Transport and attenuation of S-metolachlor at the catchment scale

Lefrancq M.¹, Guyot B.¹, Imfeld G.¹, Elsayed O.¹, Millet M.², and Payraudeau S.¹

marie.lefrancq@etu.unistra.fr

¹ Laboratory of Hydrology and Geochemistry of Strasbourg (LHyGeS - UMR 7517), University of Strasbourg/ENGEES/CNRS, France

² Atmospheric Physical Chemistry Department (LMSPC - UMR 7515), University of Strasbourg/CNRS, France
Tracking pesticides from sources to sinks

- 70% of herbicides are applied in pre-emergence
- Interpretation of transport and degradation at the catchment scale is limited
- Need for new tools to assess in situ biodegradation

Source: AERM, 2012; Oliver et al, 2012; Fenner, 2013

Specific transformation processes

Suspended solids
How tracking pesticides from sources to sinks?

At the catchment scale

<table>
<thead>
<tr>
<th>Method</th>
<th>Enantiomeric analysis</th>
<th>Compound-specific isotope analysis (CSIA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Enantiomers = different spatial orientation of their atoms</td>
<td>Measures the stable isotope ratio of a compound</td>
</tr>
<tr>
<td></td>
<td>$Enantiomeric\ excess = \frac{R-S}{S+R} \times 100$</td>
<td>$\delta \ [%] = \frac{R_{sample} - R_{std}}{R_{std}}$</td>
</tr>
</tbody>
</table>
| Interpretation| - Enantioselective degradation  
- Enantioselective toxicology | Molecules with light isotopes tend to be degraded faster |
| Main use     | - 30% of pesticides are chiral 
- Ecotoxicological studies 
- Tracking physicochemical processes | - Environmental sciences (sourcing and degradation of pollutants)  
- Biogeochemistry (carbon and nutrient cycling)  
.... |

Fenner, 2013; Milosevic, 2013; Celis, 2013
### S-metolachlor

- The principal herbicide used on corn and sugar beet in pre-emergence (Europe)
- S-metolachlor is frequently detected in surface water as well as its degradation products

<table>
<thead>
<tr>
<th></th>
<th>S-Metolachlor: S: 80 - 100% R: 0 - 20%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical structure</strong></td>
<td><img src="image" alt="Chemical structure" /></td>
</tr>
<tr>
<td><strong>Aquatic crustaceans</strong></td>
<td>Acute 96 h LC$_{50}$ [mg L$^{-1}$]</td>
</tr>
<tr>
<td><strong>Solubility in water (20°C) [mg L$^{-1}$]</strong></td>
<td>480</td>
</tr>
<tr>
<td><strong>Log $K_{ow}$ (pH 7, 20°C)</strong></td>
<td>3.05</td>
</tr>
<tr>
<td><strong>Koc [L kg$^{-1}$]</strong></td>
<td>62 - 372</td>
</tr>
<tr>
<td><strong>DT$_{50}$ (soil) [d]</strong></td>
<td>21</td>
</tr>
<tr>
<td><strong>Hydrolysis, photolysis</strong></td>
<td>stable</td>
</tr>
<tr>
<td><strong>Henry's law constant (20°C) []</strong></td>
<td>$4.13 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

*Freitas et al., 2008; Alletto, 2013; Eurostat, 2007; PPDB, 2006*
Methods for tracking biotransformation processes

Enantiomeric signature

Carbon CSIA

Novel method to analyse CSIA for S-metolachlor

\[ R = \frac{C^{13}}{C^{12}} \]

Potential biotransformation signature

Buser, 2000; Thullner, 2012
Objectives

- Evaluate the transport of S-metolachlor at the catchment scale
- Investigate the partitioning between the dissolved and sorbed phases
- Test both approaches to track in situ biotransformation at the catchment scale
**Alteckendorf catchment** (Alsace, France)

