PRESENTATIONS

Interim Reporting Workshop

Caribbean Coastal Pollution Project (CCPP)

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

21-22 January 2009
Reef Yucatan Hotel, Merida, Mexico

Day 4: Thursday, 22 Jan (continued)

Gerardo Gold-Bouchot and Victor Ceja-Moreno, Cinvestav Unidad Merida, Mexico
Organochlorine Pesticides (OCs), Polychlorinated Biphenyls (PCBs) and Poly cyclic Aromatic Hydrocarbons (PAHs) in Recent Sediments from the MBRS

Nadia Deen Ferguson, UNEP CAR/RCU, Jamaica
The Caribbean Environment Programme supporting partnerships and projects to reduce POPs

Eric Dewailly, Laval University, Canada
Arctic Lesson: from AMAP to CariMAP

Chris Metcalfe, Trent University and Watershed Sciences Centre, Canada
Passive Samplers in the Yucatan Peninsula
Report on Lab Assessments in the Wider Caribbean Region
BIOMARKERS Examples with fish: Fish tumours CYP450 activity Vitellogenin induction in males Inter-sex gonads
Emerging POPs and PTS (not presented)

Ken Drouillard, GLIER, University of Windsor, Canada
Quantitative Biomonitoring of POPs in Caribbean Coastal Zones Using Oysters
Inter-laboratory Comparison Exercise
Guidelines for Sample Preparation and Analysis
Harmonized Database (not presented)
Organochlorine Pesticides (OCs), Polychlorinated Biphenyls (PCBs) and Polycyclic Aromatic Hydrocarbons (PAHs) in Recent Sediments from the MBRS

Gerardo Gold-Bouchot and Victor Ceja-Moreno

Marine Geochemistry Laboratory
Marine Resources Department
Cinvestav Unidad Merida
Mexico

Objectives

• Determine types and concentrations of organochlorine compounds in recent sediments
  – 34 sites in the four participating countries
    • 13 in Mexico
    • 9 in Belize
    • 5 in Guatemala
    • 9 in Honduras
  – Selected by environmental agencies
• Assess the environmental risk from these pollutants
• Provide environmental managers with sound information
Study Zone

Results OCs

- **HCHs**
- **Chlordanes**
- **Drins**

Locations and samples:
- Cabo Catoche
- Isla Contoy
- Arrecife Cuevones
- Boca Lag. Bojorquez
- Puerto Morelos - El ángel
- Cozumel (Frente al Pueblo)
- Arrecife Colombia
- Punta Allen
- Niche Jabin
- Bahía Chetumal Norte
- Bahía Chetumal Centro
- Bahía Chetumal Sur
- Xcalak
- Río Bacalar Chico
- Bahía Chetumal
- Corozal
- Cayo Caulker
- Boca 2 Creek R
- Boca 1 R. Belice
- Shallow water keys
- Plascencia
- Sapodilla Keys
- Cabo 3 Puntas
- Barra Sarstún
- Río Dulce
- Río Escondido (Pto. Barrios)
- Puerto Santo Tomás del Castillo
- Barra de Motagua
- Omoa
- Quilimaco
- Ulúa
- Chamalecón
- Tela
- Utila (arrecife)
- Utila (frente al pueblo)
- Ceiba
Medians by country

OCs by country
Conclusions

- Relatively high concentrations of DDT compared to those of DDE indicate “recent” use.
- High Lindane concentrations in Chetumal Bay, including Corozal Bay
- Of all organochlorine compounds, highest were the PCBs
- PAHs have a possible petrogenic source
- It is important to continue this monitoring and track the sources
Thank You!

ggold@mda.cinvestav.mx
gerardo.gold@gmail.com
THE CARIBBEAN ENVIRONMENT PROGRAMME

SUPPORTING PARTNERSHIPS AND PROJECTS TO REDUCE POPS

Nadia Deen Ferguson
AMEP Assistant Programme Officer
UNEP CAR/RCU

Caribbean Regional Coordinating Unit (UNEP-CAR/RCU)

UNEP

Division of Environmental Policy Implementation

Regional Seas Programme

Governments of the Caribbean Region

Caribbean Environment Programme “Cartagena Convention and Protocols”

CAR/RCU

AMEP

SPAW

CETA
**Cartagena Convention**

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

Adopted in 1983
Entry into Force 1986

- **Protocol Concerning Pollution from Oil Spills**
  - Adopted in 1983
  - Entry into force in 1986
  - AMEP Sub Programme
    - RAC/REMPEITC

- **Protocol on Specially Protected Areas and Wildlife**
  - Adopted in 1990
  - Entry into force in 2000
  - SPAW Sub Programme
    - SPAW RAC

- **Protocol on Land Based Sources of Pollution**
  - Adopted in 1999
  - AMEP Subprogramme
    - RAC IMA and RAC CIMAB

---

**The Objective of AMEP is:**

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** of the **Cartagena Convention**
Obligations of the LBS Protocol

- **General Obligations**
  - National Planning including use of EIAs
  - Integrated Coastal Zone and Watershed Management
  - Environmental Monitoring and Assessment

- **Specific Obligations for Major Pollutants**
  - Effluent and Emissions limitations, Time Tables for implementation, and Classification of Recreational Waters (Annex III – Sewage)
  - Best Management Practices (Annex IV – Agricultural Run-off)
  - Most Appropriate Technologies

Annexes

- **Annex I**: Source categories, activities and pollutants of concern
- **Annex II**: Factors to be used to determine effluent and emission source controls
- **Annex III**: Domestic Wastewater
- **Annex IV**: Agricultural non-point sources
Current Projects to Reduce POPs

- Global Environment Facility Projects - IWCAM & REPCar
- Best Management Practices for Pollution Reduction - Best Practices in Agriculture
- Support to Stockholm Convention Secretariat
- Support & Collaboration with BASEL

Complementary Projects

Know Why Network Partnership
WW2BW/SIDA Project
- RAC-CIMAB, RAC-IMA, Marine Research Institute of the Ministry of Environment of Colombia (INVEMAR), IOCARIBE and IAEA
  - Lab Capacity Improvement
  - Hot Spot Diagnostic Analysis and GIS Technology used to map, analyze water quality & Pollution Loads
  - Guidelines for the classification of marine waters as per LBS Protocol
  - GIS Capacity for pollution monitoring
Complementary Projects

Technical Report 33

- Pollutant loads from the 5 sub regions of the WCR
- 13 basic parameters, 10 optional measured
- Projections 2015 & 2020
Colombia, Costa Rica y Nicaragua

Reduciendo el Escurrimiento de Plaguicidas al Mar Caribe

RESUMEN Y ESTADO DEL PROYECTO
Objetivo

Proteger el medio marino de la región del Gran Caribe, implementando prácticas de manejo integrado y medidas específicas para el control sobre el uso y la aplicación de plaguicidas en el sector agrícola.

Apoyo a los países en la implementación del Protocolo Relativo a la Contaminación Procedente de Fuentes y Actividades Terrestres (LBS), como parte del Convenio de Cartagena.

Componentes

Coordinación del proyecto: a nivel regional y nacional

Desarrollo de Proyectos Demostrativos: Validación e implementación de Buenas Prácticas Agrícolas (BPA)

Monitoreo del impacto ambiental de los plaguicidas, incluyendo Programa de Monitoreo Costero

Actividades para el fortalecimiento de la capacidad de reducción de escorrimiento de plaguicidas.
**Monitoreo impacto ambiental plaguicidas**

Monitoreo costero de plaguicidas

*Fase 1: Evaluación plaguicidas en ambientes costeros y marinos*

- Propuestas y contratación: junio – julio 2008
- SSFA por 1 año

Monitoreo impacto ambiental plaguicidas

Publicación de manual para programa de monitoreo:

- Muestreo, análisis, procesamiento de información, control de calidad
- Primer borrador junio 2008, versión final septiembre 2008
Monitoreo impacto ambiental plaguicidas

Monitoreo costero de plaguicidas

Cursos de capacitación:

- “Técnicas analíticas para la medición de residuos de plaguicidas en muestras ambientales”
- “Cuantificación de contaminantes orgánicos en sedimentos marinos”
- Junio 30 a julio 18 de 2008

Tercera reunión Comité Directivo - GEF-REPCar

Monitoreo costero de plaguicidas

Cursos de capacitación:

- “Taller en modelación de fuentes difusas de contaminación marina y descargas de sedimento”   Febrero 18 a 20 de 2008

Tercera reunión Comité Directivo - GEF-REPCar
**Monitoreo impacto ambiental plaguicidas**

Monitoreo costero de plaguicidas

**Acreditación laboratorios:**
- Compra equipos (cofinanciación), capacitación
- Programa de manejo de calidad

<table>
<thead>
<tr>
<th>CIRA</th>
<th>CICA-CIMAR</th>
<th>INVEMAR</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO17025</td>
<td>En proceso: residuos de plaguicidas</td>
<td>Calidad de agua, residuos de plaguicidas, muestreo</td>
</tr>
<tr>
<td>Manual calidad</td>
<td>Blanco de reactivo, muestra duplicada, muestra enriquecida. Durante cromatografía: blanco de solvente, blanco de equipo, estándares de recuperación (curso CICA)</td>
<td></td>
</tr>
</tbody>
</table>

**Tercera reunión Comité Directivo - GEF-REPCar**

**Monitoreo impacto ambiental plaguicidas**

**Impactos esperados**
- Mayor información sobre interacciones agricultura y medio ambiente como herramienta para desarrollo de estrategias, políticas, directrices
Fortalecimiento de la capacidad de reducción de escurrimiento de plaguicidas

Pagina web de proyecto
✓ Plataforma interactiva basada en mapas, junto con AMEP

Areas for Collaboration
- Information management
- Technical exchange
- Training in Specialized Sampling and Analytical Methodologies
- Lab capacity development
- Coordinated Support to MEAs
- Regional integrated projects for the management of POPS and other LBS of marine pollution
CLEAN BEACHES

FISHERIES

THANK YOU!!

