.1. Coordination of activities in the region

It has been stated in the Introduction of this document that the Conference of the Parties of the Stockholm Convention, adopted various agreements following decision SC-3/19, aiming at establishing a regional organization group for each of the five United Nations regions, to facilitate regional implementation of the global monitoring plan. It was decided that each regional organization group should be comprised of six members and Parties were invited to nominate members with expertise in monitoring and data evaluation to the groups. The main objectives of the regional organization group were to define and implement the regional strategy for information gathering, including capacity building, and to prepare the regional monitoring report for the first effectiveness evaluation to be performed by the Conference of the Parties in May 2009. It is relevant to say, that the mandate and terms of reference of the regional organization groups were established at the COP-3.

Each regional bureau was required to select six members to comprise its regional organization group (ROG). Dr. Malverne Spencer (Antigua & Barbuda), Ms. Sandra Hacon (Brazil), Mr. Lorenzo Caballero (Chile), Mr. Rigoberto Blanco (Costa Rica), Mrs. Carola Resabala (Ecuador) and Mrs. Ana Patricia Martínez (Mexico), were selected to serve as the members of the Regional Organisation Group (ROG) for Latin America and the Caribbean, (GRULAC).

When initiating and executing its activities to obtain monitoring information, the ROG took careful note of two concepts outlined in Article 16 of the Stockholm Convention. First, it was stated that Parties shall make arrangements to obtain comparable monitoring data and second, that the arrangements to gather data should be implemented using existing programs and mechanisms to the extent possible.

At its first and second meetings, the ROG reviewed information on existing programs based upon survey responses obtained by the Secretariat, and selected candidate programs to provide the basis for the first evaluation report. The selection was performed by application of quality and comparability criteria, which resulted in the identification of only two established international programs to be the main information sources for the first evaluation. The ROG carefully examined the sampling, analytical methodology, and data quality arrangements of each of the programs and was satisfied that such arrangements will enable the data from the identified programs to be used by the COP as baseline data and to determine changes in POPs levels over time, within those programs.

Although it was believed that it is practical and realistic to expect such internal comparability between same media programs, it is noted that each of the established programs has its own work conducting procedures, usually including constraints on the use of different analytical laboratories within each program. However, very few different programs share the same analytical laboratory. Since the use of different analytical laboratories is a major source of variance, the ROG concluded that it would be very difficult to achieve comparability among programs. Therefore, the focus was placed on efforts to promote internal comparability within programs over time for both, the present and the future. While this conclusion generally implies

that direct comparability among regions will be very limited, significant exceptions are evident, such as when a program operating in several regions has maintained a centralized analytical facility servicing all regions, such as with the WHO coordinated human milk program.

During its first and second meetings, the ROG considered how best to provide the COP with all the information requested in a concise fashion. It was decided to address these needs by providing the COP with four tiers of information: 1) a short simple summary to inform the COP of the essential elements; 2) a concise synthesis of information derived from the contributing existing monitoring programs (Chapter 3 of this report); 3) more detailed information on the nature of operation and data used from each of the contributing programs (Chapters 4 and 5), which are termed "program summaries". They were chiefly prepared by experts working in the existing contributing programs; 4) the assurance that full details on any aspect of an existing program can be accessed, usually through direct contact with the management or secretariats of each contributing program. Therefore, anybody wishing to obtain more information on the analytical methodologies, quality assurance and control, data handling, and data availability practices of a contributing program, there is a choice of the degree of detail sought for to access.

The sections following summarize the nature of each of the main sources of information used by the ROG and the results of the programs and studies selected are provided in chapter 5. Additional information compiled can be found in Annexes, 1-4.

3.2. Strategy used to collect information for existing national and international programs

The main objectives of the ROG were to define and implement the regional strategy for information gathering, including capacity building, and to prepare the Regional Monitoring Report for the first effectiveness evaluation to be performed by the COP in May 2009.

To support initiation of regional organization group activities in the GRULAC region, it was agreed a division of responsibility to facilitate communication with countries. This division was reconfirmed during the inception workshop for the first ROG-GRULAC region which was held in Mexico City, January 2008. Table 3.1 shows the division of responsibilities as convened.

Table 3.1. Division	of responsibility for	countries betwee	en the regional	coordination gr	oup
members	8				

Antigua &	Brazil	Chile	Costa Rica	Ecuador	Mexico
Barbuda					
A. Parties	A. Parties	A. Parties	A. Parties	A. Parties	A. Parties
Dominica	Guyana	Argentina	Honduras	Peru	Bahamas
Saint Lucia	Trinidad &	Bolivia	Nicaragua	Panama	Barbados
Saint Kitts & Nevis	Tobago	Paraguay			Jamaica
Saint Vincent &	Venezuela	Uruguay			Dominican
the Grenadines					Republic
					_
B. Signatories	B. Signatories	B. Signatories	B. Signatories	B. Signatories	B. Signatories
Grenada	Suriname	Cuba	Belize	Colombia	Haiti
			Guatemala		
			El Salvador		
6	5	6	6	4	6

As agreed, official information letters were sent by the Secretariat to all countries in the region, informing them of the nomination of the regional organization group members and division of responsibility for communication. Further communication within the region was performed by the ROG members with reference to these letters.

ROG members officially requested countries to fill out a questionnaire in order to find out if they have monitoring programs, sampling and analytical capacities, availability of QA/QC protocols for POPs analysis on the core media; additionally, it was asked of them to state their needs to improve laboratory capacities. Questionnaires were sent during November 2007, aiming to know the level of existing infrastructure and capacity building as well as the main gaps related to continuous monitoring programs in the region.

At the inception workshop, results of the questionnaires were presented; these can be found summarized in Annex 1. Due to lack of information from many countries, it was decided to request again not only to respond the questionnaires, but provide information about monitoring programs in the countries including some other matrices.

Following the inception workshop for the GRULAC Region, a one-day meeting of the regional organization group members was held to consolidate the proposals raised during the workshop, to endorse the outcome of the workshop and to establish the final strategy, for the GRULAC Region to develop the regional monitoring report.

During that meeting, regional organization group members reconfirmed the responsibility for a selected number of countries within their sub-region, see Table 3.1, outlined the modus operandi for collecting data and drafted the first regional monitoring report and agreed on a timetable to undertake the work. The members also agreed on a strategy to fill the identified data gaps and suggested strategic partnerships. Finally, the regional organization group members agreed on the three members to represent the region in the Coordinating Group and on a coordinator for the GRULAC Region.

The following three ROG members were selected to represent the GRULAC Region in the Coordinating Group: Dr. Malverne Spencer (Antigua & Barbuda), Mr. Lorenzo Caballero (Chile), and Mrs. Ana Patricia Martínez (Mexico), who was also selected to serve as coordinator of the ROG-GRULAC activities.

In May 2008, a workshop to facilitate the drafting of the regional report was held in Geneva, where the structure and content of the report were defined and the data management policies were established.

Due to the limited information received, a second call was done in June 2008, to request information on media other than core matrices. It was assumed that if the country did not respond to the request to submit additional information on the core media, then it would be considered as not having data to be included into the regional monitoring report for the first Global Monitoring Program evaluation.

3.3. Collecting available information on core media and other suitable monitoring results

In the region, there are two global monitoring programs, the WHO human milk survey and the GAPS. Regarding the WHO survey only Brazil took part in the 3rd round (2000-2003); some countries from the GRULAC region are taking part in the fourth round (Antigua & Barbuda, Chile and Uruguay). Results of the third round are available from the WHO survey and it is expected to have the results of the fourth round.

GAPS (Global Atmospheric Passive Sampling Program) sites in the GRULAC Region includes, Argentina (2004-2006), Brazil (2005-2008), Bolivia (2005-2006), Chile (2005-2008), Colombia (2005-2008), Costa Rica (2005), Cuba (2005-2008) and Mexico (2005-2006). Three more sites were included for one sampling period in 2008: Barbados, Brazil (Amazonas) and Ecuador (GAPS, 2009), but the results were received in 2009 and were not analyzed for this report.

Data from one regional international study were also submitted by Mexico, regarding human *primipara* maternal blood, funded by the World Bank and coordinated by the North American Commission for Environment Cooperation (CEC) and supported by CEC, Environment Canada and USEPA.

Other information sources are short term studies, the references of which are listed in Annex 3, that were provided by different countries in the region such as: Mexico Air Sampling Study 2002-2006, supported by CEC, Environment Canada and USEPA; Altitudinal and seasonal variations of persistent organic pollutants (POPs) in the Bolivian Andes Mountains, study supported by Environment Canada; Passive sampler derived air-concentrations of POPs on a north-south transect in Chile, study supported by Environment Canada, among others. Information regarding core matrices was obtained only from the governments of Brazil and Mexico. Other countries sent general information but outside the defined time window established by UNEP (1998-2008) for this first report.

National activities were also reported by countries regarding milk and blood, where very few scattered studies have been performed mainly in populations highly exposed to agricultural pesticides and DDT. In most cases also a reference population was sampled. Other media data on OCP residues are systematically monitored in many countries in water, soil, sediments, marine environment and in agricultural products.

The ROG recognizes that valuable data may be available in many programs that may be used to establish temporal trends but do not include the core matrices. In the GRULAC region, there are several studies related to POPs monitoring, and initiatives that do not report evidence of quality control/assurance and the required continuity for establishing temporal trends. The data from these programs must meet the acceptance requirements as defined in the Guidance for the global monitoring plan (UNEP, 2007) and will provide support for data in core media.

Studies sent by governments are mentioned in the regional report and their references are also included in Annex 3. All information used were made available to ROG members by governments, institutions, national reports, peer reviewed journals, among others.

3.4. Evaluation of readily available data sets according to data quality criteria and selection of data which could be used for the first evaluation

The application of quality criteria to data evaluation was done in accordance to the adopted Guidance on the Global Monitoring Plan for Persistent Organic Pollutants and the agreements reached during the Workshop for facilitating draft of the regional reports available in the document EE-GMP/2008/4 (www.pops.int). The criteria were adopted for the five UNEP regions. According to these criteria and because of the limited response from the countries, very little information was available in terms of continuous monitoring data.

The core matrices data included in this report were provided by GAPS, CEC and WHO, and the studies that accomplish QA/QC and comparability criteria that are established in the above mentioned Guidance. Additional information concerning summaries of studies, from the core and other media, sent by countries was also included in Annex 4. However, it should be considered that their data do not allow comparisons. Further compiled information from electronic sources is included in the CD attached to this report as Information Bank.

3.5 Facilitate activities to obtain supplementary data where data gaps have been identified

Establishment of strategic partnership projects for capacity enhancement and production of supplementary monitoring data to achieve better regional coverage was agreed.

The Global Atmospheric Passive Sampling Program coordinated by Environment Canada, which has been active in the region since 2005, used to monitor up to 11 sampling sites in 8 different countries: Argentina, Brazil, Bolivia, Chile, Costa Rica, Colombia, Cuba and Mexico. During the inception workshop it was noted that only 6 sites located in 5 countries were currently operated in 2008, therefore it was decided to enlarge this network by 5 additional sampling sites during one season in 2008 and make efforts to continue with the program in the future. The following countries with additional sampling sites were identified by the workshop to improve regional coverage of air data: Barbados, Brazil (Amazonas), Ecuador, Argentina and Mexico. Venezuela was also identified as a possible sampling point. Data from Barbados, Brazil (Amazonas) and Ecuador were received in 2009 but could not be analyzed for this report.

During the inception workshop it was also agreed to expand the WHO-human milk survey to include additional countries during the 4th round (2005-2008).The following countries were identified as probable participants during the workshop: Antigua & Barbuda, Brazil, Chile, Costa Rica, Ecuador, Honduras, Peru and Uruguay. Only Antigua & Barbuda and Uruguay completed the sampling in 2008.

Another outcome of the ROG was the elaboration of a GEF project proposal on strengthening monitoring capacities within the region. This project (if approved) will be coordinated by a nominated Stockholm Convention Regional Centre. During the inception workshop it was recommended that the following countries be involved in such proposal: Antigua & Barbuda, Argentina, Barbados; Brazil; Chile; Costa Rica; Ecuador; Honduras; Mexico; Nicaragua; Peru; Uruguay, Saint Lucia, Venezuela, Panama and Paraguay.

3.6. Arrangements to elaborate the regional monitoring report: Identification of the roles and responsibilities of the drafting team of experts selected by the regional organization group to prepare the report for that particular region

In order to support the ROG members to draft the regional monitoring report, it was agreed to hire a consultant. ROG elaborated the terms of reference for the consultancy work which was circulated to prospective consultants identified by the ROG. The main duties for the consultant were to develop a preliminary draft of the regional report for review by ROG members in July 2008, amendments and observations from the ROG members were included and a draft final version was circulated among the Focal Points of the region and the Secretariat during August.

This GRULAC Draft Report was sent to all the 33 Countries: 28 confirmed the reception of the report by electronic message or by telephone. The remaining 5 countries were impossible to contact due to lack of information, i.e. wrong telephone number or mail address. Some countries asked for additional time to review the document; when an extension of the review term was granted and a second call sent and both produced limited improvement.

