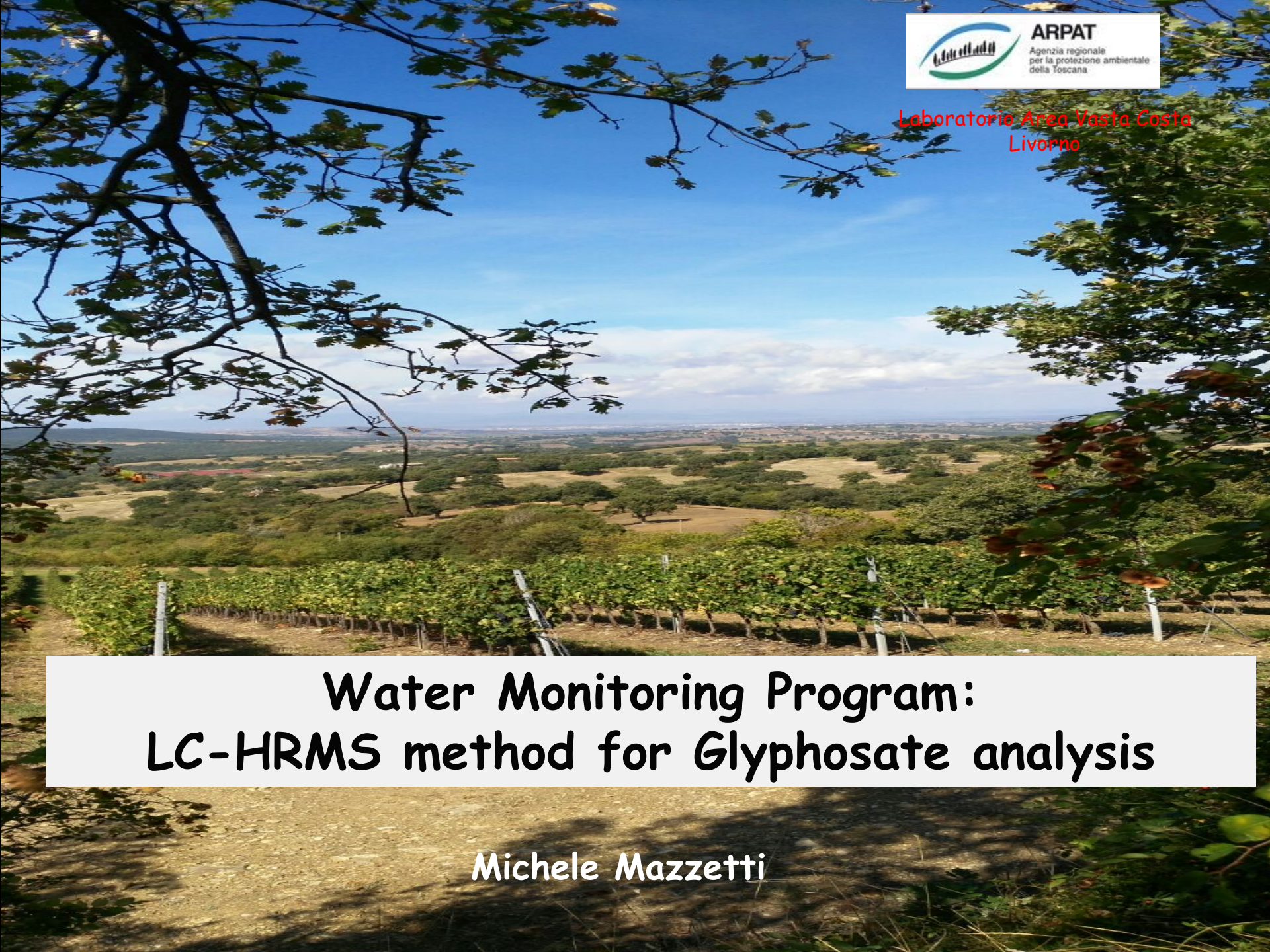


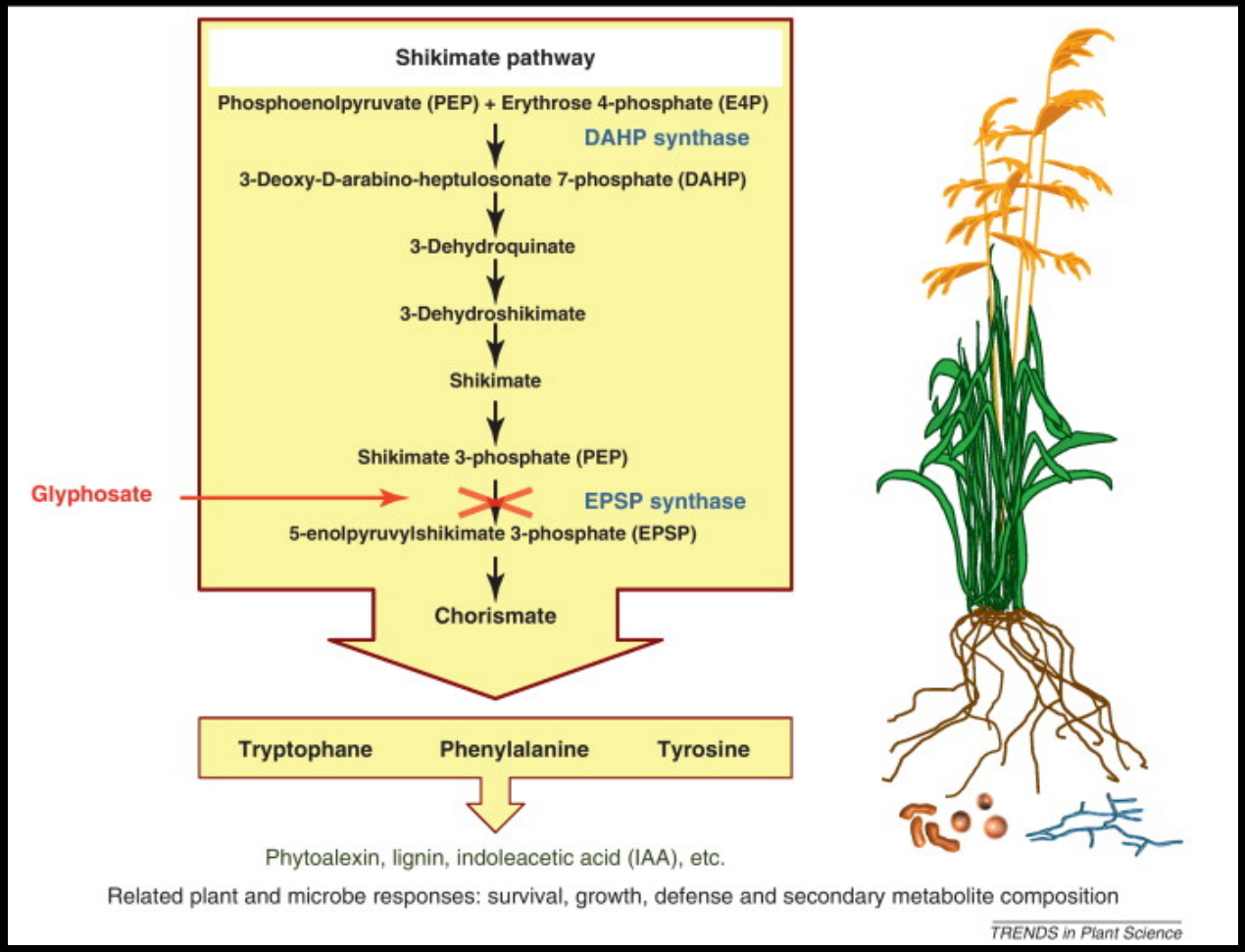
ARPAT
Agenzia regionale per la protezione ambientale della Toscana

Laboratorio Area Vasta Costa
Livorno

Water Monitoring Program: LC-HRMS method for Glyphosate analysis

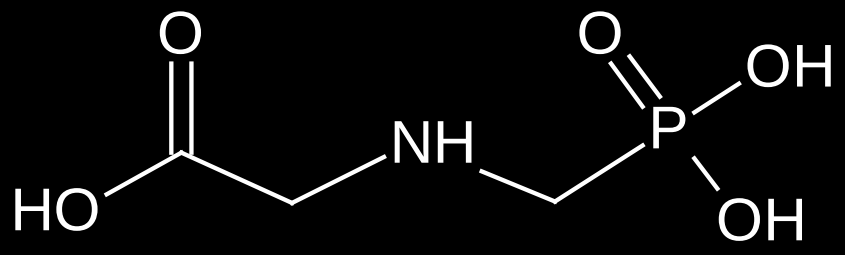
Michele Mazzetti

Glyphosate, is a broad-spectrum herbicide widely used in the world.. It is representative of a broad class of compounds, known as phosphonic acids, which contain a direct carbon-to-phosphorus (C-P) bond.



Glyphosate kills plants and bacteria by inhibiting the bacterial and plant enzyme enolpyruvylshikimate-phosphate synthase (EPSPS).

