Presence of Glyphosate and its soil metabolite aminomethylphosphonic acid (AMPA) in surface water

What does it mean for human health and the environment ?

Dr Richard P. Garnett
Chemical Regulatory Lead EMEA
Monsanto Europe

XIV Symposium in Pesticide Chemistry - Pesticides in the Environment : fate, modelling and risk mitigation

Content

- Introduction
- AMPA and aminophosphonates
- Impact of the presence of glyphosate and AMPA in surface water:
  - on the environment
  - on human health

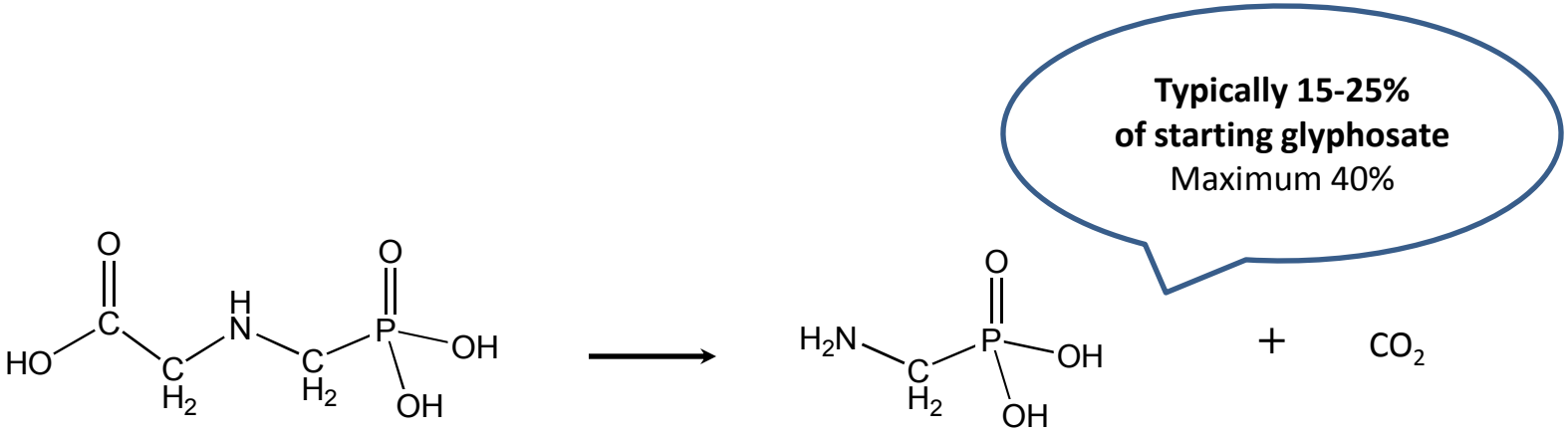
INTRODUCTION

Glyphosate has a uniquely wide range of uses

- Broad spectrum:
  - broad-leaved weeds & grasses
  - annual & perennial weeds
- Agricultural weed control
  - arable crops, grassland, fruit & vines, horticulture
  - crop selectivity
    - by timing e.g. pre-plant
    - by placement e.g directed spray
  - new developments
    - “conservation tillage”
    - “harvest aid”
- Vegetation management in non-crop areas
  - streets, roads & railways
  - parks & home gardens
  - Forestry
- Aquatic or semi-aquatic use

AMPA and Glyphosate

AMPA is the major metabolite of Glyphosate in the environment



Glyphosate

Aminomethylphosphonic acid
(AMPA)