SHIPPING

TOURISM
Arctic Lesson: From AMAP to CariMAP

Eric Dewailly MD PhD
Laval University/CHUQ and PAHO/WHO Collaborative Center in Environmental Health
and the CEHP team
CCPP Meeting, Merida, January 2009

AMAP Assessment 2002: Human Health in the Arctic
Figure 2.1 Illustration of the different physical pathways by which POPs enter the Arctic. Transport into, and within, the Arctic occurs via the currents, ocean currents, rivers, and terrestrial ice movements.

Figure 2.4 Use of DDT in the northern hemisphere in 1980 and 2000 (Li and Nielsen, 2000).
POPs in the seafood chain

- Contaminants in seafood (predators and fatty species)
- POPs in human lipid rich tissues and fluids: milk, plasma
- Effect biomarkers: EROD, thyroid, vitamin A, immune functions, etc...
- Diseases: lack of specificity
Figure 5.3: DDE concentration in blood of mothers and women of childbearing age.

Figure 5.4: β-HCH concentrations in blood of mothers and women of childbearing age.
Data available in Nunavik

- Adult blood
- Maternal blood
- Cord blood
- Human milk

Classical and emerging persistent organic pollutants in the Arctic: preliminary results from the Nunavik Health Study 2004 (adults)

<table>
<thead>
<tr>
<th>Organochlorines</th>
<th>Organobromines</th>
</tr>
</thead>
<tbody>
<tr>
<td>A) PCBs</td>
<td>E) PBBs</td>
</tr>
<tr>
<td>B) PCDDs</td>
<td>F) PBDEs</td>
</tr>
<tr>
<td>C) PCDFs</td>
<td></td>
</tr>
<tr>
<td>D) p,p'-DDE</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Perfluorinated</th>
</tr>
</thead>
<tbody>
<tr>
<td>G) PFOS</td>
</tr>
<tr>
<td>H) PFOA</td>
</tr>
</tbody>
</table>
Plasma concentrations (geometric means and 95% CI) of four major contaminants according to age categories

![Graph showing plasma concentrations of PBC 153, 4-Hydroxy-PCB107, PBDE 47, and PFOS across different age categories.]

Plasma concentrations (geometric means and 95% CI) of four major contaminants according to consumption of marine mammal fat (gr/day)

![Graph showing plasma concentrations of PBC 153, 4-Hydroxy-PCB107, PBDE 47, and PFOS across different levels of marine mammal fat consumption.]

*Note: The graphs illustrate the geometric means and 95% confidence intervals for each contaminant across different age categories and levels of marine mammal fat consumption.*
Qanuippitaa: Legacy POPs, comparison with 1992-2004

- **Aroclor 1260**: -52%
- **trans-nonachlor**: -20%
- **p,p'-DDE**: -58%
- **HCB**: -63%
- **Oxychlordane**: -49%
- **β-HCH**: -61%

Qanuippitaa: PFOS, comparison with 1992

Women of child bearing age and pregnant women only (1992 n= 49; 2004 n=31)

- **PFOS**: -53.6%
Temporal trends in exposure for pregnant women and neonates

Pregnant women and neonates are more sensitive to the effects of POPs and toxic metals

Specific Monitoring for this population

- Human milk (past project)
- Cord plasma/blood (past project)
- Maternal plasma/blood (ongoing project)

Temporal trends in exposure: 1) Human milk

Integration of several studies where human milk was collected

Time span 1989-2001, Nunavik vs. southern Quebec

Analyses of PCBs, OCs pesticides, dioxin-furans and PBDEs

- Nunavik:
  - ↓ 53 % for Total PCBs (sum of 16 PCBs)
  - ↓ 78 % for Total TEQs
  - ↑ 74 % for Total PBDEs (sum of 7 congeners)

Similar ↓ in OCs in Nunavik and South
Higher ↑ for PBDEs in south
Temporal trends in exposure: 3) Maternal plasma

- Aroclor 1260: $R^2=0.13$, $p<0.0001$, 8.1% annual decrease
- Hexachlorobenzene: $R^2=0.12$, $p<0.0001$, 7.1% annual decrease
- p,p'-DDE: $R^2=0.12$, $p<0.0001$, 7.9% annual decrease
- β-HCH: $R^2=0.07$, $p<0.001$, 6.4% annual decrease
- trans-nonachlor: $R^2=0.07$, $p<0.001$, 4.6% annual decrease
- Oxychlordane: $R^2=0.05$, $p<0.01$, 5.5% annual decrease
- Mirex: $R^2=0.30$, $p<0.0001$, 11.4% annual decrease
- Hydroxy-PCB 202: $R^2=0.35$, $p<0.0001$, 8.4% annual decrease
PCB 153 Umbilical Cord Vs Maternal Plasma

R = 0.96

Concentration in maternal plasma (ng/g lipd wt.)

Concentration in cord plasma (ng/g lipd wt.)

Time trend of POPs in cord blood in Nunavik (1993-2001)

PCB

DDE

HCB

Oxochlorane
Balancing the Risks and the Benefits of Local Fish Consumption in Bermuda

Éric Dewailly, MD, PhD
Unité de recherche en santé publique du CHUL (CHUQ), Québec, Canada

and

Philippe Rouja, PhD
Ministry of the Environment, Telecommunications and Ecommerce, Department of Conservation Services Government of Bermuda.

A Case Study in Bermuda: POPs and Heavy Metals in Newborns and Fish

| TABLE 10-3. Organochlorines in umbilical cord plasma of Bermudians (µg/L; n = 42). |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | Mean ± SE       | N               | % Detected     | Range           | NA              |
| Aroclor 1260    | 39              | 22.1%           | <0.6-0.90      | NA              |
| PCB-101         | 39              | 5.6%            | <0.06-0.96     | NA              |
| PCB-138         | 39              | 7.2%            | <0.06-0.97     | NA              |
| PCB-153         | 39              | 50.8%           | <0.66-0.11     | NA              |
| PCB-180         | 39              | 5.1%            | <0.06-0.96     | NA              |
| Θ-BHC           | 39              | 2.6%            | <0.1-0.14      | NA              |
| p,p'-DDE        | 39              | 100%            | <0.06-1.36     | 0.43 ± 0.04     |

NA = nonapplicable.
But mercury was high… 10 microg/L on average.
The POP Project of the CEHP

- Sampling
- Analytes
- Others
- Parameters
- Atlantis
Sampling Procedure

• 15 Caricom Countries
• 50 cord blood samples in each country
• Start in 2008 with Grenada.
• Sampling completed, analyses in progress
• Continue in 2009 with Barbados, St. Lucia and St. Vincent

Analytes

• 10 legacy POPs in individual samples
• Calux TEQs (non-ortho PCBs + PCDDs + PCDFs) in 5 pools/country
• Emerging POPs and metabolites (n=86) in 5 pools/country
   § OH-PCBs and MeSO-PCBs
   § Other Chlorinated pesticides and PCP
   § PBDEs, OH-PBDEs and PFOS

Analyses on Atlantis
Analyses in Québec
Urine analytes

- Metabolites for pyrethroids incl. deltamethrin (5 compounds)
- Metabolites organophosphates (6 compounds)
- Chlorophenoxy (2,4-D and metabolite 2,4-Dichlorophenol)
- Pentachlorophenol (PCP)
- Bisphenol A (BPA)
- Trichlosan