Trends in Plant Science, Volume 17, Issue 10, October 2012, Pages 569–574

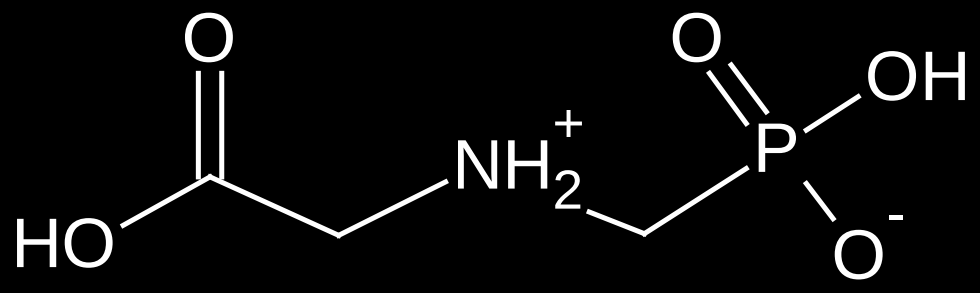


Common Name ISO: GLYPHOSATE

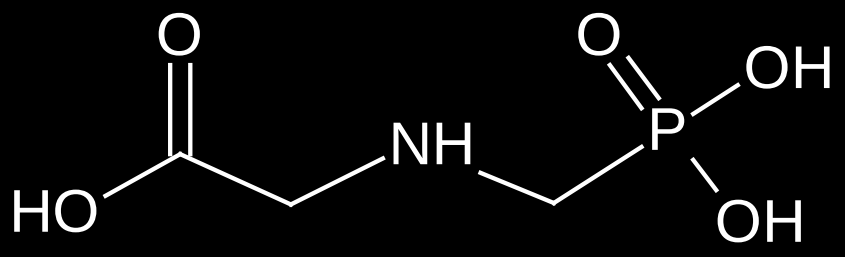
Chemical name IUPAC: N-(phosphonomethyl)-glycin

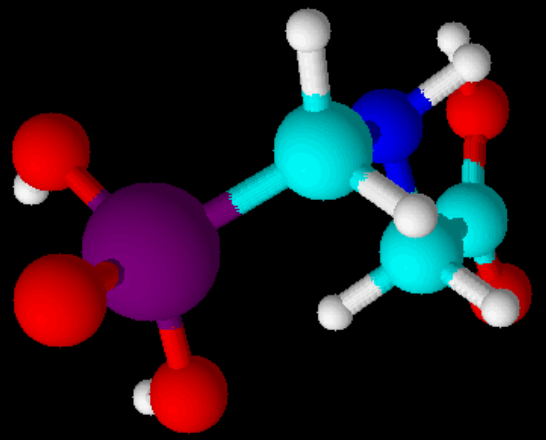
Solvent	Solubility	Solvent	Solubility
Water	**pH 2: 10.5 ± 0.2 g/l 20 °C, 995 g/kg**	Methanol	0.231 g/l
Acetone	0.078 g/l	n-Octanol	0.020 g/l
Dichloromethane	0.233 g/l	Propan-2-ol	0.020 g/l
Ethylacetate	0.012 g/l	Toluene	0.036 g/l
Hexane	0.026 g/l		

Glyphosate is a zwitterion, as illustrated in figure and has four dissociation constants (pKa),



Acid Dissociation Constants of Glyphosate	Value of Dissociation Constant of Glyphosate	Dissociated Proton in Glyphosate
pKa_1	0,8	First phosphonic
pKa_2	2,3	Carboxilate
pKa_3	6,0	Second phosphonic
pKa_4	11,0	Amine



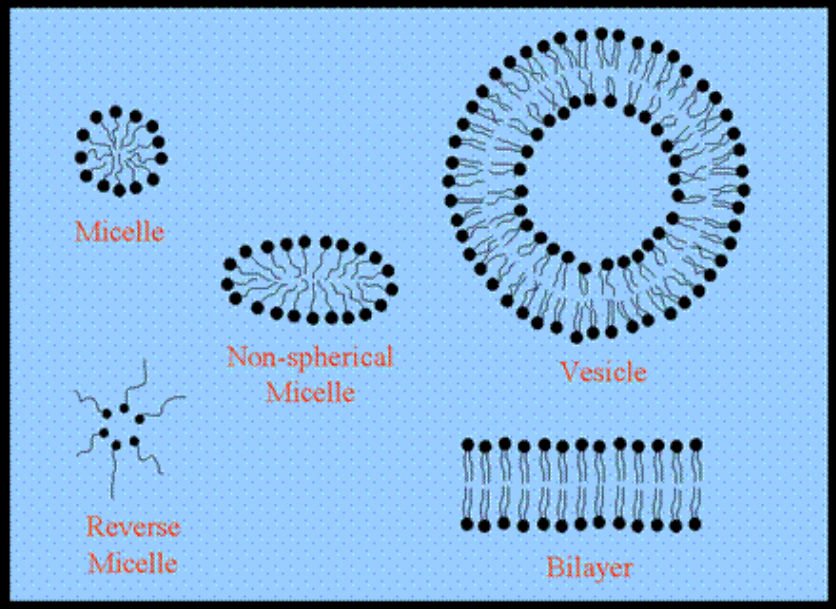


The molecule of glyphosate can be envisioned as a polydentate and/or monodentate ligand that binds to "substrates" via the oxygen atoms. These molecular characteristics of glyphosate have major implications in its mode of herbicide action and in the sorption behavior of glyphosate on soils/sediments.