48 ha
Slope: 5%
Rainfall\textsubscript{yearly}: 646 mm

- **Corn**: 68%
- **Sugar beet**: 4%
- **Wheat, oat**: 18%
- **Orchard, grass strip**: 8%
- **Roads, tracks**: 2%

Vegetal barrier
**Alteckendorf catchment** (Alsace, France)
48 ha  
Slope: 5%  
Rainfall$_{\text{yearly}}$: 646 mm

A representative plot
77 m$^2$  
Slope: 5%

- **Sugar beet growing season**
- **S-metolachlor**  
  Pre-emergence herbicide
- **2 measurements points:**  
  Outlet of the catchment and the plot

March 27 2012  
20 weeks  
August 14 2012
Sampling strategy

Catchment’s outlet
**Flow proportional sampling**
(115 mL every 10 m³)

Total suspended solids quantification by filtration (0.7 µm)

Plot’s outlet
**Flow proportional sampling**
(350 mL every 7 L)
S-metolachlor analysis

Runoff water samples

- Suspended solids (> 0.7 μm)
- Dissolved phase (< 0.7 μm)

Extraction with acetonitrile and pure water
Recovery rate: 69%

- GC-MS/MS
Uncertainty: 17%
LOQ: 0.01 μg kg⁻¹

- S-metolachlor concentration
GC-MS/MS
Uncertainty: 8%
LOQ: 0.04 μg L⁻¹

- Enantiomeric signatures
GC-MS/MS chiral
Uncertainty: 1%

- Carbon isotopic ratio
GC-C-IRMS
Uncertainty: 0.5‰
Impact of rainfall pattern

88 rainfall events: 316 mm

9 runoff events > 10 m$^3$

Total mass exported: 581 t (i.e. 1006 t km$^2$, 0.7 mm)

One single event explains 53% of the total outflow, 92% of the total SS exported
S-metolachlor off-site and partitioning

- Concentrations reached 62 µg L\(^{-1}\)<0.7 µm) and 34 mg kg\(^{-1}\) (>0.7 µm)
- Total export of 368 g, i.e. 3.4% exported

- Nearly 50% of the total loads were in the particulate phase
- 96% of the total loads corresponded to the event of May 22
Enantiomers enrichment: result of stereoselective biotransformation

- EE [%] ranged between -54% and -77%
- Similar export coefficient for R- and S-metolachlor

\[ \text{Enantiomeric excess} = \frac{R - S}{S + R} \times 100 \]
Carbon isotope fractionation

\[ \delta^{13}C \ [\%o] = \frac{R_{sample} - R_{std}}{R_{std}} \]
Carbon isotopic Vs enantiomeric signatures

- Fast flood events
- Different commercial products (Dual gold, Camix, Mercantor gold)
- Evidence of degradation at low concentrations

Milosevic, 2013
Summary

• One single event represents the majority of the pesticides and suspended solids export

• The partitioning between dissolved and sorbed phase was nearly 50%/50%

• For the first time, a combination of in situ analysis of chirality and CSIA was tested in runoff water at the catchment scale to highlight in situ biodegradation.

• First step toward the application of chirality and CSIA to evaluate the transport and attenuation of S-metolachlor at the catchment scale.

Perspectives:

- To which extent biotransformation occurred?
- Is enantioselective degradation reflected in soil and suspended solids?
Thank you for your attention

Research group: « Wetland biogeochemistry and contaminant transfer» (CNRS-UMR7517)

Scientists
Gwenaël Imfeld
Sylvain Payraudeau

Engineers – technicians
Benoît Guyot
Eric Pernin
Cyrielle Regazzoni

PhD students
Izabella Babcsányi
Omnia Elsayed
Marie Lefrancq
Elodie Maillard

Students
Maxime Combes
Thomas Dreidemy
Tristan Meyer
Angela Mutschler
Matthieu Schwob
Diogo Reis

LHYGES
Marie-Claire Pierret

Atmospheric Physical Chemistry Department (LMSPC - UMR 7515), Strasbourg.
Maurice Millet

