Regional Workshop
Assessment, Monitoring and Management of Persistent Organic Pollutants (POP) and Persistent Toxic Substances (PTS) in the Coastal Ecosystems of the Wider Caribbean Region

Hosted by the Institute of Marine Affairs (IMA)
10-12 June 2008
Crews Inn Hotel, Chaguaramas, Trinidad

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First Regional Workshop
June 10th – 12th, 2008

Assessment, Monitoring and Management of Persistent Organic Pollutants (POP) and Persistent Toxic Substances (PTS) in the Coastal Ecosystems of the Wider Caribbean Region

Opening Remarks
Peter F. Sale
UNU-INWEH

Goals for the Project

• Build partnerships among coastal managers and analytical labs to monitor pollution by PTS
• Extend data on PTS in coastal ecosystems
• Improve capacity for laboratory analysis of PTS pollution
• Trace selected cases of pollution back to their sources
• Educate about, and reduce incidence of PTS pollution

Tasks for the Workshop

• Discuss and finalize the plans for laboratory evaluation and capacity improvement
• Discuss and finalize planned sampling of coastal environments during 2008
• Identify actors and build partnerships to enable the project to proceed
• Learn and share experience in monitoring of POP and other PTS in aquatic environments
Geographic Region

The Gulf of Honduras is limited by Belize, Guatemala and Honduras and it covers approximately 10,000 Km².

The watersheds cover an area of 60,000 Km².

The principal ports part of this project are:

- Cortes Port (Honduras).
- Puerto Barrios Port and Santo Tomas de Castilla Port (Guatemala).
- Big Creek Port and Belize City Port (Belize).

Port factors

- In 2003 the 5 major ports in the Gulf region accommodated nearly 4,000 ships and handle more than 12 million metric tons of cargo.
- In 2004, approximately 7,000 ships and 14 million metric tons.
- The tendency of maritime transport is to grow. Similarly environmental risks grow.
- As a consequence there are plans to expand actual port operations and to dredge deeper channels, so bigger ships can be accommodated.
- A significant part of this interchange is the management of hazardous cargo like hydrocarbons and chemicals.
The Region as an area of localization and interchange.

**Environmental factors.**

The base line of the Mesoamerican Barrier Reef System (MBRS) project reported that out the 4 sites where the samples of the fish “White grunt” Haemulun plumieri were collected, all indicated contamination of Polycyclic Aromatic Hydrocarbons or PAHs. The sites were chosen one per country of the Gulf of Honduras region. The study indicated that the highest concentrations were found in Punta Manabique (Guatemala) and the lowest in Cayos Cochinos (Honduras). Caulker Caye (Belize) reported intermediate levels.

The actual information indicate that approximately 20 PAHs have shown carcinogenic, mutagenic and immunosuppressor activity. The most relevant toxicity is the result of bioaccumulation in medium and long terms. The main source of PAHs is the incomplete combustion that occurs in automobiles, planes, ships, power plant generators of electricity and incinerators of waste.

- **Nitrogen Delivery**
  - Annual delivery of sediments and nutrients (per watershed).

- **Chetumal Bay, Mexico**
  - Sugar cane

- **Belize**
  - Citrus
  - Banana
  - Sugar cane

- **Guatemala**
  - Banana
  - Oil palm

- **Honduras**
  - Banana
  - Oil palm
  - Citrus
  - Pineapple
  - Sugar cane

- **Annual delivery of sediments and nutrients (per watershed).**
The Gulf of Honduras project has the following objectives:

- Contribute to reverse marine and coastal ecosystem degradation within the Gulf of Honduras.
- Enhance the control and prevention of maritime transport-related pollution in the major ports and navigation lanes.
- Improve navigational safety to avoid groundings and spills.
- Reduce land-based sources of pollution draining into the Gulf.

Components

4. Improving environmental management and hazard reduction measures in the regional network of 5 ports within the Gulf of Honduras. Actions: Port Operation Diagnostic Study.

The region as an area of social interchange. Partners in the project.

**GUATEMALA**

- MINISTERS
- CIV
- MARN
- EMPORNAC
- COBIGUA

**BELIZE**

- Environment and Natural Resources
- Transportation
- Port Authority of Belize
- Port of Belize
- Port of Big Creek
The region as an area of social interchange. Partners in the project.

HONDURAS

Ministers

Environment

E N P

Programa para la Protección Ambiental y Control de la Contaminación Originada por el Transporte Marítimo en el Golfo de Honduras

Environment

and Natural Resources.

Housing and Transportation (SOPTRAVI)

Merchant Marine

Finally, it is important to recognize that these are the resources the countries and their populations have. It is imperative to protect them in order to protect the future of the people of the region. The principle that everything is interconnected in the region and planet is now more obvious. It is necessary to work for the environmental protection of the Gulf of Honduras.

Working for the environmental protection of the Gulf of Honduras.

GRACIAS.
Persistent Organic Pollutants

- POPs are a group of organic chemicals with distinct characteristics that make them particularly dangerous once released to the environment:
  - highly toxic; very stable (long residence times); tend to be mobilized over long distances after their emission
- The "dirty dozen"
  - Pesticides - Aldrin, Dieldrin, DDT, Endrin, Chlordane, Heptachlor, Hexachlorobenzene (HCB), Mirex, Toxaphene
  - Polychlorinated Biphenyls (PCBs) - Used extensively in industrial applications (e.g., dielectric fluids)
  - Dioxins and Furans - By-products of industrial processes (e.g., incomplete combustion)
- Upcoming POPs?
  - Pesticides - Lindane and chlordecone
  - Brominated fire retardants – Pentabromodiphenyl ether and hexabromobiphenyl
  - PFOS – Perfluorooctane sulfonate
HONDURAS
POPs Project 1999-2001

AFRICA
STOCKPILES PROGRAMME

Why accumulation of obsolete pesticides
- Because of Locust invasions…and other migratory pests
- Overall, management of pesticides is often inadequate in developing countries
- Weak import controls
- Lack of training on appropriate pesticide use
- Inappropriate donations and aggressive sales practices
- Poor storage and stock management
- Pressure to stockpile for unforeseen emergencies
- Lack of safe destruction technologies

Leaking containers in Gao

50,000 tonnes!
**Diethylrin Container in Gao**

**Features**
- Horizontal APL, up to 15 years duration, Cross Regional (MNA, Africa)
- Objectives: Eliminate obsolete pesticides stockpiled throughout the African continent, and prevent accumulation of new stocks
- Program funding: Overall US$ 250 million, 52 countries (planned)
  - Phase 1: US$ 50 millions, 7 countries
- Countries - Phase 1: Ethiopia, Mali, Morocco, Nigeria, S. Africa, Tanzania, Tunisia
- Status P1: 6 countries are operational in January 2007
- Donors: 12 donors (including GEF, DGF, Belgium, Canada, Denmark, EU, Finland, France, Japan, Netherlands, Sweden, Switzerland)
- Partners: FAO, UNEP, Plant Science Industries (CropLife Int’l), NGOs (Pesticide Action Network, WWF), African Union, NEPAD
- Risks: Corporate Risk Project, Category A

**Project description**
- Cp 1: Country Operations
  - Clean up and disposal
  - Prevention of accumulation
  - Capacity building
  - Project management
- Cp 2: Technical support
- Cp 3: Cross cutting activities
- Cp 4: Project coordination

**Operationnal**

<table>
<thead>
<tr>
<th>Country</th>
<th>Status</th>
<th>Next step</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tunisia</td>
<td>Project launched (Nov 05)</td>
<td>CESA, Inventory to be validated</td>
</tr>
<tr>
<td>South Africa</td>
<td>Project launched (Aug 06)</td>
<td>Work plan, inventories and CESA</td>
</tr>
<tr>
<td>Nigeria</td>
<td>Grant agreement signed (Aug 06)</td>
<td>Work plan, and inventories</td>
</tr>
<tr>
<td>Tanzania, Morocco and Mali</td>
<td>Grant agreement signed (Dec 06)</td>
<td>Work plan, inventories and CESA</td>
</tr>
<tr>
<td>Ethiopia</td>
<td>Conditions of negotiations partially fulfilled</td>
<td>Negotiations in March, Launch in May</td>
</tr>
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</table>

**Obsolete Pesticide Stocks: An issue of poverty**

**Inventories**
Training of inventory staff

Repackaging

Contaminated Soils

Transport

Challenges

- **Safeguards:** Careful assessment of risks is needed, and adequate mitigation measures must be taken (esp for collection, transport and disposal of pesticides), monitored and evaluated

- **Partnership:** the complex and diversified partnership with FAO, CLI, NGOs, NEPAD requires a lot of coordination efforts, but finally benefits to the project

- **Funds:** additional funds for future activities must be raised, and a fundraising strategy prepared
Future Perspectives

- **ASP-Phase 2** will cover 10 to 15 additional countries in Africa.
- **ASP** supports a platform for improved chemicals management in Africa, also is supported by ongoing study by WB-OECD (Mali).
- **Cross-sectoral** (ENV-HD-ARD) linkages with Integrated Pest Management (Locust Control), and Malaria Control, including safe use of DDT.
- **Prevent costly disasters** such as the current Cote d’Ivoire Toxic Waste Emergency (est at US$36m).

**MIDDLE EAST & NORTH AFRICA**

**Canadian POPs Trust Fund**

- **EGYPT**  Pesticides/PCBs $250k
- **LEBANON**  PCBs $250k
- **IRAN**  Pesticides/PCBs $450k
- **AZERBAIJAN**  Pesticides/PCBs

**Thank you**
The GEF-IWCAM Project

GEF-IWCAM Background

- Funding: Global Environment Facility (GEF)
- Project Cost: US$112M (includes co-financing)
- GEF Funding US$14M
- Implementing Agencies: UNEP & UNDP
- Executing Agencies: CEHI, UNEP-CAR/RCU, and UNOPS
- Project Coordination Unit: based at CEHI

GEF-IWCAM Background

- 13 countries involved in the Project: Antigua & Barbuda, Bahamas, Barbados, Cuba, Dominica, Dominican Republic, Grenada, Haiti, Jamaica, St. Kitts & Nevis, St. Lucia, St. Vincent & the Grenadines, Trinidad & Tobago
- All have agreed to adopt the IWCAM approach
- Required to address policy and legislative issues to fully mainstream IWCAM at the national level.

PROJECT OBJECTIVE

To assist Caribbean Small Island Developing States to adopt an integrated approach to watershed and coastal area management.