In the environmentally significant pH range of 5 to 9, the first phosphonic and carboxylate protons are fully dissociated. The dissociation of the second phosphonic proton increases above pH 6, but the amine proton is unlikely to dissociate in the environment.

The pH-dependent dissociation of glyphosate determines the speciation of glyphosate in aquatic systems. However, the estimation of environmental exposure concentration in water does not take into account the dissociation of glyphosate in water. The effect toxicity of each dissociated form of glyphosate is not known .

Colloidal transport



Particulate size in disperse phase range from 5 to 200 nanometers
3 DeLonge, L.W., Kjaergaard, and Moldrup, P. 2004. Colloids and Colloid-Facilitated Trnsport of Contaminats in Soils: An Introduction. Vadose Zone Jounar, Vol, pp 321-325.

The environmental fate studies conducted on soil and water-sediment systems do not take into account the adsorption of glyphosate onto colloidal-range particulates.

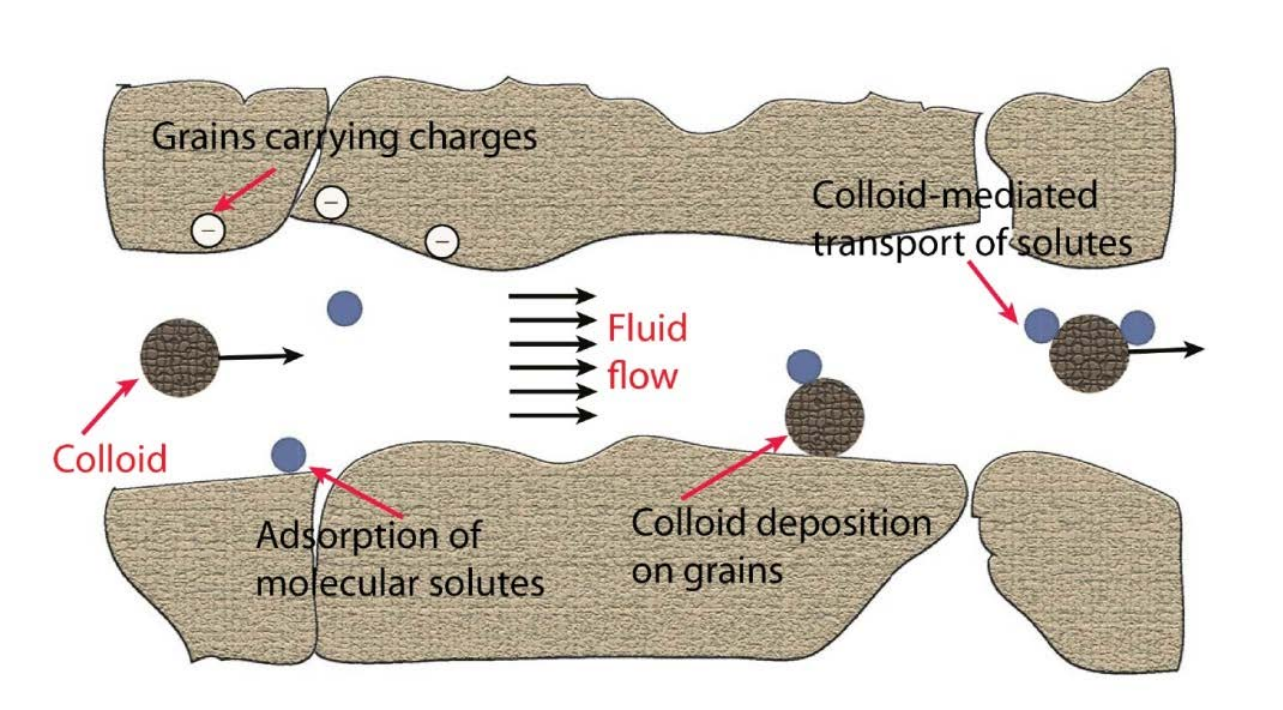
The importance of particulate matter in the transport of pollutants and subsequent deposition is recognized.

Since glyphosate adsorbs strongly to soil particulates, the higher surface area of colloidal matter may result in higher concentrations of glyphosate when compared to higher particulate sizes.