Further mineralisation

Potential to reach surface water throughout the year

MONSANTO imagine®

Diffuse sources

- Spray drift
- Run-off
- Drainage

Point sources

- Bad practices, e.g.
- Mixing & loading
- Sprayer cleaning

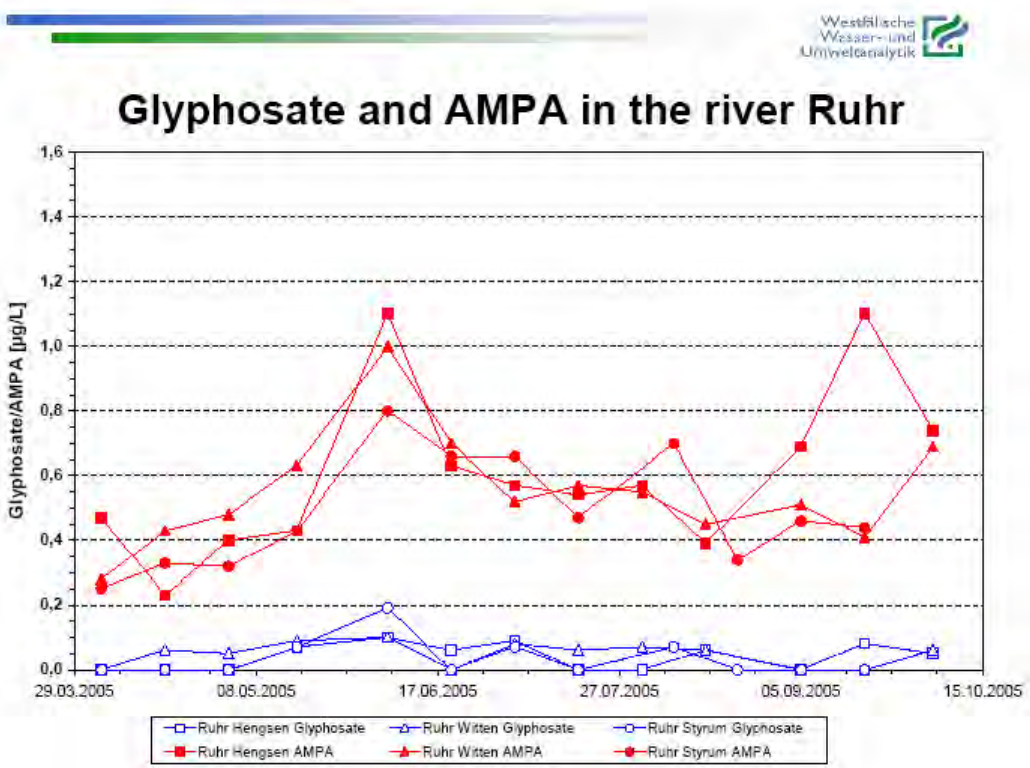
Glyphosate and AMPA presence in surface water from European monitoring studies

	Monitoring period	*No. of samples*	*No.of detects*	*% detects*
Glyphosate	**1993-2009**	**≥50805**	**≥14704**	**≥29**
AMPA	**1997-2009**	**≥33812**	**≥17119**	**≥45**

Toolbox for the sustainable use of glyphosate (http://www.egeis-toolbox.org/toolbox.html)

Monitoring data show

More frequent detects of AMPA compared to glyphosate , and at higher concentration in large rivers

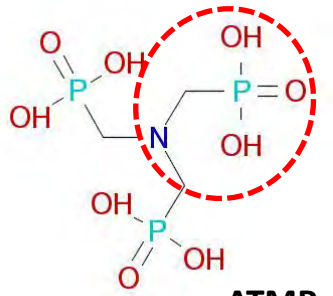


Claus Schlett (Gelsenwasser), Presentation during a Monsanto seminar 'Glyphosate and Water', Brussels, November 2005

AMPA AND AMINOPHOSPHONATES

AMPA and aminophosphonates

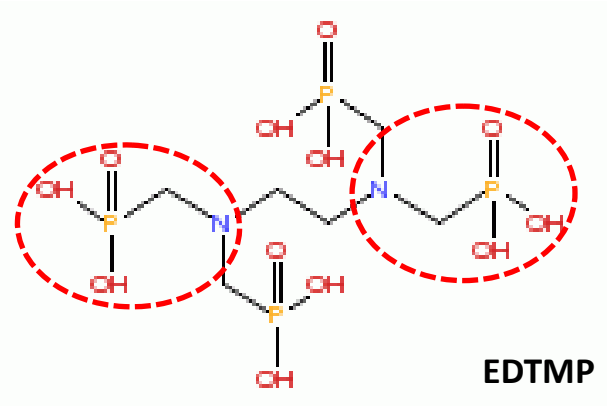
Four widely used aminophosphonates can degrade into AMPA