IHF (Freiburg)
Jens Lange
Brian Sweeney

http://lhyges.u-strasbg.fr/
marie.lefrancq@etu.unistra.fr
### Hydrological conditions

Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Meteorology</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Daily mean temperature</td>
<td>[°C]</td>
<td>15.76 ± 4.77 (4.91 - 26)</td>
</tr>
<tr>
<td>Daily mean humidity</td>
<td>[%]</td>
<td>68.15 ± 10.88 (37.83 - 89.42)</td>
</tr>
<tr>
<td>Potential daily evapotranspiration</td>
<td>[mm]</td>
<td>3.82 ± 1.19 (1.3 - 7.4)</td>
</tr>
<tr>
<td>Rainfall events amounts</td>
<td>[mm]</td>
<td>3.6 ± 6.4 (0.4 - 54.4)</td>
</tr>
<tr>
<td>Rainfall events intensities</td>
<td>[mm 6 min⁻¹]</td>
<td>0.4 ± 0.4 (0.2 - 1.8)</td>
</tr>
<tr>
<td>Rainfall events duration</td>
<td>[mn]</td>
<td>114 ± 114 (8 - 462)</td>
</tr>
<tr>
<td><strong>Hydrology</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(events &gt; 10 m³)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Outflow volume</td>
<td>[m³]</td>
<td>1314 ± 3472 (22 - 10568)</td>
</tr>
<tr>
<td>Event duration</td>
<td>[mn]</td>
<td>136 ± 116 (38 - 413)</td>
</tr>
<tr>
<td>Runoff coefficient</td>
<td>[%]</td>
<td>7.76 ± 12.64 (0.23 - 40.81)</td>
</tr>
<tr>
<td>Maximum outflow</td>
<td>[m³ s⁻¹]</td>
<td>0.15 ± 0.22 (0 - 0.71)</td>
</tr>
<tr>
<td>Drainage contribution to the total</td>
<td>[%]</td>
<td>8.59 ± 6.65 (1.48 - 22.52)</td>
</tr>
<tr>
<td>outflow volume during runoff events</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
# Hydrochemical conditions