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Geometric Mean (ng/L)</th>
<th>GM CI 95%</th>
<th>p,p’-DDE</th>
<th>p,p’-DDT</th>
<th>α- HCH</th>
<th>β- HCH</th>
<th>γ- HCH</th>
<th>δ- HCH</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCB (IUPAC #)</td>
<td></td>
<td></td>
<td>1269.5 (7909.8-12806.4)</td>
<td>54</td>
<td>79.1 (45.1-80.1)</td>
<td>99</td>
<td>154.3 (125.1-159.5)</td>
<td>199</td>
</tr>
<tr>
<td>Aroclor 1260</td>
<td></td>
<td></td>
<td>118</td>
<td>56.1</td>
<td>56.1</td>
<td>56.1</td>
<td>56.1</td>
<td>56.1</td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td></td>
<td></td>
<td>124</td>
<td>55.6</td>
<td>55.6</td>
<td>55.6</td>
<td>55.6</td>
<td>55.6</td>
</tr>
<tr>
<td>Chlordane</td>
<td></td>
<td></td>
<td>161</td>
<td>13305.0 (10746.4-16076.5)</td>
<td>131</td>
<td>15.4 (14.6-16.6)</td>
<td>157</td>
<td>116.2 (54.6-249.0)</td>
</tr>
<tr>
<td>Mirex</td>
<td></td>
<td></td>
<td>170</td>
<td>209.4 (106.6-205.5)</td>
<td>172</td>
<td>22.8 (24.0-43.2)</td>
<td>177</td>
<td>26.7 (20.3-34.9)</td>
</tr>
<tr>
<td>Oxychlordane</td>
<td></td>
<td></td>
<td>190</td>
<td>815.9 (694.0-1012.6)</td>
<td>187</td>
<td>64.1 (49.6-82.8)</td>
<td>185</td>
<td>206.8 (232.9-515.2)</td>
</tr>
<tr>
<td>cis-Nonachlor</td>
<td></td>
<td></td>
<td>194</td>
<td>6.3 (5.5-7.1)</td>
<td>193</td>
<td>6.3 (5.5-7.1)</td>
<td>195</td>
<td>6.3 (5.5-7.1)</td>
</tr>
<tr>
<td>Toxaphene</td>
<td></td>
<td></td>
<td>201</td>
<td>94.0 (11.5-100.9)</td>
<td>203</td>
<td>71.5 (54.5-94.1)</td>
<td>206</td>
<td>45.5 (32.6-58.0)</td>
</tr>
<tr>
<td>Parallels</td>
<td></td>
<td></td>
<td>209</td>
<td>12.4 (9.2-16.7)</td>
<td>209</td>
<td>12.4 (9.2-16.7)</td>
<td>209</td>
<td>12.4 (9.2-16.7)</td>
</tr>
</tbody>
</table>

Legacy and Emerging new POPs (ng/L)

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Geometric Mean (ng/L)</th>
<th>GM CI 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>p,p’-DDH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlordane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mirex</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxychlordane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Octachlorostyrene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p,p’-DDE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p,p’-DDT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toxaphene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3,4,6-Tetrachlorophenol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentachloroanisole</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentachloronitrobenzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parlar # 26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Parallels</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PFOS*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*PFOS: Perfluorooctane sulfonate
### Methylsulfone et hydroxy metabolites

<table>
<thead>
<tr>
<th>Metabolite</th>
<th>Value (Lower, Upper)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Methylsulfonyl-PCB 49</td>
<td>27.0 (21.8-33.5)</td>
</tr>
<tr>
<td>3-Methylsulfonyl-PCB 87</td>
<td>11.0 (9.1-13.4)</td>
</tr>
<tr>
<td>3-Methylsulfonyl-PCB 101</td>
<td>18.5 (14.3-23.8)</td>
</tr>
<tr>
<td>3-Methylsulfonyl-PCB 141</td>
<td>4-Methylsulfone-PCB 49</td>
</tr>
<tr>
<td>3-Methylsulfonyl-PCB 149</td>
<td>4-Methylsulfone-PCB 87</td>
</tr>
<tr>
<td>3-Methylsulfonyl-PCB 149</td>
<td>8.4 (7.0-10.2)</td>
</tr>
</tbody>
</table>

### Hydroxylated metabolites

<table>
<thead>
<tr>
<th>Metabolite</th>
<th>Value (Lower, Upper)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Hydroxy-PBDE 68</td>
<td>6.6 (3.6-7.8)</td>
</tr>
<tr>
<td>3-Hydroxy-PCB 138</td>
<td>24.5 (18.8-32.0)</td>
</tr>
<tr>
<td>3-Hydroxy-PCB 153</td>
<td>41.9 (32.4-54.2)</td>
</tr>
<tr>
<td>3-Hydroxy-PCB 180</td>
<td>4.2 (3.4-5.2)</td>
</tr>
<tr>
<td>4-Hydroxy-PCB 107</td>
<td>144.2 (120.7-172.3)</td>
</tr>
<tr>
<td>4-Hydroxy-PCB 146</td>
<td>136.6 (107.2-174.2)</td>
</tr>
<tr>
<td>4-Hydroxy-PCB 163</td>
<td>9.9 (7.9-12.3)</td>
</tr>
<tr>
<td>4-Hydroxy-PCB 172</td>
<td>18.7 (15.0-23.3)</td>
</tr>
<tr>
<td>4-Hydroxy-PCB 187</td>
<td>128.1 (105.5-155.7)</td>
</tr>
<tr>
<td>4-Hydroxy-PCB 193</td>
<td>2.9 (2.4-3.6)</td>
</tr>
<tr>
<td>4-Hydroxy-PCB 199</td>
<td>21.3 (16.8-30.0)</td>
</tr>
<tr>
<td>4-Hydroxy-PCB 200+198</td>
<td>4.8 (4.0-5.7)</td>
</tr>
<tr>
<td>4-Hydroxy-PCB 201</td>
<td>2.1 (1.8-2.4)</td>
</tr>
<tr>
<td>4-Hydroxy-PCB 202</td>
<td>7.6 (6.2-9.3)</td>
</tr>
<tr>
<td>4-Hydroxy-PCB 208</td>
<td>4.6 (3.8-5.6)</td>
</tr>
<tr>
<td>4-Hydroxy-Heptachlorostyrene</td>
<td>30.37 (25.01-36.89)</td>
</tr>
</tbody>
</table>

### Other parameters

- **Metals:** Pb, Hg
- **Zoonosis antibodies for** Hantavirus, Leptospirosis, West Nile and other flaviviruses and spotted fever rickettsiae.
- **Questionnaire**
ATLANTIS MOBILE LABORATORY: An Environmental & Public Health Tool

Self-sufficient, mobile laboratory:
- 3 laboratory modules, 3 support modules
- Standard size containers

Dedicated to:
- Environmental health research
- Environmental monitoring
- Educational outreach & technology transfer

Access remote areas
Integrate & standardize data acquisition.

Analytical Toxicological Laboratory
Biomarkers Laboratory

Atlantis Itinerary 2008-2011
Collaboration with CCPP

- Geographical, mapping, GIS
- Compounds analyzed
- QA/QC
- Risk associated with seafood consumption
- Ecotoxicology/human toxicology
- Common technical platform
- Training and capacity building
- Technology transfer

Thank you
Passive Samplers in the Yucatan Peninsula

Chris Metcalfe
Trent University, Canada

Quintana Roo, México

Cancún
Cozumel
Playa del Carmen
Tulum
Sian Ka’an Biosphere
Discharges of Freshwater into the Coastal Zone
Potential Contamination Problems

- Plans to triple recreational development in the Maya Riviera over the next 10 years
- Poor planning and enforcement of development guidelines in the region
- Potential for contamination of freshwater aquifer from domestic wastewater, surface runoff, accidental spills, agriculture, and maintenance of lawns and turf
- Potential for transport of contaminants to the coastal zone
- Need for monitoring of contamination in the region
- Pilot project supported by UNU-INWEH to evaluate contamination using passive sampling technologies
- Initial passive sampler deployment from December, 2008 to January, 2009
Semi-Permeable Membrane Devices (SPMDs)
- Polyethylene bag containing 1 g synthetic lipid (triolein)
- Accumulates hydrophobic (water insoluble) compounds, such as:
  - Organochlorine pesticides
  - PCBs
  - PAHs
- Samples 5-10 litres per day; depending on the compound
- Deploy for about 1 month; retrieve and extract contaminants; analyze

Passive Sampling Devices:
- Adsorb contaminants over time from water
- Easier and cheaper monitoring method than collecting biota or sediments
- Sampling rates are affected by water temperature, flow rates, and other environmental factors
- SPMDs – for water insoluble compounds
- POCIS – for water soluble compounds

Polar Organic Contaminants Integrated Sampler (POCIS)
- Contains sorbent for hydrophilic (water soluble) contaminants, such as:
  - Pharmaceuticals
  - Endocrine disruptors
  - Current use pesticides
- Samples 2-7 litres per day; depending on the compound
- Deploy for about 1 month; retrieve and extract contaminants; analyze
Study Objectives

- **Phase I:** Determine whether there is contamination of freshwater aquifers discharging into the coastal zone in the southeastern Yucatan, and if so, indicate the sources of contamination.
  