GEF-IWCAM Project Components

COMPONENT 1: DEMONSTRATION, CAPTURE AND TRANSFER OF BEST PRACTICES

- Implementation and management of 9 demonstration projects in 8 countries
- Capture of lessons, best practices, alternative technologies from Demonstration Projects
- Development of national, regional and global replication strategies and mechanisms

GEF-IWCAM Component #1 - Demo Projects

- Antigua and Barbuda: Mitigation of Groundwater and Coastal Impacts from Sewage Discharges from St. John’s
- Bahamas: Land and Sea Use Planning for Water Recharge Protection and Management in Andros
- Bahamas: Marina Waste Management at Elizabeth Harbour in Exuma
- Cuba: Application of IWCAM Concepts at Cienfuegos Bay and Watershed
- Dominican Republic: Mitigation of Impacts of Industrial Wastes on the Lower Haina River Basin and its Coast
GEF-IWCAM Component #1 - Demo Projects

- Jamaica: An Integrated Approach to Managing the Marine, Coastal and Watershed Resources of East-Central Portland
- Saint Kitts and Nevis: Rehabilitation and Management of the Basseterre Valley as a Protection Measure for the Underlying Aquifer
- Saint Lucia: Protecting and Valuing Watershed Services and Developing Management Incentives in the Fond D'or Watershed Area
- Trinidad and Tobago: Land-Use Planning and Watershed Restoration as part of a Focused IWCAM Demonstration in the Courland Watershed and Buccoo Reef Area

GEF-IWCAM Project Components

COMPONENT 2: DEVELOPMENT OF IWCAM PROCESS, STRESS REDUCTION AND ENVIRONMENTAL STATUS INDICATORS FRAMEWORK

- Review existing national and regional level indicator frameworks
- Development of template for national level Indicators
- Conduct hotspot diagnostic analyses (HSDA) at (non-demo) hotspots in each country
- Establish Regional centre for storage of Indicator information and for Indicator training
- Pilot IWCAM process, stress reduction and environmental status indicators (1 country)

COMPONENT 3: POLICY, LEGISLATIVE AND INSTITUTIONAL REFORM FOR IWCAM

- Review of national policy, legislation and institutional structures identifying barriers to IWCAM
- A set of regional guidelines for national policy, legislative and institutional reform
- Regional programme for amendment of national legislation and policy
- IWRM Plan development

COMPONENT 4: REGIONAL & NATIONAL CAPACITY BUILDING & SUSTAINABILITY FOR IWCAM

- National workshops on awareness and multi-sectoral sensitisation to IWCAM issues
- Stakeholder involvement in regional IWCAM
- Training and education activities
- A regional strategy for the sustainable promotion and implementation of IWCAM
- Project Networking
- A regional IWCAM Information Clearing House

COMPONENT 5: PROJECT MANAGEMENT AND COORDINATION

- Project Management (by Project Coordination Unit)
- Project Steering Committee (to provide policy level guidance)
- National Inter-sectoral Committees (to capture IWCAM concepts)
- Implementing Agency/Executing Agency Management Group
- Regional Technical Advisory Group
- Project Reporting on activities and outputs, and reviews of project work-plan and budget
- Project Evaluation ensures that indicators are measuring sustainable project success
- Develop an Information Management System for the project

Laboratory Capacity Building

- Environmental monitoring and surveillance
  - Need for building capacity, both nationally and regionally, to monitor and evaluate environmental water quality in all participating SIDS.
  - Enhancement of laboratory capacity and capability are needed – provision of equipment, technical training including QA/QC
Plans for Increasing Laboratory Capacity

- Conduct of monitoring needs capability assessments planned for first half of 2008
- Strengthen laboratory capabilities through acquisition of equipment
- Upgrade monitoring capabilities of regional laboratories

Update on Lab Strengthening Activities

- Criteria Developed for Selection of Laboratories for Assessment
  - Laboratory must have a mandate for environmental management including ambient water quality monitoring
  - Recommendation of laboratory by Demo Project Manager
  - The laboratory must indicate a willingness to support IWCAM work and the Demonstration Projects in particular, during and beyond the life of the IWCAM Project
  - The organizational structure of the lab or institution should be sustainable in terms of staffing arrangements, budget and facilities.

Laboratories Assessed

- Jamaica
  - The National Water Commission’s Eastern Laboratory
  - The National Environment and Planning Agency’s Laboratory of the Ministry of Land and Environment
  - The Mines and Geology Division Analytical Services of the Ministry of Energy, Mining and Telecommunications
  - The Environmental Health Laboratory of the National Public Health Division of the Ministry of Health and Environment
  - The Negril Coral Reef Preservation Society’s Laboratory

- Antigua and Barbuda
  - Division of Analytical Services of Ministry of Agriculture
  - Water and Sewerage Authority

- Cuba
  - Needs assessments carried out on 5 laboratories in Cienfuegos – all with a role to play in the demonstration project
  - Public Health Lab, Sugar Factory Lab, Soil Lab, Hydrology Lab and CEAC
Laboratories in the following countries are being assessed:
- Saint Lucia
  - Water and Sewerage Company
  - Gros Islet Polyclinic
- Trinidad and Tobago
  - Institute of Marine Affairs - Trinidad
  - Water and Sewerage Authority – Tobago
  - Department of Natural Resources and the Environment (carries out field testing for demo project)

Laboratories in the following countries will be assessed in July:
- Dominican Republic (by CEAC official)
- Haiti

Basic Training Needs so far Identified:
- Laboratory QA/QC - planned for July/August
  - Training in basic microbiology and use of membrane filtration technique for determination of enterococci and E.coli in marine and freshwaters

Monitoring Needs for Demo projects in Jamaica and Antigua identified:

Basic Equipment and Infrastructural Needs Identified:
- Identified for laboratories in Jamaica and Antigua
- Awaiting quotations from suppliers

Thank you for your attention.
Participating Laboratories

Selection based on information from prior evaluations, recommendations from November 2007 workshop, other recommendations.

Goal was one laboratory per country.

<table>
<thead>
<tr>
<th>Country</th>
<th>Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guatemala</td>
<td>Facultad de Ciencias Químicas y Farmacia - Universidad de San Carlos de Guatemala</td>
</tr>
<tr>
<td>Honduras</td>
<td>Centro de Estudios y Control de Contaminantes SERNA</td>
</tr>
<tr>
<td>Jamaica</td>
<td>NEPA Lab, and Pesticides Residue Lab, UWI</td>
</tr>
<tr>
<td>México</td>
<td>Lab. Geoquímica Marina, CINVESTAV-México, and Resp. Lab. Institucional de Química ECOSUR</td>
</tr>
<tr>
<td>St. Lucia</td>
<td>Caribbean Environmental Health Institute (CEHI)</td>
</tr>
<tr>
<td>Trinidad &amp; Tobago</td>
<td>Dept. of Chemistry, UWI, and Marine Chemistry Dept. IMA</td>
</tr>
</tbody>
</table>

Lab Evaluation Team

- Dr. Ken Drouillard, Univ. Windsor, Canada
- Dr. Gerardo Gold, CINVESTAV, México
- Dr. Chris Metcalfe, Trent Univ, Canada

Lab Capacity Enhancement

- Site visits by the evaluation team: report
- Technical training
- Augmentation of instrumentation
Laboratory Needs to Implement a Baseline POPS Monitoring Program

Ken Drouillard,
Great Lakes Institute for Environmental Research,
Adjunct, UNU-INWEH

Laboratory - Facilities
• Possible Models
  – Fully Functional Independent Laboratories
    • Costly, Lacks Feasibility (Facilities + Staff)
    • Inefficient use of instrument time and QA/QC needs
    • Maximum control of sample analysis priorities & facility usage
  – Regional Instrumental/Analytical Facilities
    • High throughput burden on limited # labs
    • Countries that depend on regional facilities have little say on sample priorities and processing times
    • Most efficient manner of ensuring QA/QC
  – Regional Instrumental Facilities + Independent Sample Processing Facilities
    • Maximizes instrument time (bottleneck = sample processing)
    • Sample processing priorities at instrument facilities need to negotiated
    • More difficult QA/QC needs – processing facilities need regular feedback

Laboratory – Facilities
Regional Instrument Facilities
• Priorities for regional instrument facilities
  – Staff – Laboratory manager + technicians
  – Laboratory with Quality Assurance Program
  – Analytical Instruments
    • GC-ECD – redundancy of units
    • GC-MSD – validation
  – Sample Processing facilities

Laboratory Staff
• Laboratory Head
  – Established operating budgets and ensures adequate resources
  – Directs priorities of laboratory operations
• Quality Manager –Regional Coordinator?
  – Oversees Quality Projects
  – Reviews and Updates Laboratory Quality Program
  – Performs Regular Internal Audits
  – Reviews method validation results, quality control charts
  – Reviews data output, signs off on their quality
  – Prepares quality assessment reports (QA documentation in lab, instrument/method performance, incidences of lack of compliance)
  – Can be shared across multiple-labs

*Quality Manager/Laboratory Manager Sometimes Combined
Requires permanent, full time position staffed with qualified personnel (BSc or MSc level)
Quality Manager Must Be Independent of Technicians
### Laboratory Staff (Cont.)

- **Laboratory Manager** – Full time Person for POPs project?
  - Directs day to day operations of the laboratory
  - Ensures Good Laboratory Practice and Safety
  - Method development and validation
  - Training and analyst proficiency testing,
- Ensures Standard Operating Procedures are implemented by technicians and documentation completed

- **Technicians**
  - Follow Standard Operating Procedures (SOPs)
  - Sample receiving and inventory control
  - Sample processing, extraction, clean-up
  - Sample analysis on instruments and data entry
  - Documentation of activities and problems in implementing SOPs

### Laboratory Quality Assurance Program

- **Quality Manual**
  - Specifies Quality Assurance Program
  - Standard Operating Procedures (SOPs)
  - Related Procedures

- **Quality Assurance = Auditing Components**
  - Use of SOPs to ensure data consistency
  - Auditing Operational Performance of Lab & Methods on Routine Basis
  - Maintain complete records of sample receipt, analysis, data reporting
  - Reporting of Non-conformances and Corrective Actions
  - Quality Management System Review – Internal & External Audits

- **Quality Control**
  - Procedures put in place to monitor data quality
    - Calibration of instruments (balances, analytical instruments etc.)
    - Maintaining certificates for calibration standards, Class glassware, solvents and reagents
    - Analysis of certified reference materials
    - Blanks, Surrogate Recovery Standards, Sample Duplicates
    - Produce Quality Control Charts
    - Participation in Inter-laboratory Comparisons

### Laboratory Quality Assurance Program Implementation of Laboratory QA/QC Program is Not Easy

- **Resource-consuming**
  - Staff members independent of lab cost recovery exercises
- **Time-consuming**
  - Can represent upwards of 30% or more of laboratory activities
  - Data entry into quality control charts
  - Only way to ensure data integrity
  - Data to be used for legal measures
  - Data to be used for peer review
- **Value added aspects of...**
  - Non-accredited laboratory procedures and laboratory users benefit from well operating lab
  - Instruments are maintained in top condition or taken offline when not functioning
  - Benefits of training of highly qualified personnel

### Quality Control Procedures Specific to POPs Analysis

- **Method validation & method validation checks**
  - Spiking & recovery of representative matrices
  - Certified analytical standards
  - Surrogate recovery standards
  - 13C-chemicals or non-environmental surrogates e.g. PCB-430, Tribromobenzene...
  - Blanks
  - Certified Reference Samples
  - Sample duplicates