That is, colloidal particulates could behave as "scavengers" of glyphosate. Transport of glyphosate by colloids have the potential for off-site deposition

Colloidal transport

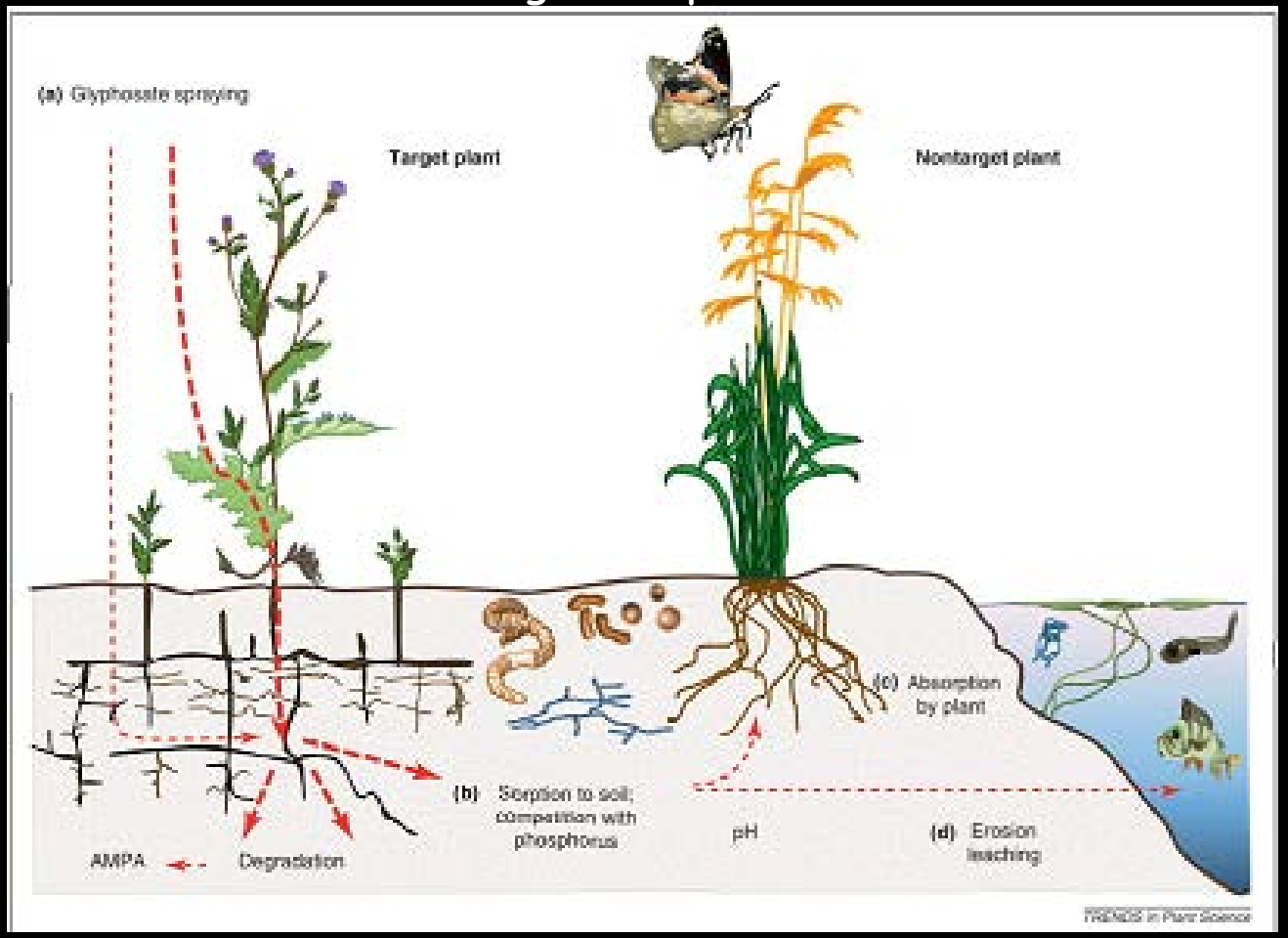
Presence of colloidal matter in natural waters can vary with season. Furthermore, the concentration distribution of the chemical through a water body is not likely to be omogenous. Therefore, the estimated environmental concentrations in water could be overestimated or underestimated at specific sites.



Geological Disposal of Nuclear Waste: Fate and Transport of Radioactive Materials,

By Prabhakar Sharma DOI: 10.5772/50391

In the soil environment, glyphosate is resistant to chemical degradation, is stable to sunlight, is relatively nonleachable, and has a low tendency to runoff (except as adsorbed to colloidal matter). It is relatively immobile in most soil environments as a result of its strong adsorption



Glyphosate is highly soluble in water. The hydrolysis half-life is >35 days (Kollman and Segawa, 1995). Studies conducted in Manatoba Canada (Kirkwood, 1979) suggest that glyphosate's loss from water is through sediment adsorption and microbial degradation

Trends in Plant Science, Volume 17, Issue 10, October 2012, Pages 569–574

Glyphosate's primary route of decomposition in the environment is through microbial degradation in soil (Franz et al. 1997). The herbicide is inactivated and biodegraded by soil microbes at rates of degradation related to microbial activity in the soil and factors that affect this activity (Eriksson, 1975).