  **WORK IN PROGRESS**

- **Phase II:** If there is contamination, determine whether the contaminants are distributed in the coastal zone in the region

  **FUTURE WORK, IF FUNDING IS SECURED**
## Target Analytes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Source</th>
<th>Analytical Method</th>
<th>Lead Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCBs</td>
<td>Industry, urban sources</td>
<td>GC-ECO</td>
<td>CINVESTAV</td>
</tr>
<tr>
<td>OC pesticides</td>
<td>Agriculture</td>
<td>GC-ECO</td>
<td>CINVESTAV</td>
</tr>
<tr>
<td>PAHs</td>
<td>Urban runoff, industry</td>
<td>GC-MB</td>
<td>CINVESTAV</td>
</tr>
<tr>
<td>PBDEs</td>
<td>Industry, sewage</td>
<td>GC-MB</td>
<td>Windsor</td>
</tr>
<tr>
<td>Synthetic musks</td>
<td>Sewage</td>
<td>GC-MB</td>
<td>Trent</td>
</tr>
<tr>
<td>Alkylphenol surfactants</td>
<td>Industry, sewage</td>
<td>LC-MS/MS</td>
<td>Trent</td>
</tr>
<tr>
<td>Antibacterials (triclosan)</td>
<td>Sewage</td>
<td>LC-MS/MS</td>
<td>Trent</td>
</tr>
<tr>
<td><strong>POCIS Extracts:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Herbicides (atrazine, 2,4-D)</td>
<td>Agriculture, turf care</td>
<td>LC-MS/MS</td>
<td>Environment Canada</td>
</tr>
<tr>
<td>Fungicides</td>
<td>Agriculture, turf care</td>
<td>LC-MS/MS</td>
<td>Environment Canada</td>
</tr>
<tr>
<td>Caffeine</td>
<td>Sewage</td>
<td>LC-MS/MS</td>
<td>Trent</td>
</tr>
<tr>
<td>Human use pharmaceuticals</td>
<td>Sewage</td>
<td>LC-MS/MS</td>
<td>Trent</td>
</tr>
<tr>
<td>Illicit drugs</td>
<td>Sewage</td>
<td>LC-MS/MS</td>
<td>Trent</td>
</tr>
<tr>
<td>Veterinary pharmaceuticals</td>
<td>Agriculture (livestock)</td>
<td>LC-MS/MS</td>
<td>U. Pharmacy, Copenhagen</td>
</tr>
</tbody>
</table>

* Inter-lab comparisons between CINVESTAV and Trent

---

## Passive Sampler Deployment Locations in the Riviera Maya

**December, 2008**

- **Puerto Aventuras**
  - 5 cave systems
  - 41+ km of caves

- **Tulum**
  - 13 cave systems
  - 348+ km of caves
  - The 3 largest subterranean rivers in the world, and the largest cave in Mexico

- **Chac Ha Al caleta, Dec. 6 (2)**
- **Tree** cenote, Dec. 6 (2)
- **Casa cenote**
- **Carwash cenote, Dec. 5 (2)**
- **Ak Tulum cave, Dec. 13 (1)**
- **Herradura cave, Dec. 14 (1)**
“Carwash” cenote

INLAND = 30 x 10 m trunk passage
COASTWARD = phreatic tubes 2 - 4 m tall

Salt water along the floor

Assumed coastward water flow

Cenote Car Wash post-genetic offset collapse

Cenote Luke’s Hope

Deployment location

restrictions

Car Wash/Aktun cenote
Golf Course

"Tree" cenote

Puerto Aventuras
Partners and Acknowledgements

Thanks to:
- Patricia Beddows, Northwestern University, IL, USA
- Tracy Metcalfe and Hongxia Li, Trent University, Canada
- Victor Ceja, CINVESTAV, Mexico
- Cave divers:
  - Dennis Weeks, Puerto Aventuras
  - Robert Schmittner, Tulum
  - Jeff Clark, Tulum

Partners:
UNU-INWEH, Canada
CINVESTAV, Merida, Mexico
Trent University, Canada
Amigos de Sian Ka’an, Cancun, Mexico
Quantitative Biomonitoring of POPs in Caribbean Coastal Zones Using Oysters

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
Biomonitors

• Integrated Water Samplers
  – Passive Samplers
  – Low Trophic Level Biomonitors
    • Native collections
    • Quantitative Biomonitoring (Deployed Animals)

• Integrated water samplers accumulate chemical from water until steady state is achieved or until sampler is retrieved

• Mussels/oysters can also be used to assess toxicity/stress at given site

Biomonitors

• Passive
  – Oysters collected from site of interest
  – Examine: POPs concentrations, lipid, glycogen

• Active (Quantitative Biomonitoring)
  – Animals collected from a reference site and caged at different locations
  – Toxicity assays – lipid/glycogen provide temporal information
  – Models required to extrapolate contaminant measured in animal at collection to steady state conc.
Steady State Correction of Biomonitors

Contaminant Bioaccumulation Kinetics In Deployed Integrated Sampler

\[ \frac{dC_m}{dt} = C_m k_1 - C_m k_2 \]

Steady State Correction

\[ C_{m\text{(ss)}} = \frac{C_{m\text{(o)}} - (C_{m\text{(o)}} \cdot \exp(-k_2 t))}{(1 - \exp(-k_2 t))} \]

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

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

\[ C_{m\text{(ss)}} = \frac{C_{m\text{(o)}} - (C_{m\text{(o)}} \cdot \exp(-k_2 t))}{(1 - \exp(-k_2 t))} \]

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

Provide baseline of water quality to contrast with white grunt results
- oysters can be collected in mangrove areas where white grunt aren’t available

- Calibration of native oysters in each country for use as quantitative biomonitor

Involvement of graduate students (Training)
CINVESTAV, UWI – Trinidad, Jamaica campuses
1) Classic Biomonitoring Program (Year 1)
- collect native oysters from each study location and submit chemical analysis

Oyster Biomonitorors

- Native oysters
  - 3 sites per country, 5 replicates per site
  - 2 contaminated (suspected areas), 1 reference site
  - Trinidad, Jamaica and Mexico (Others?)

- Measure
  - OC-pesticides, PCBs, PAHs, PBDEs other scan for emerging chemicals of concern
Oyster Biomonitoring

Quantitative Biomonitoring

- Native oysters (n=20) from reference sites
- Oysters dosed with performance reference compounds PCB: 23, 43, 61, 86, 109, 129, 173 and 198;
- The PRC-dosed oysters will be transplanted in cages to the three study areas sampled objective 1.
- Replicate oysters (n=5 per time point) will be destructively sampled after 0, 60 and 120 d of deployment
- Measure PCB, OCs, PAHs, PBDEs
- Measure lipid and glycogen content

---

Oyster Biomonitoring

- **Objective 1**
  - Supplemental Monitoring dataset
  - Wider variety of pollutants can be assessed due to limitations in metabolic capacity of oysters compared to fish

- **Objective 2**
  - More academically driven questions
  - Are are inter- and intraspecific (across site) differences in POP kinetics in oyster biomonitors?
  - Can we detect stress via glycogen and lipid reserve changes in deployed mussels?
Questions

• Are there other regions that would like to contribute oyster samples for analysis in phase 1?
  – Limited funds available for field collections
  – Additional analysis costs can be accommodated at University of Windsor

• Mexico, Trinidad, Jamaica
  – Are suitable graduate students available for completing phase 2 of project and can this be used as part an existing thesis project?
Report on Lab Assessments in the Wider Caribbean Region

Chris Metcalfe, Trent University, Canada
Ken Drouillard, University of Windsor, Canada
Gerardo Gold Bouchot, CINVESTAV, Mexico

Objectives

Evaluate the capacity of laboratories for monitoring and research on POPs and PTS in the Wider Caribbean Region (WCR),

Make recommendations that:

i) Encourage networking among laboratories to achieve the project objectives at both regional and Caribbean-wide scales

ii) Develop capacity in as many laboratories as possible, within the constraints of the project budget
## Laboratories Evaluated

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Date</th>
<th>Assessors</th>
</tr>
</thead>
<tbody>
<tr>
<td>IMA, Trinidad</td>
<td>June, 2008</td>
<td>KGD, CDM, GGB</td>
</tr>
<tr>
<td>UWI St. Augustine, Trinidad</td>
<td>June, 2008</td>
<td>KGD, CDM, GGB</td>
</tr>
<tr>
<td>CEHI, St. Lucia</td>
<td>June, 2008</td>
<td>KGD, CDM, GGB</td>
</tr>
<tr>
<td>UWI Mona, Jamaica</td>
<td>June, 2008</td>
<td>KGD, CDM, GGB</td>
</tr>
<tr>
<td>NEPA, Jamaica</td>
<td>June, 2008</td>
<td>KGD, CDM, GGB</td>
</tr>
<tr>
<td>CINVESTAV, Mexico</td>
<td>Aug. 2008</td>
<td>KGD, CDM, GGB</td>
</tr>
<tr>
<td>ECOSUR, Mexico</td>
<td>Aug. 2008</td>
<td>KGD, CDM, GGB</td>
</tr>
<tr>
<td>CESSCO, Honduras</td>
<td>Aug. 2008</td>
<td>KGD, CDM, GGB</td>
</tr>
<tr>
<td>U. San Carlos, Guatemala</td>
<td>Aug. 2008</td>
<td>KGD, CDM, GGB</td>
</tr>
<tr>
<td>U. Santo Domingo, DR</td>
<td>Oct. 2008</td>
<td>GGB</td>
</tr>
</tbody>
</table>

## Basis of the Evaluation

- Physical infrastructure
- Analytical equipment
- Analytical expertise
- Sampling capacity
- Monitoring program capacity
- Research capacity
Results of the Evaluation

• Pesticide Laboratory at the UWI Mona, Jamaica and the Marine Geochemistry Laboratory at CINVESTAV in Merida, Mexico currently have the greatest capacity to take lead roles in regional monitoring networks for POPs and PTS
• These 2 laboratories and UNU-INWEH will need to develop partnerships in order to collect marine samples for POPs and PTS analysis throughout the WCR
• Faculty in the Chemistry Department at UWI in St. Augustine, Trinidad have the expertise, equipment and interest in developing research projects on POPs and PTS
• The other laboratories in the WCR vary in their capacity for research and monitoring of POPs and PTS and will require modest to extensive investment from UNU-INWEH in order to develop this capacity.