### Regional Laboratory Facilities

- **Needs to be fully functioning laboratory**
  - Full sample processing + Instrumentation
  - Implement method validations, Instrument calibration
  - Share in sample processing activities of POPs Program
- **Needs to implement QA/QC within its own laboratory + satellite processing laboratories**
  - Most provide timely feedback to satellite laboratories regarding sample QA
  - Needs to provide database management capabilities
- **Ideally such facilities already exist**
  - Need investments related to staffing, QA-Program, Method development, etc.
Regional Laboratory Facilities

Instrumentation

• GC-ECD
  – High sensitivity and moderate selectivity
  – High linear dynamic range
  – Robust detector
  – High duty cycle
  – Intermediate Cost ~30-50 k

• GC-MSD (Low Resolution - MSD)
  – Validate Peak Identities
  – Cross Check GC-ECD Performance
  – Incorporate additional analytes
  – Less robust and higher maintenance
  – Moderate Cost ~120 k

Regional Laboratory Facilities

Sample Processing Facilities

• Sample Processing Facilities
  • Storage of Standards, CRMs, etc.
    – Standard Refrigerator/Freezer
    – Certified Analytical standards
      – PCBs, OC-pesticides Stocks and Working Solutions
      – Surrogate Standard Solutions
      – Certified Reference Materials
  • Solvent Storage and Waste Handling
    – Solvent cabinets for solvent storage
    – Reagent storage – Sodium Sulfate, florisil, alumina, silica gel
    – Dessicators, Muffle Furnace, Drying Ovens
  • Sample Receiving and Sample Storage
    – Refrigerators, Chest Freezers, Cold rooms
  • Storage of Sample Extracts
    – Refrigerator

Satellite Laboratory Facilities

• The needs of satellite labs will vary depending on sample matrix and SOP
• Ideally, satellite lab receives samples from field program and submits sample extracts to Regional Analytical Facility
• Requires – laboratory processing facilities, surrogate spiking standards, CRMs, analytical blanks, reagents, solvents, sample extraction + clean-up infrastructure

Satellite Laboratory Facilities

• Minimum Needs:
  – Laboratory & benchtop space, water + power supply (excluded from price)
  – Solvent cabinets, reagent storage (1.5 k)
  – Spiking standards & CRM storage (refrigerator ~ 1k)
  – Sample storage – freezers and refrigerators (~ 4 k)
  – Fume hood (1) desirable (~15 k)
  – May or may not be required depending on method
  – Roto-evaporator or solvent concentrator (~5 k)
  – Analytical balances (~2.5 k)
  – Blenders/sample homogenizers (~1.5k)
  – Glassware related to sample homogenization, extraction, clean-up (~15k)
• Estimated start-up cost (excluding building): ~45 k
## Satellite Laboratory QA Program
- Analyst training and proficiency testing performed at regional analytical facility
  - Must pass proficiency test prior to operating in satellite laboratory
- Satellite Laboratory Proficiency Testing
  - Must pass CRM testing criteria before satellite laboratory can commence processing samples
- External audits of satellite laboratory
  - Performed by quality manager from regional facility
- Examination of Within Batch Quality Control Data
  - Which each batch of samples (5-6 samples extracted):
    - Blanks
    - Sample duplicates
    - Performance of CRMs
- Regular communication between Regional Facility and Satellite Laboratory regarding batch quality control performance results
- Participation in international round-robin testing programs

## Regional Laboratory QA Program
- External audits of regional laboratories
  - Performed by independent quality managers
  - Documentation of QA/QC, quality control charts etc.
- Develop cross regional quality assessment reports
- Participation in international round-robin testing programs

## Database Management
- Centralized repository for data
- Receives – QA checked data from regional facilities
- Data security/accessibility to project PI’s
  - Need to sort out data ownership issues
  - Confidentiality and cross region data sharing
Los arrecifes del mundo no están lo suficientemente protegidos / The world’s reefs are not sufficiently protected

- 40 países no tienen áreas de arrecifes protegidas / 40 countries have no reef areas protected
- La mayoría de las metas de las áreas marinas protegidas no son alcanzadas / Most of the goals of marine protected areas are not met

Cuencas / Watersheds
- El 80% de la contaminación marina se deriva de tierra firme / 80% of marine pollution originates from the mainland.
- Incrementos en la sedimentación/nutrientes de las deforestaciones y prácticas agrícolas.
- Destrucción de hábitats.
- Descargas de Aguas residuales urbanas.

RESULTADOS DE NUESTRAS ACTIVIDADES HUMANAS

Sobreexplotación y desarrollo costero son las grandes amenazas del hombre para los arrecifes

Overuse and coastal development are the greatest threats to the coral reefs.

Monitoréo Sinóptico / Synoptic Monitoring

- El Programa de Monitoréo Sinóptico incluye:
  - Nutrimentos (solo nitrogenados y fósforo)
  - Plaguicidas en organismos y sedimentos
  - Biomarcadores:
    - Metabolitos de PAHs en bilis (petróleo y derivados)
    - Actividad de colinesterasas en músculo (plaguicidas organofosforados y carbámicos)
  - Un esquema de muestreo estratificado al azar
**Introducción / Background**

**Primer monitoreo en el SAM / The first monitoring in the MBRS region was conducted in June 2005.**

Sediment and white grunt (*Haemulon plumieri*) samples were collected from 17 MBRS sites.

The concentrations of the different fractions of petrohydrocarbons, such as aliphatic hydrocarbons, unresolved complex mixture (UCM), polycyclic aromatic hydrocarbons (PAHs) and total hydrocarbons (HCs); and organochlorine pesticides (including polychlorinated biphenyls, or PCBs) were analyzed in the sediment samples and in the liver of the grunts. In addition, cholinesterase activity was measured in the liver, muscles and brain of the fishes, as well as the concentrations of PAHs metabolite in bile.

All the analyses were implemented according to the detailed procedures in the Manual of Methods for the MBRS Synoptic Monitoring Program (Almada-Villela et al., 2003).

---

**Naphthalene and Phenanthrene**

- **Highest Phenanthrene median concentrations were found in Cayos Cochinos and Xkalak.**
- **Highest Naphthalene median concentrations were found in P. Manabique and Xkalak.**

---

**Pyrene and Benzo(a)Pyrene**

- **Xkalak had the highest Pyrene and Benzo(a)Pyrene median concentrations.**
- **But Punta Manabique had the highest absolute concentrations.**

---

**Median concentrations of hydrocarbons in the livers of white grunts**

- The greatest concentrations of hydrocarbon fractions were found in Xkalak, Mexico and the smallest in Punta de Manabique, Guatemala.
Median concentrations of organochlorine pesticides in the livers of white grunts

The concentrations of PCBs were the largest of all the organochlorine components. As for pesticides, the pattern found is different in each site. Thus, in Cayos Cochinos the hexachlorocyclohexanes (HCHs) prevail, while in Punta de Manabique and Caye Caulker DDTs are the most abundant and tetrachlorobenzene is the predominant one in Xcalak.

As in the case of PAHs, the highest concentrations of pesticides were found in the northern part of the study area, in the Belize River, Corozal, Chetumal Bay and Xcalak. In particular, the high concentration of DDTs is to be noted in sediments in Xcalak, as well as the high concentrations of chlorobenzenes in Corozal and Chetumal.

The least cholinesterase activity in the muscle of fish was found in Cayos Cochinos, which may indicate that there are more organophosphorous or carbamic pesticides in this site; however...
The probable effect levels (PEL)

Monitoring sites showing the levels of chlordanes in sediments with respect to PEL and TEL. Green dots indicate those stations where there is a low probability of finding a toxic effect.

The probable effect levels (PEL) are defined as the concentration of a pollutant in sediments, above which adverse effects are frequently found in fauna. On the other hand, if the concentrations of a pollutant exceed the PEL, there is a high probability that the sample is toxic to marine fauna.

Concentration values above the PEL were only found for hexachlorocyclohexanes (HCHs) and chlordanes. In the case of the HCHs, the PEL was exceeded in 25% on the sediment samples analyzed, and only in one sample in the case of the chlordanes.

The sites:
- Placencia Lagoon
- Corozal Bay
- Xcalak

Twenty five percent (25%) of the sediment samples exceeded NOAA’s Probable Effects Level (PEL) for Lindane (γ-HCH); therefore, harmful effects to the fauna due to the presence of this pesticide may be expected.

The concentrations of PAHs metabolites and of some pollutants in the selected indicator organism (Haemulon plumieri) exceeded the concentrations of the same pollutants found in the Mayan Cichlid (Ariopsis assimilis) in Chetumal Bay, a site considered to be impacted by pollution.

With the information available at this moment, it is not possible to determine the sources of the pollutants found, or their potential dispersion throughout the MBRS. It is also important to consider the probable transport of the pollutants by wind (Alegría et al., 2000) and not only by marine currents.

Conclusion
Overview of available information and data on POPs and PTS in the eight project countries

Hanneke Van Lavieren

Internal Working Document

• Summary based on prior studies done, web searches, National Implementation Plans under Stockholm Convention (if available)
• What we know - useful as background information to project
• Focus on summarizing potential sources, data available from coastal environment, what as sampled & where, which chemicals to expect, data gaps
• Summarizes the regional evidence of the presence of POPs and PTSs in marine environment, with some information on environmental levels and trends
• To serve as working document - information incomplete - to be added to as necessary & updated

Previous & ongoing studies

• UNEP GEF project: Regionally Based Assessment of Persistent Toxic Substances - Central America & the Caribbean (2002)
  collection, assembly & evaluation of data on sources, environmental levels & impacts of persistent toxic substances across the globe
• Meso American Barrier Reef Systems Project – Pollution Component (Belize, Guatemala, Honduras, Mexico)

Previous & ongoing studies

• Reducing pesticide runoff to the Caribbean – UNEP GEF - Colombia, Costa Rica, Nicaragua (2005-2009)
• Integrating Watershed and Coastal Area Management (IWCAM) in Small Island Developing States of Caribbean - Dominican Republic demo project
• International Mussel Watch Project 1991-1992

Other sources of info

• Occasional studies of environmental levels of PTSs conducted during past 3 decades in almost all countries of the Region
• University research groups or governmental institutes conducted most studies - many in collaboration with and/or supported by universities, institutions from the US, Canada or Europe, or by international agencies

Marine & Coastal Data

• Few data available on Organochlorine pesticides and PCBs in water samples marine environment
• Sampling was done in potentially contaminated areas such as estuaries, coastal areas & harbors & no data available for the open ocean
• Most of scarce data in region from sediment and biota samples from coastal lagoons
Main Sources POPs & PTS

- Major anthropogenic sources in the Region are agriculture, energy, industry, waste management, and the marine sector
- Broad categories of PTSs are pesticides, unintended byproducts, industrial compounds and PTSs of emerging concern

What was sampled

- Water
- Sediments
- Marine biota:
  - Mussel (*Brachidontes exustus*), white mullet (*Mugil curema*), oyster (*Crassostrea rhizophorea*), white grunt or “Ronco blanco” (*Haemulon plumieri*), bivalve (*Anadara tuberculosa*), Trinidad swamp mussel, or “mok” (*Mytila guyanensis*)
- Marine mammals:
  - Spotted dolphin (*Stenella attenuata*), long snouted dolphin (*Stenella longirostris*), short finned pilot whale (*Globicephala macrorhynchus*)

Thanks for your input to this document!
Field Sampling Design

Ken Drouillard, Great Lakes Institute for Environmental Research, Adjunct, UNU-INWEH

Design Requires a Project Objective!