## Table 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Plot</th>
<th>Drain</th>
<th>Catchment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Erosion</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total suspended solids (&gt; 0.7μm)</td>
<td>[mg L⁻¹]</td>
<td>1.7 ± 2.57 (0.05 - 7.66)</td>
<td>0.16 ± 0.29 (0 - 1)</td>
<td>5.85 ± 11.27 (0.02 - 59.7)</td>
</tr>
<tr>
<td>Volatile organic carbon (&gt; 0.7μm)</td>
<td>[%]</td>
<td>18.73 ± 12.9 (11.04 - 46.32)</td>
<td>24.27 ± 22.62 (3.03 - 75.76)</td>
<td>11.1 ± 5.16 (4.76 - 30.16)</td>
</tr>
<tr>
<td><strong>Hydrochemistry</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrite (NO₂⁻)</td>
<td>[mg L⁻¹]</td>
<td>0.5 ± 0.36 (0.11 - 1.22)</td>
<td>0.13 ± 0.03 (0.11 - 0.19)</td>
<td>0.83 ± 1.31 (0.11 - 5.6)</td>
</tr>
<tr>
<td>Nitrate (NO₃⁻)</td>
<td>[mg L⁻¹]</td>
<td>114.05 ± 157.02 (10.17 - 425.15)</td>
<td>31.52 ± 12.87 (18.75 - 62.66)</td>
<td>27.16 ± 20.71 (2.32 - 92.18)</td>
</tr>
<tr>
<td>Ammonium (NH₄⁺)</td>
<td>[mg L⁻¹]</td>
<td>12.11 ± 23.95 (0.42 - 69.45)</td>
<td>1.16 ± 1.63 (0.12 - 3.04)</td>
<td>4.14 ± 7.39 (0.12 - 29.59)</td>
</tr>
<tr>
<td>Ion phosphate (PO₄³⁻)</td>
<td>[mg P L⁻¹]</td>
<td>1.85 ± 2.32 (0.13 - 6.38)</td>
<td>0.36 ± 0.39 (0.01 - 1.05)</td>
<td>0.44 ± 0.37 (0.01 - 1.61)</td>
</tr>
<tr>
<td>Total inorganic carbon (TIC)</td>
<td>[mg C L⁻¹]</td>
<td>22.51 ± 35.43 (1.46 - 93.4)</td>
<td>87.37 ± 2.79 (82.32 - 91.42)</td>
<td>74.9 ± 18.47 (18.71 - 107.77)</td>
</tr>
<tr>
<td>Total organic carbon (TOC)</td>
<td>[mg C L⁻¹]</td>
<td>64.86 ± 78.55 (10.43 - 221.51)</td>
<td>2.87 ± 1.08 (1.72 - 5.23)</td>
<td>20.44 ± 28.1 (1.2 - 120.42)</td>
</tr>
<tr>
<td>Dissolved inorganic carbon (DIC)</td>
<td>[mg C L⁻¹]</td>
<td>23.97 ± 38.55 (0.09 - 87.44)</td>
<td>80.07 ± 22.76 (3.74 - 92.31)</td>
<td>58.42 ± 27.26 (0.12 - 93.17)</td>
</tr>
<tr>
<td>Dissolved organic carbon (DOC)</td>
<td>[mg C L⁻¹]</td>
<td>50.11 ± 75.65 (3.16 - 228.9)</td>
<td>4.12 ± 3.85 (1.84 - 14.46)</td>
<td>21.6 ± 26.45 (1.3 - 111.8)</td>
</tr>
<tr>
<td>Total phosphorus (P)</td>
<td>[mg L⁻¹]</td>
<td>2.87 ± 1.9 (1.44 - 6.2)</td>
<td>0.64 ± 0.38 (0.35 - 1.26)</td>
<td>7.43 ± 7.2 (0.84 - 29)</td>
</tr>
<tr>
<td><strong>S-metolachlor</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Detection frequency in water</td>
<td>[%]</td>
<td>100</td>
<td>63</td>
<td>64</td>
</tr>
<tr>
<td>Water concentration (&lt; 0.7μm)</td>
<td>[μg L⁻¹]</td>
<td>26.98 ± 20.21 (0.36 - 64.1)</td>
<td>0.28 ± 0.53 (0 - 2.21)</td>
<td>4.14 ± 12.79 (0 - 62.09)</td>
</tr>
<tr>
<td>Enantiomeric excess (EE)</td>
<td>[μg kg⁻¹]</td>
<td>0.72 ± 0.05 (0.6 - 0.75)</td>
<td>0.68 ± 0.12 (0.34 - 0.74)</td>
<td>0.71 ± 0.15 (0.02 - 0.77)</td>
</tr>
<tr>
<td><strong>Acetochlor</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Detection frequency in water</td>
<td>[%]</td>
<td>40</td>
<td>38</td>
<td>45</td>
</tr>
<tr>
<td>Water concentration (&lt; 0.7μm)</td>
<td>[μg L⁻¹]</td>
<td>0.28 ± 0.55 (0 - 1.75)</td>
<td>0.15 ± 0.24 (0 - 0.85)</td>
<td>3.86 ± 12.32 (0 - 59.33)</td>
</tr>
<tr>
<td>SS concentration (&gt; 0.7μm)</td>
<td>[μg kg⁻¹]</td>
<td>7.43 ± 7.2 (0.84 - 29)</td>
<td>6.45 ± 6.2 (0.84 - 29)</td>
<td>7.12 ± 7.2 (0.84 - 29)</td>
</tr>
</tbody>
</table>
Focus on the event of May 22 2012

- T ≈ 40 year return period
- 20% rainfall, 53% total outflow
- 92% of suspended solids exported

What is the contribution of this large event for pesticides export?
Integrative approach at the catchment outlet