The ROG members and Consultants met at a regional drafting workshop in Costa Rica at the end of August 2008 in order to revise and include comments and observations from the countries and to finalize the regional report.

The final version was translated into Spanish in September 2008 and presented to the Coordination Group in November 2008. The final edition in Spanish and English will be published in March 2009.

4 METHODS FOR SAMPLING, ANALYSIS AND DATA HANDLING

The GRULAC region lacks a regional approach for monitoring POPs in the environment and humans either in the core matrices (air, human milk and/or blood) or in other media. This is an important starting point since the data reported in this document is mainly derived from data provided by existing international programs such as Global Atmospheric Passive Sampling (GAPS) and WHO human milk survey and on information provided by the countries.

The issue of comparability was discussed and it was agreed that only data belonging to the same program should be compared i.e., comparisons could be done only within programs. In the case of international reports, data can be compared only when it belongs to the same monitoring program and the corresponding analyses were performed by a unique analytical laboratory. In this same respect, the GRULAC region presents a wide variety of climatic conditions that may possibly confer undefined implications on data comparability; however, it may be possible to establish some trends within the region by utilizing a regional monitoring plan.

As mentioned in Chapter 3, some regional partnerships have been developed with global programs, such as the case of the Global Atmospheric Passive Sampling Network program, coordinated by Environment Canada, and the WHO-human monitoring survey.

4.1 Programs/activities related to air monitoring4.1.1 GAPS Network in the GRULAC region

Key Message

Two different types of samplers, PUF and XAD, were used by the GAPS program in eleven sites. The data available for this report come from nine sites in eight countries for the PUF sampling and from seven sites in six countries for XAD sampling in 2005, and from six sites in six countries for XAD sampling in 2006. However, only four sites accomplished the criteria based on 75% data completeness; there was insufficient information to evaluate the precision and accuracy of the data.

The first year results (January–December 2005) from the GAPS Network provided baselines for air concentrations of persistent organic pollutants (POPs) at nine sampling sites in the GRULAC region. In many cases, these data represent the first POPs measurements in this region and will be useful for assessing temporal and spatial trends as well as regional and global POPs transport in air (GAPS, 2008).

Background

The GAPS Network is a key program for producing comparable global-scale POPs data. The project was initiated in December 2004 as a two-year pilot study before it evolved into a network, comprising more than 60 sites on seven continents. Its objectives are to: i) demonstrate the feasibility of passive air samplers (PAS) for POPs; ii) determine POPs spatial and temporal

trends in air; and iii) contribute useful data for assessing regional and global long-range atmospheric POPs transport. Passive air samples are advantageous because of their low cost, simple construction and electricity-free operation. Deployment of PAS worldwide over several years will allow for temporal trends to be established and thus, to evaluate the effectiveness of POPs control measures.

The GAPS Network has been active at eleven sites in the GRULAC region since 2005, see Table 4.1, and Figures 4.1 and 4.2 (GAPS, 2008). The countries involved have been supporting all the field work contributing with logistics, deployment and sample collection and providing meteorological data on a regular basis.

Site ID	Location	Country	Site Type	Latitude	Longitude	Elevation (masl*)
GR01	La Palma	Cuba	BA	22.752° N	83.535° W	47
GR02	Veracruz	Mexico	RU	19° 12 N	96° 08 W	
GR03	Tapanti NP	Costa Rica	BA	9.69354° N	83.86544° W	2830
GR04	Arauca	Colombia	RU	7° 00' 46.25" N	70° 44' 36.332" W	100-120
GR05	Huayna Potosí 5200 m a.s.l, La Paz	Bolivia	BA	16° 16' 19.7" S	68° 08' 10" W	5192
GR06	Chungara Lake	Chile	BA	18° 13 S	69°10 W	4320
GR07	Indaiatuba (near Campinas)	Brazil	BA	23° 09' 27.1" S	47° 10' 06.6" W	624
GR08	Bahia Blanca	Argentina	AG	38° 45' S	62° 15' W	
GR09	Coyhaique	Chile	BA	45° 35' S	72° 02' W	
GR10	Tláhuac	Mexico	UR	19° 14' 44" N	99° 00' 36" W	2260
GR11	St. Peter and St. Paul Rocks	Brazil	BA	00° 56' N	29° 22' W	

Table 4.1. Information on sampling locations in the GRULAC region (BA = background; RU = rural; AG = agricultural and UR = urban) (GAPS, 2008).

* metres above mean sea level



Figure 4.1. Sampling sites and years in Mexico, Central America and the Caribbean



Figure 4.2. Sampling sites and years in South America (GAPS, 2008).

Sampling

Two types of PAS are used: the PUF-disk sampler is deployed for three-month periods to capture seasonal differences and the XAD sampler is exposed for a full year, as noted below (Fig. 4.3).



Figure 4.3. Schematic diagrams of passive air samplers (GAPS, 2008).

The PUF-disk sampler is described in Shoeib and Harner (2002) and Pozo *et al.* (2006), and the XAD sampler is described in Wania *et al.* (2003). Both types of PAS are installed outdoors far away from potential sources of contamination to the site (e.g., exhaust vents, electronics and sources of combustion or human activity). They are mounted approximately two meters above the ground in an open area with unobstructed airflow.

Sample analytical procedures

PUF Disk PAS

Details for the extraction and analysis of the PUF-disk samples and field blanks are given in Pozo *et al.* (2006). The following QA/QC procedures were employed for the PUF-disk sampler:

- Field blanks A PUF disk field blank was collected once a year from each site to assess possible contamination caused by shipping, handling and storage.
- Method blanks A solvent blank was extracted with every set of eight samples to assess
 possible contamination during laboratory analysis (i.e., from sample preparation to
 instrumental analysis). Also, during PUF disks preparation for deployment, one sample from
 each batch was extracted and checked for purity.
- Instrument blanks A solvent blank was analyzed with every set of twelve field samples to assess any instrument contamination.
- Surrogate spikes Prior to extraction, PUF-disk samples were spiked by means of a recovery standard method consisting of ¹³C-PCB-105, $d_6-\alpha$ -HCH, and d_8-p,p '-DDT to confirm analytical integrity.
- Matrix spikes Analytical (method) recoveries were determined by spiking clean PUF disks with known quantities of the target chemicals and treating them as samples to assess matrix effects on extraction efficiencies.
- Field collected samples Duplicate samples were collected at several sites in the GAPS Network to assess overall precision of both sampling and laboratory methods.
- Mirex was added as an internal standard to correct for volume differences in sample extracts.

All samples and field blanks were quantified for target compounds including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs). OCPs, PCBs, and PBDEs were analyzed through a Hewlett-Packard 6890 gas chromatograph-5973 mass spectrometer (GC-MS) using electron impact (EI) for PCBs and negative chemical ionization (NCI) for OCPs and PBDEs in the selected ion monitoring mode.

XAD PAS

Cleaning the XAD-2 resin, and packing the XAD PAS samples were carried out as described previously by Wania *et al.* (2003). Cleaning, preparation and extraction of PAS were done in a clean lab.

The XAD-2 resin was Soxhlet extracted with dichloromethane for 20 hours. Prior to extraction, the resin was spiked with standards consisting $d_6 - \alpha$ -HCH, ${}^{13}C_{10}$ -HEPX, ${}^{13}C_{10}$ -TN, ${}^{13}C_{12}$ -dieldrin, d_8 -*p*,*p*'-DDT and ${}^{13}C_{12}$ -PCB-32, ${}^{13}C_{12}$ -PCB-77, ${}^{13}C_{12}$ -PCB-118 and ${}^{13}C_{12}$ -PCB-126 to test for the loss of the compounds during the extraction and clean-up procedures. The extracts were volume reduced using a rotary evaporator and concentrated to around 1 mL using a gentle nitrogen stream. The extracts from first year samples were cleaned using alumina columns, but not those from the second year. After reducing samples to 3 mL using a rotary evaporator, the extracts from second year samples were passed through sodium sulphate columns (baked at 450 °C overnight) to remove any water present. The extracts from the first year air samples were cleaned using a column with 1 g of 6% deactivated alumina (baked at 450 °C overnight) and 0.5 cm of sodium sulphate. The samples were eluted with 20 mL of DCM:PE (5:95 v/v). The extracts were concentrated to 1 mL using a nitrogen stream and then were solvent-exchanged to isooctane. The final volume of the extracts was 1 mL, and 100 ng of mirex was added to the sample as an internal standard for correcting volume differences in the sample.

The sample and blank (field and laboratory) extracts were analyzed for Stockholm Convention POPs as well as pesticides not classified under Stockholm Convention POPs using an Agilent 6890 gas chromatograph (GC) coupled to a 5973 mass selective detector (MSD) with a negative chemical ionization source for organochlorine pesticides (OCPs) in selected ion mode. The analyzed non-Stockholm Convention pesticides in air samples are: α -HCH, γ -HCH, α -endosulfan, β -endosulfan, endosulfan sulfate, dacthal, chlorothalonil, pendimethalin and trifluralin.

Quality assurance and control measures were used to monitor all analytical procedures. Field blanks were collected to determine the contaminants levels introduced by handling, shipping and storage and one laboratory blank was analyzed for every set of sample extractions to determine the contaminants levels introduced during extraction and clean-up. The laboratory blanks and field blanks were processed in the same way as the samples. Air samples were not spiked with surrogates for the pesticides that are not classified under the Stockholm Convention POPs, such as chlorothalonil, dacthal, metribuzin, pendimethalin and trifluralin. To test for the loss of these compounds during the extraction and clean-up procedures, six 20 g XAD-2 samples were spiked with the pesticides, then extracted and cleaned in the same way as the samples.

Data comparability

All PUF-disk samples are prepared and analyzed in the same laboratory (Hazardous Air Pollutants (HAPs), Environment Canada, Toronto) to ensure that the data can be compared spatially and temporarily. The HAPs laboratory participates in international inter-calibration studies for POPs and performs well in these exercises¹.

Data storage

Sample extracts are capped tightly in GC vials and stored in a freezer at a temperature of about -20°C. Air concentration results and relevant sample information (e.g. sample ID, site ID,

¹ Contact: Dr. Tom Harner, 4905 Dufferin Street, Downsview, Ontario, Canada, M3H 5T4

location name, sampling duration, meteorological conditions, among others) were recorded in Excel® spreadsheets.

4.1.2 High volume air sampling

Key message

Comparisons between active and passive air (PUF Disk) sampling were conducted in Mexico between 2002-2004 (Alegria et al. 2008), to measure organochlorine pesticides and PCBs in ambient air concentrations. Concentrations of OC pesticides measured with passive samplers agreed well with those measured using high volume samplers, the concentration ratios of PAS to high volume air were between 0.76 and 1.5.

Background

This study used two types of sampling strategies: high volume air and passive air sampler (PUFdisk sampler). The sampling campaigns were carried out in southern Mexico during 2002-2004 to measure ambient air concentrations of OC pesticides and polychlorinated biphenyls (PCBs. Air parcel back trajectories were examined to determine possible sources and transport pathways of the chemicals detected.

Sampling

Air samples were collected during 24 h every 14 days by drawing 500 m³ air through a 10 cm diameter glass fibre filter (Whatman 2000, Maidstone, England) followed by a polyurethane foam (PUF) trap consisting of one or two 8.0 cm diameter x 7.5 cm long plugs (polyether type, density 0.022 g/cm^3 , Pacwill Environmental, Grimsby, ON, Canada).

Passive air samplers of the type designed by Harner *et al.* (2004), and Shoeib and Harner (2002), and used in other field investigations (Jaward *et al.*, (2004), Pozo *et al.* (2004), Gouin *et al.* (2005)), were also deployed at the four study sites, see Figure 4.4. These were PUF disks, 14 cm diameter x 1.35 cm thick and of the same PUF type as that used for high volume sampling, suspended inside two stainless steel bowls, the upper inverted one being slightly larger to allow air flow between the two bowls, as illustrated in Figure 4.3 (Harner *et al.* (2004)).



Figure 4.4. Air sampling stations and direction of origin of air masses in southern Mexico. Alegria *et al.* 2008).

Analytical procedures

Cleaning of filters and PUF plugs for high volume sampling as well as the analysis, followed published procedures (Alegria *et al.* 2006, Harner *et al.* 2004, Shoeib and Harner, 2002).

Filters and front PUF plugs were extracted together and back PUF plugs were extracted separately. Prior to extraction, PUF sampling media were fortified with a mixture containing 20 ng each of $[^{2}H_{6}] \alpha$ -hexachlorocyclohexane (α -HCH), $[^{13}C_{10}]$ heptachlor exoepoxide (HEPX), $[^{13}C_{10}]$ transnonachlor (TN) and $[^{13}C_{12}]$ dieldrin (DIEL), 100 ng of $[^{2}H_{8}]p,p$ DDT, 1 ng $[^{13}C_{12}]$ PCB77, 10 ng $[^{13}C_{12}]$ PCB118 and 0.5 ng $[^{13}C_{12}]$ PCB126, which served as surrogates for assessing method recoveries for each sample. In this study 51 PCB congeners were analyzed from di-chlorinated to deca-chlorinated (PCB: 8, 18, 17, 15, 16+32, 31, 28, 33, 52, 49, 44, 42, 37, 74, 70, 66, 56+60, 95, 101, 99, 87, 123, 128, 110, 151, 123, 149, 118, 153,105, 137+138, 187, 183, 185, 174, 177, 171, 156, 157, 180, 194, 195, 199, 200, 170, 203, 205, 206, 207, 209).

