EXPOSURE TO GLYPHOSATE: SHOULD WE WORRY?

Sílvia Lacorte
Department of Environmental Chemistry, IDAEA-CSIC, Barcelona
Top 10 pesticides by usage in Spain (out of 350)

- Glyphosate
- Metam sodium
- Mancozeb
- Chlorpyriphos
- 2,4-D
- Dimethoate
- MCPA
- Fosetil-al
- Isoproturon
- Oxifluorfen

Total consumption: 2,880 tonnes
4,941-3,303,816 ha treated

11% treated area in Spain

Tonnes of glyphosate
(Spain, 2013)
**Glyphosate**

**Formulation:** more than 130 formulations

**Active ingredient:** from 0.7% for domestic use to 68% for agriculture

**Application:** more than 60 types of crops

**Amount applied:** 0.59-1.49 kg/ha, 1 or 2 times/year

**Action mode:** systemic pesticide, resistance identified

**ECHA:** High production chemical

**Legislation:** Reg. EC 1107/2009 until 31/12/2017
## Glyphosate

![Glyphosate Structure](image)

<table>
<thead>
<tr>
<th>Property</th>
<th>Glyph</th>
<th>AMPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility (g L⁻¹)</td>
<td>10.5</td>
<td>&gt; 100</td>
</tr>
<tr>
<td>VP (mPa)</td>
<td>0.0131</td>
<td>0.0231</td>
</tr>
<tr>
<td>Kd (mL g⁻¹)</td>
<td>5-900</td>
<td>15-1554</td>
</tr>
<tr>
<td>GUS</td>
<td>-0.25</td>
<td>0.03</td>
</tr>
<tr>
<td>DT50 soil (d)</td>
<td>15</td>
<td>121</td>
</tr>
<tr>
<td>DT50 water (d)</td>
<td>74</td>
<td>132</td>
</tr>
<tr>
<td>BCF (L kg⁻¹)</td>
<td>0.5</td>
<td>-</td>
</tr>
</tbody>
</table>
Trace level analytical determination

AMP A,  
$m/z$ 112.0158

Glyphosate,  
$m/z$ 168.0067

Analytical problems
- Extraction difficulties
- Sensitivity
- Time consuming methods
- Complex instrumentation

High cost

Reliability of results
Not many studies...

Le Fur et al., 2000. Analyst 28;
Hanke et al., 2008. anal. Bioana.Chem 391
Use patterns and fate

- Formulation
- Doses
- Application period
Degrades

Volatilization

Leaching

Bioaccumulation
Degrades
Run-off to surface waters
Sorb to soil and may accumulate in crops
European Drinking Water Directive 98/83/EC prescribes maximum admissible concentrations of 0.1 µg L\(^{-1}\), but this level does not reflect ecological or human toxicity.

<table>
<thead>
<tr>
<th>Europe</th>
<th>Sites</th>
<th>Sample</th>
<th>%&lt; 0.1</th>
<th>%&gt; 0.1</th>
<th>µg L(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surface waters</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glyph.</td>
<td>3716</td>
<td>50805</td>
<td>29</td>
<td>23</td>
<td>0.03-427</td>
</tr>
<tr>
<td>AMPA</td>
<td>2728</td>
<td>33612</td>
<td>50</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td><strong>Groundwater</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glyph.</td>
<td>8925</td>
<td>36298</td>
<td>1.3</td>
<td>0.7</td>
<td>0.02-4.8</td>
</tr>
<tr>
<td>AMPA</td>
<td>7678</td>
<td>27254</td>
<td>1.7</td>
<td>0.9</td>
<td></td>
</tr>
</tbody>
</table>

Battaglin et al, 2014, JAWRA, 50
Padilla-Sanchez et al., 2012, J. Mass Spectrom. 47, 1458
Foodstuff 60-240 µg kg⁻¹