- Principal Component Analysis: 15 variables, 31 objects

- Hydrochemical conditions differed during May 22
- Samples before and after May 22 clustered together
**SOLID PHASE EXTRACTION (SPE)**

1. RINSING (MeOH, EA, DCM)
2. CONDITIONING (MeOH)
3. LOADING
4. WASHING & DRYING
5. ELUTION (DCM & EA)
6. CONCENTRATION

**GAS CROMATOGRAPHY (GC-MS/MS)**

- 190 µl of sample
- +
- 10 µl of internal standards Metolachlor D6 and Alachlor D13

**Extracted and concentrated sample**

Add 2 ml of DCM into GC vial

**RESULTS**

Program: Initial temperature 50°C (held for 2 min), 30°C min⁻¹ to 150°C, 5°C min⁻¹ to 250°C and finally 30°C min⁻¹ to 300°C held for 5 min. Inlet temperature is 280°C.
**Chloroacetamides extraction**

- **Conditionning**: 10 mL MeOH + 10 mL pure water
- **Sample loading**: Approximately 1 L at 10 mL/min
- **Washing**: 5 mL EA + 5 mL DCM
- **Drying** under nitrogen flux
- **Elution**: 3 mL EA, 2 mL DCM
  Evaporation under nitrogen flux and dissolution in 1 or 2 mL DCM
Enantiomeric analysis
Carbon isotopic composition reported as difference in CO$_2$ isotope ratio relative to an international standard (VPDB) in $\delta^{13}C$ [%] unit.
# GC-C-IRMS: Method validation

<table>
<thead>
<tr>
<th>Compound</th>
<th>EA- IRMS (standards)</th>
<th>GC-C-IRMS (standards)</th>
<th>GC-C-IRMS (extracted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetochlor</td>
<td>-29.8 ± 0.21</td>
<td>-29.5 ± 0.34</td>
<td>-30.1 ± 0.16</td>
</tr>
<tr>
<td>alachlor</td>
<td>-33.8 ± 0.05</td>
<td>-33.9 ± 0.19</td>
<td>-33.9 ± 0.33</td>
</tr>
<tr>
<td>metolachlor</td>
<td>-30.2 ± 0.06</td>
<td>-31.0 ± 0.22</td>
<td>-30.7 ± 0.26</td>
</tr>
</tbody>
</table>

- No significant difference between EA-IRMS and GC-C-IRMS
- Solid phase extraction method causes no significant fractionation
- Signal is linear within the measurement range

**EA-IRMS:** Elemental Analysis - Isotope Ratio Mass Spectrometry

**GC-C-IRMS:** Gas chromatography combustion isotope ratio mass spectrometry
Enantiomers enrichment: result of stereoselective biotransformation

- Enantiomeric Excess (EE) ranged between -0.02 and 0.77
- Export coefficient similar

\[ EE = \frac{S - R}{S + R} \]

- Enantiomeric shift before large application and in November
- Short sampling period
**Hydrology and erosion**

Mean runoff coefficient: 6% (0.03 – 57)

4.36 g L⁻¹ (0.02 – 24.72)

Total mass exported: 581 t
**Herbicides**

In water (< 0.7 µm):

<table>
<thead>
<tr>
<th></th>
<th>Number of samples (n)</th>
<th>S-metolachlor [%] (µg L⁻¹)</th>
<th>Acetochlor [%] (µg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Plot</strong></td>
<td>10</td>
<td>100% (64.1)</td>
<td>40% (1.8)</td>
</tr>
<tr>
<td><strong>Catchment</strong></td>
<td>33</td>
<td>60% (62.1)</td>
<td>45% (59.3)</td>
</tr>
</tbody>
</table>

**Detection frequency (Maximal concentration)**

- **Decreasing concentrations at the plot scale**
- **Export:** 198 g (S-metolachlor) and 347 g (acetochlor)
- >90% explained by 22, May.
- **Export rate?**