Data comparability

All samples were prepared and analyzed in the same laboratory. Data belonging to a particular strategy in the case of the active sampling is comparable. Information on air concentrations using the passive samplers was expressed as estimated values and averaged.

Data Storage

After sampling, filters and PUF plugs were stored in a freezer for up to one month until analyzed. Data were retrieved from a paper in press and stored in a Excel® file.

4.1.3. Air study –2000/2001 – Dioxins in Brazil (de Assunção et al. 2005)

Key message

This study is the only one reporting dioxins and furans data in air samples in the region. The work corresponds to a monitoring project undertaken during 2000/2001 in three urban sites in Brazil.

Background

In this work, three urban sites in São Paulo City were chosen on the basis of local differences in the type, distribution, and proximity of emission sources, as well as differences in wind direction frequencies.

Sampling

Sampling locations were not geo-referenced, but major details are reported in the publication Sampling of dioxins and furans was performed according to US EPA Method TO-9A (US EPA, 1999) using Andersen GPS1 samplers equipped with quartz micro fibre filters for particle collection and a polyurethane foam plug for gas retention. Simultaneous 24h samples were collected at three sampling sites in November 29, 2000, February 21, May 30 and August 28, 2001 (total number of samples taken = 12). Samplers were calibrated before and after sampling, using a U-tube water manometer. Prior to sampling, filters and PUF cartridges were cleaned and spiked with ${}^{13}C_6$ 1, 2, 3, 7, 8, 9-HxCDD (field surrogate). After sampling, samples and blanks were placed in an original glass container and wrapped with aluminium foil.

Analysis

The PCDD/Fs analyses were carried out in a laboratory (Analytical Solutions Laboratory) in Rio de Janeiro City, Brazil, according to the US EPA Method 8290 (US EPA, 1994). Samples were transported in a refrigerator with dry ice. Each filter and the corresponding PUF were combined and spiked with twelve ¹³C₁₂PCDD/F internal standards, and then Soxhlet extracted with dichloromethane for 16h. Each extract was then cleaned-up in a sulphuric acid–silica gel column using hexane as eluent and a Florisil column using dichloromethane as eluent. The extracts were concentrated to almost dryness and ¹³C₆-1, 2, 3, 4 -TCDD was added in 15µl of nonane immediately before analysis. Extracts were analyzed in a Hewlett Packard 6890 model high-resolution gas chromatograph/VG Autospec Ultimate mass spectrometer (HRGC/HRMS). Recoveries ranged from 48% to 121%, and recovery of field surrogate ranged from 77% to 132%. The detection limits of the PCDD/Fs congeners, calculated by signal-to-noise ratio, ranged from 0.006 to 0.009pg/m³.

Data comparability

Samples were processed according strict quality assurance criteria, and only one laboratory was involved in the analysis of the results

Data storage

The data were stored in Excel® files.

4.2 **Programs/activities related to human tissues (milk and/or blood)**

4.2.1 Monitoring of Human Milk for Persistent Organic Pollutants in the framework of the WHO survey

Background

Since the mid-seventies, WHO in collaboration with UNEP has implemented the food component of the Global Environment Monitoring System - Food Contamination Monitoring and Assessment Programme (GEMS/Food), which collects, collates and evaluates data on the levels and trends of contaminants in food and human milk. These contaminants include the organochlorine pesticides POPs, which were the initial focus of attention. In the beginning of the mid-eighties, WHO coordinated several surveys of the dioxin-like polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) levels. These surveys were carried out in collaboration with other international organisations and national institutions, and concentrated particularly on the infant's health risk, due to exposure through contaminated human-milk, and aiming to prevent and control exposure to these chemicals through food.

More recently, the WHO protocol for these surveys has been revised to include the objective of providing accessible, reliable and comparable data on POPs levels in human milk for the purposes of the Stockholm Convention. The latest protocol (used for the ongoing 4th survey) is different from the early protocol because it: a) emphasizes the protection, promotion and support of breastfeeding; b) specifies a minimum of 50 donors for one pooled sample, and; c) includes the analysis of all 12 POPs currently covered by the Convention. The latest version of WHO Guidelines (October 1, 2007) is currently available at:

http://www.who.int/foodsafety/chem/POPprotocol.pdf.

The only country that has participated in the WHO's 3rd round survey in the GRULAC region is Brazil, though it is planned that in the fourth round of the WHO survey, more countries will be involved within the GRULAC region. This is a key step towards a more comprehensive and comparative monitoring program within the region.

Sampling

In order to promote reliability and comparability, participating countries were encouraged to adhere as closely as possible to the WHO protocol. It was also recognized that the countries exhibited considerable variability of circumstances, so that some flexibility was required.

Guidance was provided to assist countries in developing their national protocols. Donors were selected according to the protocol of the third round of WHO-coordinated exposure study on "Levels of PCDDs, PCDFs and PCBs in Human Milk", which include also the application of a standardized questionnaire about individual characteristics and food habits to each mother. The study's objectives were explained to all mothers who gave their consent. Only *primipara* mothers, exclusively breastfeeding one infant, apparently healthy and living at the same residence for at least 5 years were included in the study. Sampling was carried out between 2 and 8 weeks after delivery. At each area, 10 samples of 100 ml each were collected from breastfeeding mothers and in most cases (81%) the whole amount was collected once. Milk was

extracted manually directly in a jar and kept frozen at -20° C. Previously, each jar was decontaminated and three tablets of potassium dichromate were added to avoid degradation during shipping. After finishing the collection of the 10 sub-samples, they were sent frozen to the central laboratory in Rio de Janeiro where they were defrosted at room temperature and pooled to give a total volume of 1000 ml. One part of 500 ml was sent to the reference lab in Freiburg/Germany and the other aliquot was kept frozen for contingency purposes (e.g. damage during transportation).

Sample analytical procedures

PCDDs, PCDFs and PCBs

Analytical procedures were executed at the State Institute for Chemical and Veterinarian Analysis in Freiburg/Germany, which is the WHO reference laboratory for dioxin analysis in human milk. All steps of the analytical method for the determination of PCDD/Fs, DLPCBs, and marker PCBs were performed following the same procedure as used in WHO interlaboratory quality assessment study realized in 2000. Fat and contaminants of interest were extracted from freeze-dried samples in a hot extraction device ("Twisselmann extractor") with Toluene/Methanol (70:30) for 8 hours. The crude fat extract was purified with butyl methyl ether and a 3 g fat aliquot was spiked with ¹³C-labeled internal standards (17 PCDD/Fs, 5 non-ortho PCBs [37, 77, 81, 126, 169], 6 mono-ortho PCBs [28, 60, 105, 118, 156, 189] and 7 di-ortho PCBs [52, 101, 138, 153,180, 194,209]). Fat was removed by gel permeation chromatography Bio Beads S-X3 followed by a silica column impregnated with sulphuric acid. Then PCDD/Fs and PCBs were separated on a florisil column. The PCDD/F fraction was purified on Carbopack B column and then, after addition of the recovery standard $(1, 2, 3, 4-{}^{13}C_{12}-TCDD)$ evaporated to the final volume of 20 µl. PCBs were separated into three fractions (di-ortho, mono-ortho and non-ortho) on a Carbopack B column; the recovery standard $({}^{13}C_{12}$ -PCB) was added to each fraction, then they were evaporated to a final volume of 60 µl (non-ortho) or 500 µl (mono- and di-ortho). The four groups were determined in separate runs by HRGC/HRMS using a Fisons Auto Spec at 10000 resolution using a DB5-MS column. With every acquisition sequence, a 5 point-calibration curve was acquired in duplicate.

POPs pesticides

The applied analytical method for organochlorine pesticides followed the principles of Official Methods in Germany (DFG S-19). For the determination, human milk samples were centrifuged and the cream layer was extracted with light petroleum after addition of sodium sulphate. After evaporation, the fat content was determined by weighing out the mass of the remainder. Up to 0.5 g of the fat extract was dissolved in cyclohexane/ethyl acetate and the internal standards were added. For separation of fat, gel permeation chromatography was performed on Bio-Beads S-X3 with cyclohexane/ethyl acetate as eluting solvent. The extract was evaporated almost to dryness under a gentle stream of nitrogen and isooctane was added. Chromatography on a small column packed with partially deactivated silica gel was performed as final clean up step and toluene was used as eluent. Routine determination was achieved using GC/ECD, generally two different GCs (Fisons Mega 2), with two columns of different polarity (no. 1: 30 m PS-088, 0.32 mm i.d., 0.32 µm film thickness, no. 2: 30 m OV-1701-OH, 0.32 mm i.d., 0.25 µm film thickness). Results were confirmed routinely by GC-LRMS (GC: HP 6890 / MS: HP 5973; 30 m HP5-MS, 0.25 mm i.d., 0.25 µm film thickness + 2.5 m pre-column; detection mode: MSD – EI.
Data comparability

To ensure reliability of exposure data and to improve comparability of analytical results from different laboratories, WHO has coordinated a number of inter-laboratory quality assessment studies. A study on levels of PCBs, PCDDs and PCDFs in human milk was conducted between February 1996 and April 1997, to identify laboratories, whose results could be accepted by WHO for exposure assessment studies (Malisch *et al.*, 2000; WHO, 2000). Only the State Institute for Chemical and Veterinary Analysis of Food Freiburg met all the pre-set criteria for analyses of PCDDs, PCDFs, DLPCBs, marker PCBs and fat in human milk and was thus selected as the WHO Reference Laboratory for the third and fourth round of the WHO human milk studies.

As noted above, the sample collection protocol may vary from country to country and therefore, data comparability between countries is not advised without a previous review of the national protocols. However, temporal trends should be possible based on the use of a consistent protocol for collection and handling of samples and of stringent criteria to assure that analytical quality assurance and control over long periods of time.

It should also be noted that the calculation of levels of PCDDs, PCDFs and DLPCBs may be slightly different for earlier surveys, which use international toxic equivalence factors (I-TEQs) in comparison to the more recent surveys, which use WHO toxic equivalence factors (WHO-TEQs). However, the levels reported for the earlier surveys should only be considered indicative of exposures because of the limited sampling plan and therefore, the differences between I-TEQs and WHO-TEQs are not considered to be minor.

Data storage

Data are stored at the GEMS/Food database located at WHO in Geneva, Switzerland and is password-accessible through the WHO Summary Information and Global Health Trends portal.

4.2.2. POPs and Metals in Pregnant Women's Blood (Riojas et al, 2007)

In 2007, Mexico participated in a tri-lateral maternal blood contaminant monitoring study of persistent organic pollutants and metals under the North American Commission for Environmental Cooperation's (CEC) program, Environmental Monitoring and Assessment, Human Health Subgroup (United States Centers for Disease Control, Health Canada and National Institute of Public Health, Mexico). This program was supported by the World Bank, the three countries of the North American Free Trade Agreement and the CEC.

The project was undertaken in Mexico by the National Institute of Public Health with the participation of the National Centre of Research and Environmental Training (CENICA) (from the National Institute of Ecology) and the Autonomous University of San Luis Potosí (UASLP). The laboratories from CENICA and UASLP participated in a capacity building exercise by analysing the samples while utilizing the expertise of the "Centre de toxigologie du Quebec²" to

² Centre de toxicologie, Institut national de santé publique du Québec, 945, avenue Wolfe, Québec (Québec) G1V 5B3, Canada.

analyze and validate results on duplicate samples. This globally recognized centre of expertise organizes external quality assessment schemes for toxic substances in blood and urine, with over 250 participants from 30 countries. Samples of blood from 240 first birth mothers from 10 regions in Mexico were collected in their last trimester of pregnancy and analyzed according to established protocols.

Background

The purpose of this initiative was to develop and implement a human blood biomonitoring project in Mexico in order to obtain an initial profile of population exposure to persistent organic pollutants (POPs) and toxic metals. Through the collection of samples in a consistent and comparable manner; through standard analytical techniques and through accepted quality assurance and quality control methodologies, this initiative was intended to provide a preliminary integrated baseline that could be used to determine priorities for and track progress in management of these toxicants both domestically and on a broader cooperative basis within North America. Canada and the USA worked cooperatively with Mexico to develop a comparable population exposure profile in order to identify population risk and potential environmental hotspots on a continental basis.

Sampling

Health care centre sampling locations were identified by experts in the participating countries including 10 sites in Mexico (see Table 4.2 below), 5 in the USA and 5 in Canada. As there has been little national or regional monitoring in Mexico, selection of sites were made according to knowledge and qualitative information provided by Mexican partners. Unique to this study is the knowledge gained from sampling at 5 sites in Mexico where some contaminants were anticipated to be above "average" values and 5 sites where baseline values were anticipated.