Recommendations

• Develop a network of laboratories for monitoring and research on POPs and PTS in the WCR
• Pesticide Laboratory at UWI Mona take a lead role in a monitoring network for POPs among English speaking partners in the Caribbean (i.e. “AngloPOPs” group)
• Marine Geochemistry Lab at CINVESTAV take a lead role in a monitoring network for POPs among Spanish speaking partners in the Caribbean and Belize (i.e. “HispanoPOPs” group)
• For the white grunt monitoring survey, the UWI Mona and CINVESTAV labs will rely on partner institutions in the WCR to collect and provide the samples for the analysis of POPs, and will conduct all analyses
• Purchase 2 new GC-ECD instruments with autosamplers to support these labs
• If sufficient funding is secured for other phases of the project, UNU-INWEH should increase the capacity for the preparation of samples and the analysis of POPs in other partner laboratories
Recommended Organizational Structure

HispanoPOPs Group
- CINVESTAV
- U. San Carlos, Guatemala
- ECOSUR, Mexico
- CESSCO, Honduras
- U. Santo Domingo, DR
- Belize*

AngloPOPs Group
- UWI Mona
- UWI St. Augustine
- CEH, St. Lucia
- IMA, Trinidad
- NEPA, Jamaica

* Lead institution not yet identified

University of Windsor, Trent University

Data Gaps

- Biomarkers of exposure to contaminants
- Analysis of dioxins and dibenzofurans
- Analysis of emerging POPs and PTS, such as:
  - Chlorinated naphthalenes and paraffins
  - Brominated flame retardants
  - Personal care products
Biomarkers

“Physiological, biochemical and histological alterations that occur as a result of exposure to environmental pollutants”

Monitor organisms in the field (in situ monitoring)
• monitor wild organisms
• monitor caged organisms
  • plants
  • invertebrates
  • fish
  • birds
  • mammals
We can monitor:

Spatial Trends
  e.g., polluted vs non-polluted
  (reference)

Temporal Trends
  e.g., eggshell thinning (next slide)
Brown bullheads in Lake Ontario & Lake Erie

BIOMARKERS

<table>
<thead>
<tr>
<th>Location</th>
<th>HSI (%)</th>
<th>Skin Lesions (%)</th>
<th>Liver Tumours (%)</th>
<th>EROD Activity pmol/min/mg protein</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hamilton Hbr</td>
<td>2.39</td>
<td>50</td>
<td>2</td>
<td>54.7</td>
</tr>
<tr>
<td>Black R</td>
<td>2.00</td>
<td>60</td>
<td>3</td>
<td>42.0</td>
</tr>
<tr>
<td>Detroit R</td>
<td>3.02</td>
<td>25</td>
<td>5</td>
<td>59.5</td>
</tr>
<tr>
<td>Old Woman R *</td>
<td>1.75</td>
<td>0</td>
<td>0</td>
<td>18.9</td>
</tr>
<tr>
<td>Bay of Quinte *</td>
<td>1.97</td>
<td>0</td>
<td>0</td>
<td>18.9</td>
</tr>
</tbody>
</table>

* Reference (clean) sites
Phase I Oxidation

Catalyzed by:
Cytochrome P450 (CYP450) enzymes
(aka Mixed Function Oxidases, Mono-oxygenases)
1. A family of enzymes that catalyze oxidative metabolism
2. Located on endoplasmic reticulum of cells (“microsomal”) – high activity in liver
3. “Inducible” enzymes that increase in activity in response to exposure to halogenated contaminants, polynuclear aromatics, etc.
4. Induction of CYP450 enzymes used as a “biomarker” of exposure to contaminants (e.g. ethoxyresorufin de-ethylase [EROD])

EROD Assay

Ethoxyresorufin

Ethoxyresorufin-O-deethylase (a CYP450 enzyme)
O-dealkylation

Hydroxyresorufin (fluorescent)
Coking plant
Stelco Steel Mill
Hamilton
Outfall of Stelco coking plant

HAMILTON HARBOUR
TOTAL POLYNUCLEAR AROMATIC HYDROCARBONS IN SEDIMENT

PAHs (µg/g)
- 0-17
- 20-67
- 76-184
- 215-650
- 1400-1470

Outfall of Stelco coking plant
White Perch (Morone americana)

Map of Study Sites.
Hypothalamic-Pituitary axis and control of VtG synthesis in oviparous vertebrates

VtG in males used as a biomarker of exposure to xenoestrogens

Western Blot Analysis of VtG in White Perch, Coote’s Paradise
Male White Perch – Coote’s Paradise, Ontario

Prevalence of Intersex Testes in Male White Perch

<table>
<thead>
<tr>
<th>Site</th>
<th>Year</th>
<th>Total No. Males</th>
<th>% Intersex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bay of Quinte</td>
<td>1999</td>
<td>37</td>
<td>22</td>
</tr>
<tr>
<td>Bay of Quinte</td>
<td>2000</td>
<td>16</td>
<td>44</td>
</tr>
<tr>
<td>Cootes Paradise</td>
<td>1998</td>
<td>16</td>
<td>50</td>
</tr>
<tr>
<td>Cootes Paradise</td>
<td>2000</td>
<td>12</td>
<td>83</td>
</tr>
<tr>
<td>L. St. Claire</td>
<td>2000</td>
<td>11</td>
<td>45</td>
</tr>
<tr>
<td>Hatchery</td>
<td>2002</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>Deal Lake, NJ</td>
<td>2002</td>
<td>13</td>
<td>0</td>
</tr>
</tbody>
</table>

(Reference)
Emerging POPs and PTS

Chris Metcalfe
Trent University, Canada

Persistent Contaminants of Emerging Interest

- Produced in large quantities (>1,000 tonnes per year)
- Persistent in organisms and in abiotic environment (i.e. air, water, soil)
- Potential for:
  - Bioaccumulation (log Kow >3.5; BCF>1,000)
  - Biomagnification (log Kow >5; BCF>5,000)
  - Long range transport from source of contamination (log Kaw >-6)
- Toxic

Persistent, Bioaccumulative and Toxic (PBT)
**Contaminants of Emerging Interest**

- Brominated flame retardants
  - Polybrominated diphenyl ethers (PBDEs)
  - Hexabromocyclododecane (HBCD)
- Perfluorinated surfactants
- Chlorinated paraffins
- Synthetic musks

![PBDEs structure](image1)

**Annual Global Market Demand for PBDEs**

<table>
<thead>
<tr>
<th>BFR</th>
<th>Americas</th>
<th>Europe</th>
<th>Asia</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deca-BDE</td>
<td>24,300</td>
<td>7,500</td>
<td>23,000</td>
<td>54,800</td>
</tr>
<tr>
<td>Octa-BDE</td>
<td>1,370</td>
<td>450</td>
<td>2,000</td>
<td>3,825</td>
</tr>
<tr>
<td>Penta-BDE</td>
<td>8,290</td>
<td>210</td>
<td>-</td>
<td>8,500</td>
</tr>
</tbody>
</table>

*Polybrominated Diphenyl Ethers (PBDEs)*

Widely used as a fire retardant in plastics, foams, textiles and building materials.
Brominated diphenyl ethers

Chlorinated Dibenzofurans

ΣPBDE Trends in Herring Gull eggs (Norstrom et al. 2002)

Doubling time ≈ 6-8 years
Temporal trends of PBDEs in Great Lakes fish
(Zhu and Hites 2004)
Doubling times of ~ 3 years in all lakes

<table>
<thead>
<tr>
<th>Location</th>
<th>Organism</th>
<th>Concentration (ug/kg lipid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>East China Sea</td>
<td>Skipjack tuna</td>
<td>23-34</td>
</tr>
<tr>
<td>Baltic Sea</td>
<td>Salmon</td>
<td>220-290</td>
</tr>
<tr>
<td>Baltic Sea</td>
<td>Herring</td>
<td>3.2-32</td>
</tr>
<tr>
<td>San Francisco, CA</td>
<td>Harbour seal (blubber)</td>
<td>1,730</td>
</tr>
<tr>
<td>Baltic Sea</td>
<td>Grey seal (blubber)</td>
<td>208-730</td>
</tr>
<tr>
<td>U.K.</td>
<td>Cormorant</td>
<td>300-6,400</td>
</tr>
<tr>
<td>U.K.</td>
<td>Harbour porpoise (blubber)</td>
<td>350-7,670</td>
</tr>
<tr>
<td>Netherlands</td>
<td>Whitebeaked dolphin (blubber)</td>
<td>7,700</td>
</tr>
<tr>
<td>Faeroe Islands</td>
<td>Pilot whale (blubber)</td>
<td>126-3,160</td>
</tr>
</tbody>
</table>
Hexabromocyclododecane (HBCD)

- Most widely used aliphatic BFR (~16,000 t/yr)
- Primary BFR in polystyrene (thermal insulation)
- Upholstery textiles (residential and commercial)

HBCD isomers in the Lake Ontario food web (Tomy et al. 2004)
Polyfluoro-alcohols/amides are incorporated into polymer based coatings heavily used in consumer products

**Uses**
- Stain repellent coatings
- Shampoo, cosmetics, paint, batteries, waxes, polishes, anti-static, anti-fog, food wraps
- Electronics production, metal plating baths.
- Fire fighting foams (AFFFs).
- Insecticide (sulfuramid)

**Global production**
- Fluorotelomer alcohols = 5x10⁶ kg/yr
  - 40% in North America; 80% used in polymers
- Perfluorooctane sulfonates = 4x10⁶ kg/yr in 2000 (phased out in 2001-03)
  - 75% in NA; 75% in polymers

**Compounds Monitored**

<table>
<thead>
<tr>
<th>PARENT</th>
<th>End Product</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="N-EtFOSE" /></td>
<td><img src="image" alt="PFOS" /></td>
</tr>
</tbody>
</table>

**Metabolites**

- ![N-EtFOSAA](image)
- ![PFOSAA](image)
- ![PFOSulfinate](image)
- ![PFOA](image)

![Graph showing PFOS trend over years with log[PFOS] = 0.0567(Year) - 116, r^2 = 0.49, p<0.0001. Doubling Time ~12 yrs.]