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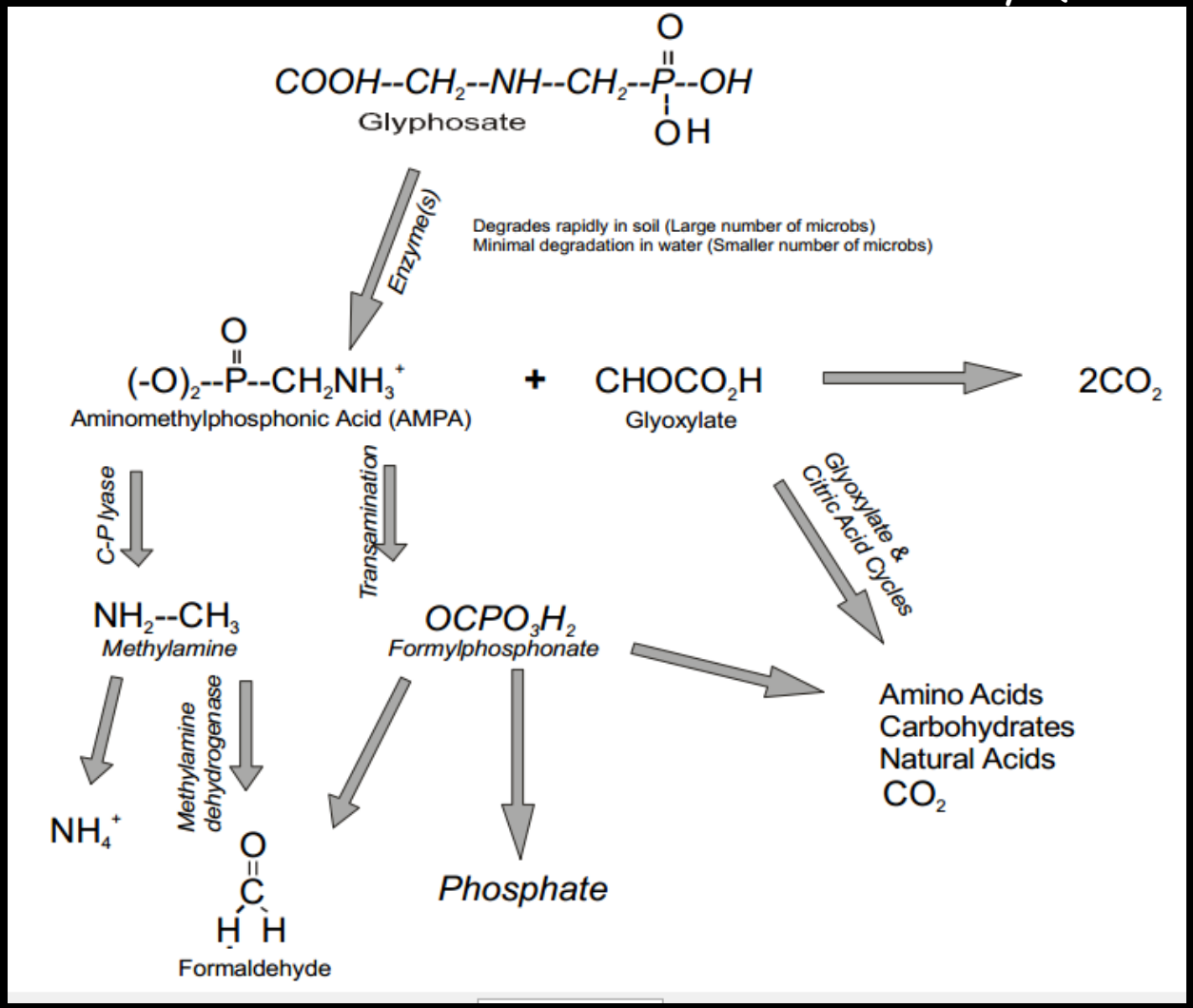
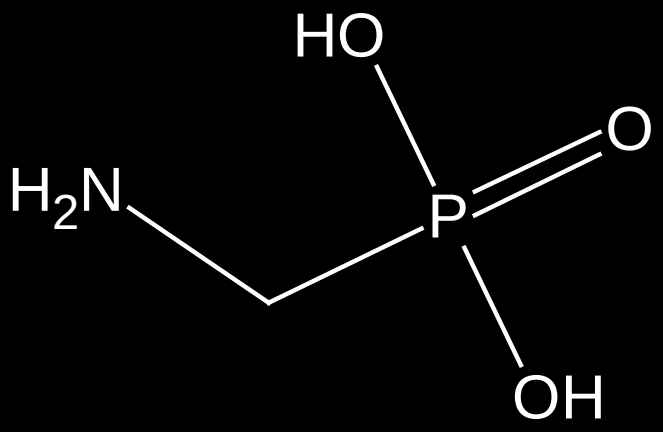
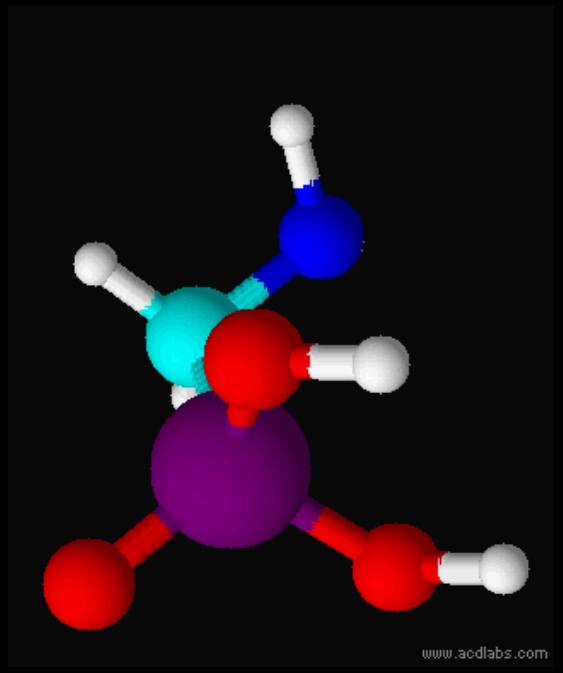