Table 4.2.	Sampling Sites a	nd Actual Sample	Numbers for Blo	od Biomonitoring Project
	1 0	1		0 5

Mexico (10 sites)							
Anticipated Hotspots	Samples Collected						
Córdoba	(25)						
Coatzacoalcos	(25)						
Salamanca	(25)						
Tultitlán	(25)						
Obregón	(25)						
Potential Background							
Guadalajara	(15)						
Hermosillo	(25)						
Mérida	(25)						
Monterrey	(25)						
Querétaro	(25)						

Resource allocation covered costs of sample collection, chemical analysis, data analysis, preparation and delivery of a report and data mail outs. In Mexico, 250 mothers were proposed to be selected for sampling and ultimately, 240 *primipara* mothers were actually sampled and

their blood analyzed. There was some difficulty in accessing the selected age range of mothers in Mexico, despite lowering the age selection criterion from 18 to 16 years of age.

The first-birth mothers were required to have lived in the proximity of the testing region for at least 10 years. The methodology developed for this project, together with Spanish-language materials and capacity building approach, has provided a product that can be readily adapted for use in other nations or regions, particularly in the Spanish-speaking nations in the Central America and Caribbean (LAC) region and South America. Mexico's participation in this respect served as a 'pilot project' that could be incorporated in other LAC nations through subsequent projects.

Blood samples from 240 Mexican mothers were taken in standard "purple top" tubes prepared for this type of testing and split into predetermined aliquots. These samples were then sent to two of three analytical laboratories for subsequent determinations of contaminant concentrations. The Autonomous University of San Luis Potosi in Mexico (reported as INSPMx) received one suite of samples, (blood plasma), for the measurements of POP's. Another suite of duplicate plasma samples were sent to the Centre de Toxicologie du Québec, Canada (CTQ), for analysis of the same compounds. Similarly, for heavy metal measurements, whole blood samples were sent to the National Centre for Environmental Research and Training, National Institute of Ecology (Centro Nacional de Investigación y Capacitación Ambiental, CENICA), and again duplicate samples were sent to the CTQ for analysis of the same metals. This duplication of analysis is of paramount importance for capacity building, in verifying the results and for ensuring the accuracy and precision of the work.

Aliquots of blood plasma were also taken, pooled and analysed for dioxins/furans and coplanar PCBs. This analytical work comprised a significant portion of the in-kind support provided by the USA through the expertise of their Centers for Disease Control (CDC) in Atlanta, Georgia. In order to collect sufficient volume of a representative sample from the region of interest, each single donor blood sample could not be analysed individually. Rather, 2 ml from each of the 25 individual maternal blood plasma samples per sample region were pooled in order to collect 2 representative aliquots from each hospital/sampling site. Since there were usually 25 samples of maternal blood at each site, 13 of the collected plasma samples were mixed into one tube i.e. 26 ml and a second aliquot of 12 samples was mixed into a second tube for 24 ml of sample. Each of these two tubes were sent to the US CDC's National Centre for Environmental Health and analyzed for dioxins, furans as well as coplanar and other PCB's in order to derive a "dioxin toxic equivalent, (TEQ)".

Sample analytical procedures

Persistent Organic Pollutants (POPs) in Plasma: PCB Congeners: 28, 52, 99, 101, 105, 118, 128, 138, 153, 156, 170, 180, 183, 187. Organochlorinated Pesticides: Aldrin, cis-chlordane, trans-chlordane, pp'-DDE, pp'-DDT, heptachlorepoxide, hexachlorobenzene, beta-HCH, alpha-HCH, gamma-HCH, mirex, cis-nonachlor, trans-nonachlor, oxychlordane. Dioxins/furans/coplanar PCBs: One or two pools per site.

The method used was based in the Guidelines for the Accreditation of Pesticide Residue Testing Laboratories [Interpretation and Amplification of CAN-P-4 (General Requirements for the Accreditation of Calibration and Testing Laboratories)] Laboratory Accreditation Program for Pesticide Residues (LAPPR) the Standards Council of Canada 1995-07-10.

Data comparability

All POPs and heavy metals were analysed at the CTQ, while in Mexico, POPs were analyzed at UASLP and metals were analyzed at CENICA. All dioxin/furan samples were prepared and analyzed in the same laboratory (CDC Atlanta Georgia, USA) to ensure minimal interlaboratory analytical error, and were accepted as valid results. Generally levels of dioxins in Mexican primapara mothers tended to be lower than their counterparts in the USA, as determined by an assessment of NHANES data.

In the final report, the analyses provided by the CTQ, referee laboratory were utilized to assess the levels of contaminants. While results indicate that the levels of both POP's and heavy metals are within anticipated ranges for the general population, there are several anomalous results that warrant further investigation. Valuable lessons were learned from this capacity building exercise and the need for an inter-laboratory validation program was paramount among these. The CEC in cooperation with Canada, USA and Mexico is developing such a program as a result of this blood monitoring project.

Data storage

Concentration results and relevant sample information (e.g. sample ID, site ID, location name, sample duration, meteorological conditions, among others) were recorded in Excel® spreadsheets.

4.3 **Programs/activities related to other media**

Some GRULAC countries submitted, to the ROG members and also to UNEP, information regarding monitoring programs and surveys; even when the data are not part of a Regional Program, they could be considered useful for future evaluations and are included as Annex 4.

Mexico, through the CEC, has undertaken a study of various information sources that may contain relevant data relating to POP's. This "Gray Literature" exercise has identified several hundred valuable information pieces such as academic theses from graduate student studies, regional data from academic research, and state generated data relating to site's specific concerns. These sources provide information of levels of DDT in environmental and biota samples, Lindane and other HCH isomers in the dairy sector and in human tissues. Chlordane in soil samples, PCB's in contaminated soils, etc. This report will be published at <u>www.cec.org</u> in 2009.

5 **RESULTS**

This chapter presents the results of the ongoing monitoring programs in the GRULAC region. The focus is in the core matrices of the GMP, i.e. air, human/blood samples. The chapter is divided in four sections: ambient air, human tissue, other media and long range atmospheric transport.

In the ambient air section, the results from air sampling, the GAPs program and other air studies in the region, are presented as box plot figures for a better representation of the variability of the data (see Annex 5 for a description of a box plot diagram). A value of half the detection limit was assigned to the GAPs results reported as "Not Detected" (ND) or "Below Detection Limit" (BDL) in order to have a representation of the data in the box plot diagrams.

In order to benefit from a better comparison, the GAPS data were grouped according to the four subregions named: Mesoamerican subregion, Caribbean subregion, Andean subregion and Southern Cone subregion, which are shown in Figure 5.1 using different colours. The data were also grouped by zone or site type i.e. background, rural/agricultural and urban areas, according to the sampling strategy of the GAPS programme.



Figure 5.1. GRULAC subregions used in this report to group the results of the GAPS program that were delivered to the ROG in May 2008.

Results from human tissue come from the WHO-human milk survey and the POPs and Metals in Pregnant Women's Blood, Mexico. The data are presented according to the sampled compound and the sampling site.

5.1 Ambient air

The data available for baseline concentrations in air media mainly come from the GAPS program (2005-2006), as mentioned; also, some results from other studies are included. The GAPS program established a network of eleven sampling sites in eight countries.

Monitoring systems employed by GAPS involved the use of PUF and XAD samplers, with different deployment times and temporal resolution as was described in chapter 4. The main difference is that the PUF gives short time temporal resolution (usually three months) while the other gives a one year average, since the equilibrium is reached after a longer period in such type of samplers (Wania et al, 2003).

PUFs were more often used in the region, deployed at nine sampling sites in eight countries; the results from 2005 are shown in the next section 5.1.1. XAD samplers were deployed in seven sites, six countries for 2005 and in six sites, six countries for 2006; the results are shown in section 5.1.2. PUFs and XAD samplers were deployed together in some sites allowing for comparison between the two sampling systems, section 5.1.3. The PUFs samplers were analyzed for PCBs and some chlorinated pesticides, and XAD for chlorinated pesticides only.

Only four of the eleven sites accomplished the 75% data completeness criterion from which no evidence was received to evaluate the precision and accuracy of the data from the GAPS program, the ROG-GRULAC decided to perform the comparisons with all the data available no matter if the site accomplished the said criterion.

Additional information from the GAPS programme regarding PUF sampling from one period in 2008 in three countries, Barbados, Brazil and Ecuador (GAPS, 2009), was received in 2009 and the data were included in the data bank, Annex 6.

Air quality studies which used active air sampling are presented in section 5.1.4 and other air studies in progress in the Region are mentioned in section 5.1.5.

The data were analyzed using some basic statistical parameters such as median values and the geometric mean. The average values, even when reported in tables, are not useful parameters since few values having large variability can contribute with larger changes in this parameter. The median and geometric mean avoid the bias caused by few exceptionally high values. The standard deviations are reported as well. As mentioned, there are many values reported as below the detection limits or not detected, for which case a number corresponding to the half of the detection limit reported by the GAPS program was used for calculating both the median and the geometric mean.

5.1.1 PUFs Levels

The GAPS program established a network of PUFs sampling sites in different countries within the GRULAC region since 2005. This network expanded its activities during 2008. The number of analyzed compounds comprises 4 pesticides of the Stockholm Convention (dieldrin, chlordane, heptachlor and DDTs) and one industrial product PCB. Results from the data of the 2005 sampling period show that the detection % frequency values were higher for chlordanes and their metabolites, ranging from 50 to 60%, followed by PCBs 42%, dieldrin 33% and p,p'-DDE with 25%. The lowest detection frequencies were observed for heptachlor epoxide and heptachlor with 19% and 4% respectively Figure 5.2 shows the detection frequency in the GAPS program for PUFs samplers.



Figure 5.2. Frequency of POPs detection in the PUFs samplers (Source: GAPS, 2008)

The GAPS data are presented in two different box plots, one where median values of background sites are compared according to the geographical sub-region as indicated in Figure 5.1, another where a comparison among zones is presented, grouping the data according to the type of sampling sites, background/remote sites versus rural/agricultural sites. Also the complete statistical parameters for PUF sampling are shown in Table 5.1. In general, POPs detected were in the order of pg/m^3 .

Figure 5.3 shows the box plots of PCBs levels in PUF passive samplers compared by geographical subregions and zones. Whereas the variability in the observed concentrations of the subregions was higher in the Caribbean and Southern Cone, it's worth mentioning that only one site was deployed in the Caribbean while three sites were deployed in the Southern Cone. Larger variability in PCBs levels was observed in the background zones when the data were grouped according to the type of sampling site. Six sampling sites were deployed in background zones and three in rural/agricultural.

The background median values found in the Mesoamerican, Caribbean, Andean, and Southern cone subregions were 0.06, 16.03, BDL and 18 pg/m^3 , respectively. The geometric means for the same subregions were 0.21, 1.92, BDL and 7.74 pg/m^3 , respectively. Aside of the fact that some extreme values were detected in the Mesoamerican subregion, high variability was observed in the Caribbean and Southern Cone subregions preventing evaluation of statistical differences between them.. Most of the higher values come from background areas, reaching up to 146 pg/m^3 (Figure 5.3) perhaps reflecting the potential long range transport aspect from source areas.



Figure 5.3. PCBs box plots in air/PUF samplers from background GRULAC subregions and zones (statistical parameters in table 5.1) (Source: GAPS, 2008).

In the case of p,p'-DDE (Figure 5.4), no statistical differences were noted between medians in the different geographical subregions (reported values were below the detection limit, in the order of 0.05 pg/m³ for the four subregions). The highest variability in p,p'-DDE concentration values were found in the Caribbean and the Southern Cone subregions. The highest value was detected in rural areas, which is expected because of their greater DDT consumption (Lopez-Carrillo *et al.*, 1996). The geometric means were 0.17 and 0.23 pg/m³ for the Caribbean and the Southern Cone subregions respectively.



Figure 5.4. *p,p*'-DDE box plots in air/PUF samplers from background GRULAC subregions and zones (statistical parameters in table 5.1) (Source: GAPS, 2008).

The other pesticides reported in the GAPs program were the chlordanes that present very low concentrations, without statistically significant differences between subregions and zones (Figure 5.5). However, cis-chlordane's median value was higher in the Caribbean subregion (1.5 pg/m^3) , while trans-chlordane and trans-nonachlor were higher in the Southern Cone subregion (2 pg/m^3) and 0.03 pg/m³). It is interesting to note the extremes values at the background zones, perhaps due to transport from sources. Variability was higher in rural/agricultural zones, probably reflecting their use in those zones.



Figure 5.5. Chlordanes and nonachlor box plots in air/PUF samplers from background GRULAC subregions and zones (statistical parameters in table 5.1) (Source: GAPS, 2008).

The median concentration of heptachlor epoxide (Figure 5.6) resulted higher in the Mesoamerican region (median value 32.5 pg/m^3); heptachlor exhibited BDL values in all background samplers and dieldrin (median values 5.04 pg/m^3 in the Caribbean and 1.2 pg/m^3 in the Southern cone) was also detected at very low concentration in the PUF samplers. The background area presented the highest variability in heptachlor epoxide and dieldrin concentrations, probably due to transport from sources areas.



