Exposure Assessment of Environmental Samples and Contaminants: TIE Approach

Jong Seong Khim and John P. Giesy

Toxicology Centre, University of Saskatchewan, CANADA
Only a few studies reported for classical POPs for sediments of the Korean coast, and no reports on some EDCs.

Moreover, above studies focused sorely on analytical concentrations.

The current risk assessment paradigm of the U.S. and Canada, which considers biological effects in addition to chemical concentrations, has never been introduced for Korean coastal sediment.

Thus, the concept of biological effects together with measurement of chemical concentrations was first employed in Korea during our study.
lots of industrial complexes along the Korean coastal areas
some sediment samples collected from Korean coastal areas
Scheme

Korean Sediments (>700 stns)

- sediment property
- metal analysis
- Organic analysis
- Chemical Concentration
- In Vitro bioassay
- benthic community
- in vivo bioassay

COMPARISON

Biological Response

4th ISPTS, Beijing, Nov 19, 2007
ACTIVITIES

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

DATA obtained in Dec 2001
(~700 stations)

SURVEYS in Korean coast

<table>
<thead>
<tr>
<th>122</th>
<th>238</th>
<th>121</th>
<th>63</th>
<th>133</th>
<th>11 locations</th>
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<td>Shihwa (20)</td>
<td>Ulsan (30)</td>
<td>Pohang (34)</td>
<td>Gwangyang (11)</td>
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<td>Masan (31)</td>
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<td>Jinhae (70)</td>
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<td>Shihwa (8)</td>
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ANALYSES of

Sed. Property

Metal

Community

Organics

In vitro bioassay

Amphipod bioassay

Microtox bioassay

Sea-urchin bioassay
SEDIMENT TIE STUDY

- applied since 1998
(analyzed for samples >150 among total of >700)

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<th>n</th>
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OBJECTIVES

Assessment of Sediment Contamination

Sediment TIE
- Bioassay-directed Fractionation
- Mass Balance Analysis

Specific Objectives

Concentration (Level)  Distribution (Sources)  Dioxin-like Activity  Estrogenic Activity
KEY CONCEPT (1)

Bioassay-directed Fractionation

Pollutants (Mixture)

fractionation

TIE fractionation

bioassay

chemcial treatment

stop!

further fractionation

TIE start

TIE end

F1  F2  F3

F4  F5  F6  F7

F1  F2  F3

sig.*

*
KEY CONCEPT (2)

**Instrumentally derived**
- Calculated by multiplying the analytical concentrations of compounds identified by their REPs and summing.
- For example, TEQs or EEQs.

**Bioassay derived**
- Estimated directly from dose-response curves from bioassay analysis of a sample and standard.
- For example, TCDD-EQs or E2-EQs.

**Mass Balance Analysis**

\[ \Sigma (\text{Conc. } \times \text{REPs}) \]

\[ \frac{EC50_{\text{std}}}{EC50_{\text{sample}}} \]
TARGET COMPOUNDS

Compounds

1. PCBs\textsuperscript{a}: Polychlorinated biphenyls
2. OC pesticides: Organochlorine pesticides
   - HCB: Hexachlorobenzene
   - CHLs: Chlordanes
   - HCHs: Hexachlorocyclohexanes
   - DDTs\textsuperscript{b}: Dichloro diphenyl trichloroethanes
3. PAHs\textsuperscript{c}: Polycyclic aromatic hydrocarbons
4. APs: Alkylphenols
   - NP\textsuperscript{d}: Nonlyphenol
   - OP: Octylphenol
   - BP: Butylphenol
5. BPA\textsuperscript{e}: Bisphenol A

(used for / found in)

- coolants, lubricants, capacitors
- insecticides, herbicides
- coal tar, crude oil, dyes, plastics
- detergents, paints, agents
- plastics, resins, containers, dental sealants

(Structure)

