Quality Assessment of Contaminated Sediment in Korean Coastal Areas: Application of Sediment Triad Approach

Dr. Jong Seong Khim
KU, KOREA

Dr. John P. Giesy
U of S, CANADA

Dr. Chul-Hwan Koh
SNU, KOREA

Nov 21st 2009
SETAC North America 30th Annual Meeting
New Orleans, Louisiana, USA
To review our study efforts and experiences
To draw down limitations and future things to do
To get some advice from all of you at SETAC

10 yrs of experiences following lessons

Outline & Perspectives of this presentation

CONTENTS
- Introduction
  - Backgrounds
  - Objectives
  - Approach
- Methods
  - Activities
  - Field work
  - Lab work
- Results
  - Key Results
  - Findings
  - Publications
- Discuss
  - Limitations
  - Significance
  - Summary
- Ending!
  - Next Step
  - About KU
  - Acknowledge
INTRODUCTION

Pollution issues in Korea

Before Our Study: mid 1990s

- Only a few studies reported for classical POPs pollution for Korean sediments and no reports made on some EDCs
- Above pollution studies focused sorely on analytical concentrations
- The risk assessment paradigm of the U.S. and Canada, which considers biological effects, never been introduced in Korea

the concept of biological effects together with measurement of analytical concentrations first employed in Korea during our study
Why sediments?

lots of industrial complexes along the coasts
ultimate sink and potential sources,
but no regulations in Korea → assessment needs
**BACKGROUNDs**

*Instrumental analysis vs. Bioassay*

**Exposure vs. Effects**

- **Exposure**: typically studied by **instrumental analysis**

- **Effects (Potency)**: determined by **bioassay** (i.e., animal studies)
  1. biological relevance
  2. integrated measure (viz. mixture effects)
  3. can account for unknowns (or unidentified chemicals)
  4. can account for non-additive interactions between chemicals
  5. in some cases, more sensitive than instrumental analysis

but also bioassay is **limited** to inability to **quantify** the concentration of active agent(s) present and inability to **identify** the active agent(s) → **combination use needs**
### BACKGROUNDS

*Where are we?: mid 1990s*

#### Research Item

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Korea</th>
<th>USA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td><img src="low.png" alt="low" /></td>
<td><img src="high.png" alt="high" /></td>
</tr>
<tr>
<td>Sediment</td>
<td><img src="low.png" alt="low" /></td>
<td><img src="high.png" alt="high" /></td>
</tr>
<tr>
<td>Biota</td>
<td><img src="high.png" alt="high" /></td>
<td><img src="high.png" alt="high" /></td>
</tr>
</tbody>
</table>

#### Effect com.

<table>
<thead>
<tr>
<th>Community disturbance</th>
<th>Korea</th>
<th>USA</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="low.png" alt="low" /></td>
<td><img src="low.png" alt="low" /></td>
<td><img src="high.png" alt="high" /></td>
</tr>
</tbody>
</table>

#### Effect ind.

<table>
<thead>
<tr>
<th>Fertilization/development test</th>
<th>Korea</th>
<th>USA</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="low.png" alt="low" /></td>
<td><img src="low.png" alt="low" /></td>
<td><img src="high.png" alt="high" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Microtox assay</th>
<th>Korea</th>
<th>USA</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="low.png" alt="low" /></td>
<td><img src="low.png" alt="low" /></td>
<td><img src="high.png" alt="high" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Amphipods mortality test</th>
<th>Korea</th>
<th>USA</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="low.png" alt="low" /></td>
<td><img src="low.png" alt="low" /></td>
<td><img src="high.png" alt="high" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Growth/reproduction test</th>
<th>Korea</th>
<th>USA</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="low.png" alt="low" /></td>
<td><img src="low.png" alt="low" /></td>
<td><img src="high.png" alt="high" /></td>
</tr>
</tbody>
</table>

#### Effect sub-ind.

<table>
<thead>
<tr>
<th>Histopathology (tumor)</th>
<th>Korea</th>
<th>USA</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="low.png" alt="low" /></td>
<td><img src="low.png" alt="low" /></td>
<td><img src="high.png" alt="high" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cell line test</th>
<th>Korea</th>
<th>USA</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="low.png" alt="low" /></td>
<td><img src="low.png" alt="low" /></td>
<td><img src="high.png" alt="high" /></td>
</tr>
</tbody>
</table>
Approach

Integrated measure

Scheme

Korean Sediments (>700 stns)

- Grain size
- TOC
- LOI
- SEM/AVS
- Cu/Cd/Zn/Pb
- POPs
- EDCs

Sediment property

Metal analysis

Organic analysis

Chemistry data

Comparison

Benthic community

In vivo bioassay

In vitro bioassay

Tox/Ecology Data

- Species comp.
- Density
- Biomass
- Sea urchin
- Microtox
- Amphipod
- H4IIIE-luc
- MVLN
- RLT 2.0
- PLHC-1

Species comp.