1. Ecosystem Health Assessment
   - Requires exposure routes be characterized
   - Food web sampling
   - Toxicity bioassays
   - Population and Community Structure Characterization

2. Human Health Assessment
   - Focus on exposure routes
     - Drinking water, edible fish/shellfish, food
     - Biomarkers of human exposure
     - Blood work, enzyme function...

Utility of Models in Field Sampling Design

- Models provide conceptual and computational framework to interpret data sets representing different spatial/temporal scales
  - Hydraulic models:
    - Translating loadings information to pollutant dispersion throughout water and sediments (mass balance)
    - Predicting sediment scouring and pollutant mobilization during storm events (event-based modeling)
  - Bioaccumulation models:
    - Linking water and sediment contamination to sport fish & wildlife consumption advisories (bioaccumulation)
    - Developing management scenarios to assess cost-benefits of alternate clean-up strategies
  - Statistical designs:
    - Facilitate detection of hot spots and contaminant dispersion
    - Randomized designs, stratified random design
  - Weight of Evidence:
    - Use what you know about possible sources to establish sampling sites, media of interest
    - Can lead to bias e.g. perpetuate myth of heavy contamination by only sampling hotspots

Need for Models in Management

- Calibrated models provide scientifically defensible interpretation of integrated datasets
  - Can indicate knowledge/data gaps and provide guidance on the types of monitoring programs necessary to fill gaps
- Multi-stakeholder investment into single model framework ensures agreement on approaches taken
- Weight-of-evidence assessments used in absence of management model framework
  - Can lead to biased conclusions if available studies are not representative of the entire system
  - Not very good at cause-effect linkages or establishing effective remediation strategies

What do we sample?

- Water:
  - Not overly effective for POPs (low C_{ow}), but useful for current use pesticides
  - Transient signal related to advective processes
  - Event – driven residues may need high resolution sampling
  - Passive samplers can be used as a surrogate
- Sediments:
  - Longer term record of loadings – although variable by location
  - Sediment cores can give historical profile
  - High concentrations, ease of detectability
  - Need appropriate sediment types – matrix effects & heterogeneity
- Organisms:
  - Consistent matrix (lipids) for chemical extraction and model interpretation
  - Animal movement, growth, reproductive output, age, feeding ecology can influence residue levels
  - Useful for human risk assessment if edible organisms/tissues monitored

1. Human Health Assessment
2. Ecosystem Health Assessment
   - Multi-calibrated interpretation and management
   - Focus on exposure routes
     - Food web sampling
     - Toxicity bioassays
     - Population and Community Structure Characterization
   - Can-need remediation monitoring of Great Lakes Institute for Environmental Research, Adjunct, UNU-INWEH
   - Weight of Evidence...
**Water**

- Low solubility of POPs necessitates large volumes be extracted (100 – 1000 L)
- High Volume Extractors – e.g. AXYS’ Infiltrex System
  - Pumps water across filter and over solid phase resin at sampling site
- Labor Intensive
  - 1 h to 3 h extraction at a site
  - Provides only 1 replicate/unit
- Expensive
  - Unit costs 25 k
  - Consumables ~ $300/sample

**Steady State Correction of Biomonitors**

Contaminant Bioaccumulation Kinetics In Deployed Integrated Sampler

\[
\frac{dC_m}{dt} = C_m \cdot k_1 \cdot C_{m0} \cdot k_2
\]

Steady State Correction

\[
C_{m\text{ss}} = \frac{C_{m0} \cdot e^{-k_2 \cdot t}}{1 - e^{-k_2 \cdot t}}
\]

- \( C_{m\text{ss}} \): steady state corrected matrix conc.
- \( C_{m0} \): initial concentration in matrix (day 0)
- \( k_2 \): chemical depuration rate from sample
- \( t \): time over which sampler was deployed

**Sampling Design**

- Integrated Water Samplers
  - Advantages
    - Replicate Analyses at sampling station
    - Time integration – considers pulses
    - Although it reports pulses as raised integrated average \( C_m \)
    - Consistent matrix – ease of extractions, standardized equipment
    - PRC as trip blanks for satellite lab. performance
  - Disadvantages
    - Most be moored on-site for 20-d or longer
    - Biofouling, vandalism, disturbances can destroy samplers
    - PRCs – require centralized pre-processing of samplers
  - Can be moored to docks, navigation buoys and other structures

**Water**

- Integrated Water Samplers
  - Passive Samplers
  - Biomonitors
    - deployed/caged animals
- Integrated water samplers accumulate chemical from water until steady state is achieved or until sampler is retrieved
- Need to understand chemical kinetics into sampler to interpret data (requires models)
- Provides estimates of bioavailable water residues
- Consistency of sample matrix (ease of analysis)

**Performance Reference Compound Approach**

- Integrated sampler spiked with chemicals (PRCs) that possess similar properties as analytes, but not present in environment
- Release of PRCs from sampler provides estimate of \( k_2 \) and sampling rates
- PRCs also act as field QA recovery by providing trip blanks

\[
C_{m\text{sox}} = \frac{C_{m0} \cdot e^{-k_2 \cdot t}}{1 - e^{-k_2 \cdot t}}
\]

\( k_2 \) values in field generally 2-3 fold in mussels, 100-1000 in passive samplers

**Sediments**

- Provides longer time-integration of loads than water
  - Depends on sediment load, OC-content, mean particle residence time, particle origin
- Often more contaminated than water
  - Typically 100-200 g sample required
- Differences in sediment characteristics lead to matrix problems or sampling problems
  - Grain size differences, organic content & origin
  - Requires sorting by laboratory e.g. Sieving or other
  - More stringent analytical requirements
    - Soxhlet, ACE, microwave assisted digestion
Sampling Design

- Appropriate for deposition areas, river mouths, soft-sediment regions
- Sediment Cores – can provide a history of loadings in depositional areas
  - (can be expensive)
- Appropriate Statistical Design (preselected sites):
  - Distributed
  - Randomized
  - Stratified Random
- Sample Replicates taken at each sample
  - Replicate = individual grab not a pooled grab
- Can provide benthos biomass

Sediment Assessment

- Stratified Random Design
  - a priori selection of sample sites
  - different longitudinal zones
  - Political boundaries
  - Dispersion criteria
  - Depth categories

Food Web Sampling

- Provides information about trophic transfer
- Consistent sampling matrix (neutral lipids) standardizes analytical requirements
- Can provide data on human exposures to POPs via food
- Different organisms integrate different spatial and temporal contaminant signatures
- Growth – effects, age-effects, metabolic signatures, trophic position

Food Web Sampling

- Choice of Study Animals
- Pandemic Distribution
  - Found throughout participating areas
  - Found at low and high contamination areas
- Feeding Ecology
  - Phytoplankton / net seston
    - transient time signature similar to water
  - Filtering invertebrates – mussels
    - Longer lived, shell length allows age-standardization
  - Polychaetes
  - Grazing herbivores
  - Gastropods
  - Fish
    - Lower vs. Upper trophic level
    - Ease of identification and capture
  - Seabird eggs
    - Migration artifacts

Food web sampling

- Recommend 2 or 3 trophic levels of candidate animals
  - Lower Trophic Level Animal
    - Filter-feeder or grazer
  - Pandemic fish species
  - Edible fish species
  - Fish – Sample Information
    - Length/weight
    - Age
    - Capture location
    - Stomach contents
    - Whole fish vs. fillet
Discussion

• What environmental media to sample?
  – Water, sediments, food web components....
• What is the sampling design?
  – Spatial scale & resolution?
• How will they be collected?
  – Sampling requirements & infrastructure?
• Who will collect them?
  – Partnerships – Government, Researchers, Fishers?
  – Is the infrastructure in place to do so?
• How Many Samples?
  • Site replicates, seasonal sampling
• What are the quality assurance measures for sampling?
  – Sample integrity
  – Trip blanks etc.
SOUND MANAGEMENT OF HAZARDOUS CHEMICALS IN LATIN AMERICA AND THE CARIBBEAN: A REGIONAL STRATEGY

ACTIVITIES

Information sharing
1) Development of a hemispheric network which will include private and public actors;
2) Development of a preliminary inventory of PTS (including POPs) for Latin America and the Caribbean and of an on-line database;
3) Compilation of existing legal and management systems, and of institutional capacities;

Outreach, Communication, Participation
4) Identification of opportunities to sustain a regional program for the sound management of chemicals;
5) Organization of sub-regional technical meetings
6) Collaboration and exchange with different groups through outreach activities;

Strategic Planning

INFORMATION SHARING

Regional Network of Sound Management of Hazardous Chemicals

The network consists of National Coordinators for the OAS/CIDA project (officially selected from the responsible Ministries and Secretaries and from the Stockholm Convention National Focal Points), as well as other government, academia and NGO representatives. Up to February 2008, 32 NCs and other 60 experts joined the network.

Three Reference Directories have been created for the region (NCs, NGOs, Mercury experts).

INFORMATION SHARING

On line PTS and Heavy Metals Inventory and Database

Identify gaps in current management practices
Facilitate information exchange on use levels, risks, alternative products and best practices
- Information gathering
- Technical Questionnaires (7)
- Creation of an on-line database

Compilation of legal/institutional frameworks and best practices on chemical management
- Analysis of the legal and institutional frameworks for the management of POPs has been completed for Nicaragua and Chile.
- Regional level: questionnaire

Data Base Structure

48 PTS:
36 Pesticides
7 Industrial comp.
3 Heavy Metals
1 Organometalic c.
1 unintentional gener

Classification
Chemical Info
Environmental fate
Country Info
Legal/Institut. Info
Trade Info

Different combi - nations

Algorithms

"Link Tables"

NEW INFORMATION!!
**Data Base Structure**

- Description of the substance
  - Common name
  - Commercial name
  - Type of crop
  - Importation
  - Production
  - Use
  - Storage
  - Treatment & Elimination
  - Final Disposal
  - Area (ha)
  - Doses/ha
  - Quantity per year

**OVERVIEW - THE CARIBBEAN**

**National Priorities**
- Inventory of obsolete stockpiles
- Inventory of sites contaminated by PTS
- Public Awareness
- Creation of NSPs

**Cross-cutting activity**
- Exchange of information among countries

**Regional Priorities**
- Inventories of PTS & PCBs
- Registration & licensing procedures
- Capacity building
- Identification of proper storage and disposal facilities

**Institutions**
- National Environment Management Authority (NEMA), St. Lucia
- Caribbean Agricultural Development and Research Institute (CARDI), St. Lucia
- Caribbean Environmental Health Institute (CEHI), Headquarters in St. Lucia
- Marine Resources Assessment Group (MRAG Ltd.), UK based consulting firm

**OVERREACH, COMMUNICATION, PARTICIPATION**

Identification of opportunities to sustain a regional program for the sound management of chemicals