Figure 5.6. Heptachlors and dieldrin box plots in air/PUF samplers from background GRULAC subregions and zones (statistical parameters in table 5.1) (Source: GAPS, 2008).

Considering the annual extension of the passive sampling using PUFs (4 samples within a year) and the recent starting of the GAPS program within the region, no temporal trend could be established, mainly due to the small amount of samples giving positive results and the still few results reported. (Annex 6 shows the figures with the time trends for several POPs).

Since data can be analyzed using different statistical parameters, Table 5.1 shows the main statistical parameters expressed as mean, geometric mean and median, as well as the standard deviation by compound and region, for future evaluations. It suggests that the large variability of the reported data produce large variation coefficients, almost all above 100%. Such high variability precludes the use of mean values and points out the need to use both median and geometric mean as the selected parameters for comparing regional levels and trends. It is important to note that many values are below the detection limits, that is, the concentrations are very low. To visualize temporal trends will require many years of monitoring. The spatial representation of the GAPS data is also weak, since large territories are not represented by the existing monitoring network.

Table 5.1. Statistical parameters for POPs in air (pg/m3) reported by the GAPS program for PUF samplers in each sub-region (background data only) and zones (includes all data) (Sources: GAPS, 2008).

PUF statistical by subre	parameters gion	cis- chlordane	trans- chlordane	trans- nonachlor	Heptachlor	Heptachlor epoxide	Dieldrin	ppDDE	PCBs
	Mean	0.53	0.20	0.16	BDL	29.76	BDL	BDL	2.30
Mesoamerican subregion	Geometric mean	0.47	0.16	0.16	BDL	7.25	BDL	BDL	0.21
(includes only	Median	0.40	0.23	0.18	BDL	32.50	BDL	BDL	0.06
background	SD	0.32	0.12	0.05	BDL	22.70	BDL	BDL	4.47
data)	VC	60%	60%	29%	BDL	76%	BDL	BDL	195%
	Min	0.31	0.05	0.10	BDL	0.05	BDL	BDL	0.06
	Max	1.00	0.30	0.20	BDL	54.00	BDL	BDL	9.00
	Ν	4	4	4	4	4	4	4	4
0.11	Mean	1.48	0.79	0.73	BDL	0.29	7.29	1.54	37.53
subregion	Geometric mean	1.12	0.37	0.27	BDL	0.11	0.98	0.17	1.92
(includes only	Median	1.50	0.60	0.15	BDL	0.05	5.04	0.05	16.03
background	SD	1.02	0.85	1.18	BDL	0.48	9.11	2.98	55.72
data)	VC	69%	108%	163%	BDL	165%	125%	193%	148%
	Min	0.30	0.05	0.10	BDL	0.05	0.07	0.05	0.06
	Max	2.60	1.90	2.50	BDL	1.00	19.00	6.00	118.00
	Ν	4	4	4	4	4	4	4	4
A 1	Mean	0.65	0.53	0.33	BDL	62.29	BDL	BDL	BDL
Andean subregion	Geometric mean	0.36	0.22	0.18	BDL	0.42	BDL	BDL	BDL
(includes only	Median	0.20	0.53	0.10	BDL	0.05	BDL	BDL	BDL
data)	SD	0.90	0.55	0.45	BDL	124.48	BDL	BDL	BDL
uala)	CV	138%	104%	138%	BDL	200%	BDL	BDL	BDL
	Min	0.20	0.05	0.10	BDL	0.05	BDL	BDL	BDL
	Max	2.00	1.00	1.00	BDL	249.00	BDL	BDL	BDL
	Ν	4	4	4	4	4	4	4	4
0 1	Mean	1.28	1.51	0.43	BDL	BDL	6.61	1.22	50.24
Cone	Geometric mean	0.71	0.85	0.27	BDL	BDL	0.73	0.23	7.74
subregion	Median	0.50	2.00	0.30	BDL	BDL	1.20	0.05	18.00
(includes only	SD	1.65	1.31	0.42	BDL	BDL	14.27	2.11	64.34
data	CV	129%	87%	97%	BDL	BDL	216%	174%	128%
uala)	Min	0.30	0.20	0.10	BDL	BDL	0.07	0.05	0.06
	Max	5.00	3.50	1.20	BDL	BDL	44.00	5.70	146.00
	N	9	9	9	9	9	9	9	9

BDL: Below Detection Limit

Table 5.1. Continuation: Statistical parameters for POPs in air (pg/m3) reported by the GAPS program for PUF samplers in each subregion (background data only) and zones (includes all data) (Sources: GAPS, 2008).

PUF statistical para by zone	meters	cis- chlordane	trans- chlordane	trans- nonachlor	Heptachlor	Heptachlor epoxide	Dieldrin	ppDDE	PCBs
Rural/Agricultu	Mean	2.27	19.08	1.60	9.04	0.30	3.64	15.33	61.73
re (includes data	Geometric mean	0.98	1.21	0.66	0.14	0.08	0.66	0.52	3.44
from Andean, Mesoamerican	Median	1.10	0.90	0.50	0.05	0.05	0.80	0.05	8.00
and Southern	SD	2.98	47.17	2.23	23.79	0.66	6.19	36.13	148.78
Cone	CV	131%	247%	140%	263%	220%	170%	236%	241%
subregions)	Min	0.20	0.05	0.10	0.05	0.05	0.07	0.05	0.06
	Max	8.50	126.00	6.00	63.00	1.80	17.00	97.00	399.00
	Ν	7	7	7	7	7	7	7	7
	Mean	1.05	0.94	0.42	BDL	17.61	4.25	0.83	29.13
Background	Geometric mean	0.63	0.41	0.22	BDL	0.22	0.32	0.12	1.18
(includes data	Median	0.40	0.30	0.15	BDL	0.05	0.07	0.05	0.06
from all	SD	1.23	1.07	0.59	BDL	55.04	10.26	1.88	51.50
subregions)	CV	117%	114%	141%	BDL	313%	242%	225%	177%
	Min	0.20	0.05	0.10	BDL	0.05	0.07	0.05	0.06
	Max	5.00	3.50	2.50	BDL	249.00	44.00	6.00	146.00
	N	21	21	21	21	21	21	21	21

BDL: Below Detection Limit

5.1.2 XAD Levels

Passive samplers using XAD resins were deployed for one year, in 7 sites in 2005 and 6 sites in 2006. Some of the sites were the same as those used for the PUF samplers. XAD data were classified by subregion and the location where the samplers were deployed (background, urban and rural areas). Differences could be observed between the two types of samplers, in particular those related to the detection frequency where Dieldrin and p,p'-DDT were not detected in any of the XAD samples analysed (Figure 5.7). The higher detection frequencies were observed for trans-chlordane, trans-nonachlor and cis-chlordane.



Figure 5.7. Frequency of POPs detection with the XAD samplers (Source: GAPS, 2008)

Figure 5.8 shows the p,p'-DDE median concentrations in air samples and the outliers. It is clear that p,p'-DDE levels in air show no statistical differences in the median values. Concentrations were not detectable in most of the samplers. However, the highest value detected by the XAD samplers was found in a background area in the Southern Cone (29 pg/m³). Data present higher variability in the samplers deployed in agricultural areas.



Figure 5.8. *p*,*p*'-DDE box plots in air/XAD samplers from background GRULAC subregions and zones (statistical parameters in table 5.2) (Source: GAPS, 2008).

Figure 5.9 shows the levels detected in air samples for cis- and trans-chlordanes and transnonachlor in the XAD samplers. Median values in background zones where higher, $(0.3, 0.73, 0.23 \text{ pg/m}^3, \text{ in the Southern Cone subregion. The zone' comparison shows larger concentrations in the urban area, 4.45, 6.05 and 3.95 pg/m³ for cis-, trans-chlordane and trans- nonachlor, respectively.$



Figure 5.9. Chlordanes and nonachlor box plots in air/XAD samplers from background GRULAC subregions and zones (statistical parameters in table 5.2) (Source: GAPS, 2008).

While heptachlor levels (Figure 5.10) were detected only in the background Andean and Southern Cone sub region, with median values of 7.65 and 1.95 pg/m^3 , respectively, the heptachlor epoxide was detected only in the urban zone, having a 3.43 pg/m^3 median value. The high levels of heptachlor in remote zones may reflect usage patterns for this pesticide. Most of the data showed values not detectable.



Figure 5.10. Heptachlors box plots in air/XAD samplers from background GRULAC subregions and zones (statistical parameters in table 5.2) (Source: GAPS, 2008).

The correlation among the two sampling periods (2005 and 2006) using the XAD samplers is shown in the Figure 5.11, where the variation in concentrations between both sampling periods did not show discrepancies for cis- and trans-chlordanes and heptachlore ($r^2 = 0.7872 P < 0.05$); this may indicate that a longer sampling period should be considered for the evaluation of temporal trends. The comparison shows only those sites where the measurements ran for the two years.



Figure 5.11. Correlation on XAD air derived concentrations between sampling years. GR: sampling locations in the GRULAC region; cC: cis-chlordane, tC: trans-chlordane and Hept: heptachlor. (Source: GAPS, 2008).

Table 5.2 shows the statistical parameters for the XAD samplers' data; as indicated in Chapter 4, the number of sites are lower than for PUF samplers. Similar to PUF measurements, a high variability is observed in the data and the values of the coefficient of variation are in most of the cases higher than 100%.

Table 5.2. Statistical parameters for POPs in air (pg/m3) reported by the GAPS program for XAD samplers in each subregion (background data only) and zones (includes all data) (Sources: GAPS, 2008).

XAD by subregion		cis- chlordane	trans- chlordane	trans- nonachlor	Heptachlor	Heptachlor epoxide	p,p´-DDE
	Mean	0.20	0.17	0.18	ND	ND	ND
Mesoamerican subregion	Geometric mean	0.17	0.11	0.12	ND	ND	ND
	Median	0.20	0.17	0.18	ND	ND	ND
(includes only	SD	0.14	0.18	0.18	ND	ND	ND
background	CV	71%	108%	101%	ND	ND	ND
uala)	Min	0.10	0.04	0.05	ND	ND	ND
	Max	0.30	0.30	0.30	ND	ND	ND
	Ν	2	2	2	2	2	2
	Mean	ND	0.28	BLD	7.65	ND	ND
Andean subregion	Geometric mean	ND	0.16	BLD	2.12	ND	ND
(includes only	Median	ND	0.28	BLD	7.65	ND	ND
hackground	SD	ND	0.32	BLD	10.39	ND	ND
data)	CV	ND	116%	BLD	136%	ND	ND
)	Min	ND	0.05	BLD	0.30	ND	ND
	Max	ND	0.50	BLD	15.00	ND	ND
	Ν	2	2	2	2	2	2
	Mean	0.45	1.10	0.33	1.95	ND	7.59
The Southern	Geometric	0.27	0.22	0.26	1.04	ND	1.27
Cone subregion	Madian	0.27	0.32	0.20	1.04	ND	0.45
cone subregion	Median	0.30	0.73	0.23	1.93	ND	0.43
(includes only	SD	0.47	1.30	0.20	1.91	ND	14.28
background		105%	123%	80%	98%	ND	188%
data)	Min	0.10	0.05	0.15	0.30	ND	0.45
	Max	1.10	2.90	0.70	3.60	ND	29.00
	N	4	4	4	4	4	4

BDL: Below Detection Limit ND: Not Detected.

Table 5.2. Continuation: Statistical parameters for POPs in air (pg/m3) reported by the GAPSprogram for XAD samplers in each subregion (background data only) and zones (includes all
data) (Sources: GAPS, 2008).

XAD statistical param by zone	eters	cis- chlordane	trans- chlordane	trans- nonachlor	Heptachlor	Heptachlor epoxide	<i>p,p</i> ^-DDE
Background	Mean	0.30	0.66	0.23	2.99	ND	4.02
	Geometric						
(includes data	mean	0.19	0.20	0.16	0.98	ND	0.76
from all sub-	Median	0.10	0.18	0.15	0.43	ND	0.45
regions)	SD	0.35	1.02	0.21	5.07	ND	10.09
	CV	118%	154%	92%	169%	ND	251%
	Min	0.10	0.04	0.05	0.30	ND	0.45
	Max	1.10	2.90	0.70	15.00	ND	29.00
	Ν	8	8	8	8	8	8
	Mean	0.33	0.83	0.22	ND	ND	7.30
Rural/agricultural	Geometric						
	mean	0.20	0.75	0.17	ND	ND	1.62
(includes data	Median	0.10	0.60	0.30	ND	ND	0.45
from the Andean	SD	0.40	0.49	0.14	ND	ND	11.86
and Southern	CV	121%	59%	67%	ND	ND	163%
Colle sub-regions	Min	0.10	0.50	0.05	ND	ND	0.45
	Max	0.80	1.40	0.30	ND	ND	21.00
	Ν	3	3	3	3	3	3
Urban	Mean	4.45	6.05	3.95	ND	3.43	ND
	Geometric						
(includes data	mean	4.43	5.96	3.83	ND	1.86	ND
only from the	Median	4.45	6.05	3.95	ND	3.43	ND
Mesoamerican	SD	0.64	1.48	1.34	ND	4.07	ND
sub-region)	CV	14%	25%	34%	ND	119%	ND
	Min	4.00	5.00	3.00	ND	0.55	ND
	Max	4.90	7.10	4.90	ND	6.30	ND
	N	2	2	2	2	2	2

BDL: Below Detection Limit ND: Not Detected.

