AMPA in the Vilaine watershed: sources, behavior and fate

Nancy, 05.16.2017

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AMPAn natural waters: its sources, behavior and environmental fate

Legend:
- Al-Fe oxides
- Soil particles
[reported maximum concentrations]
Reported half-life of AMPA in days

Grandcoin et al., 2017
Objectives

Is the AMPA in natural waters, mainly derived from glyphosate or phosphonates?

What sector (and how much) contributes to AMPA loads in natural waters?
Bibliography

Current knowledge of the AMPA contamination of the watershed

Determination of relevant locations for AMPA monitoring

Experimentations

Ponctual sampling of natural waters, 2 campaigns:
Classic conditions (10-20 mm rainfall)
Low water (no rain for 2 months)

Balance of in/outputs of WWTP (24h)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equipment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp, pH, cond, fDOM, Chlorophyll, %O₂, salinity, redox</td>
<td>EXO 2 probe</td>
</tr>
<tr>
<td>Diuron, DCPU, DCPMU, 3,4-DCA, chloroacetamids and ESA/OXA forms of chloroacetamids</td>
<td>HPLC-MS/MS</td>
</tr>
<tr>
<td>Glyphosate, AMPA</td>
<td>HPLC-Fluorimetry</td>
</tr>
<tr>
<td>NO₂, NO₃, NK, NH₄, Ptot, PO₄, UV Spectra, DOC, TOC, MES, DCO, DBO.</td>
<td>Various</td>
</tr>
</tbody>
</table>
Preliminary results
AMPAn and glyphosate in the watershed-1

Rennes upstream

<table>
<thead>
<tr>
<th>Condition</th>
<th>AMPA FOD (%)</th>
<th>Glyphosate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Classic</td>
<td>100</td>
<td>33</td>
</tr>
<tr>
<td>Low water</td>
<td>92</td>
<td>46</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Condition</th>
<th>Min (µg/L)</th>
<th>Max (µg/L)</th>
<th>Median (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Classic</td>
<td>0.23</td>
<td>2.10</td>
<td>0.72</td>
</tr>
<tr>
<td>Low water</td>
<td>0.10</td>
<td>2.48</td>
<td>1.09</td>
</tr>
</tbody>
</table>

Classical conditions (19 samples)

Min (µg/L) 0.08
Max (µg/L) 0.17
Median (µg/L) 0.11

Flux AMPA = 79 kg/day
Gly < LQ

Rennes downstream

<table>
<thead>
<tr>
<th>Condition</th>
<th>AMPA Flux</th>
<th>Glyphosate Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Classic</td>
<td>809 kg/day</td>
<td>100 kg/day</td>
</tr>
<tr>
<td>Low water</td>
<td>693 kg/day</td>
<td></td>
</tr>
</tbody>
</table>

Classic
Gly < LQ

Low water
Flux AMPA = 98 kg/day
Gly < LQ
AMP A and glyphosate in the watershed-2

Vilaine (Main river)

Classic
Flux AMPA = 288 kg/day
Gly < LQ

Low water
Flux AMPA = 60 kg/day
Gly < LQ

« Oust » (Main affluent)

Q ≈ 40% Q(Vilaine)

Classic
Flux AMPA = 37 kg/day
Flux Gly = 12 kg/day

Low water
Flux AMPA = 8 kg/day
Gly < LQ
### Correlation matrices (Pearson)

<table>
<thead>
<tr>
<th>Classic conditions</th>
<th>Positive correlation</th>
<th>AMPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>fDOM</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>NH4</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>PO4 / P total</td>
<td>0.62 / 0.45</td>
<td></td>
</tr>
<tr>
<td>TOC / DOC</td>
<td>0.44 / 0.29</td>
<td></td>
</tr>
</tbody>
</table>

### Influencing parameters

- AMPA is not correlated to Gly

- AMPA is correlated to Gly

<table>
<thead>
<tr>
<th>Negative correlation</th>
<th>Glyphosate</th>
<th>pH</th>
<th>O2 dissolved</th>
<th>NO3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glyphosate</td>
<td>-0.13</td>
<td>-0.31</td>
<td>-0.40</td>
<td>-0.65</td>
</tr>
<tr>
<td>pH</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O2 dissolved</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Pesticides and influencing parameters

Classique

- AMPA (µg/L)
- NH4 (mg/L)
- PO4 (mg/L)
- Glyp (µg/L)

Distribution along the river-1

Concentration

Stream flow (m³/s)

Upstream Downstream

Ille Meu Seiche Oust Isac

Rennes
Distribution along the river-2

Pesticides and influencing parameters

AMP A (µg/L)
NH4 (mg/L)
PO4 (mg/L)
Glyp (µg/L)

Low water

Upstream: Ille, Meu, Seiche
Downstream: Oust, Isac
Balance of in/outputs of a WWTP

AMPA is quantified in all samples
Glyphosate is quantified in only 1 sample

Elimination of AMPA 30-70% (Biological treatment)
55-90% (Membranes treatment)

Inlet
[AMPA] = 3 - 15 µg/L
[Gly] = 0 - 1.64 µg/L

Outlet
[AMPA] = 1 - 5 µg/L
[Gly] < LQ

Upstream
[AMPA] = 0.66 µg/L
[Gly] = 0.11 µg/L

Downstream
[AMPA] = 2.35 µg/L
[Gly] < LQ
Comparison of fluxes WWTP/Stream

Outlet
- $Q (B) = 2161 \text{ m}^3/\text{day}$
- Flux (B) AMPA = 8.01 kg/day
- $Q (M) = 1402 \text{ m}^3/\text{day}$
- Flux (M) AMPA = 2.91 kg/day

Low water
- $Q = 3400 \text{ m}^3/\text{day}$
- Flux AMPA = 2.24 kg/day

Upstream
- $Q (B) = 2161 \text{ m}^3/\text{day}$
- Flux (B) AMPA = 8.01 kg/day
- $Q (M) = 1402 \text{ m}^3/\text{day}$
- Flux (M) AMPA = 2.91 kg/day

100m 300m
Conclusions

AMPA in the Vilaine watershed, is derived from both glyphosate and phosphonates

Urban area increases AMPA load in the Vilaine, and with more reason in low water conditions

WWTP increases x5 the AMPA loads in the receiving stream under low water conditions
Thank you for your attention!