- Regional Survey
- Four Regional Workshops

Central America (Nicaragua, October 2007)
Caribbean (St. Lucia, October 2007)
South America (Panama, February 2008)

SAICM Regional Committee Coordination Meeting (Trinidad & Tobago, June 2008)

**PRIORITY TOPICS ON SMOC FOR LAC COUNTRIES**

<table>
<thead>
<tr>
<th>Strategic Direction</th>
<th>Recommended Priority Actions</th>
<th>Sub-Regions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - Address Areas of Priority Health Hazards and Environmental Risk</td>
<td>Disposal of Stockpiles of Obsolete Pesticides</td>
<td>The Caribbean</td>
</tr>
<tr>
<td>2 - Promote Legal, Policy and Institutional Reforms</td>
<td>Reducing the Impacts of Mercury</td>
<td>South America</td>
</tr>
<tr>
<td></td>
<td>Regional Policy on Chemical Security</td>
<td>Central America</td>
</tr>
<tr>
<td></td>
<td>Facilitating the Adoption of Pollutant Release and Transfer Register - PRTR</td>
<td>throughout the LAC Region</td>
</tr>
</tbody>
</table>

**PREFERENCES, GAPS, AND ON-GOING ACTIVITIES AT NATIONAL LEVEL SURVEY MARCH 2007**

**REGIONAL PRIORITIES SURVEY SEPTEMBER 2007**

Latin America & the Caribbean

Central America
NEXT STEP: TOWARDS STRATEGIC PLANNING

FIRST COORDINATION MEETING OF THE SAICM REGIONAL COMMITTEE FOR LATIN AMERICA AND THE CARIBBEAN

• Towards the development of a Regional Strategy for the implementation of SAICM in Latin America and the Caribbean,
• Mechanisms to develop a regional consultation process and ad-hoc tools, such as virtual forums, surveys, evaluations, etc.
• Implementation of SAICM in LAC: analysis of the thematic and geographic distribution of projects at national and multi-national level.
• Identification of geographic and thematic gaps with respect to the priorities of countries and to the SAICM Global Plan of Action.
• Planning new projects on priority topics and their distribution in the region. Design of a long-term regional program framework for systematic approach to projects implementation at national and regional level.

FIRST COORDINATION MEETING OF THE SAICM REGIONAL COMMITTEE FOR LATIN AMERICA AND THE CARIBBEAN

• Divulgation and replication of lessons learned from the projects.
• Mechanisms of horizontal cooperation within the region (network of laboratories, institutions, universities; capacity building courses, divulgation and educational material, etc.)

Achievements so far

Outsputs
• On-line database for a selected set of persistent, bio-accumulative and toxic chemicals, including pesticides from agricultural or sanitary uses, as well as emissions of mercury, PCBs, and industrial by-products such as dioxins and furans. The DB includes existing legal, management systems and institutional capacities in support of the management of chemicals
• Gap-analysis on the management of toxic and bio-accumulative substances, as well as emissions of mercury;
• Information, capacity-building and institutional needs assessment;
• Countries priority assessment, set up of a baseline to define a Regional Strategy for LAC
Biomarkers in Environmental Monitoring and Assessment

Gerardo Gold-Bouchot
Marine Resources Department
Cinvestav Unidad Mérida
México
Port of Spain
June, 2008

Definition

“A biomarker is a xenobiotically induced variation in cellular or biochemical components or processes, structures, or functions that is measurable in a biological system or sample” (National Research Council 1987)

“A cellular, tissue, body fluid, physiological, or biochemical change in individuals that is used quantitatively during biomonitoring to either imply presence of significant pollutant or as an early warning system for imminent effects.”

Types of biomarkers

• Biomarkers can be classified as:
  – Exposure. Indicate if the organisms has been exposed to a xenobiotic.
    • The simplest biomarker of exposure is the concentration of the pollutant itself.
  – Effect. Indicate if exposure to a xenobiotic is producing a deleterious effect on the organism.
  – Susceptibility. Indicate if the individual (or population) is more or less susceptible to effects.

Uses

• Environmental monitoring and assessment
• As a complement of chemical data
• Screening

Ideal biomarker

• The characteristics of an “ideal” biomarker would be:
  – Specific
  – Sensitive
  – Easy and cheap to measure
  – Reflects possible damages
Examples

• Exposure biomarkers
  – Concentration of pollutants
  – Metabolites in bile (or urine)
  – EROD, ECOD, etc. activities

• Effect biomarkers
  – Inhibition of Acetylcholinesterase
  – Changes in the antioxidant system:
    • CAT, SOD, Gt, etc.
    • Lipid peroxidation
    – Histological lesions
      • Including tumors
    – Endocrine disruption
      • Vitellogenin (and other proteins) induction

Cytochrome P-450

• The best known biomarker is the group of enzymes in the CYP-450 group
• Particularly the 1A group
  – Inducible proteins
  – Regulated by the Ah receptor
  – Part of the Phase I metabolism of xenobiotics
  – Under some circumstances, can be “quantitative”

Cytochrome P-450

• Phase I
  – Makes compounds more polar
    • Produces hydroxil, diol, peroxide, etc.
    • Derivatives
  – Phase II
    • Conjugates the compounds from Phase II
      • Glucuronates, sulfates, etc.
Cytochrome P-450

Examples

Acetylcholinesterase Inhibition
- Has a role in nervous impulse transmission

Acetylcholinesterase Inhibition
- Are inhibited by organophosphorous and carbamate pesticides
- In fish it is usually measured in muscle
  - In muscle it is a biomarker of exposure
  - In brain it is a biomarker of effect

Metallothioneins
- Small proteins
- Chelate some metals
  - Their role is to control the intracellular pool of Zn and Cu
- Cytosolic
- High content of cisteine
- In plants, phytochelatins
Problems

• Of course, there are some difficulties with the use of biomarkers
  – Most are not specific enough
    • EROD responds to PAHs, planar PCBs, dioxins and furans
    • AchE is sometimes inhibited by PAHs and metals
    • Most biomarkers based on enzyme activity are affected by metals
  – There are changes due to season, sexual maturity, gender, age, etc.
  – There is a need to characterize the biomarker for the species used

Conclusions

• Biomarkers are great:
  – Screening
    – Complement chemical data
    – Add new bang to results
      • Weight of evidence approach
  – But . . .
    – You have to make sure you understand the species in question
      • If not, be prepared to do a lot of “basic” science

Thank you!

Comments, complaints, etc. to:
  ggold@mda.cinvestav.mx
  gerardo.gold@gmail.com
Methods for Biological Monitoring

Biological Monitoring Techniques:
- Bioassessment
- Bioindicators
- Biomonitoring
- Biomarkers

Bioassessments

Population or Community - Level Changes
- Biomass or Abundance ↑ or ↓
- Species Diversity ↓
- Food Web Structure simplified
- Predator / Prey Relationships

Bioindicators

e.g.
- Tubificid worms (degraded)
- Cold water salmonids (healthy)

Biomonitoring

Used to monitor the concentrations of environmental contaminants in biota
A) Passive – Sample natural populations e.g. “Mussel watch” program or archived samples
B) Active - Organisms transplanted to monitoring site e.g. Caged mussels

ANSWERS BASIC QUESTIONS:
1) What contaminants are present in the environment?
2) Are contaminants present at concentrations above guidelines (consumption, water quality, sediment quality, etc.)?
3) What are the spatial trends?
   Polluted vs non-polluted (reference) sites
   Source tracking
4) What are the temporal trends?
   Is contamination getting better or worse?
   Is remediation having an effect?

Contaminants in zebra mussels (From Metcalfe et al)
Concentrations of Contaminants in Pooled Herring Gull Livers

Temporal trends of PBDEs in Great Lakes fish (Zhu and Hites 2004)
Doubling times of ~3 years in all lakes. Some evidence for a recent decline in Lakes Michigan and Ontario

Choice of Biomonitoring Organism
- Widely available and easily sampled
- Likely to accumulate target analyte(s)

AND/OR
- "Valued Ecosystem Component"
  - Keystone species in ecosystem
  - Species causing an impact (e.g. invasive species)
- "Valued Social Component"
  - High cultural, economic or recreational value
  - Species at risk
  - May need non-lethal sampling techniques
    - Eggs, placental cord, hair, skin, feathers, teeth
    - Biological fluids (blood, urine)
    - Biopsies of fat

Problems with Biomonitoring Techniques
- Biological variability (sex, age, size, condition, reproductive status, metabolism)
- Availability of organisms (especially at grossly polluted sites); even caged organisms may die or be moribund
- Complex sample matrix (e.g. lipid removal required)
**Passive Samplers**

- Determines time-weighted average concentrations over the deployment period (14-30 d)
- Simplifies sample collection and preparation
- No metabolism
- Low variability among replicates
- Less complex sample matrix
- Low maintenance and cost

“Semi-permeable membrane devices (SPMDs) for hydrophobic chemicals
“Polar Organic Contaminant Integrative Sampler” (POCIS) for hydrophilic chemicals

---

**Sampling Characteristics of POCIS and SPMDs**


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**Sampler Deployments in the Great Lakes**

- Boat-based deployments at:
  - near shore locations (5-20 m of water)
  - mid-lake monitoring buoys
- 28 day deployments
- Samplers deployed 4 – 5 m below the surface
- “Trip blanks” at each deployment site

---

Monitoring of persistent contaminants released from the carcasses of Chinook salmon that spawn in the Credit River watershed of L. Ontario

O’Toole and Metcalfe, 2005

SPMDs deployed every month from Sept, 2001 to Nov, 2002.
Disadvantages of SPMDs

- Deployed SPMDs are subject to loss (e.g. from currents or storm surge), vandalism or mischief
- Reflect contaminant levels only in the truly dissolved phase of water
- Contaminant profiles in SPMDs do not always match the profiles in biota
- Difficulty in calculating average concentrations in water from the amounts accumulated in the SPMDs

SPMDs

\[ K_{\text{SPMD}} = \frac{k_u}{k_s} \]

- \( k_u \) and \( k_s \) vary with:
  - Target analyte
  - Temperature
  - Water flow and turbulence
  - SPMD thickness (biofouling)
  - SPMD volume

Therefore: Difficult to estimate concentrations of analytes in water from the concentrations of analyte accumulated in the SPMD under different environmental conditions. (\( C_w = C_{\text{SPMD}} K_{\text{SPMD}} \))
Performance Reference Compounds (PRCs)

- Method of estimating concentrations of target analytes in water from measurements of analyte concentrations in SPMD
- Involves spiking PRCs into SPMDs before deployment and determining loss over deployment period

**PRC Method**

**Assumptions:**
- The effects of environmental variables (temperature, flow, biofouling) on the uptake rates of target analytes can be approximated by effects on the loss rates of PRCs under the same conditions
- The PRCs are governed by the same rate controlling mechanisms as the target analytes; ideally, every target analyte should have a PRC surrogate, but this is not feasible

---

Exposure Adjustment Factors (EAFs)

Huckins et al., 2002, ET&C 36:85-91

\[
EAF = \frac{k_{ePRC-field}}{k_{ePRC-cal}}
\]