5.1.3 Comparative analysis between PUF and XAD samplers, in the subregions and zones within the GRULAC region

This section compares the results obtained with both sampling media, PUF and XAD, by region and zone. Given the large variability of the data, the parameters median and geometric mean were considered appropriate. It is important to consider that several samplers (7 out 11) were deployed in background sites where no nearby POPs sources were apparent, in order to establish some baseline values for several POPs in air. In some cases statistical analyses could not be performed due to the limited amount of information available. The number of samples processed was notably greater for PUF samplers than for XAD, and obviously some differences become apparent for air concentrations. The correlation between both samplers is shown in Figure 5.12 that reveals a good agreement between the concentrations observed for both type of samplers, considering different sites and compounds.

For future monitoring programs within the GRULAC region, the temporal and spatial resolution that is required for a regional air monitoring program must be discussed, PUFs have a higher temporal resolution since the deployment period varied from days to months, but there are involved greater samples analyses and transport costs. On the other hand, since the XAD samplers are deployed for an entire year, annual resolution is provided.



Figure 5.12. Correlation observed among levels in air by using XAD and PUFs samplers in the same sites during 2005. cC: cis-chlordane, tC: trans-chlordane, tN: trans-nonachlor (Source: GAPS, 2008).

Table 5.3 shows a comparison in median values observed for both XAD and PUFs samplers deployed in different type of sites within the GRULAC region: urban, rural/agricultural and background; it's worth to mention that only XAD samplers where deployed in urban sites.

	Zone or type of sampling site								
Compound	Urban	Rural/ag	gricultural	Background					
	XAD	XAD	PUF	XAD	PUF				
cis-chlordane	4.5	0.1	1.1	0.1	0.4				
trans-chlordane	6.1	0.6	0.9	0.2	0.3				
trans-nonachlor	4.0	0.3	0.5	0.2	0.2				
Heptachlor	ND	ND	0.1*	0.4	0.1*				
Heptachlor epoxide	3.4	ND	0.1*	ND	0.1*				
Dieldrin	ND	ND	0.8	ND	0.1*				
<i>p,p´</i> -DDE	0.5*	0.5*	0.1*	0.5	0.1*				
PCBs	-	_	8.0	_	0.1*				

Table 5.3. Comparison of median values (pg/m^3) for PUFs and XAD samplers, considering all
the data (tables 5.1 and 5.2).

* Value below the detection limit

ND: Not Detected.

In general, the differences between the median values of the compounds sampled in remote sites from de GRULAC subregions, are low, except for the heptachlor in the Andean subregion and the heptachlor epoxide in the Mesoamerican subregion (Table 5.4). Most median values fall within the sub pg/m^3 concentrations. The data show that PCBs concentrations in air are greater than most of the pesticide concentrations in air.

Table 5.4. Median POPs values (pg/m³) in air from different geographical subregions within GRULAC, considering background data only. (Tables 5.1 and 5.2)

	Subregions									
Compound	Mesoan	nerican	Caribbean	Caribbean And		Souther	Southern Cone			
	Sub-region		Sub-region	Sub-	region	Sub-region				
	XAD	PUFs	PUFs	XAD	PUFs	XAD	PUFs			
cis-chlordane	0.2	0.4	1.5	ND	0.2	0.3	0.5			
trans-chlordane	0.2	0.2	0.6	0.3	0.5	0.7	2.0			
trans-nonachlor	0.2	0.2	0.2	0.1*	0.1*	0.2	0.3			
Heptachlor	ND	0.1*	0.1*	7.7	0.1*	2.0	0.1*			
Heptachlor epoxide	ND	32.5	0.1*	ND	0.1*	ND	0.1*			
Dieldrin	ND	0.1*	5.0	ND	0.1*	ND	1.2			
<i>p,p</i> - DDE	ND	0.1*	0.1*	ND	0.1*	0.5*	0.1*			
PCBs		0.1*	16.0		0.1*		18.0			

* Value below the detection limit

ND: Not Detected.

A summary of the comparison of the results obtained by the GAPS program in the GRULAC region is shown in Table 5.5; in general some similarities exist among the spatial trends observed in the different zones where sampling took place. However, it must be taken into consideration

that there are also differences between both samplers type in terms of the concentrations found. No conclusions can be reached on time trends using any of the samplers.

Trend in air concentrations (median)	XAD	PUF ¹
Urban >Rural/agriculture ≥ background	cis-chlordane, trans- chlordane, trans- nonaclor, heptachlor epoxide	cis-chlordane, trans- chlordane, trans- nonachlor, Dieldrin, PCBs
Urban = rural/agricultural = background	<i>p,p</i> ² -DDE ² Dieldrin	Heptachlor ² , heptachlor epoxide ² , p,p -DDE ²
Background > rural/agricultural = urban	heptachlor	

Table 5.5. Summary of the results in air concentrations by using PUFs and XAD samplers

¹Only deployed in the rural/agricultural and background zones.

² Values are in the detection limit order.

Based on the results from the GAPS program, it is possible to indicate the background values (in terms of i.e. mean, median and geometric mean concentrations detected in background areas) for several POPs, as shown in Table 5.1 and Table 5.2. These values could be used as a preliminary baseline for environmental levels in air in pg/m^3 for several POPs of the Stockholm Convention within the GRULAC region, using both the XAD and the PUF samplers' results. However, it must be taken in consideration that there are still many important uncertainties associated to geographical cover, high variability in the observed data, differences in the results obtained in the two different sampling methods, among others.

5.1.4 Active Air samples (high volume samplers).

Two studies were identified in the region regarding air sampling with high volume systems: one was performed in México where selected POPs pesticides and PCBs were analyzed during a two year period on a regular basis. The other study was to determine dioxins and furans levels in air samples in an urban area (Sao Paulo, Brazil)

5.1.4.1 High volume sampling in Mexico

The available information on active samplers in air is limited to a study performed in Mexico between 2002 and 2004 for seven compound families (Alegria et al., 2008). The interesting fact is that these studies focus on the Stockholm Convention POPs corresponding to urban, suburban and rural areas. In the Mexican study, the compounds analyzed and frequencies of detected POPs are detailed in figure 5.13. PCBs were detected in almost 98% of the samples, independently of their origin. A similar situation was observed for DDTs, their metabolites and chlordane.

Heptachlor shows a higher proportion of samples detected in urban areas (14%) and a low detection frequency in suburban and rural areas (5% each). Dieldrin's frequency of detection was more homogeneous with proportions of 26, 22 and 18% in each area. In México such products were banned during the eighties.



Figure 5.13. Frequency of detection of the analyzed compounds (Alegria et al., 2008)

PCBs.

Median values of PCBs found in rural, urban and suburban areas were 116, 93 and 41 pg/m^3 , respectively (Figure 5.14). The rural area data presented the highest median value and variability; these parameters were attributed to long range atmospheric transport processes from source areas (Alegria et al., 2008).



Figure 5.14. Boxplot Σ PCBs (in order to know the congeners that were analyzed see chapter 4).

Since this was a high frequency sampling program that covered two years, it was possible to retrieve a temporal trend for some POPs compounds. Figure 5.15 shows the occurrence of a high PCBs concentration episode in the rural zone, between March and August 2002. This pattern was not observed during the same period in the other two zones that remained at relatively constant values, showing no temporal trend. A similar situation of high PCBs concentrations episodes in air were also reported in the Arctic region, associated with the long range atmospheric transport processes from east Europe (Eckhardt et al., 2007).



Figure 5.15. Temporal trends of PCBs levels in air samples from Mexico.

DDTs

The highest DDT levels were found in rural areas with a median value of 2010 pg/m³. For urban and suburban areas, the respective median values were 1242 and 536 pg/m³ (Figure 5.16). The ratio p,p'-DDT/p,p'-DDE in the rural area is greater than 1, suggesting a recent use of DDT in the rural area. Seasonal changes were determined for DDT levels in air. Higher concentrations are observed in warmer periods.





Chlordanes and nonachlor

Figure 5.17 illustrates the air concentrations for cis and trans-chlordane and trans-nonachlor. Active sampling shows very similar values to those of passive samplers. The median concentrations nearly ranged between 2-4 pg/m^3 , although the suburban areas displayed greater variability.



Figure 5.17. Air concentrations in different zones in Mexico, for cis-, trans-chlordane, and nonachlor

Figure 5.18 shows the results of heptachlor, dieldrin and toxaphene; the observed concentrations were similar for all pesticides in all sampled zones besides toxaphene, presenting remarkably higher concentrations in suburban zones, reaching a median value of 160 pg/m^3 .



Figure 5.18. Air concentrations of heptachlor, dieldrin and toxaphene in rural, urban and suburban areas

5.1.4.2 High volume sampling of dioxins in air in Brazil

One of the data gaps observed in the region regarding POPs is related to dioxins and furans measurements in air. Even when there is no routine analysis for dioxin and furans in air, few data have been released in the GRULAC region. Neither dioxin data in air from background sites, nor from rural/agricultural sites were available; only one study carried out at an urban area was reported. This recent report from Brazil (de Assunção *et al.* 2005), shows results from samples collected simultaneously at three urban sites in São Paulo City, in winter, spring, summer and fall (in 2000 and 2001). Andersen PUF samplers were used for gas and particles sequential sampling. Samples were analyzed using HRGC/HRMS according to US EPA Method 8290. The greater metropolitan area of São Paulo is one of the largest industrialized cities of Latin America and has a highly polluted atmosphere. Concentrations of dioxins and furans, ranged from 1.14 pg m^{-3} to 13.8 pg m^{-3} (0.047 pg I-TEQ m $^{-3}$ to 0.751 pg I-TEQ m $^{-3}$), Figure 5.19.

Principal component analysis showed that all the variables are highly correlated with one another, except the 2, 3, 7, 8-TCDD one. This is consistent with the similar concentration profiles observed for the tetra, penta, hexa, hepta and octa-homologous groups of the three sampling sites studied. At all sites, the most abundant compounds were the hepta and octa congeners. The 2, 3, 4, 7,8-PeCDF accounted for 37–46% of the total TEQ and the 2,3,7,8-TCDD accounted for 7–16%. The greatest mass concentrations of PCDD/Fs were found in the site where there is influence of industrial activities and heavy vehicular traffic fuelled by gasohol, diesel, and ethanol.



Figure 5.19. Dioxins and furans in air in a highly industrialized city in Brazil (Sao Paulo)

For all sites, the greatest concentrations in I-TEQ were observed in May (fall) while the smallest concentrations were observed in November (spring). As mention, the greatest mass concentrations of PCDD/Fs were found in a site located near an industrial area. Local industrial activities and heavy vehicular traffic from a nearby highway are the main emission sources at this site. The PCDD/Fs contribution of the incinerator emissions at a residential area was not observed because most of the wind directions were not favourable in the sampling periods and the work capacity of the incinerator was reduced during the study. However, the dioxin levels of this study are in the same range than the values for São Paulo City reported in another study conducted in 1995/96 (Mahnke,1997).

Although a small number of measurements were recorded in this study, the results show that dioxins and furans are present in air in São Paulo City at significant concentrations. Certainly, further investigation is still necessary to gain a better understanding on the emission sources for these pollutants in air. Long term monitoring is fundamental to elucidate the relationship between dioxins and furans emissions into the atmosphere from primary anthropogenic sources.

5.1.5 Other GRULAC air studies in progress (passive and high volume)

A number of ongoing programs and studies are being carried out in some GRULAC countries, namely:

a. Chile. In order to establish the atmospheric concentrations and sources of PCBs in the city of Santiago de Chile, the *Laboratorio de Química Ambiental* (LQA) of the *Centro de Tecnologías Ambientales* (CETAM) of the *Universidad Técnica Federico Santa Maria* (UTFSM) carried out an air quality monitoring campaign in the winter seasons of the

years 2002 and 2003. This study is financed by CONAMA (National Environmental Commission) and the CONICYT (National Commission for Scientific and Technological Research). The data will be available mid 2009. (Annex 4)

- b. A UNEP supported project aimed to use XAD-type passive samplers to evaluate altitudinal gradients of POPs (PCB, Pesticides) in different areas of the world such as Nepal, Bostwana, Costa Rica and Chile. The institutions involved are the University of Toronto at Scarborough, Environment Canada (National Water Research Institute, Burlington, Ontario), the Regional Institute for Studies of Toxic Substances, University of Heredia in Costa Rica, and the EULA-Chile Environmental Sciences Centre, University of Concepción, Chile. These data are expected to be available in 2009.
- c. The laboratory of Environmental Biogeochemistry located at the University of La Plata in Argentina, has started an air passive sampling study in different areas of Argentina, using PUF-type samplers, in collaboration with Mazarek University, Brno, Czech Republic.
- d. México has established the Mexican Dioxin Air Monitoring Network (MDAMN), designed under the umbrella of the Program of Sound Management of Chemicals of the Commission for Environmental Cooperation, CEC, which has been working on a regional plan to reduce the risk from POPs in North America. The main objective of this network is to generate the baseline information of dioxins and furans in background ambient air for the National Implementation Plan of the Stockholm Convention, as well as to the Regional Initiative of the CEC. The MDAMN started its operation in March 2008 at 9 sites (8 background and 1 urban, as reference), samples are taken four times per year, using high volume samplers (Tisch, PS-1 model) with quartz fibre filter (QFF) and polyurethane foam (PUF) cartridge. For each sample, an approximate volume of 8,400 m³ of air is sampled during 580 operation hours. QFF and PUF samples are analysed for dioxin, furans and coplanar PCBs, in the laboratories of USEPA. As mentioned, the results will serve to determine the baseline for these pollutants in ambient air, and to evaluate the effectiveness of measures implemented to reduce emissions of non intentional POPs and ambient concentrations.