Standards for Bioassays

6. 2,3,7,8-TCDD\textsuperscript{f}: 2,3,7,8-tetrachlorodibenzo-\textit{p}-dioxin (most toxic dioxin)
7. E2\textsuperscript{g}: 17-\textit{\beta}-estradiol (natural estrogen)
METHODS

1. Sediment Samples
   Raw Extract (RE)

2. H4IIE/MVLN (1 ml DCM)

3. Florisil Column Fractionation: FEs (F1, F2, & F3) (1 ml each for 3 FEs)
   - F1 (1 ml Hex)
   - F2 (1 ml Hex)
   - F3 (1 ml ACN)

4. H4IIE/MVLN (0.5 ml) H4IIE/MVLN (0.5 ml) H4IIE/MVLN (0.5 ml)

5. GC (0.5 ml) GC/HPLC (0.5 ml) HPLC (0.5 ml)
   - PCBs
   - HCB, p,p'-DDE
   - PAHs
   - HCHs, CHLs, DDTs
   - APs (NP, OP, BP)
   - Bisphenol A

organic extraction
initial bioassay screening
bioassay-directed fractionation
second bioassay determining potencies
instrumental quantification
IN VITRO BIOSSAYS

H4IIE-luc or MVLN Cells

72 hr of Exposure (dosing)

Sediment Extracts (RE or FEs)

Standard for H4IIE-luc assay
2,3,7,8-TCDD

Standard for MVLN assay
17-β-estradiol

ARNT

AhR-luc.

Luc.-mRNA

ER-luc.

ER

Luciferase

Luciferin

Light

4th ISPTS, Beijing, Nov 19, 2007
RESULT (1): CHEMICAL CONCENTRATIONS

POPs in Korean Sediments

1) Concentration
- inland > bay

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

3) Sources
- generally agree between inland and bay
- hot spot and multiple sources

4) Overall,
- low to moderate, compared with other studies
- mostly lower than SQGs
RESULT (2): BIOLOGICAL EFFECTS

Dioxin-like Activity (H4IIE-luc Cells)

1) Screening Response
- >90% of REs showed significant responses

2) Fraction Response
- F2 ≥ RE > F3 > F1; PAHs responsible
- \( \Sigma \) FEs > RE; interaction between compounds

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

4) Mass Balance
- TEQs < TCDD-EQs
- Sometimes good agreement (TEQs = TCDD-EQs)
Estrogenic Activity (MVLN Cells)

1) Screening Response
- ~50% of REs showed significant responses

2) Fraction Response
- RE > F2 > F3 > F1; PAHs and APs responsible
- \( \Sigma \) FEs > RE; interaction between compounds
- Cytotoxic in many F3

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

4) Mass Balance
- EEQs << E2-EQs (average 20%)
Summary: Comparison

- POPs & EDCs levels: low to moderate
- Localized distribution: point sources from inland
- Major contaminants: PAHs and APs
- RE < FEs responses interaction (non-additive)
- F2 (H4IIE-luc) & F2-3 (MVLN) greatest responses
- F3 (MVLN) sometimes, cytotoxic

Korean Sediments n=154

Chemical Concentration: TEQs < TCDD-EQs EEQs << E2-EQs

Biological Response
TIE and MBA were useful to determine chemical composition and concentrations that responsible for the biological responses.

However, known composition and concentrations of target chemicals could not fully account for biological responses.

More elaborate characterization of compounds associated with some fractions should improve further understanding.
FUTURE TIE WORKS

MORE INTEGRATED APPROACH & UNDERSTANDING NEEDED

Chemicals
- existing POPs
- emerging EDCs

for
- PCDD/DFs
- PAHs
- APs
- PFCs
- PBDEs

Media
- environmental samples

with
- Sediment
- Water
- Biological Samples

Tools
- bioanalytical methods

by use of
- in vitro
- in vivo
- in situ
Thank You!

Acknowledgement to:
Research Teams of Profs. Giesy & Koh