Density

Biomass

Sea urchin

Microtox

Amphipod

H4IIIE-luc

MVLN

RLT 2.0

PLHC-1
Objectives

General: component-wise

Integrated Assessment (Exposure & Effect)

Triad approach
- chemistry, toxicology, ecology
- bioassay-directed fractionation
- mass-balance analysis

Specific Objectives

Concentration (levels)

Distribution (sources)

Response (in vitro or In vivo)

Response (benthic community)
Study began in Dec 1995 (long-term research plan)

DATA obtained in Dec 2001 (~700 stations)

Sediment TIE study (>200 stations)

Study areas (no. of stations surveyed)

- 122 Namyang (5)
- 238 Gwangyang (75)
- 121 Shihwa (20)
- 63 Ulsan (30)
- 133 Pohang (34)
- 11 locations

- Incheon (7)
- Mokpo (91)
- Masan (31)
- Onsan (23)
- Masan (24)

- Shihwa (20)
- Incheon (9)
- Jinhae (70)
- Ulsan (30)
- Onsan (33)

- Gyeonggi (60)
- Ulsan (63)
- Onsan (33)
- Shihwa (8)

- Gwangyang (11)

Analyses

- Sed. Property
  - Metals
  - Community
    - Organics
    - In vitro bioassays
  - Sea-urchin bioassay

- Amphipod bioassay
- Microtox bioassay
METHODS

Target chemicals?

Compounds (used for / found in)

Dioxins/Furans (incineration, industrial use)
PCBs: Polychlorinated biphenyls (coolants, lubricants, capacitors)
OC pesticides: Organochlorine pesticides (insecticides, herbicides)
- HCB: Hexachlorobenzene
- CHLs: Chlordanes
- HCHs: Hexachlorocyclohexanes
- DDTs: Dichloro diphenyl trichloroethanes
PAHs: Polycyclic aromatic hydrocarbons (coal tar, crude oil, dyes, plastics)
APs: Alkylphenols (detergents, paints, agents)
- NP: Nonlyphenol
- OP: Octylphenol
- BP: Butylphenol
BPA: Bisphenol A (plastics, containers, dental sealants)
Metals: Cu, Cd, Zn, Pb etc. (industrial use etc.)

a
\[
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\]

b
\[
\begin{array}{c}
\text{Cl}_\text{m} \\
\text{Cl}_\text{n}
\end{array}
\]

m+n=1-10

c
\[
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\]

d
\[
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\end{array}
\]

e
\[
\begin{array}{c}
\text{C}_9\text{H}_{19} \\
\text{OH}
\end{array}
\]

f
\[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{OH} \\
\text{OH}
\end{array}
\]

\text{CCl}_3
METHODS

Field work: photo description
METHODS

Field work: survey vessel
METHODS

Field work: industrial activities around bay
METHODS

Field work: sediment grab sampling
METHODS

Field work: imagine contamination!

[Image of a bucket with a sample]
METHODS

Field work: sub-sampling for chemical analyses
METHODS

Field work: samples for *in vitro* & *in vivo* bioassays
METHODS

Field work: biological samples
METHODS

Field work: sediment core samples
**METHODS**

*Lab work: organic analyses & in vitro bioassays (TIE)*

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Wet Sediment (water removal)</td>
</tr>
<tr>
<td>2</td>
<td>Soxhlet Extraction (40 g in 400 ml DCM)</td>
</tr>
<tr>
<td>3</td>
<td>S-Removal (Cu treatment)</td>
</tr>
<tr>
<td>4</td>
<td>Raw Extract: RE (2 ml)</td>
</tr>
<tr>
<td>5</td>
<td>H4IIE-luc/MVLN (1 ml)</td>
</tr>
<tr>
<td>6</td>
<td>Florisil Column Fractionation: FEs (F1, F2, and F3) (1 ml)</td>
</tr>
<tr>
<td>7</td>
<td>H4IIE-luc/MVLN (0.5 ml)</td>
</tr>
<tr>
<td>8</td>
<td>GC (0.5 ml), GC/HPLC (0.5 ml), HPLC (0.5 ml)</td>
</tr>
</tbody>
</table>

For all RE & FEs
40 g sed. extracts final volume 1 ml

- 98 PCBs
- HCB, p,p′-DDE
- 16 PAHs
- HCHs, CHLs, DDTs
- APs (NP, OP, BP)
- Bisphenol A
**METHODS**

*Lab work: in vivo bioassays (amphipod, sea urchin, & microtox)*

**Organism collection**
- Field amphipod collection
- Acclimation (18 °C, 28 ‰)
- Allocation of 20 individuals in 1 L beakers