5.2 Human tissues (milk and/or blood)

There are few data related to human matrices in the region; the identified studies that meet the comparability and quality requirements were the WHO-human milk survey and the POPs and Metals in Pregnant Women's Blood, Mexico.

In the human milk survey only one GRULAC country participated, Brazil. The analysis of the samples was performed at the WHO reference laboratory in Germany. The results became the only data set, at the Global level to meet the comparability requirements agreed to at the Drafting ROGs workshop in May 2008, Geneva.

5.2.1. Human milk study 2002 – Dioxins, PCBs and organochlorine pesticides (Braga *et al.*, 2002; Krauss *et al.* 2004)

Human milk samples were collected at 10 different locations, mostly from human milk banks (Figure 5.20). They were chosen with special attention to select at least one capital from each of the five territorial Brazilian regions, except for the State of São Paulo where two cities were selected: São Paulo (capital) and Cubatão. Following the protocol of the study, this area was considered, in advance, as a highly polluted one due to 33,000 tons of toxic industrial waste stored in landfills in this region. The local coordinators trained the professionals involved in the activities of the human milk banks to identify donors, helping to answer the questionnaires and also, in collecting the samples, which were all obtained in 2001.



Figure 5.20. Human milk sampling locations in Brazil

This study was part of the third round of the WHO-coordinated exposure study on "Levels of PCDDs, PCDFs and PCBs in Human Milk". The age of sampled Brazilian mothers varied from 13 to 40 years old, (22, on average), with 63% between 13 and 21, 27% between 22 and 31 and 10% between 32 and 40. The results for dioxins and PCBs are shown in Table 5.6.

SAMPLING Location City/State	PCDD/F pg WHO-TEQ/g fat (lower bound- upper bound limits)	Dioxin-like PCBs * pg WHO-TEQ/g fat	Marker PCBs** ng/g fat	% difference upper/lower bound
Brasília/Federal District	2.73	1.81	17.3	0.2
	(2.72-2.73)	(1.81-1.81)		0.2
Curitiba/Paraná	5.08	1.52	14.2	0.1
	(5.07-5.08)	(1.51-1.52)		0.1
São Paulo/São Paulo	3.89	1.40	9.9	0.0
	(3.89-3.89)	(1.40-1.40)		0-0
Cubatão/São Paulo	5.34	2.78	33.1	0.1
	(5.34-5.34)	(2.78-2.78)		0.1
Rio de Janeiro/Rio de	4.40	1.72	15.3	0.0
Janeiro	(4.40-4.40)	(1.72-1.72)		0.0
Belo Horizonte/Minas	4.81	2.04	17.1	0.0
Gerais	(4.81-4.81)	(2.04-2.04)		0.0
Recife/Pernambuco	2.87	1.82	12.8	0.2
	(2.87-2.87)	(1.81-1.82)		0.2
Caaporã (João Pessoa)	3.93	12.30	96.5	0.0
/Paraíba	(3.93-3.93)	(12.30-12.30)		0.0
Fortaleza/Ceará	3.69	1.64	16.4	0.0
	(3.69-3.69)	(1.64-1.64)		0.0
Belém/Pará	3.92	1.30	10.1	0.2
	(3.91-3.92)	(1.30-1.30)		0.2

Table 5.6. Concentration of PCDD/Fs, PCBs and DLPCBs in human milk, Brazil 2002.

* PCB - IUPAC No. 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189

** PCB - IUPAC No. 28, 52, 101, 138, 153, 180

The median of PCDD/F in human milk was 3.93 pg WHO-TEQ/g fat ranging from 2.73 to 5.34 pg WHO-TEQ/g fat. Dioxin-like PCBs varied from 1.30 to 12.30 pg WHO-TEQ/g fat with a median of 1.77 pg WHO-TEQ/g fat. Marker PCBs varied from 9.9 to 96.5 ng/g fat with a median of 15.9 ng/g fat. The pooled sample from Cubatão showed, as expected, the greatest values for all compounds, though not considering the PCBs values from Caaporã. In comparison with the results from the other 25 participating countries, the Brazilian samples showed the lowest contamination of PCBs (third lowest place for dioxins).

Organochlorine pesticides were analyzed only in two out of the ten pooled samples, from São Paulo City and Belo Horizonte, since organochlorine pesticides were not included in the third round; the results are given in Table 5.7.

 Table 5.7. Organochlorine pesticide concentrations in human milk from São Paulo and Belo

 Horizonte Brazil 2002.

Compound	São Paulo µg/g fat	Belo Horizonte µg/g fat
НСВ	0.006	0.003
o,p'-DDE	< 0.001	< 0.001
o,p'-DDD	< 0.001	< 0.001
o,p'-DDT	< 0.001	< 0.001
<i>p</i> , <i>p</i> '-DDE	0.596	0.155
<i>p</i> , <i>p</i> ′-DDD	< 0.001	< 0.001
<i>p,p'</i> -DDT	0.010	0.009
dieldrin	0.001	0.001
endrin, endrin ketone	< 0.001	< 0.001
heptachlor	< 0.001	< 0.001
cis-heptachlor epoxide	0.001	0.001
α -chlordane, γ -chlordane	< 0.001	< 0.001
oxy-chlordane	0.003	0.001
trans-nonachlor	0.002	0.002
Σ Parlar (toxaphene)	< 0.001	< 0.001
α-HCH	< 0.001	< 0.001
β-НСН	0.027	0.022
ү-НСН	< 0.001	< 0.001
Σ Endosulfane	< 0.001	< 0.001

The high p,p'-DDE/p,p'-DDT ratios, 59.6 for São Paulo and 17.2 for Belo Horizonte, indicate that exposure happened through past DDT application since the DDE/DDT ratio increases as the DDT use ceases. Previous application can be assumed also for the HCH group, as only the more stable *beta* isomer was present in both pooled samples.

In 1985, the use of DDT and HCH has been restricted to public health campaigns for vector control by the Brazilian Government. Until 1998, both compounds were used against the malaria vector, which is concentrated in the Amazon region in the northern part of Brazil (98% of cases). Both sampled capitals are located in the central part of Brazil.

5.2.2. POPs and Metals in Pregnant Mexican Women's Blood

Mexico participated in a tri-lateral maternal blood contaminant monitoring study of persistent organic pollutants organized by the North American Commission for Environmental Cooperation (CEC). This study included 240 women (15 to 30 years old) from ten different communities. The results show that the cities with the highest geometric p,p -DDE mean were in the industrialized areas of Coatzacoalcos and Cordoba with 1071 and 615 µg/Kg Lipid respectively; nevertheless, the highest value was found at the North in the Yaqui Valley in Sonora (19753 µg/Kg Lipid), believed to be due to a long history of organochlorine insecticide use. The summarized data are shown in the Figure 5.21.



Figure 5.21. Summary of POPs concentrations in blood samples of pregnant women in Mexico (source Riojas *et al.* 2007).

Data were also reported as medians. Figure 5.22 shows the median values for two POPs that represent the higher detected concentrations (p,p'-DDE and HCB) for both hot spot and baseline (background areas).



Figure 5.22. p,p'-DDE and HCB medians in the different sampled zones. The considered hot spots are shown in red while the considered baseline zones are in blue.

Dioxins and furans were also reported in this study, and the summary of the results is shown in the Table 5.8

"Hot spot" sites	PCDD TEQ ¹ (WHO-	PCDF TEQ ¹	cPCB TEQ ¹	mPCB TEQ ¹	Total TEQ ²	Sum PCB ppt (pg/g) ³
	TEQpg/g					
Cuatitlan	3.17	2.04	1.49	0.80	7.50	284.2
Coatzacoalcos	14.66	1.99	1.30	0.94	18.89	351.9
Salamanca	3.71	1.16	1.20	0.61	6.68	320.5
Cordoba	2.88	1.80	0.75	0.67	6.10	369.4
Obregon	2.13	2.26	0.65	0.30	5.34	182.6
Mean	5.31	1.85	1.08	0.66	8.90	301.7
Baseline sites						
Queretaro	3.10	1.38	1.08	0.71	6.27	223.6
Merida	2.79	1.41	0.89	0.80	5.89	369.6
Guadalajara	3.34	2.08	1.23	0.42	7.07	304.7
Monterrey	4.37	2.14	1.13	0.35	7.99	258.3
Hermosillo	2.60	1.50	1.08	0.35	5.53	154.9
Mean	3.24	1.70	1.08	0.53	6.55	262.2

Table 5.8. Mean values of dioxins per site as provided by US CDC^{*}

* These analyses were provided by US CDC and are the result of pooled samples from each site

¹ WHO TEQ 1995

² Sum of TEQ by class (PCDD, PCDF, cPCB and mPCB)

³ Sum of PCBs in ppt (pg/g) on a whole weight basis

5.3 Other media

Different GRULAC countries reported information relative to the presence of POPs in matrices other than the core matrices. Information relative to soils and sediments were provided by Antigua & Barbuda, human adipose tissue was also reported by Mexico. Brazil reported several studies relative to the POPs in human matrices. The Barbados Water Authority and the EPD routinely monitor groundwater wells in Barbados and a wide-spectrum analysis of groundwater samples from one or two of these water supply wells are carried out on annual basis. These analyses have not, to date, detected the presence of PCBs in the groundwater. The results of the most recent analysis, in June 2004, have shown PCB concentrations to be below the reliable quantification limit of 0.010 μ g/L, additionally, in the early 1990s, sea-urchin tissue was tested for a variety of toxic substances, including PCBs. No PCBs were detected in the samples analysed. Annex 3, presents a table listing the references of the studies received by the GRULAC countries. Summaries from some studies reported by the countries to the ROG-GRULAC members can be found in Annex 4.

5.4 Long-range atmospheric transport

In the GRULAC region no specific assessments have been conducted in order to understand if the POPs analyzed are transported long distances from the sources areas. This is a capacity building issue that will require further development since expertise is needed to accomplish such a scope. The data provided by the different air monitoring programs shows clear differences in the various types of sites as classified in this report. High concentrations have been observed in background zones within the GAPS program but are difficult to explain.

Detection of a substance at remote locations where it has never been used indicates evidence for long-range atmospheric transport, LRT, by natural and/or anthropogenic pathways; however, the detection of a sole 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 POPs in the GRULAC region, more extensive investigations are required. Such research should include sampling along latitudinal or altitudinal gradients in one or more environmental media to provide information on changes in concentrations when moving away from identified point source areas.

Altitudinal and latitudinal gradients in the Andes Cordillera have been measured in soils (Borghini *et al.* 2005) and mosses (Grimalt *et al.* 2004). In both studies a strong temperature dependence of POPs concentrations was found, which means that higher concentrations of some POPs (such as PCBs, HCB) were found in colder and higher altitude areas. Recently, Tremolada *et al.* (2008), studying soils in the Peruvian Andes, also found a precipitation effect on PCBs and DDTs detected levels.

Over long latitudinal gradients also a fractionation of PCBs has been described in mussel samples along the Chilean coast (Mendoza *et al.* 2006). Higher concentrations of low molecular weights PCBs in southern and colder areas were found. This preliminary evidence supports the "global fractionation" hypothesis of Wania and Mackay (1993).

Recent scientific peer reviewed papers indicate the presence of PCBs in snow samples in the Andes (Quiroz *et al.* 2008), where levels ranging from 20-190 pg/L were detected in the Aconcagua mountain, the highest point in the Andes. In the Bolivian Andes, Estellano and co workers (Estellano *et al.* 2008) describe some altitudinal profiles of POPs in air samples using PUF samplers.

Even in remote lakes in the Southern cone area, the presence of POPs and related compounds has been reported (Pozo *et al.* 2007), however in the latter case it is not clear if the source comes from long range transport or is due to local sources. Passive air PUF sampler reults in Chile by Pozo *et al.* (2004), and subsequent back trajectory analyses, suggest the LRT of POPs from distant source areas.