ATMP

Amino tris(methylenephosphonate)

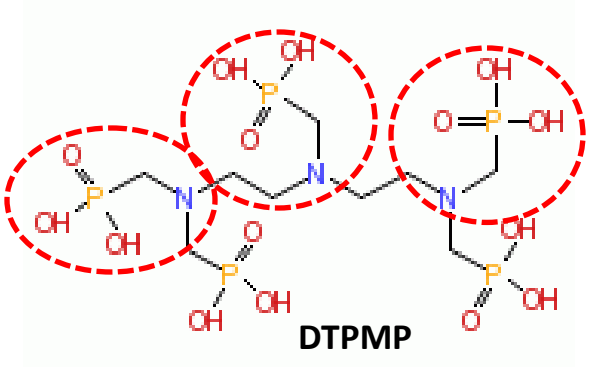
Industrial boilers/ cooling



EDTMP

Ethylenediamine tetra(methylenephosphonate)

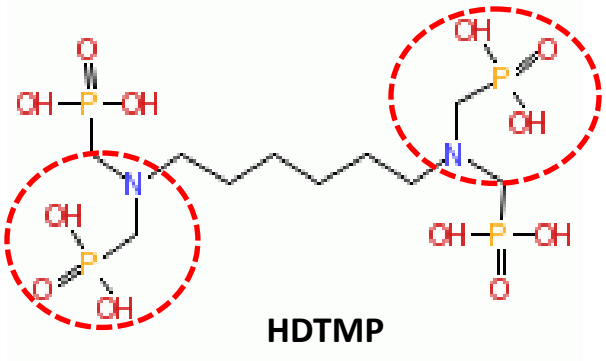
Laundry detergents



DTPMP

Diethylenetriamine penta(methylenephosphonate)

Laundry detergents



HDTMP

Hexamethylenediamine tetra(methylenephosphonate)

Industrial boilers/ cooling

AMPA and laundry detergents

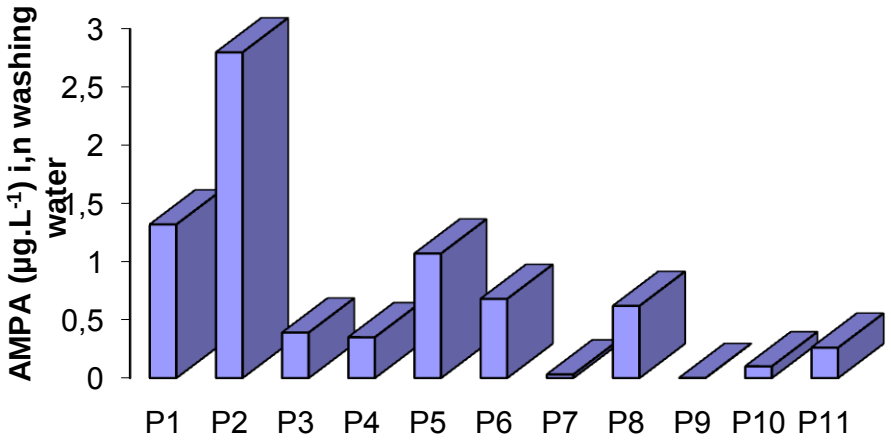
- Study conducted to determine the:
  - Presence of AMPA in commercial laundry detergents
  - Presence of AMPA in technical phosphonates
  - Formation of AMPA during a laundry washing cycle
- 17 detergents tested
  - Powders and liquids – different brands
- Detergent concentrations in accordance with the recommendations of the manufacturers
- Washing cycle of 1 hr with 10 L of water was simulated at different temperatures

A. Jadas-Hécart, G.Morin, P.Y. Communal, (2010) Aminophosphonates des lessives : une potentielle source d'AMPA ?

AMPA and laundry detergents

Powder detergent	AMPA in µg/L "washing" water	AMPA in µg/g detergent
P1	1.32	0.18
P2	2.8	0.27
P3	0.39	0.04
P4	0.35	0.04
P5	1.07	0.11
P6	0.68	0.07
P7	0.03	0.003
P8	0.62	0.09
P9	0	0.00
P10	0.1	0.01
P11	0.26	0.025