ENVIRONMENTAL FATE OF GLYPHOSATE Jeff Schuette Environmental Monitoring & Pest Management Department of Pesticide Regulation Sacramento, CA 95824-5624 (Revised November 1998)

The primary metabolite of glyphosate is aminomethylphosphonic acid (AMPA). Degradation of AMPA is generally slower than that of glyphosate possibly because AMPA may adsorb onto soil particles more strongly than glyphosate and/or because it may be less likely to permeate the cell walls or membranes of soil microorganisms (USDA, 1984).





Aminomethylphosphonic acid (AMPA).

ENVIRONMENTAL FATE OF GLYPHOSATE Jeff Schuette Environmental Monitoring & Pest Management Department of Pesticide Regulation Sacramento, CA 95824-5624 (Revised November 1998)

TUSCANY
Active Substances Sales data
Year 2009
Kg

ARPAT

GLYPHOSATE	122603
COPPER	290023
SULFUR	1490397
Whole sales data	2505814
Sales data excluding Copper and sulfur	725394
Glyphosate Percentage	17%

International Agency for Research on Cancer

World Health Organization

20 March 2015

IARC Monographs Volume 112: evaluation of five organophosphate insecticides and herbicides

Lyon, France, 20 March 2015 – The International Agency for Research on Cancer (IARC), the specialized cancer agency of the World Health Organization, has assessed the carcinogenicity of **five organophosphate pesticides**. A summary of the final evaluations together with a short rationale have now been published online in The Lancet Oncology, and the detailed assessments will be published as Volume 112 of the IARC Monographs.

What were the results of the IARC evaluations?

The herbicide **glyphosate** and the insecticides **malathion** and **diazinon** were classified as *probably carcinogenic to humans* (Group 2A).

For the herbicide **glyphosate**, there was *limited evidence of carcinogenicity* in humans for non-Hodgkin lymphoma. The evidence in humans is from studies of exposures, mostly agricultural, in the USA, Canada, and Sweden published since 2001. In addition, there is convincing evidence that glyphosate also can cause cancer in laboratory animals. On the basis of tumours in mice, the United States Environmental Protection Agency (US EPA) originally classified glyphosate as *possibly carcinogenic to humans* (Group C) in 1985. After a re-evaluation of that mouse study, the US EPA changed its classification to *evidence of non-carcinogenicity in humans* (Group E) in 1991. The US EPA Scientific Advisory Panel noted that the re-evaluated glyphosate results were still significant using two statistical tests recommended in the IARC Preamble. The IARC Working Group that conducted the evaluation considered the significant findings from the US EPA report and several more recent positive results in concluding that there is *sufficient evidence of carcinogenicity* in experimental animals. Glyphosate also caused DNA and chromosomal damage in human cells, although it gave negative results in tests using bacteria. One study in community residents reported increases in blood markers of chromosomal damage (micronuclei) after glyphosate formulations were sprayed nearby.