Then:
\[
k_{ua-field} = k_{ua-cal} \cdot EAF
\]

Where: \(k_u = \text{Uptake rate for target analyte}\)

Therefore, in order to determine the rate of accumulation for a target analyte under any environmental conditions, we need to determine:
- \(k_{ePRC-field}\): Spike PRCs into SPMDs deployed in field
- \(k_{ePRC-cal}\): Spike PRCs into SPMDs in lab
- \(k_{ua-cal}\): Determine uptake rate for target analytes in lab (literature)

---

Model PRCs:

- Spike into triolein compounds not detected in environmental samples
  - PCB congener 8
  - PCB congener 13
  - Phenanthrene-d3
  - PCB congener 203 added as a recovery surrogate (i.e. no elimination from SPMD over the deployment period)
Outline of Presentation

- Purpose of Project
- Safety Training Course
- Site Commissioning
- Repackaging
- Site Decontamination & Decommissioning
- Remedial Activities
- Transportation
- Disposal

Purpose of Project

- Provide HAZWOPER training
- Repackage 24 tonnes of DDT
- Remediate impacted areas as required
- Transport and dispose of DDT and hazardous waste
- Supply and outfit ERV

Safety Training Course

- Hazardous Waste Operations and Emergency Response (HAZWOPER) training course
  - Hazard identification
  - Waste characterization
  - Personal protective equipment (PPE) selection & use
  - Implementation and use of hazardous waste site procedures
- Completed by Hazco in March of 2007
- Attendees included:
  - 7 staff from SWMCOL
  - 2 staff from the Ministry of Health
  - 2 staff from the Pesticides and Toxic Chemicals Control Board
  - 4 staff from Green Engineering

Training Course - March 2007
Site Commissioning

- Determination of site area layout
- Mobilization of supplies
- Site set-up including enclosure construction
- Establish hot, warm, decontamination, and supply zones
- Emergency planning
- Define worker roles and responsibilities

Site Area Layout

Assembly Point

- Daily site safety meeting
- Job safety analysis (completed prior to new task)
- Location of Health and Safety documents
- Lunch and breaks
- Personal protective equipment storage

Assembly Point

Site Access Area
Support Zone
- First aid supplies
- Eye wash station
- Fire extinguisher
- Tools
- Spill abatement equipment
- Personal protection equipment
- General supplies

Fire Protection & Spill Containment

Enclosure Set-Up

Enclosure Set-Up

Work Area Entry Point & Decontamination Zone
Work Area Entry Point & Decontamination Zone

DDT Repackaging

- Daily health and safety meeting and job safety analysis
- Bring new overpack drum to hot zone
- Remove DDT from existing container in hot zone
- Transfer DDT into overpack drum in hot zone
- Lift, clean and weigh overpack drum in warm zone
- Stack overpack drum in new container
- Decontamination

Health and Safety Meeting

Personal Protective Equipment
Site Decommissioning

- Plywood cut up and placed in salvage bins
- Decontaminate all supplies and work area
- Reposition containers for shipment
- Final site inspection

Summary of DDT/Soil Shipped

<table>
<thead>
<tr>
<th>Contents of Drums</th>
<th>Quantity of Drums</th>
<th>Weight of DDT + Drums (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDT</td>
<td>98</td>
<td>16,110</td>
</tr>
<tr>
<td>DDT debris</td>
<td>8</td>
<td>565</td>
</tr>
<tr>
<td>Shipping Container # 1</td>
<td>Total</td>
<td>16,675</td>
</tr>
<tr>
<td>DDT</td>
<td>16</td>
<td>2,610</td>
</tr>
<tr>
<td>DDT debris</td>
<td>2</td>
<td>115</td>
</tr>
<tr>
<td>Soil with DDT</td>
<td>33</td>
<td>6,690</td>
</tr>
<tr>
<td>Other debris</td>
<td>3</td>
<td>280</td>
</tr>
<tr>
<td>Shipping Container # 2</td>
<td>Total</td>
<td>9,695</td>
</tr>
<tr>
<td>OVERALL TOTAL (for both shipping containers)</td>
<td>160</td>
<td>26,370</td>
</tr>
</tbody>
</table>
Weight of DDT/Soil

<table>
<thead>
<tr>
<th></th>
<th>DDT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total weight (kg)</td>
<td>19,400</td>
</tr>
<tr>
<td>Total weight of drums at 36 kg/drum (kg)</td>
<td>4,465</td>
</tr>
<tr>
<td>Total weight of DDT shipped (kg)</td>
<td>14,935</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Soil with DDT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total weight (kg)</td>
<td>6,970</td>
</tr>
<tr>
<td>Total weight of drums at 36 kg/drum (kg)</td>
<td>1,295</td>
</tr>
<tr>
<td>Total weight of DDT shipped (kg)</td>
<td>5,675</td>
</tr>
</tbody>
</table>

Containers Ready for Shipment

Remedial Activities

Preliminary Delineatory Sampling

Three soil samples taken by Green prior to repackaging

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Sample Description &amp; Location</th>
<th>DDT Concentration Detected (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1227/07</td>
<td>Fine sand from sand pad – Western side, front of container near doors</td>
<td>243.83</td>
</tr>
<tr>
<td>A1228/07</td>
<td>Fine sand from sand pad – Southern side of container</td>
<td>1.95</td>
</tr>
<tr>
<td>A1229/07</td>
<td>Eastern side outside fence of container</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Remediation Phase

- Removal of 0.1 – 0.15 m impacted surficial soil
- Soil and rusted floor placed in salvage drums to be transported to Canada

Floor of Old DDT Storage Container
Disposal of Former DDT Storage

- Container decontaminated with kerosene and detergent
- Washwater contained and captured for use in solidification process
- Container cut up by 3rd party steel reclamation and recycling contractor and transported to Mittal Steel mill for recycling

Solidification of Residual Bedding Sand

- Bedding sand materials from former DDT storage area treated onsite by Green
- Sand materials solidified using Green’s proprietary solidification process
  - Process immobilizes contaminants in solidified cementitious slurry
- Sand materials combined with wastewater to ensure containment of all waste streams

Stabilization Process

Cut Up Container

Solidification of Residual Bedding Sand (cont.)

- Sand, wastewater, and stabilization materials were combined and placed in drums
- 61 drums were left onsite to solidify
- Drums were transported to SWMCOL’s Forres Park Landfill for final disposal

Mixing of Bedding Sand
Assessment, Monitoring and Management of POP and PTS in the Coastal Ecosystems of the Wider Caribbean

Biological Monitoring
Haffner, G.D. Hebert, C. Whittle,M

Exposure and Effects
- All chemicals toxic, not sufficient to just know presence and concentration
- Require kinetic models to calculate dose and understand factors regulating dose.
- Without exposure-effect models, monitoring programs become ‘data rich and information poor’

Why Biological Monitoring
- Best way to determine dose and to develop cause – effect relationships.
- Provides broader information on environmental health and places contaminant issues within context of other stressors.
- Multiple stressor management is the key!

Biological Monitoring
- Two programs: Great Lakes Fish Contaminant Monitoring Program and Herring Gull Monitoring Program.
- Linked under the Great Lakes International Surveillance Plan.
- Provide examples of successful monitoring programs that not only track chemical dynamics through time but provide critical information on environmental health.

Paracelsus, 1490 – 1541
“The Father of Toxicology”
(Philippus Aureolus Theophrastus Bombastus von Hohenheim)

“All things are poison and nothing is without poison, only the dose permits something not to be poisonous.”
Usually quoted as: “the dose makes the poison”
GLWQA PROGRAM OBJECTIVE

"TO SURVEY COLLECTIVELY, THE CONCENTRATION OF CONTAMINANTS IN SELECTED SPECIES OF GREAT LAKES FISH AND OTHER BIOTA WITH THE SPECIFIC PURPOSE OF DETERMINING ENVIRONMENTAL TRENDS IN CONTAMINANT LEVELS AND RELATING THESE, WHERE POSSIBLE, TO SOURCES OF SUCH POLLUTION, THE EFFECTIVENESS OF REMEDIAL ACTIONS, AND THE POTENTIAL IMPLICATIONS TO GREAT LAKES FISH STOCKS."

PROGRAM FRAMEWORK
GREAT LAKES WATER QUALITY AGREEMENT

- ANNEX 11 - Surveillance & Monitoring
  (Trend Evaluation & Emerging Problems)
- ANNEX 12 – Persistent Toxic Substances
  (Early Warning System, Spatial & Temporal Trends & Biological Tissue Bank)
- ANNEX 2 – RAPs & LaMPS
  Critical Pollutants & Impairment of Beneficial Uses

GREAT LAKES FOOD WEB - REVISED

<table>
<thead>
<tr>
<th>TOP PREDATOR:</th>
<th>LAKE TROUT (VALLEYE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FORAGE SPECIES:</td>
<td>SCULPIN ALINFE SMELT</td>
</tr>
<tr>
<td>INVERTEBRATES:</td>
<td>DIPOREIA MYSIS PLANKTON</td>
</tr>
<tr>
<td>DEPOSITIONAL BASIN</td>
<td>SEDIMENTS</td>
</tr>
</tbody>
</table>

WHAT IS MEASURED - ROUTINELY

- Metals:
  - Hg
  - As
  - Se
  - Cu
  - Zn
  - Ni
  - Pb
  - Cr
- Pesticides/Organics:
  - ΣPCB
  - ΣDDT & Metabolites
  - Heptachlor Epoxide
  - Dieldrin
  - Chlordane (α,γ)
  - Lindane (α, HCH)
  - HCB
  - Mirex

WHAT IS MEASURED – INTENSIVELY

- Analytes
  - A-BHC
  - HCB
  - B-BHC
  - G-BHC
  - D-BHC
  - HEPTACHLOR
  - ALDRIN
  - OCS
  - EPOX.(B)
  - EPOX.(A)
  - O-CHLOR
  - A-CHLOR
  - DIELDRIN
  - ENDRIN
  - B-ENDOSULF
  - PP.TDE
  - OP.DOT
  - PP.DDT
  - OP.DDE
  - PP.DDE
  - TOXAPHENE
  - PHOTOMIREX
  - PP.METHOX
  - MIREX
  - PCF’s
WHAT IS MEASURED – BIOLOGICAL

• Total Length, Fork Length, Weight
• % Lipid
• Age (CWTs, Scales, Otoliths, Fin Clips
• [lake trout migration also]
• Lamprey Scars
• Condition Factor (prey species)
• Length Frequency (recruitment)
• Diet (predators)
• Caloric Content (prey species)
• Fin Ray Asymmetry Incidence
• Skeletal Anomalies (X-Rays)
• Backbone Composition
• Morphological Anomalies

OMOE & Great Lakes Contaminant Surveillance Program Data – Walleye (45-55 cm)

• OMOE’s sport fish monitoring program (dorsel muscle, skin off fillet) produces different temporal trends than DFO/EC’s whole fish monitoring program
• May be related to lipid content differences in fillet vs. whole body
• May implicate ecological factors – such as changes in growth & energy density in walleye populations over time