AMPA was present in all 11 commercial **powder** detergents (different brands) and in the corresponding 'washing water'[1]

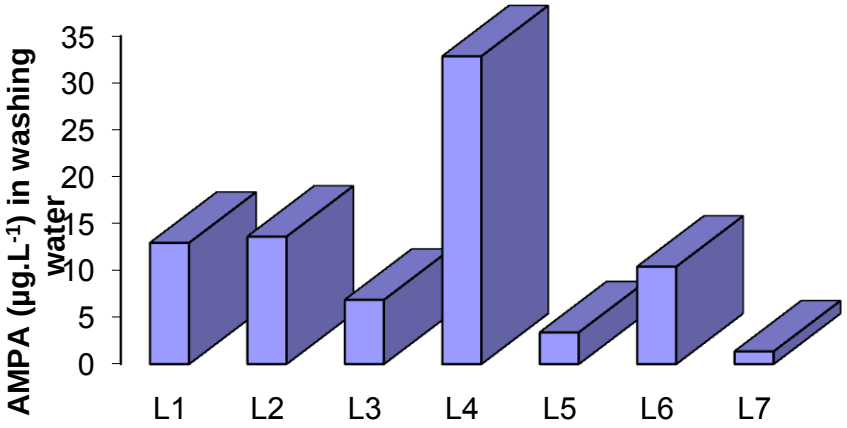


[1] i.e. the content in the water at the output of the washing machine

AMPA and aminophosphonates

Liquid detergent	AMPA in µg/L "washing" water	AMPA in µg/g detergent
L1	12.94	3.50
L2	13.6	3.68
L3	6.85	1.85
L4	32.85	5.21
L5	3.38	0.43
L6	10.39	0.82
L7	1.35	0.17

AMPA present in all 7 commercial **liquid** detergents (different brands) and in the corresponding 'washing water'[1]



