BIOAVAILABILITY OF TRIAZINE RESIDUES IN AGED SOILS

William C. Koskinen
USDA-ARS, St. Paul, MN

Enrique Barriuso
INRA, Grignon, France

Jussara B. Regitano
Universidade de Sao Paulo, Brazil

Michael J. Sadowsky
University of Minnesota

Triazines

- The chemicals that launched 1000’s of careers
- Atrazine, simazine, terbuthylazine, cyanazine, propazine, prometryn, etc
Availability/Bioavailability

- Availability/Bioavailability is the integration of various processes in soil and controls:
  - transport to water and air
  - exposure to and uptake by target and nontarget organisms
Availability/Bioavailability

Availability/Bioavailability is the integration of various processes in soil and controls:
- transport to water and air
- exposure to and uptake by target and nontarget organisms
- degradation

Sorption–desorption is arguably the most important process; it directly or indirectly controls all other processes.
Characterization of Availability

- Indirect methods
- Direct methods
Characterization of Availability – Indirect Methods

- Aqueous extractable

- Organic solvent extractable (supercritical fluids for pesticides in soil water at typical field moisture levels)
Characterization of Availability – Indirect Methods
- Aqueous extractable
- Organic solvent extractable (supercritical fluids for pesticides in soil water at typical field moisture levels)
- Isotopic exchange technique

Characterization of Bioavailability – Indirect Methods
- Aqueous extractable
- Solvent extractable
- SFC method – pesticide in soil water at typical field moisture levels
- Isotopic exchange technique
- Batch equilibration method; $K_d$; $K_{oc}$; $K_f$, 1/n
Potential Problems/Criticisms

- Little data to support aqueous or solvent extractable = availability

- Slurry method doesn’t represent reality
Potential Problems/Criticisms

- Little data to support solvent extractable = bioavailability
- Slurry method doesn’t represent reality
- Desorption hysteresis

Potential Problems/Criticisms

- Little data to support solvent extractable = bioavailability
- Slurry method doesn’t represent reality
- Desorption hysteresis
- $K_{oc}$ - Sorption on mineral surfaces?
Potential Problems/Criticisms

- Little data to support solvent extractable = bioavailability
- Slurry method doesn’t represent reality
- Desorption hysteresis
- $K_{oc}$ - Sorption on mineral surfaces?
- Changes in availability with time

Direct Methods

- Measured uptake by plants, earthworms, microorganisms
Direct Methods

- Measured uptake by plants, earthworms, microorganisms
- Degradation by specific pesticide-degrading microorganisms

Potential Problems/Criticisms

- Direct characterization of pesticide bioavailability in soil using plants or microorganisms can be expensive and time-consuming
Potential Problems/Criticisms

- Direct characterization of pesticide bioavailability in soil using plants or microorganisms can be expensive and time-consuming.
- It requires identifying a plant or microorganism that can rapidly take up and/or degrade the pesticide.

Objectives

- Characterize solvent extractability of aged triazine residues.
Objectives

- Characterize solvent extractability of aged triazine residues
- Determine mineralization of aged triazine residues by a triazine-degrading organism
- Correlate bioavailability (mineralization) of aged triazine residues to solvent extraction
Chemicals

- UL-ring-$^{14}$C-atrazine (>98% pure), unlabeled atrazine (>99% pure)
- UL-ring-$^{14}$C-simazine (>98% pure), unlabeled simazine (>99% pure)

Soil Properties

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Orig.</th>
<th>%OC</th>
<th>%clay</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>US</td>
<td>0.5</td>
<td>3</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.1</td>
<td>35</td>
<td>6.7</td>
</tr>
<tr>
<td>Simazine</td>
<td>US</td>
<td>1.0</td>
<td>4</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.3</td>
<td>19</td>
<td>6.3</td>
</tr>
<tr>
<td>BR</td>
<td></td>
<td>1.0</td>
<td>22</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.3</td>
<td>40</td>
<td>5.5</td>
</tr>
<tr>
<td>HW</td>
<td></td>
<td>2.6</td>
<td>15</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.4</td>
<td>74</td>
<td>5.5</td>
</tr>
</tbody>
</table>
Methods

- Soil Treatment and Incubation
  - Air-dry soils (10 g) treated with $^{14}$C-triazine solution placed into centrifuge bottles
  - Soil moisture content adjusted to -33 kPa.
Methods

- Soil Treatment and Incubation
  - Air-dry soils (10 g) treated with $^{14}$C-triazine solution placed into centrifuge bottles
  - Soil moisture content adjusted to -33 kPa.
  - Vial containing 5 mL 1 N NaOH was placed in bottles.
  - Soils were incubated at 25 °C for up to 8 weeks.
At each sampling time

Soil
  - unextracted
  - Aq. extracted
  - Solv. extracted

Inocc/ incubate
  - 14CO2

extract
  - 14C
  - combust
Soil
- unextracted
- Aq. extracted
  - 14C
  - Inocci/ incubate
    - 14CO2
      - extract
      - 14C
      - combust
- Solv. extracted
Inoculation/Incubation

- Triazine-degrading organism: *Pseudomonas* sp. strain ADP

Inoculum density = 1 x 10⁸ ADP cells g⁻¹ soil
Inoculation/Incubation

- Triazine-degrading organism: *Pseudomonas* sp. strain ADP
- Inoculum density = $1 \times 10^8$ ADP cells g$^{-1}$ soil
- Soil moisture = -33kPa

Incubated up to 20 d at 25 °C.
Inoculation/Incubation

- Triazine-degrading organism: *Pseudomonas* sp. strain ADP
- Inoculum density = $1 \times 10^8$ ADP cells g$^{-1}$ soil
- Soil moisture = -33kPa
- Incubated up to 20 d at 25 °C.
- $^{14}$CO$_2$ evolution monitored

RESULTS
**14C-atrazine residue distribution**

![Graph showing the distribution of 14C-atrazine residue in Zimmermann and Webster soils over time.](image)

- **Zimmermann Soil**
  - Mineralized
  - Water extracted
  - Methanol extracted
  - Bound residues

- **Webster Soil**

**14CO2 evolution from 14C-simazine-treated soils after inoculation with Pseudomonas sp. strain ADP.**

![Graph showing the evolution of 14CO2 from 14C-simazine-treated soils over time.](image)

- **BR-1**
- **BR-2**
- **US-1**
- **US-2**
- **HW-1**
- **HW-2**

- Time after inoculation (h)
  - 0 30 60 90 120 150
Extractable vs. Mineralizable

% of 14C initially applied

(a) % of 14C initially applied

Extractable vs. Mineralizable (water-extractable removed)

(b) % of 14C initially applied

% of 14C initially applied

(c) % of 14C initially applied
Extractable vs. Mineralizable
(water-, methanol-extractable removed)

% of 14C initially applied

% 14C mineralized

% 14C methanol + water extractable

INEX

IN - inoculation

EX - extraction

Clay loam soil regression
(y = 1.31x - 6.16, r² = 0.976)

Fine sand soil regression
(y = 1.33x - 6.77, r² = 0.932)

Atrazine
Extractable vs. Mineralizable
Simazine residues distribution before and after inoculation with *Pseudomonas* sp. strain ADP in aged soils.

Simazine extractable vs. mineralizable
After 40 years of research, there is still no universal method to characterize bioavailability.

The topic is wide open and we need to look for innovative methods.

Sequential solvent extraction correlated to bioavailability is a start.

Possibilities – biosensors???