**Sediment collection**
- Sieving & Homogenization
- Field sediment collection
- Sediment, water placement in 1L beakers (overnight)

Starting assay – day 0

Aeration and monitoring WQ

Ending assay – day 10

Determining amphipod survival

Korean amphipod, *Mandibulophoxus mai*
POPs in Korean Sediments

1) Concentration:
- inland > bay

2) Distribution:
- APs: much greater in inland (~ppm)
- PAHs: widespread distribution (~ppm)
- PCBs & OCPs: relatively uniform (~ppb)

3) Sources:
- hot spot and multiple sources

4) Overall,
- low to moderate
- mostly ≤ SQGs
RESULTS

e.g., Chemistry: *metals*

**Metals in Korean Sediments**

1) **Concentration:**
- *inner area > outer bay*

2) **Distribution:**
- *Cu*: greater in inland (>ppm)
- *Zn & Pb*: widespread distribution (>ppm)

3) **Sources:**
- *hot spot* and multiple sources

4) **Overall,**
- *moderate to high*
- *mostly ≥ SQGs*
RESULTS

e.g., Toxicology: in vitro response

Dioxin-like Activity (H4IIE-luc Cells)

1) Screening Response:
   - >90% of REs > control

2) Fraction Response:
   - F2 ≥ RE > F3 > F1; PAHs responsible
   - ΣFEs > RE; non-additive → interaction

3) Distribution:
   - inland > bay
   - very high in river; point sources

4) Mass Balance,
   - mostly TEQs < TCDD-EQs
   - Sometimes good agreement (viz. TEQs = TCDD-EQs)
RESULTS

e.g., Toxicology: *in vivo* response

Sea Urchin Test

1) Screening Response:
- mostly significant for **both** PW & RE
- sensitive to Fertilization test

2) Fraction Response:
- PW ≥ RE
- both metals & organics responsible

3) Distribution:
- inner area > outer bay
- very high in river; **point sources**

4) Mass Balance,
- good agreement with chemistry data
RESULTS

e.g., Ecology: benthic community response

Benthic Community Structure

1) Species composition:
- divided into 4 groups
- consistent with pollution gradient
- inner area > outer bay

2) Species no. of polychaeta:
- relatively low in inner area
- reflects pollution gradient
- comparable to station groups
- opportunistic species in polluted areas

3) Overall,
- good agreement with chemistry data
Chemistry: low-moderate for organics & moderate-high for metals

Toxicology or ecology: in vitro > in vivo > community response

Relationship: relatively good agreement between chemistry & toxicology or ecology data

Limitations: known composition & concentrations of target chemicals could not fully account for biological responses

need more works on
- TIE method development (viz. techniques)
- bioavailability study (viz. mechanism)
- mass balance model improvement (viz. interpretation) etc.
SIGNIFICANCE

Data Accumulation

Chemistry, Toxicology, & Benthic Community Data for >700 stations and >1,000 samples in Korea
Key findings

1) TIE first applied to coastal sediment  
PUBLICATIONS
- EST 99 > 100
- ETC 99 > 50

2) TIE further applied to biological samples  
- AECT 00 > 30

3) TIE next applied to water and porewater  
- AECT 01 > 50
- ETC 02 > 30

4) Assessment extended to inland area  
- EP 04 > 30
- EES 05 > 10

5) TIE method improvement  
- ET 02 > 50

5) REPs for environmental chemicals  
- AECT 00 > 100
- AT 01 > 20
- EST 09 -

ca. > 600 times cited
**Instrumental analyses using**
- LC (PFCs, Hormones)
- GC (PAHs, APs, BPA)
- HRGC (PCDD/DFs, co-PCBs, PBDEs)
- CIC (Total F)
- ICP-MS (metals)

**Bioassays using**
- Dioxin-like activities (HII4E-luc)
- Estrogenicity (MVLN)
- Steroidogenesis (H295R)
- Mutagenicity (Mutatox®)
- Other in vivo studies

**NEXT STEP**
Towards integrated sediment assessment

**Chemistry**

**Ecology**
Community indices

**Toxicology**
RESEARCH PERSPECTIVES

in Environmental Chemistry Lab at Korea University
http://lifesci.korea.ac.kr/~eco/eng

INTEGRATED Environmental Assessment

‘source’ oriented approach

Environmental Chemistry

back and forth approach

Ecological Response

‘receptor’ oriented approach

Toxicological Response

Environmental Chemodynamics

Exposure Assessment

Effect Assessment

for Ecosystem Human Health

Human resource development of Next generation
Thank You!

Thanks to:
Former & Current
Research Teams & Individuals of Profs. Koh & Giesy