[1] i.e. the content in the water at the output of the washing machine

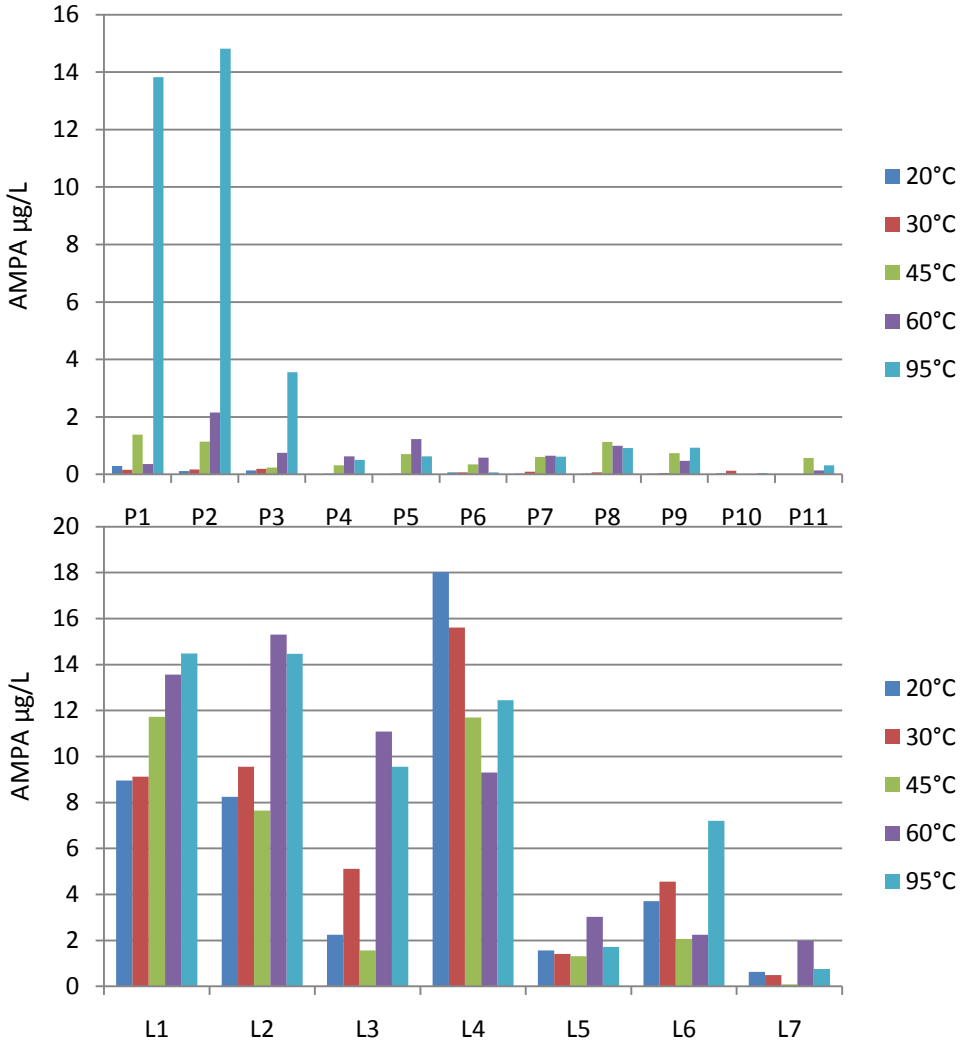
AMPA and aminophosphonates

Presence of AMPA in technical phosphonates

- A sample of technical DTPMP (used in laundry detergents) contained 1240 µg AMPA/g DTPMP (~0.1% w/w)
- This could explain the presence of AMPA in liquid detergents
  - assume 70 g detergent /washing cycle (10L water)
    - 70 g/10L water – 7g detergent/L water
  - assume 0.2 – 0.4% of aminophosphonate in detergents
    - 14-28 mg phosphonate/L water
  - with AMPA present as a 0.1% impurity
    - 14-28 µg AMPA/L water
- An IPCS (http://www.inchem.org/) publication lists AMPA as a 1% impurity in technical ATMP

AMPA and aminophosphonates

Formation of AMPA during laundry washing cycle at different temperatures



<u>Powder detergents</u>

- Significant increase in AMPA formation for 3 powder detergents at 95°C

<u>Liquid detergents</u>

- No significant impact of temperature on AMPA formation

AMPA and aminophosphonates

Is AMPA removed during sewage treatment ?

Laundry washing effluents are not directly discharged into surface water, but are usually[1] cleaned in a sewage plant

Locations/time	Influent (total mass g)	Effluent (total mass g)	% effluent/influent
Doordrecht (May)	219.5	318.3	145
Doordrecht (Sept)	407.1	398.3	98
Zwijndrecht (May)	259.8	347.4	134
Papendrecht (June)	141.5	336.9	238

Withagen et al (2004) Resultaten monitoring afspoeling glyphosaat and AMPA en waarnemingen van onkruidbeelden in zeven proefgemeentes (voorjaar and najaar 2003) , Plant Reseach International, Nota 297

→ **AMPA is not removed by sewage treatments**

[1] Note that, in some countries, there are no treatment facilities in smaller villages and so household waste water enters surface waters untreated.

IMPACT ON ENVIRONMENT

Impact on the environment

- Monitoring data are often compared to the drinking water standard : 0.1 µg/L
  - Surrogate zero without protective or ecotoxicological significance
- Surface water concentrations should be compared to a biological effect concentration or Environmental Quality Standard (EQS).
  - EQS values can be well above 0.1 µg/L
- For glyphosate and AMPA, no European EQS value has been set
  - biological effects are observed at concentrations well above 0.1 µg/L (*http://www.egeis-toolbox.org/toolbox.html*)
    - Lowest NOEC (EU review) *0.28 mg a.e./L* (marine alga *Skeletonema costatum)*
    - Using statistical evaluation (Species Sensitivity Distribution), an acceptable concentration for long term effects could be up to 425 µg/L
  - Sweden has set an EQS of 10 µg/L for glyphosate (based on conservative assumptions) and 500 µg/L for AMPA
  - These values are well above the levels observed in surface water