LAKE SUPERIOR – LAKE TROUT

<table>
<thead>
<tr>
<th>Age</th>
<th>N</th>
<th>Total Length (Size Range)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3+</td>
<td>4</td>
<td>25.5 - 34.0</td>
</tr>
<tr>
<td>4+</td>
<td>3</td>
<td>30.0 - 38.0</td>
</tr>
<tr>
<td>5+</td>
<td>37</td>
<td>40.0 - 55.0</td>
</tr>
<tr>
<td>6+</td>
<td>31</td>
<td>41.0 - 65.0</td>
</tr>
<tr>
<td>7+</td>
<td>20</td>
<td>48.0 - 62.0</td>
</tr>
<tr>
<td>8+</td>
<td>5</td>
<td>55.0 - 73.0</td>
</tr>
<tr>
<td>9+</td>
<td>6</td>
<td>55.0 - 77.0</td>
</tr>
<tr>
<td>10+</td>
<td>3</td>
<td>62.0 - 74.0</td>
</tr>
</tbody>
</table>

LAKE ONTARIO – LAKE TROUT

<table>
<thead>
<tr>
<th>Age</th>
<th>N</th>
<th>Total Length (Size Range)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3+</td>
<td>4</td>
<td>26.0 - 34.0</td>
</tr>
<tr>
<td>4+</td>
<td>3</td>
<td>30.0 - 38.0</td>
</tr>
<tr>
<td>5+</td>
<td>31</td>
<td>40.0 - 55.0</td>
</tr>
<tr>
<td>6+</td>
<td>20</td>
<td>45.0 - 65.0</td>
</tr>
<tr>
<td>7+</td>
<td>11</td>
<td>49.0 - 62.0</td>
</tr>
<tr>
<td>8+</td>
<td>6</td>
<td>40.0 - 56.0</td>
</tr>
<tr>
<td>9+</td>
<td>6</td>
<td>49.0 - 61.0</td>
</tr>
<tr>
<td>10+</td>
<td>18</td>
<td>54.0 - 64.0</td>
</tr>
<tr>
<td>11</td>
<td>6</td>
<td>56.0 - 68.0</td>
</tr>
<tr>
<td>12</td>
<td>2</td>
<td>56.0 - 70.0</td>
</tr>
<tr>
<td>13</td>
<td>2</td>
<td>57.0 - 71.0</td>
</tr>
<tr>
<td>14</td>
<td>1</td>
<td>59.0 - 69.0</td>
</tr>
</tbody>
</table>

Herring Gull Program

• Initiated in response to reproductive failure observed in the 1960-70 period
This is where it all started...

"100 nests but only 10 young!" - Michael Gilbertson, 1971

The Herring Gull (Larus argentatus)

Why is it a good indicator species?

- Breeds on all five Great Lakes
- It eats fish and is at top of the aquatic food web
- High egg lipid content
- Accumulates elevated contaminant levels but not "sensitive"
- Well studied and visible to the public

But most importantly...

Herring Gulls do not migrate – all their contaminants are from the Great Lakes.

Great Lakes Herring Gull Monitoring Program

- Have changes in Great Lakes food webs affected chemical exposure in herring gulls?

Change-point Regression analyses - results fall into four categories:

- Faster in recent years
- Constant rate
- Slower in recent years
- No trend

Biological Monitoring of Environmental Contamination

- Use high trophic level species – Why?
- Accumulate high levels facilitating measurement
- Integrate exposure through whole food web
- Temporal and spatial trends in environmental contamination
- Toxic effects
DEVELOPING A CARIBBEAN CONTAMINANTS MONITORING & ASSESSMENT PROGRAM

- **BE CONSISTENT**
- **BE RELEVANT**
  - Adapt to Changing Conditions Without Losing The Central Theme.
  - Do Not Let Chemists *Unduly* Influence What Chemicals and What Biota Are Analysed.
  - Understand What Is An Environmentally Relevant Concentration of a Chemical.
  - Understand More About The Biology Of The System Than The Chemistry.

SOME COMMANDMENTS

- Treat Every Sample Collected With Respect. (They can never be duplicated – exactly.)
- Do Not Be An Undisciplined Collector
- Share Your Wealth. (Every sample should generate as much information as possible.)
- When In Doubt – Archive A Subsample (See 1st Point)
The Caribbean Environment Programme
Supporting Partnerships and Projects to reduce POPs

Nadia-Deen Ferguson
AMEP Assistant Programme Officer
UNEP CAR/RCU

CARTAGENA CONVENTION

Only legally binding, regional agreement for the Protection and Development of the Marine Environment of the Wider Caribbean Region

The Contracting parties shall take all appropriate measures to prevent, reduce and control pollution:

- Article 5: Pollution from Ships
- Article 6: Pollution from Dumping
- Article 7: Pollution from Land-Based Sources
- Article 8: Pollution from Sea Bed Activities
- Article 9: Air Pollution
- Article 10: The Contracting parties shall take all appropriate measures to prevent, reduce and control pollution:

CARTAGENA CONVENTION

Protocol Concerning Specially Protected Areas and Wildlife (SPAW)
Adopted in 1990
In force since 2000

LBS PROTOCOL

- General Obligations
  - national planning
  - integrated coastal area management
  - monitoring and assessment
- Specific Obligations for Priority Sources
  - Sources, Categories, Associated Pollutants of Concern (Annex I)
  - Domestic Wastewater effluent and emissions limitations with schedules for implementation (Annex III)
  - Agricultural Non-Point Sources best management practices (Annex IV)
AMEP Sub Programme

To control, prevent and reduce pollution of the coastal and marine environment from land and marine-based sources and activities thereby enabling Countries of the Wider Caribbean to meet their obligations under the Land Based Sources of Marine Pollution and Oil Spills Protocols.

Current Projects to Reduce POPs

- WW2BW/SIDA Project
- RAC Cimab, RAC IMA, INVEMAR
  - Lab Capacity Improvement
  - Water quality data for regional “hot spots”
  - Guidelines for the classification of marine waters as per LBS Protocol
  - GIS Capacity for pollution monitoring
  - IOCARIPE, IAEA, UdO, CEHI.

Areas for Collaboration

- Information management
- Training in Specialized Sampling and Analytical Methodologies
- Technical exchange
- Information dissemination
- Lab capacity development
Coastal Monitoring Program

The coastal monitoring program is an integral part of the REPCar project. Keeping in mind the importance of the oceanographic inter-connectivity in the region, the regional program of coastal monitoring is projected like the base for a long-term monitoring program, with the participation of different oceanographic and academic institutes.

The objective of the coastal monitoring programme is to monitor and evaluate pesticide run-off in specific zones (watersheds), to provide agricultural users with this information and thus promote best practices in the use of pesticides. The information generated will serve as a baseline and will, in the long run, become an indicator of the environmental benefits generated by the project, among others.

Marine and Coastal Research Institute
“José Benito Vives de Andrés” INVEMAR

Linked to Environmental, Dwelling and Territorial Development Ministry (MAVDT)

- INVEMAR is a non-profit civil corporation, according to the terms of the Law 29 of 1990 and the Decree 393 of 1991, by which the system of science and technology in Colombia is regulated. It counts with legal status, administrative autonomy and own patrimony.
- Their mission is to carry out basic and applied investigation in the renewable natural resources and in the national interest seaways and oceanic and marine ecosystems, in order to provide the necessary scientific knowledge for the formulation of politics, for to take decisions, and for the elaboration of plans and projects which conduct to the development of the national coasts, based on the sustainable management principles for the recovery of the coastal and marine environment, and for to improve the Colombian people life quality.

Center for the investigation in Aquatic Resources of Nicaragua (CIRA-UNAN)

The center for the investigation in Aquatic Resources of Nicaragua (CIRA-UNAN) is part of the Universidad Autónoma Nacional de Nicaragua (UNAN/MANAGUA). It is an academic institute dedicated to contribute to the use and the protection of the water resources of Nicaragua.

The CIRA/UNAN offers services of diagnoses, advising, consultant, training and have specialization and master programs for graduate students in topics of water resources quality and in the integrated management basins.

Center of Investigation in Environmental Pollution CICA and Center for Research in Marine and Limnology Sciences CIMAR

The Center of Investigation in Environmental Pollution, is a scientific investigation unit of the University of Costa Rica, it is dedicated to study environmental pollution, its causes, and its effects in humans, animals, plants, food and in the physical environment.

The Center for Research in Marine and Limnology Sciences (CIMAR) is a multidisciplinary academic research unit linked to the University of Costa Rica. The center is organized in research programs and projects, besides support modules for to execute specific projects.
Work Plan
Second Meeting of the Pesticides Coastal Monitoring Programme
March 27 y 28, 2008, Kingston Jamaica

Workshop objectives:
• Discuss the progress made in developing the Pesticides Coastal Monitoring Programme
• Review the capacity of participating institutions
• Define the most appropriate sampling techniques
• Select the matrices, compounds and methods of analysis to be used as well as the quality control standards to be developed
• Assess monitoring alternatives in the marine environment and complete the general framework for the Programme.

Conclusions
• Make a training course on sampling and pesticide analysis techniques, at the CICA, in San José, Costa Rica.
• The compounds to be monitored was selected through a matrix representing the pesticides most frequently used in the main agricultural crops of the three countries. This was further complemented with information on the physical and chemical properties of these compounds, and with techniques used in their analysis.

Molecules selected:
- Sediments: longer average life span (t½), and higher dissociation constant Octanol – Water (Koc): zoles (ciproconazole, propiconazole, among others), chlorpirifos, diuron, endosulfan, ethofumesate, fenamiphos, glyphosate, imazalil, methylation, triadimefon/triadimenol, triazines, tridemorph.
- Agua: dissociation constant Octanol – Water (Kow), and techniques used in their analysis: Bromacil, carbendazim, carbofuran and tiabendazol.
- Tracers: chlorpirifos y endosulfan, because these molecules have a longer life cycle. As well as DDT.

Matrices to be monitored:
- Surface sediment: 0.5 cm in the floculate layer Agua.
- Water
- Particles in suspension
- Ronco Blanco fish (Haemulon plumieri)

Monitoring Recommendations
- Nicaragua will conduct monitoring only in coastal zones, coastal lagoons and watersheds but not in marine zones, as it does not have much experience in monitoring on the open seas.
- Colombia will conduct monitoring in the coastal and marine zone, including San Andrés in order to obtain first-hand information on the boundary between Colombia and Nicaragua.
- Costa Rica, will work together with the IAEA project, for the taking of samples in marine zones.

After conducting the baseline monitoring, each country will, on the basis of the results obtained, conduct a new review of the zones and stations, compounds and matrices to be monitored. This monitoring scheme will be circulated among participants and members of the expert panel for their review, comments and suggested changes.

Cooperation with other Regional Projects
Project “Use of Nuclear Techniques to Address the Management Problems of Coastal Zones in the Caribbean Region”:
• Training course
• Base line in the marine zone to Costa Rica

Project “Assessment and Management of Environmental Pollution”:
• Measurement of other variables as salinity, temperature, suspended solids, nutrients and coliforms.

