Effect of Aging on Contaminant Bioavailability

Allison Taylor, Jie Wang, Daniel Schlenk and Jay Gan

Department of Environmental Science
University of California, Riverside, CA 92521
“Priority” Organic Pollutants (HOCs)

✓ Chlorinated pesticides
✓ PCBs/PBDEs
✓ PAHs
✓ Dioxins

FACT 1: Strong sorption

✓ Chlorinated pesticides
✓ PCBs/PBDEs
✓ PAHs
✓ Dioxins

FACT 2: Aged
DDT

- Paul Hermann Müller, Nobel Prize in Physiology or Medicine, 1948
- During World War II, control malaria and typhus among civilians and troops
- Agricultural insecticide since 1945
- Banned in 1972 in the U.S.
Aging and Bioavailability

- Plant roots
- Organic matter
- Microbes
- Dissolved OM
- Benthic invertebrates
- Freely dissolved
Aging and Bioavailability

- Plant roots
- Organic matter
- Dissolved OM
- Microbes
- Benthic invertebrates

- Bioaccessible
- Freely dissolved
Aging and Bioavailability

- Plant roots
- Organic matter
- Benthic invertebrates
- Microbes

- Freely dissolved
- Bioaccessible
- Non-accessible
Aging and Bioavailability

plant roots

organic matter

benthic invertebrates

dissolved OM

microbes

Non-accessible

Bioaccessible

Freely dissolved
Measuring Bioavailability

- Irreversibly bound
- Reversibly bound
- Freely dissolved

Total concentration

Bioaccessibility

\[ C_{\text{free}} \]

Reichenberg and Mayer, ET&C, 2006, 1239-1245
Bioavailability

**Freely dissolved concentration** $C_{\text{free}}$

The potential for a chemical to undergo spontaneous processes, e.g., diffusion and partitioning

**Bioaccessibility**

The actual amount of a chemical that is or may become available within a given time and under given conditions

Reichenberg and Mayer, 2006, Environ. Toxicol. Chem. 25, 1239-1245
Bioavailability Methods

Bioaccessibility

- Partial desorption
  - Weak acid extraction
  - Mild solvent extraction
  - Gut fluid extraction
  - Cyclodextrin extraction
  - Tenax adsorption extraction
- Isotope dilution method (IDM)

$C_{\text{free}}$

- Passive samplers
  - DGT
  - Polyethylene devices (PEDs)
- Semi-permeable membrane devices (SPMDs)
- Polyoxymethylene (POM)
- Solid phase micro-extraction (SPME)
Study I. Aged POPs at the Palos Verdes Superfund Site

US EPA, 2010
A Sediment Core Experiment

Hypothesis:

Contaminant aging has resulted in reduced bioavailability.
$^{210}\text{Pb}$ Dating

3C: JW512

$^{210}\text{Pb}$ Date

Depth (cm)

CRS

CIC

8C: JW514

$^{210}\text{Pb}$ Date

Depth (cm)

CRS

CIC
Total concentration profiles of PCBs and DDTs in (A) 8C and (B) 3C cores in µg/kg dry weight (d.w.) of sediment.
Conclusions I

- DDT residues were extensively "aged".
- Due to aging, only a very small fraction of DDTs in the marine sediment was "bioaccessible".
- DDTs in surface sediment also showed very low bioaccessibility.
  - DDT residues were "aged" elsewhere before deposition onto the ocean floor.

Implications:
- Risks much lower than expected from total concentration.
- EPA decided to use MNA ("monitored natural attenuation") instead of capping.
Study II. A Direct Method to Test Aging

- Isotope-labeled HOCs
- Historically-contaminated soil
- *Eisenia fetida*

Bioaccumulation assay:
- Ultrasonic extraction
- SPE purification
Isotope-labeled HOCs

Historically-contaminated marine sediment

*Nereis virens*

Bioaccumulation assay

ultrasonic extraction

SPE purification
Isotope-labeled HOCs

Historically-contaminated freshwater sediment

Lumbriculus variegatus

Bioaccumulation assay

SPE purification

ultrasonic extraction
Isotope-labeled HOCs

Historically-contaminated soil/sediment

Spiked soil/sediment

Tenax beads

Tenax desorption

transferring
ultrasonic extraction
centrifuging & transferring beads
Tenax $F_{24h}$ of native HOCs were consistently smaller than those for isotope labeled HOCs, suggesting reduced bioaccessibility due to aging.
The BSAF values of native HOCs were consistently lower than those for isotope labeled HOCs, clearly indicating aging effect on bioavailability of POPs in environmental matrices.
Ratios of labeled HOCs to native HOCs accumulated in earthworm, against against with the ratios of Tenax $F_{24h}$.

Highly significant linear correlation, with $R^2 = 0.82$, and slope close to 1.
Conclusions II

- Compared to freshly spiked chemicals, bioaccumulation of aged residues was much lower.
- The same conclusion was made in marine sediment, freshwater sediment, and soil, for different invertebrates.
- The use of chemically based measurement closely predicted bioaccumulation.
- The use of isotope labels is a direct and convincing technique to demonstrate the effect of aging on contaminant bioavailability.
Review

Methods to assess bioavailability of hydrophobic organic contaminants: Principles, operations, and limitations

Xinyi Cui\textsuperscript{a,c}, Philipp Mayer\textsuperscript{b}, Jay Gan\textsuperscript{c,*}

\textsuperscript{a} State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210046, China
\textsuperscript{b} Department of Environmental Science, Aarhus University, Frederiksbergvej 399, 4000 Roskilde, Denmark
\textsuperscript{c} Department of Environmental Sciences, University of California, Riverside, CA 92521, USA
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