Widespread Biota Contamination

Source: Researchers of Michigan State University, University of Minnesota, University of Iowa, ESRI
Chlorinated Paraffins

- Used in flame retardants, additives in metal-working fluids, paints, sealants, and as plasticizers
- Short chain (C\textsubscript{10}-C\textsubscript{13}), medium chain (C\textsubscript{14}-C\textsubscript{17}) and long chain (C\textsubscript{18}-C\textsubscript{30})
- SCCPs have greatest potential for release and greatest toxicity
- Log K\text{ow} = 5.9 – 8.1
- Production in NA: 8,000 tonnes for SCCPs and 18,000 tonnes for MCCPs

SCCPs and MCCPs in the Lake Ontario food web (Houde et al. 2008)
Personal Care Products in the Environment

- Sun-tan lotions and sun blocks
- Skin creams
- Insect repellents (e.g. DEET)
- Antibacterial agents (e.g. Triclosan)
- Fragrances (e.g. synthetic musks)

Synthetic Musks

- Synthetic musks emulate the odour but not the structure of the expensive, natural product.
- Polycyclic musks
- Nitro-musks
- Synthetic musks are relatively hydrophobic ($K_{ow} = 3 - 5$) and have been found in fish, marine mammals and fish eating birds
Fish Collection Sites

Musks in Fish from Hamilton Harbour, Ontario

O'Toole & Metcalfe, 2006

Parts per Billion (ug/kg wet wt)
HHCB in Marine Biota

<table>
<thead>
<tr>
<th>Organism</th>
<th>Location</th>
<th>Concentration (ug/kg ww)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atlantic salmon</td>
<td>New York</td>
<td>&lt;1-3.2</td>
</tr>
<tr>
<td>Sharpnose shark</td>
<td>Florida</td>
<td>4.6-5.2</td>
</tr>
<tr>
<td>Haddock (liver)</td>
<td>Norway</td>
<td>29-43</td>
</tr>
<tr>
<td>Hammerhead shark (liver)</td>
<td>Japan</td>
<td>16-48</td>
</tr>
<tr>
<td>Harbour seal (blubber)</td>
<td>California</td>
<td>4.4-5.5</td>
</tr>
<tr>
<td>Bottlenose dolphin (blubber)</td>
<td>Florida</td>
<td>4.2-20.5</td>
</tr>
<tr>
<td>Striped dolphin (blubber)</td>
<td>Florida</td>
<td>8.1-25</td>
</tr>
<tr>
<td>Finless porpoise (blubber)</td>
<td>Japan</td>
<td>22-149</td>
</tr>
</tbody>
</table>

Overview of POPs of Emerging Concern

<table>
<thead>
<tr>
<th>Chemical/group</th>
<th>Comments/highlights</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfluoro-octane sulfonic acid (PFOS) and amide derivatives (&quot;ScotchGard&quot;)</td>
<td>PFOS in eagle eggs, marine mammals, fish; Endocrine disruptor?</td>
</tr>
<tr>
<td>Perfluoro carboxylic acids and related perfluoro alcohols</td>
<td>PFOA found with PFOS; terminal residues of perfluorinated alcohols?</td>
</tr>
<tr>
<td>Brominated diphenyl ethers and other BFRs (hexabromocyclododecane)</td>
<td>Increasing PBDE concentrations in eggs of fish eating birds and in fish; Evidence of biomagnification; Endocrine (thyroid) disruptor</td>
</tr>
<tr>
<td>Chlorinated paraffins (chlorinated alkanes)</td>
<td>Evidence of biomagnification; Potential for long range atmospheric transport of SCCPs</td>
</tr>
<tr>
<td>Chlorinated naphthalenes</td>
<td>Low concentrations, but contribute to toxicity of dioxins and planar PCBs in fish and fish eating birds</td>
</tr>
<tr>
<td>Volatile, bioaccumulative personal care products (e.g. synthetic musks)</td>
<td>HHCB and AHTN found in fish, marine mammals and fish eating birds, Global transport; Endocrine disruptor (thyroid, anti-estrogen)</td>
</tr>
</tbody>
</table>
“New” POPs have been selected mainly by the “analogue” method

PCBs, dioxins ➔ PBDEs, Chlorinated naphthalenes

HCB, DDT, chlordane ➔ Endosulfan, hexachlorobutadiene, pentachlorophenol

Advances in instrumentation are crucial to identifying new classes of chemicals e.g. perfluorinated chemicals, musks

Analytical standards?  
Certified Reference materials?  
Available Instrumentation?  
Extraction/isolation?
Quantitative Biomonitoring of POPs in Caribbean Coastal Zones Using Oysters

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
Biomonitors

• Integrated Water Samplers
  – Passive Samplers
  – Low Trophic Level Biomonitors
    • Native collections
    • Quantitative Biomonitoring (Deployed Animals)

• Integrated water samplers accumulate chemical from water until steady state is achieved or until sampler is retrieved

• Mussels/oysters can also be used to assess toxicity/stress at given site

Biomonitors

• Passive
  – Oysters collected from site of interest
  – Examine: POPs concentrations, lipid, glycogen

• Active (Quantitative Biomonitoring)
  – Animals collected from a reference site and caged at different locations
  – Toxicity assays – lipid/glycogen provide temporal information
  – Models required to extrapolate contaminant measured in animal at collection to steady state conc.
**Steady State Correction of Biomonitors**

**Contaminant Bioaccumulation Kinetics In Deployed Integrated Sampler**

\[
\frac{dC_m}{dt} = C_m k_1 - C_m k_2
\]

Steady State Correction

\[
C_{m(t)} = \frac{C_{m(0)} - \left( C_{m(0)} \cdot \exp(-k_2 \cdot t) \right)}{1 - \exp(-k_2 \cdot t)}
\]

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

**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

\[
C_{m(t)} = \frac{C_{m(t)} - \left( C_{m(0)} \cdot \exp(-k_2 \cdot t) \right)}{1 - \exp(-k_2 \cdot t)}
\]

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

Provide baseline of water quality to contrast with white grunt results
- oysters can be collected in mangrove areas where white grunt aren’t available

- Calibration of native oysters in each country for use as quantitative biomonitor

Involvement of graduate students (Training)
CINVESTAV, UWI – Trinidad, Jamaica campuses
Oyster Biomonitor Project

1) Classic Biomonitoring Program (Year 1)
   - collect native oysters from each study location and submit chemical analysis

Oyster Biomonitors

• Native oysters
  – 3 sites per country, 5 replicates per site
  – 2 contaminated (suspected areas), 1 reference site
  – Trinidad, Jamaica and Mexico (Others?)