The atmospheric circulation in the Amazon Basin is dominated by winds from the tropical equatorial Atlantic Ocean, entering Amazonia from the Northeast. The wind circulation goes to the southwest, and is forced by the Andes Mountains to the south. The main air masses leave Amazonia in the southern part of South America. A small component that is able to pass through the Andes reaches the Tropical Pacific Ocean (Artaxo, 2008).

There are no specific studies for long range transport of POPs in Brazil and the small data base of air levels cannot be used for estimation of this kind of transport. Especially for non-intentional POPs like dioxins there are no emission data published which could be helpful to better understand atmospheric transport.

A study carried out in November 1995 to assess organochlorine levels in the atmosphere, performed on board the Brazilian Navy Oceanographic and Antarctic Supply Ship "Ary Rongel", during the XIV Brazilian Antarctic Expedition (Montone *et al.* 2005) showed trends relating of chlorinated pesticides, DDT and HCB, and for PCBs in the atmosphere of the southwest Atlantic and Antarctic oceans. The data can be considered an atmospheric baseline study. This is the only southern regional data from a remote area available that informs about the transport of pollutants and allows comparison of the background levels in the future. This study may provide comparable monitoring information to evaluate the effectiveness of the Stockholm Convention.

Sampling was performed in the open ocean between 23° and 62° latitude transects of the Southwest Atlantic and Antarctic Oceans. Fourteen samples were obtained and the following organochlorines were identified: hexachlorobenzene (HCB), p,p-DDE, p,p-DDD, p,p-DDT and 11 PCB congeners (18, 28, 44, 52, 101, 118, 128, 138, 153, 180 and 187).

Organochlorine levels in the atmosphere ranged from not detected (<0.6) to 25.3 pg/m³ for HCB, $3.7-102.6 \text{ pg/m}^3$ for $\sum \text{DDTs}$) and $46.2 - 985.0 \text{ pg/m}^3$ for PCBs. HCB levels increased slightly towards the Antarctic Peninsula. DDT levels are one order of magnitude less with respect to the preliminary study carried out from January to March 1987 (Weber and Montone, 1990), in a similar transect. These results may indicate a global drop in atmospheric DDTs. Data from the Southern Ocean during the last decades have confirmed this trend. In the early 1980s, Tanabe *et al.* (1982), reported DDT levels ranging between 110 and 240 pg/m³ for the Southern Ocean. A few years later, Kawano *et al.* (1985), detected lower levels (8.4–11 pg/m³) at the northern and southern sites in the Southern Ocean (December 1983–January 1984). Tatsukawa *et al.* (1990), reported a global decrease of DDT levels in the open ocean atmosphere between 1975 and 1983.

Total PCB concentrations showed similar trends to total DDT, indicating a decrease with increasing latitude. Despite the difficulty in comparing former PCB levels with recent measurements, it is apparent that atmospheric PCB concentrations over the Southwest Atlantic Ocean have not decreased rapidly in the last decades. Individual PCBs congener levels are in the same order of magnitude as those measured by Schreitmüller and Ballschmiter (1994) in the latitudes 25-47 °S during north–south cruises across the Atlantic Ocean in 1990. The lower chlorinated congeners (PCB-101 and below) predominated in the air samples, mainly between 51 and 62 °S latitude. A relatively larger proportion of less chlorinated congeners were reported in the high latitudes, such as in the Southern Ocean, as compared to those in mid and low latitudes (Iwata *et al.* 1993). Heavier PCB congeners (128, 187 and 180) occurred only in the samples near South America. The presence of these congeners and the other heavier congeners (138 and 153) can be associated with local source contributions (waste burning and dumping sites) from the Antarctic station such as was described by Larsson *et al.* (1992) and Montone *et al.* (2003).

The influence of the continental air masses arriving during the transect was observed mainly through the PCB and DDT data. The highest concentrations were between latitudes 23 to 36 °S, where the sampling points were nearer the coast. The air mass back trajectories show that the air mass travelled mainly over the continent, meaning that they presented some continental contribution. OC levels in air in the southwest Atlantic Ocean decreased with increasing latitude, with exception of HCB which increased slightly. In spite of the fact that some tropical countries are still using DDT for limited agricultural purposes, the lower proportion of p,p -DDT observed in the Antarctic sector of the South Atlantic air implies a decrease from the 1990s. No significant temporal trend was observed in atmospheric PCB data over the period from 1987 to 1995 in the Antarctic Peninsula.
6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

6.1.1. Baseline concentrations

Air

The data available for baseline concentrations in air media come mainly from the GAPS program which involves currently 8 countries out of 33 from the GRULAC region, namely, Argentina, Bolivia, Brazil, Chile, Colombia, Costa Rica, Cuba, and Mexico. Considering the complexity of the ecological characteristics, the geographical dimension of the region and the different levels of social and economic development, those 8 countries should not be considered to represent the whole region.

The GAPS program generally shows very low concentrations in air measured through passive samplers, usually in the low pg/m^3 range. To detect changes in concentrations with some reliability, the temporal and spatial resolutions must be taken into consideration to properly design a regional monitoring program. The preliminary background values provide result from sites located far from point emission sources and could be used for future comparisons of temporal trends. As mentioned before, more monitoring sites are needed to expand the network thereby providing proper coverage of the region.

Concentrations of several pesticides are greater in rural/agricultural areas and may be related to the pattern of use of such products; however, many pesticides did not show values above the detection limits. It is important to note that the GAPS Program does not cover all the 12 POPs of the Stockholm Convention. The lack of data of airborne dioxins and furans is considered a shortcoming of data for the region.

The employment of passive samplers has proven to be very useful for comparing the different sub regions and zones but there are still many questions to be answered that relate to: spatial and temporal resolution, the large variability in the results observed and the differences between the two sampling systems, PUF vs. XAD. Additionally, in order to follow a 25% variation from current concentration values, it is estimated that a monitoring program should last about 5-15 years (Annex 7).

The use of active atmospheric sampling in the region was limited to two studies (Dioxins in air São Paulo and high volume sampling of POPs in Mexico). Results using passive and active sampling indicate some differences in concentrations for some compounds (i.e. DDTs).

While active sampling needs more infrastructure and resources, this method represents the standard methodology for analyzing air pollution that should be used for calibrating and

comparing passive sampling techniques. As with passive sampling, the active sampling studies' results did not allow the establishment of a baseline for the whole region.

Human milk/blood

The data available from the Third Round WHO-coordinated exposure study on -levels of PCDDs, PCDFs and PCBs- in human milk, provides information only from Brazil (2001-2002) and it was supported financially and technically by the national government. Another source of information was the study administrated by the North American Commission for Environmental Cooperation (Riojas *et al.* 2007), which provides data for human maternal blood in Mexico (2005-2006). Unfortunately, this information is insufficient to allow defining a baseline for the whole region, evidencing the need for a regional human biomonitoring program.

Human monitoring data reveal low POPs concentrations (including dioxins and furans, PCBs and selected pesticides) in the analyzed samples in both studies. In a very few sites significant levels were detected. It is important to mention that this report does not include a comparison between milk and blood data. Future monitoring should consider the relationships between both kinds of measurements to better understand the exposure of vulnerable groups as indicators to protect the future generations, as stated in the Millennium Goals and the Stockholm Convention.

6.1.2 Evidence of temporal trends and long range transport

In the GRULAC region the only existing monitoring program that has been running for more than one year is the GAPS program for air media. The available data do not currently allow definition of any temporal trend for the region. This limitation of the available data points to the need for the implementation of long term monitoring programs.

Diverse references from the scientific literature exist regarding long range transport (LRT), within the GRULAC region; peer reviewed scientific studies point out that POPs LRT is occurring in the region, but the actual source areas have not yet been identified. More research is needed to assess POPs transport through the atmosphere within the regional boundaries and from outside the region.

Due to the Antarctic Continent's proximity to the GRULAC region, the former exerts influence on the latter's environment, thus it is important to start planned research activities within the framework of the Global Monitoring Program.

It can be concluded that more systematic studies should be designed and implemented to address this issue within the GRULAC region. Air monitoring with the GAPS program and active sampling could be used for modelling the transport of POPs between source and receptor areas, but the need is recognized for an evaluation and increase of the GAPS sampling sites aimed to model POPs transport. It is recommended that POPs modelling capabilities and training should be stimulated within the region.

6.1.3 Gaps in data coverage and the resources needed to overcome them or establish/strengthen the capacity within the region

The absence of continuous monitoring programs covering the entire GRULAC region is one of the limiting factors to the establishment of temporal and spatial trends, representing the most important gap. The region should define monitoring networks considering the ecosystems' similarities and differences and local capabilities. Monitoring should be extended as much as possible, but individual country participation is needed in this regard. Resources will be needed to support the extension of existing GAPS program, the WHO-human milk survey, and the human blood monitoring survey. The region should build its own capabilities since these programs are currently managed by organizations from outside the region. Spatial coverage should also be improved; it might be possible to establish monitoring programs defining subregions sharing some similarities (e.g. eco-regions that cross country boundaries).

Furthermore, the region should make efforts in order to unify criteria to develop a comprehensive and sustainable long term monitoring program involving the core matrices and others that may be of regional interest. To develop and implement a monitoring program, a political commitment is necessary in order to provide ongoing financial resources and establish priorities for a regional program.

6.1.4 Ongoing programs/activities

As mentioned before, the GAPS program has been active in the GRULAC, since 2005, and some sites were included for the current evaluation. The recommendation is to maintain these sites and to expand the spatial coverage to the regions presently not covered, in close relation with the needs and interests of a regional program. This regional program should be supported by the countries in the region with the capacity to fund such monitoring. If countries wish to introduce a local component to this program, they should ensure that their program is designed in such a way that it allows for comparability of results with the broader regional program.

The WHO-human milk survey had minimal participation from the countries in the region, with only Brazil participating in this global study during the Third Round. Antigua & Barbuda and Uruguay are now participating in the UNEP-WHO human milk survey, Fourth Round that was undertaken in the second half of 2008. These countries completed the sampling and the results are expected in the autumn of 2009. It is also expected that more countries will be involved in the Fourth Round which is still in progress. Countries should realize the advantages of participating in such global studies and consider contributing samples. It is proposed that PAHO play an important role in promoting such activities in the GRULAC region. The Ministries of Health could also be significant contributors to this work if they were made aware of the benefits of participating in such global programs.

Countries in the region should discuss if levels in other media such as marine mammals, mussels and soils, could be used as supplemental indicators for temporal trend evaluation within an interregional monitoring program.

6.2 Recommendations for the future

The absence of synergies between countries is noted. Interaction between government, academia, industry and NGOs is needed both at national and regional levels to build a successful strategy for facing the challenge of monitoring POPs levels in the core matrices of the GMP. The regional involvement in monitoring programs requires a common strategy, ongoing financial support, human resources and capacity building to accomplish the task of gathering comparable and high quality data for contribution to the GMP and the effectiveness evaluation of the Stockholm Convention. In each country, the cooperation and participation of other key Ministries such as Health, Agriculture, among others, should be encouraged.

The GRULAC should formalize a coordinating structure for developing a Regional Action Plan (RAP). The ROG could be strengthened in order to be part of the coordinating structure, which would play a key role in setting the preparation of the medium/long term Regional Action Plan (RAP). The formulation of a RAP would allow: (i) evaluation of options available and actions necessary to meet the requirements of the Stockholm Convention for POPs monitoring, (ii) development of a regional monitoring program indicating scope, limitations, costs and benefits and, (iii) identification of requirements for capacity building and external assistance in the implementation of the RAP.

The countries should make an effort to optimize the existing resources in terms of infrastructure, human resources and quality assurance and quality control systems. The more experienced countries within the region should promote capacity building activities at sub regional level through the Regional Nominated Centres. Some countries have enough human and infrastructure facilities to promote training courses and long term cooperation initiatives with their neighbours, aiming to accomplish the Stockholm Convention's objectives.

In the future, the main functions of the ROG-GRULAC could be as follows: (i) to raise awareness within governments of the POPs monitoring and the need to develop a RAP; (ii) to facilitate co-ordination within the region to allow the successful development and implementation of the RAP; (iii) to develop the structure, framework and procedures for the development of the RAP; (iv) to establish a mechanism for planning, managing and supervising the development and implementation of the RAP; and (v) to plan and initiate information dissemination campaigns.

Some other technical recommendations related to the development of the regional monitoring plan should be considered including the criteria for the definition of air sampling sites and analytical programs, QA/QC, determination of sample size for human monitoring and limitations associated with costs and benefits.

The existing air monitoring networks need to be expanded by using both passive and active sampling techniques and an effort should be undertaken in order to cover all POPs of the Stockholm Convention.

The need for baselines values in human samples is urgent, since the small amount of data available did not allow a meaningful comparison. The selection of sites for providing human milk samples as a priority, but also blood samples, should be made as soon as possible.

It is worth mentioning that there are several species of non-migratory endemic wildlife (birds, marine mammals, mussels, and others) as well as soils and mosses that can be used as regional indicator sentinels (ecomarkers) of local or regional POPs contamination for future evaluation but a regional agreement between countries is required to define these.

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