...Thanks for your attention
**Why Demo Projects?**

**Project Goals**

- Capacity Training
- Regional Data
- Laboratory Risk Assessment Approaches
- Baseline Conc.
- Sources / Health Effects

**Demo Projects**

- Provides richer data at expense of comprehensive coverage
  - We can’t have a demo project in each country
- Hands on experience with more advance level interpretation of data
  - Teaches concepts of design and data interpretation beyond sample collection and analytical analysis
- 2 Components
  - 1) Baseline data – regional patterns of contamination
  - 2) Risk assessment – focussed determination of health implications or sources

**Spatial Pattern of Contamination**

- Water
  - Passive samplers (SPMDs/POCIS Samplers)
  - Simplicity of matrix, commonality of design and extractions
  - Ability to be placed in freshwater/marine systems
- Sediment
  - Ease (relative) of collection
  - Heterogenous matrix
    - Size fraction, organic carbon content, turnover & burial
    - More rigorous analytical requirements
      - *e.g.* Soxhlet + clean-up methods
- Biomonitoring
  - Existing Database (White Grunt)
    - MBRS, Gulf of Honduras: Project (Up-coing)
  - Simplicity of matrix - lipids
  - Ease of analytical processing
    - Cold column chromatography

**Design Requires a Project Objective!**

1. **Spatial patterns of contamination**
2. **Source Identification and Control**
   - Requires high resolution sampling + additional information
     (e.g. Hydraulic models, end of pipe sampling or other to facilitate litigation).
3. **Ecosystem Health Assessment**
   - Requires exposure routes be characterized
   - Food web sampling
   - Toxicity bioassays
4. **Human Health Assessment**

**Demo 1: White Grunt as a Regional Biomonitor?**

- Coastal fish, may not be found at all locations
  - Find Ecological Equivalent Species
  - Similar size and feeding ecology
- Size range to be considered
  - 300 – 500 g
- Regional coverage of single species
  - Scope of sampling exceeds foraging range
  - Compliments and strengthens past & existing projects
    - Gulf of Honduras/MBRS
- Supports Project Scope – Establish Baseline Data
**Spatial Trends In PCB Trophodynamics**

- Is white grunt the most effective biomonitor?
- Representativeness of spatial patterns of contamination?
- Representativeness of level of contamination – is it the most contaminated or least contaminated?

**Food web sampling as a Demo Project**

- Food web sampling at 3 locations
  - Hasn’t been completed for region
  - Places white grunt into context of food web exposures
    - degree of contamination
    - spatial integration
  - Can be used to validate food web bioaccumulation models (Risk assessments)
- Can be linked with existing initiatives
  - E.g. Gulf of Honduras
    - Reference + Contaminated Site;
    - 3rd site???

**GLIER Food Web Biomonitoring Sites**

Historical Data Sets Available for:
- Peche Island (1992-1993; R. Russell PhD)
- Middle Sister Island (1992, 95/96; S. Kowalski MSc, H. Morrison PhD)

**Spatial Trends In PCB Trophodynamics**

**PCBs in Biota vs. Sediment**

- Large Organisms Integrate Large Spatial Areas
- Smaller Organisms More Representative of Local Environments
- Ecological Information on Species specific Time Budgets in Contaminated Regions Often Lacking!
Temporal Trends in PCB Trophodynamics
1991 – 2001 (GLIER Dataset)

Peche Isl., Detroit River

Middle Sister Isl., Lake Erie

• No major changes in PCB food web trophodynamics between 1990-2000
República Dominicana
Proyecto IWCAM-RD

Proyecto

Integrando la Gestión de Cuencas y Áreas Costeras en Pequeños Estados Isleños en Vía de Desarrollo

Alcance IWCAN-RD

Mitgar los Impactos de Desechos Industriales en la Cuenca Baja del Río Haina y su Costa

Objetivos IWCAN para los Estados Isleños

- Fortalecer el compromiso y la capacidad de los países participantes para implementar un enfoque integrado de la gestión de cuencas y áreas costeras.
- Aumentar la capacidad de los países para planificar y gestionar sus recursos acuáticos y ecosistemas sobre una base sostenible a largo plazo.

Antecedentes del inicio del Proyecto

- Valor Inicial del Proyecto: 112 Millones de USD.
- Fuente de financiamiento: Global Environment Facility (GEF) y contrapartida de los países participantes.
- Agencias implementadoras:
  - 1. Programa de Naciones Unidas para el Medio Ambiente (PNUMA)
  - 2. Programa de Naciones Unidas para el Desarrollo (PNUD).
- Agencias ejecutoras:
  - 1. Secretariado de la Convención de Cartagena, Unidad Coordinadora Regional Caribeña del PNUMA (UNEP – CAR/RCU
  - 2. Caribbean Environmental Health Institute (CEHI).

Antecedentes

- Países Participantes: Antigua & Barbuda, Islas Bahamas, Barbados, Cuba, Grenada, Dominica, República Dominicana, Haití, Jamaica, San Kitts y Nevis, Santa Lucía, San Vicente & las Granadinas y Trinidad & Tobago.
- Duración del proyecto: 5 años, comenzando en el último trimestre del 2005.
- Unidad coordinadora del proyecto: está localizada en el CEHI, por acuerdo entre las agencias implementadoras y ejecutoras y los países participantes; y fue establecida en mayo 2006, cuando el Coordinador Regional del Proyecto asumió sus funciones.
Cambios actuales

**Nombre Actual:** Mitigación de los Impactos de Desechos Industriales en la Cuenca Baja de Río Haina y su Cuenca  
**Valor del Proyecto:** 1,163,220.00 USD  
**Fuentes Financieras:**  
1. Global Environment Facility (GEF): 520,470.00 USD  
2. Contrapartida de República Dominicana: 642,750.00 USD

Agencia ejecutora

El Proyecto será ejecutado de la Secretaria de Estado de Medioambiente y Recursos Naturales (SEMARENA), a través de la Subsecretaría de Gestión Ambiental (SGA).

Duración del proyecto

**4 años**  
Iniciando en noviembre del año del 2006

Objetivos IWCAM-RD

- Reducir la contaminación ambiental de la cuenca baja del Río Haina y su costa.
- Crear las condiciones para un efectivo manejo ambiental integrado de la cuenca baja del Río Haina y su costa

Objetivos específicos y productos

- **Establecer una infraestructura y estrategia para el manejo de la cuenca baja del río Haina y su costa:**  
  * Establecimiento de una Unidad Ejecutora del Proyecto (UEP).  
  * Establecimiento de un Consejo de Manejo y Desarrollo de la Cuenca Baja del Río Haina, (CMD-HAINA)
- **Identificar e implementar mecanismos para reducir las fuentes contaminantes de la cuenca baja del río Haina y su costa.**  
  * Revisión de legislación y políticas para proporcionar incentivos, para la reducción de descargas y emisiones, además establecer responsabilidades para los monitoreo y cumplimiento de las normas de Calidad Ambientales.
Objetivos específicos y productos

* Desarrollo e implementación de una estrategia para la limpieza de la cuenca baja del río Haina.

Objetivos específicos y productos

* Establecer un mecanismo de financiamiento sostenible, para el monitoreo, por parte del Consejo de Manejo y Desarrollo de la Cuenca Baja del Río Haina (CMD-HAINA), con relación a las variables de importancia medioambiental.

Objetivos específicos y productos

* Desarrollar un mecanismo que permita replicar en otras cuencas las experiencias positivas del proyecto.

Cambios y mejoras esperados

* Contar con un organismo gestor, efectivo y sostenible, para la cuenca baja del río Haina y su sector industrial relacionado con recursos, apoyo político y responsabilidades definidas en relación a:
  * Requisitos de Estudios de Impactos Ambientales.
  * Monitoreo de la calidad de agua de la cuenca.
  * Monitoreo del cumplimiento y aplicación de la legislación correspondiente.

Cambios y mejoras esperados

* Una mejoría significativa de las industrias y la realización de mediciones de:
  * Calidad del agua
  * Manejo de residuos sólidos industrial.
  * Reducción de las emisiones atmosféricas contaminantes.

Otros cambios y mejoras esperados

* Mejoras significativas relacionada con las descargas de aguas residuales, las emisiones atmosféricas y los desechos sólidos, a través de un mecanismo de Evaluación de Impacto Ambiental efectivo y responsable, apoyado por un monitoreo de cumplimiento y por la aplicación de la ley Ambiental 64-00 y sus normas.
Mejoras esperadas

- Establecer mecanismos y tecnologías para la reducción de emisiones, descargas y desechos sólidos, que puedan ser transferidos a otras áreas industriales de importancia en el país.

Estado Actual del Proyecto IWCAM-RD

- El 15 de febrero del 2008, fue contratado el Coordinador Nacional del Proyecto.
- Se han iniciado las acciones para la conformación y funcionamiento de la oficina del proyecto:
  - Elaboración de plan de trabajo
  - Elaboración de presupuesto febrero-junio
  - Solicitud de compra de equipos y material de oficina.
  - Elaboración de términos de referencia para la contratación del personal e inicio de la selección del mismo.

Actividades realizadas

- Se seleccionaron los indicadores del proyecto.
- Hasta la fecha todavía no se han utilizado los fondos presupuestados.
- Actualmente fue realizado un taller sobre educación ambiental, para los representantes de la zona.

Fin

MUCHAS GRACIAS
Conceptos básicos de las capas de agua dulce y agua salada de una región kárstica

Manglares; Dunas; Playa; Selva; Arrecife
Nivel del mar: Capa freática
Dirección regional del flujo de las aguas
Acuífero de agua dulce; de agua salobre, y de agua salada

Flujo del agua y potencial de contaminación en la geología kárstica
Flujo de agua dulce
Flujo de agua salada
Contaminación

Flujos Subterráneos en la Península de Yucatán

Desemboca de agua dulce cerca la costa en la Península de Yucatán

Potential for Contamination in Karst Geological Zones
- Urban pollution
  - Domestic wastewater
  - Hydrocarbons
  - Metals
- Agriculture (citrus, banana, palm oil, pineapple, sugarcane)
- Tourism and recreation

Potencial para contaminación:
Contaminación urbana
- Agua desecho doméstico
- Hidrocarburos
- Metales
Agricultura (cítricos; banana; palma; piña, caña)
Turismo y recreación
Impacts of Recreational Activities

- Wastewater discharges or septic leakage
  - Hotels and resorts
  - Recreational homes, boats
- Hydrocarbons from boats, vehicles
- Maintenance of lawn and turf
  - Homes
  - Hotels and resorts
  - Golf courses

Exacerbated by reduced "ecological integrity" (e.g. removal of mangrove, wetlands)

Studies to Evaluate Sources of Contamination in Karst Geological Zones

**Design**
- Passive samplers deployed in wells, artesian zones (e.g. cenotes), mangrove and nearshore zones
- Collection of biota (crabs, mussels, polychaetes) and sediments in mangrove and/or nearshore zones

**Analysis**
- Pesticides (current use, legacy)
- PCBs, hydrocarbons and metals
- Surfactants
- Tracers of domestic wastewater (disinfectants, synthetic musks)