• Measure
  – OC-pesticides, PCBs, PAHs, PBDEs other scan for emerging chemicals of concern
Oyster Biomonitoring

Quantitative Biomonitoring

- Native oysters (n=20) from reference sites
- Oysters dosed with performance reference compounds PCB: 23, 43, 61, 86, 109, 129, 173 and 198;
- The PRC-dosed oysters will be transplanted in cages to the three study areas sampled objective 1.
- Replicate oysters (n=5 per time point) will be destructively sampled after 0, 60 and 120 d of deployment
- Measure PCB, OCs, PAHs, PBDEs
- Measure lipid and glycogen content

Oyster Biomonitoring

- Objective 1
  – Supplemental Monitoring dataset
  – Wider variety of pollutants can be assessed due to limitations in metabolic capacity of oysters compared to fish
- Objective 2
  – More academically driven questions
  – Are are inter- and intraspecific (across site) differences in POP kinetics in oyster biomonitor?
  – Can we detect stress via glycogen and lipid reserve changes in deployed mussels?
Questions

• Are there other regions that would like to contribute oyster samples for analysis in phase 1?
  – Limited funds available for field collections
  – Additional analysis costs can be accommodated at University of Windsor

• Mexico, Trinidad, Jamaica
  – Are suitable graduate students available for completing phase 2 of project and can this be used as part an existing thesis project?
**Inter-laboratory Comparison Exercise**

- **Participating labs:**
  - UWI-MONA (Jamaica)
  - CINVESTAV
  - Trent University (Water Quality Lab)
  - University of Windsor (GLIER Organic Lab)

- **Short term Goals of Inter-lab comparison:**
  - Establish working methods for POPs analysis by GC-ECD
  - Use of common standards
  - Perform inter-laboratory comparison of analytical results on CRMs

**Long Term Objectives – Regional Labs**

1) Participate in a preliminary inter-laboratory analytical comparison exercise prior to commencing POPs analysis of biomonitoring samples

2) Implement a Quality Assurance Program (QuAP) during the analysis of biomonitoring samples for POPs

3) Perform analysis of fish tissue samples generated by the white grunt biomonitoring program

4) Provide training opportunities and technical advice to satellite laboratories using a scheduled approach.
Inter-laboratory Analytical Comparison Exercise

- Establish working SOPs for POPs analysis
- Harmonize selection of standards and certified reference materials (CRMs) used for quality assurance purposes.
- Provide an initial quality check to ensure consistency in analytical results between laboratories

Inter-laboratory Analytical Comparison Exercise

- UNU-INWEH distributed to each laboratory:
  - certified analytical standards
    - Organochlorine pesticides
    - PCB Standard
  - spiking internal standard
    - 2,4,6-trichlorobiphenyl
  - CRM
    - IAEA tuna homogenate
# Inter-laboratory Analytical Comparison Exercise

## OC-Pesticides

<table>
<thead>
<tr>
<th>Chemical</th>
<th>PCB Congeners (IUPAC #)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldrin</td>
<td>17, 18, 28/31, 33, 44, 49, 53, 70</td>
</tr>
<tr>
<td>cis-chlordane</td>
<td>74, 82/151, 87, 95, 99, 101</td>
</tr>
<tr>
<td>trans-chlordane</td>
<td>105, 132, 110, 118, 128, 138</td>
</tr>
<tr>
<td>oxy-chlordane</td>
<td>149, 153, 156/171, 158, 170, 177</td>
</tr>
<tr>
<td>p,p'-DDD</td>
<td>180, 183, 187, 191, 194, 195/208, 199/201, 205, 206, 209</td>
</tr>
<tr>
<td>p,p'-DDE</td>
<td>Sum PCBs</td>
</tr>
<tr>
<td>p,p'-DDE</td>
<td></td>
</tr>
<tr>
<td>p,p'-DDE</td>
<td></td>
</tr>
<tr>
<td>p,p'-DDT</td>
<td></td>
</tr>
<tr>
<td>p,p'-DDT</td>
<td></td>
</tr>
<tr>
<td>p,p'-DDT</td>
<td></td>
</tr>
<tr>
<td>Dieldrin</td>
<td></td>
</tr>
<tr>
<td>Dieldrin</td>
<td></td>
</tr>
<tr>
<td>Heptachlor</td>
<td></td>
</tr>
<tr>
<td>cis-heptachlorepoxide</td>
<td></td>
</tr>
<tr>
<td>trans-heptachlorepoxide</td>
<td></td>
</tr>
<tr>
<td>p,p'-heptachlorepoxide</td>
<td></td>
</tr>
<tr>
<td>Hexachlorobenzene</td>
<td></td>
</tr>
<tr>
<td>Mirex</td>
<td></td>
</tr>
</tbody>
</table>

## Stock Solution Preparation

1. Create stock solution by dissolving 1 mL of vial contents into 50 mL isooctane.
   
   *Store stock solution in a sealed vial in the freezer.*

2. Create working standard solution by dissolving 1 mL of stock solution into 10 mL isooctane.
   
   *Store working standard solution in a sealed vial in the refrigerator.*

Note use of GC vial inserts (200 µL) will extend the life of working standard solutions.
### PCB 30 – Spiking Recovery Standard - Protocol

Shipped via: 1 mL x 35 μg/mL (35 000 ng/mL) in iso-octane.

1) **Stock solution (700 ng/mL):**
   - Dissolve 1 mL of contents in shipped vial into 50 mL iso-octane
   - Store solution in sealed vial in freezer

2) **Working Sample Spiking Solution (70 ng/mL):**
   - Dilute 1 mL Stock Solution into 10 mL iso-octane
   - Store solution in sealed vial in refrigerator

3) **Working Recovery Standard (7 ng/mL):**
   - Dilute 1 mL Stock Solution into 100 mL iso-octane
   - Store solution in sealed vial in refrigerator

### Sample spiking protocol.

Following sample homogenization and addition of homogenate to extraction solvent, spike 100 μL/mL of final volume into the extraction solvent. I.e., in the final volume following sample clean-up will be 2 mL, spike 200 μL of sample spiking solution into the extraction solvent.

Quantify internal standard recovery using the working recovery standard solution. Note use of GC-vial inserts (200 μL) will extend the life of working internal standard recovery solution.

**Retention time:** 12.310 min. Based on performance using a DB-5 column (J&W Scientific) 60 m x 0.25 mm i.d. 0.10 μm film thickness. Splitless injection. Temperature program: 50°C start hold 1 min, ramp 20°C/min until 200°C, hold 2 min, ramp 3°C/min until 280°C hold 5 min. Total run 40.16 min.

---

<table>
<thead>
<tr>
<th>PCB/UPAC #</th>
<th>Shipped Vial (μg/mL)</th>
<th>Stock Solution (μg/mL)</th>
<th>Working Sample Spiking Solution (μg/mL)</th>
<th>Working Recovery Standard (μg/mL)</th>
<th>R.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>17</td>
<td>100</td>
<td>570</td>
<td>570</td>
<td>570</td>
<td>12.992</td>
</tr>
<tr>
<td>18</td>
<td>200</td>
<td>1140</td>
<td>1140</td>
<td>1140</td>
<td>14.523</td>
</tr>
<tr>
<td>28</td>
<td>200</td>
<td>1140</td>
<td>1140</td>
<td>1140</td>
<td>14.523</td>
</tr>
<tr>
<td>31</td>
<td>300</td>
<td>1710</td>
<td>1710</td>
<td>1710</td>
<td>15.050</td>
</tr>
<tr>
<td>32</td>
<td>400</td>
<td>2280</td>
<td>2280</td>
<td>2280</td>
<td>15.594</td>
</tr>
<tr>
<td>40</td>
<td>500</td>
<td>2850</td>
<td>2850</td>
<td>2850</td>
<td>16.020</td>
</tr>
<tr>
<td>50</td>
<td>600</td>
<td>3420</td>
<td>3420</td>
<td>3420</td>
<td>16.480</td>
</tr>
<tr>
<td>70</td>
<td>700</td>
<td>4000</td>
<td>4000</td>
<td>4000</td>
<td>16.947</td>
</tr>
<tr>
<td>75</td>
<td>800</td>
<td>4500</td>
<td>4500</td>
<td>4500</td>
<td>17.413</td>
</tr>
<tr>
<td>85</td>
<td>900</td>
<td>5000</td>
<td>5000</td>
<td>5000</td>
<td>17.869</td>
</tr>
<tr>
<td>95</td>
<td>1000</td>
<td>5500</td>
<td>5500</td>
<td>5500</td>
<td>18.325</td>
</tr>
<tr>
<td>105</td>
<td>1100</td>
<td>6000</td>
<td>6000</td>
<td>6000</td>
<td>18.781</td>
</tr>
<tr>
<td>105/122</td>
<td>1200</td>
<td>6500</td>
<td>6500</td>
<td>6500</td>
<td>19.236</td>
</tr>
<tr>
<td>110</td>
<td>1300</td>
<td>7000</td>
<td>7000</td>
<td>7000</td>
<td>19.690</td>
</tr>
<tr>
<td>128</td>
<td>1400</td>
<td>7500</td>
<td>7500</td>
<td>7500</td>
<td>20.145</td>
</tr>
<tr>
<td>128</td>
<td>1500</td>
<td>8000</td>
<td>8000</td>
<td>8000</td>
<td>20.590</td>
</tr>
<tr>
<td>152</td>
<td>1600</td>
<td>8500</td>
<td>8500</td>
<td>8500</td>
<td>21.041</td>
</tr>
<tr>
<td>158</td>
<td>1700</td>
<td>9000</td>
<td>9000</td>
<td>9000</td>
<td>21.496</td>
</tr>
<tr>
<td>158</td>
<td>1800</td>
<td>9500</td>
<td>9500</td>
<td>9500</td>
<td>21.941</td>
</tr>
<tr>
<td>170</td>
<td>1900</td>
<td>10000</td>
<td>10000</td>
<td>10000</td>
<td>22.296</td>
</tr>
<tr>
<td>171</td>
<td>2000</td>
<td>10500</td>
<td>10500</td>
<td>10500</td>
<td>22.751</td>
</tr>
<tr>
<td>177</td>
<td>2100</td>
<td>11000</td>
<td>11000</td>
<td>11000</td>
<td>23.206</td>
</tr>
<tr>
<td>192</td>
<td>2200</td>
<td>11500</td>
<td>11500</td>
<td>11500</td>
<td>23.661</td>
</tr>
<tr>
<td>183</td>
<td>2300</td>
<td>12000</td>
<td>12000</td>
<td>12000</td>
<td>24.116</td>
</tr>
<tr>
<td>183</td>
<td>2400</td>
<td>12500</td>
<td>12500</td>
<td>12500</td>
<td>24.571</td>
</tr>
<tr>
<td>181</td>
<td>2500</td>
<td>13000</td>
<td>13000</td>
<td>13000</td>
<td>25.026</td>
</tr>
<tr>
<td>194</td>
<td>2600</td>
<td>13500</td>
<td>13500</td>
<td>13500</td>
<td>25.481</td>
</tr>
<tr>
<td>194</td>
<td>2700</td>
<td>14000</td>
<td>14000</td>
<td>14000</td>
<td>25.936</td>
</tr>
<tr>
<td>194</td>
<td>2800</td>
<td>14500</td>
<td>14500</td>
<td>14500</td>
<td>26.391</td>
</tr>
<tr>
<td>194</td>
<td>2900</td>
<td>15000</td>
<td>15000</td>
<td>15000</td>
<td>26.846</td>
</tr>
<tr>
<td>194</td>
<td>3000</td>
<td>15500</td>
<td>15500</td>
<td>15500</td>
<td>27.301</td>
</tr>
<tr>
<td>205</td>
<td>3100</td>
<td>16000</td>
<td>16000</td>
<td>16000</td>
<td>27.756</td>
</tr>
<tr>
<td>205</td>
<td>3200</td>
<td>16500</td>
<td>16500</td>
<td>16500</td>
<td>28.211</td>
</tr>
<tr>
<td>205</td>
<td>3300</td>
<td>17000</td>
<td>17000</td>
<td>17000</td>
<td>28.666</td>
</tr>
<tr>
<td>205</td>
<td>3400</td>
<td>17500</td>
<td>17500</td>
<td>17500</td>
<td>29.121</td>
</tr>
<tr>
<td>205</td>
<td>3500</td>
<td>18000</td>
<td>18000</td>
<td>18000</td>
<td>29.576</td>
</tr>
</tbody>
</table>