Fruit, vegetable and derivatives

Farm animals

Tap water

Crops

Food

12% samples 0.2-2.3 mg kg⁻¹

7-12000 µg L⁻¹

7-12000 µg kg⁻¹

Few studies (n=635), 12% of samples, low residues

levelshttp://www.glyphosate.eu/database/fact-sheet
### Maximum Residue Levels (Reg. EU No 293/2013)

<table>
<thead>
<tr>
<th>Category</th>
<th>mg kg(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citrus</td>
<td>0.1-0.5</td>
</tr>
<tr>
<td>Tree nuts</td>
<td>0.1</td>
</tr>
<tr>
<td>Pome &amp; stone fruits</td>
<td>0.1</td>
</tr>
<tr>
<td>Berries</td>
<td>0.1-0.5</td>
</tr>
<tr>
<td>Miscellaneous fruits</td>
<td>0.1</td>
</tr>
<tr>
<td>Vegetables, fresh, frozen</td>
<td>0.1-3</td>
</tr>
<tr>
<td>Brassica</td>
<td>0.1</td>
</tr>
<tr>
<td>Leaf vegetables</td>
<td>0.1</td>
</tr>
<tr>
<td>Legumes</td>
<td>0.1</td>
</tr>
<tr>
<td>Fungi</td>
<td>0.1-50</td>
</tr>
<tr>
<td>Pulses</td>
<td>2-10</td>
</tr>
<tr>
<td>Oilseeds and oil fruit</td>
<td>0.1-20</td>
</tr>
<tr>
<td>Cereals</td>
<td>0.1-20</td>
</tr>
<tr>
<td>Teas and infusions</td>
<td>0.1-20</td>
</tr>
<tr>
<td>Species</td>
<td>0.1</td>
</tr>
<tr>
<td>Meats</td>
<td>0.05</td>
</tr>
</tbody>
</table>

#### Exposure (mg kg\(^{-1}\) bw d\(^{-1}\))

\[
EDI = \frac{\sum F_i x C_i}{bw} = \frac{0.6 mg}{60 kg} = 0.01
\]

\[
ADI = \frac{\sum F_i x C_i}{bw}
\]

- 0.3 EU
- 0.5 EFSA
- 1.75 USA

#### % ADI

\[
% ADI = \frac{0.01 \times 100}{0.3} = 3.3\
\]

Impact on human health

**Glyphosate**
- Toxicity 2000 mg/kg rat
- Skin irritant
- Eye irritant
- Potential carcinogen
- Potential EDC

**AMPA**
- 8300 mg/kg rat
- Tract irritant
- Skin sensitizer
- Eye irritant
- Phototoxicant
- Probable liver and kidney toxicant

**Risk?**
- Dose
- Frequency of exposure
- Vulnerability
- Formulation

Richard et al., (2005) EHP 113
Effects in humans

Toxicological endpoints at **low concentration level**: estrogenicity, genotoxicity, oxidative stress, reproduction, neurologic, metabolism, behaviour, etc.

Permitted level in EU tap water

0.1 1

Mammary tumors
Séraline 2014 Environmental Sciences Europe 26

MRL in foodstuff

10

No myeloma
Sorahan 2015, IJERPH 12

Permitted level in US tap water

100 700 1000 ppb

Urine
Not in breast milk
Mcguirre 2016 AJCN 103

Mesured exposure range (biomonitoring)
Solomon 2016 Crit. Rev. Toxicol, 46
Conclusions

**ENVIRONMENTAL CONTAMINANTS**

- **Detected in the environment and foods**
- **Produced in large quantities**
- **Some adverse effects known**
- **Why not legislated?**

**NEEDS**

- **Analytical**: ensure reliability of the results for waters and soil: intercomparison studies.
- **Environmental**: higher sampling frequency required to provide a conclusive picture of pesticide occurrence.
- **Food**: far more food quality control analysis.
- **Toxicity**: identification of toxicological endpoints at low concentration level.
Thank you for your attention