Impact on the environment

90th percentiles of the levels observed in surface water monitoring in France

Monitoring period	*97-06*	*1997*	*1998*	*1999*	*2000*	*2001*	*2002*	*2003*	*2004*	*2005*	*2006*
Glyphosate (µg/L)	**0.71**	**1.23**	**0.86**	**0.92**	**0.76**	**0.70**	**0.76**	**0.80**	**0.62**	**0.80**	**0.67**
AMPA (µg/L)	**1.3**			**1.05**	**0.92**	**0.93**	**0.90**	**1.67**	**1.20**	**1.30**	**1.30**

The risk to the aquatic environment from the levels observed in surface water is negligible

ISL (Février 2009, Analyse de donne de suivi de l'AMPA et du glyphosate dans les eaux de France – Periode 1999-2006 (*unpublished report*)

IMPACT ON HUMAN HEALTH

Impact on human health

- Humans are exposed to surface water through the consumption of abstracted drinking water
- Studies have shown that glyphosate and AMPA are efficiently removed by chemical/oxidative disinfection
  - the oxidation by-products are also degradation products of natural substances[1]
- Complemented by other water treatment processes
  - less efficient but usually not used in isolation
- Most water treatment processes are necessary when there is no glyphosate or AMPA (or other pesticdes) present
- Glyphosate and AMPA are of low toxicity to humans, and the toxicological threshold for drinking water is 4 orders of magnitude higher than the 0.1 µg/L EU drinking water trigger (EU ADI : 0.3 mg/kg bw/day – 70 kg person – 21 mg/day – 10% allocated to water – 2L water /day – thus 1000 µg/L)

Brosillon, S., Wolbert, D., Lemasle, M., Roche, P. and Mehrsheikh, A. (2006). Chlorination kinetics of glyphosate and its by-products: modelling approach. *Water Research,* Vol. 40, no. 11, pp. 2113-2124.

Removal of glyphosate and AMPA by standard drinking water processes

Treatment Process	Glyphosate removal (%)	AMPA removal (%)
Bank and dune filtration	20 to 50	25 to 95
Aluminium coagulant and clarification	15 to 40	20 to 25
	Not a reliable barrier for Glyphosate and AMPA	
Iron coagulant and clarification	40 to 70	20 to 85
	Not a reliable barrier for Glyphosate and AMPA	
Slow sand filtration	Insufficient information but likely to be less effective than bank or dune filtration and therefore of little practical benefit	
Chlorination	74 to > 99	40 to >95
	Likely to provide the main barrier to Glyphosate and AMPA at most water treatment works	
Ozonation	60 to >99	25 to 95
	Provides an additional barrier at works where already installed for other pesticides and micropollutants	
Activated carbon adsorption	10 to 90	20 to 70
	Higher removals relate to virgin GAC and are unlikely to be achieved under practical conditions. Not a reliable barrier for Glyphosate and AMPA.	
Membrane filtration	>90 (NF/RO) >50 (UF)* *depending on membrane type	>95 (NF/RO) No information found for UF
	Membrane processes not widely used in water treatment, and unlikely to be installed solely as a barrier to pesticides and other organic micropollutants.	

Toolbox for the sustainable use of glyphosate (http://www.egeis-toolbox.org/toolbox.html)

Performance of typical water treatment processes for glyphosate

Assumption of glyphosate removal (conservative)

Bankside/dune infiltration	30%
Chemical coagulation/clarification/filtration	20%
Slow sand filtration	20%
Ozonation	95%
GAC	20%
Chlorination	95%

Using the above assumptions, the maximum level of glyphosate allowed in raw water can be calculated for different process streams, in order to achieve the 0.1 µg/L level in drinking water

Conclusion

- Glyphosate can be found in surface water due to its wide range of applications
- AMPA is the major soil metabolite of glyphosate, but also a degradate of other aminophosphon
- These industrial chemicals contribute significantly to the presence of AMPA in surface water.
- Although Glyphosate and AMPA can be found in surface water, the levels observed are well below the biological effect levels and are thus not a threat to the aquatic environment
- The toxicologically based threshold for glyphosate and AMPA in drinking water is 4 orders of magnitude higher than the 0.1 µg/L trigger.
- Glyphosate and AMPA are effectively removed by common surface water treatment processes – their presence in surface water are thus not a threat to human health