**Note:** Shipped sample out of vials and inserted into capsules for spiking and analysis.
Quebec Ministry of Environment Standard

GC-ECD with 60 m DB-5 column

GC-ECD of supplied OC-Standard Mixture (60 m DB-5 column)
Co-elution issues – Pest. Mix & PCBs

• Heptachlor epoxide / oxychlorodane/ PCB 70
• p,p’-DDE/dieldrin/PCB 87
  – p,p’-DDE/dieldrin readily resolved on new 60 m column
• o’p’-DDE/PCB110
• Endosulfan II/PCB118
• p,p’-DDE with cis-nonachlor (Resolved on our system)
• Trans-nonachlor with PCB 99 (Resolved on our system)

• **Some issues with supplied standards:
• mixed heptachlor epoxide + oxychlorodane and p,p’-DDE/dieldrin could result in quantitation errors for these compounds unless good chromatography is realized
### Appendix 5. CRM - IAEA-435 Tuna Homogenate

<table>
<thead>
<tr>
<th>OCC-Pesticides</th>
<th>PCB congeners (UPAC #)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-D</td>
<td>19.6</td>
</tr>
<tr>
<td>2,3,7,8-TCDD</td>
<td>89.6</td>
</tr>
<tr>
<td>p,p'-DDD</td>
<td>49.8</td>
</tr>
<tr>
<td>p,p'-DDE</td>
<td>81.9</td>
</tr>
<tr>
<td>p,p'-DDE</td>
<td>96.9</td>
</tr>
<tr>
<td>p,p'-DDT</td>
<td>101.6</td>
</tr>
<tr>
<td>p,p'-DDD</td>
<td>101.6</td>
</tr>
</tbody>
</table>

*This CRM is to be used to facilitate the inter-laboratory comparison exercise. Each lab is to run 3 separate extractions of this homogenate along with 2 blanks and submit results to UNJ-INVHE for the initial inter-laboratory comparison exercise.*

### Appendix 6. CRM - NIST- SRM 1974 Lake Michigan Fish Tissue

<table>
<thead>
<tr>
<th>OCC-Pesticides (Certified Value)</th>
<th>PCB congeners (Certified Value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-D</td>
<td>19.6</td>
</tr>
<tr>
<td>2,3,7,8-TCDD</td>
<td>89.6</td>
</tr>
<tr>
<td>p,p'-DDD</td>
<td>49.8</td>
</tr>
<tr>
<td>p,p'-DDE</td>
<td>81.9</td>
</tr>
<tr>
<td>p,p'-DDT</td>
<td>96.9</td>
</tr>
<tr>
<td>p,p'-DDD</td>
<td>101.6</td>
</tr>
</tbody>
</table>

Note. The NIST CRM is suggested as a reference material for use in routine extractions of white grunt biomonitoring samples. This CRM was chosen because of its long term availability and because the concentrations of individual analytes are high enough to afford low extraction weights, economizing the homogenate investment. Costs of the NIST-CRM are $300.00 USD for 5 aliquots of 8 g (40 g). Concentrations are high enough to permit extractions of 0.2 g for quantification. Thus, 1 unit is sufficient for 130 extractions. If homogenates are run at a frequency of every 8 samples, this permits 780 sample analyses i.e. additional cost per sample for homogenate investment is ~ $1/sample.
Quality Assurance Document

i) Laboratory Personnel and Reporting Structure
ii) Statement of data security, data storage and confidentiality
iii) Analytical Quality Control Procedures:
   - Instrument Calibrations (analytical balances and instruments)
   - Cross validation of working standard solutions (procedure and frequency)
   - Spiking Standard Recoveries (census rules or quality control charts)
   - Sample blanks
   - Sample duplicates
   - Certified reference materials
   - Maintenance of and interpretation of quality control charts
   - Participation in inter-laboratory comparison exercises
iv) Quality Assurance Documentation for:
   - Sample reception and storage procedures
   - SOP for analysis of POPs and evidence of implementation of SOPs
   - Method validation and Method Detection Limits for each analyte
   - Criteria for acceptance or rejecting quality control parameters
   - Updated quality control charts
   - Results on file of inter-laboratory comparison exercises
   - Non-compliance and corrective action reports

Analysis of white grunt samples

- Regional laboratories will receive white grunt samples (5-10 g, dorsal muscle fillet) from each of the participating laboratories
- Assign a unique laboratory code to each sample that can be tracked to the sample I.D. Information
- The regional laboratory will analyze (2-4 g portion of sample, with skin-removed) and store remainder of tissue
- The laboratory will utilize 2,4,6-trichlorobiphenyl (PCB #30) as the sample spiking standard
- With each batch of sample: laboratory blank and CRM (NIST SRM1974) is analyzed
- A sample duplicate, randomly chosen within the batch, will be run every 2 batches
- Instrumental analysis will be completed by GC-ECD using the certified analytical standards. At the laboratory discretion, alternative methods, e.g. GC-MSD, maybe used for validation. However, all reported results should reflect values determined by GC-ECD.
- An electronic spreadsheet report of data which has passed QC procedures will be prepared according to a common template (to be provided) and submitted to UNU-INWEH.
  - spiking standard recovery,
  - Blanks
  - CRM results
  - duplicates
  - % extractable lipid,
  - Analyte concentrations will be blank-adjusted (if required) and expressed in units of ng/g wet wt.
  - Analyte concentrations will not be corrected for sample spiking recoveries, although recovery information will be provided with the data report.
Guidelines for Sample Preparation and Analysis

- **Target fish:** White Grunt (*Haemulon plumieri*)

- Three fish of appropriate size per site. Recommend collect 5-10 fish per site for storage if possible.

- **Size Range:**
  - 120 – 250 g
  - 19 – 26 cm total length

- **Alternative Species:**
  - Other Grunt Species (first priority)
  - Other benthic feeding species of appropriate target size range.

- **Capture method:** Any
Sample Storage

• On Site:
  • Place each whole fish into its own Zip-lock freezer bag.
  • On a piece of cardboard stock, write out pencil:
    • Unique Sample I.D., date, site, country.
    • Place the cardboard stock into the bag with the fish.
  • Place bagged fish on ice in cooler immediately at capture.
  • Fill out the appropriate information on a Sample Collection Sheet

• At laboratory (Temporary)
  • Place bagged fish, frozen whole, in a freezer at -20°C.
  • Keep all fish collected for the project in the same location and freezer.
  • Submit an electronic copy of the sample collection sheet to the UNU-INWEH FTP site.
Long term storage:
- remove ~10 g dorsal muscle as indicated in red square above
- use clean, solvent rinsed fillet knife for each sample
- retain scales and skin
- wrap dorsal muscle in solvent rinsed aluminum foil
- place foil wrapped muscle in zip-lock bag or whirl-pack bag
- write out unique sample i.d. Cardboard stock in pencil and place in bag. Write unique i.d. In marker on bag.
Harmonized Database

• Physical location and management?
• On-line (access?)
• Types of data made available for presentation
  • Raw data
  • Data summaries
  • Location maps (GIS)
• Additional information?