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Consiglia Condividi 3,3Mila Tweet 61 46 LinkedIn 22

"Quel pesticida è un probabile cancerogeno": è battaglia tra Iarc e Monsanto, produttore della sostanza

Utilizzato in 750 prodotti per l'agricoltura, per l'Agenzia internazionale per la ricerca sul cancro di Lione l'erbicida potrebbe essere pericoloso. Ma Monsanto, la multinazionale che lo distribuisce, smentisce. Intanto gli agricoltori biologici chiedono la messa al bando

di ANTONIO CIANCIULLO

CORRIERE DELLA SERA / AMBIENTE

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INSIEME AD ALTRI QUATTRO DIFFUSI INSETTICIDI

Il diserbante più usato al mondo è cancerogeno

Il glifosato inserito nell'elenco dall'Agenzia internazionale per la ricerca sul cancro: favorisce la comparsa di linfomi non-Hodgkin

di Valeria Balboni

Il glifosato è stato inserito nell'elenco dei probabili cancerogeni dall'Agenzia internazionale per la ricerca sul

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LA STAMPA TUTTOGREEN

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Impennata del vino bio made in Italy: il Belpaese è ai primi... | #Filierasporca scrive al ministro Martina: una filiera trasp... | Venezia72: "Behemoth" di Zhao Liang vince il premio della so... | Sustainability ... | A Venezia72 "Ritorno al futuro", con la indimenticabileDeLor...

"Probabilmente cancerogeno" il glifosato, un erbicida diffusissimo e alla base del "Round Up" di Monsanto

Per l'autorevole IARC, l'Agenzia internazionale per la ricerca sul cancro, organismo collegato all'OMS, la sostanza è sospettata di provocare tumori e danni al Dna. "È scienza spazzatura", replica la multinazionale Monsanto

REGULATION (EC) No 1107/2009

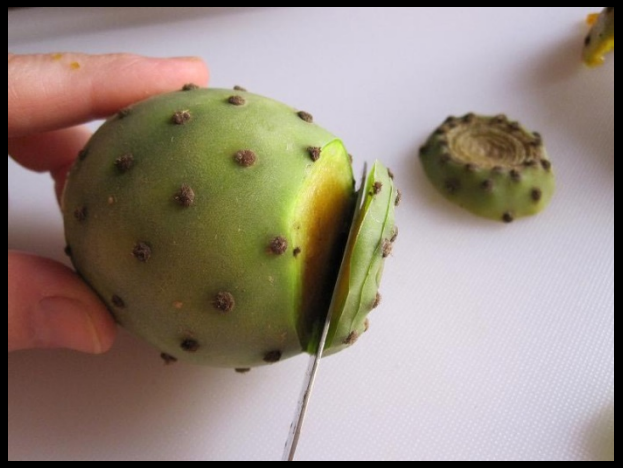
CHAPTER I
GENERAL PROVISIONS
Article 1
Subject matter and purpose

3. The purpose of this Regulation is to ensure a high level of protection of both human and animal health and the environment and to improve the functioning of the internal market through the harmonisation of the rules on the placing on the market of plant protection products, while improving agricultural production.

REGULATION (EC) No 1107/2009

Introduction of « cut-off » criteria

Reasons of the introduction of « cut-off » criteria



- Council report and Resolution of EU Parliament on the COM report on implementation of Directive 91/414/EEC in 2001 and 2002
- Consistency with other policies and legislative measures such as 6th Community Environment Action Programme, workers safety, Endocrine Disruptors Community strategy 1999, REACH
- Facilitation of decision making process
- Increase protection of human, animal health and Environment

REGULATION (EC) No 1107/2009

CHAPTER II

ACTIVE SUBSTANCES, SAFENERS, SYNERGISTS AND CO-FORMULANTS

SECTION 1

Active substances

Subsection 1

Requirements and conditions for approval

Article 4

Approval criteria for active substances

The assessment of the active substance shall first establish whether the approval criteria set out in points 3.6.2 to 3.6.4 and 3.7 of Annex II are satisfied. If these criteria are satisfied the assessment shall continue to establish whether the other approval criteria set out in points 2 and 3 of Annex II are satisfied.

REGULATION (EC) No 1107/2009
Annex II,

3.6 Impact on human health

3.6.3

An active substance, safener or synergist shall only be approved, if, on the basis of assessment of carcinogenicity testing carried out in accordance with the data requirements for the active substances, safener or synergist and other available data and information, including a review of the scientific literature, reviewed by the Authority, it is not or has not to be classified, in accordance with the provisions of Regulation (EC) No 1272/2008, as carcinogen category 1A or 1B

29/07/2015

Glyphosate monograph is on-line

30/07/2015

EFSA is to assess the findings of a report by the International Agency for Research on Cancer (IARC) which concludes that the herbicide glyphosate is probably carcinogenic to humans.

The report…….will be considered as part of EFSA's on-going peer review of the re-evaluation of glyphosate.

EFSA's finalised conclusion will be sent to the European Commission and published later this year.

Re-Evaluation

In the EU, active substances used in plant protection products are evaluated or re-evaluated using a phased approach.

First, an initial draft risk assessment report is produced by a designated rapporteur Member State (RMS). In the case of glyphosate the RMS is Germany. The report is peer-reviewed by EFSA, which sends its conclusion to the European Commission. The Commission then decides whether or not to include the substance in the EU's list of approved active substances. Find out more here .

30/07/2015

www.bfr.bund.de

BfR

Bundesinstitut für Risikobewertung

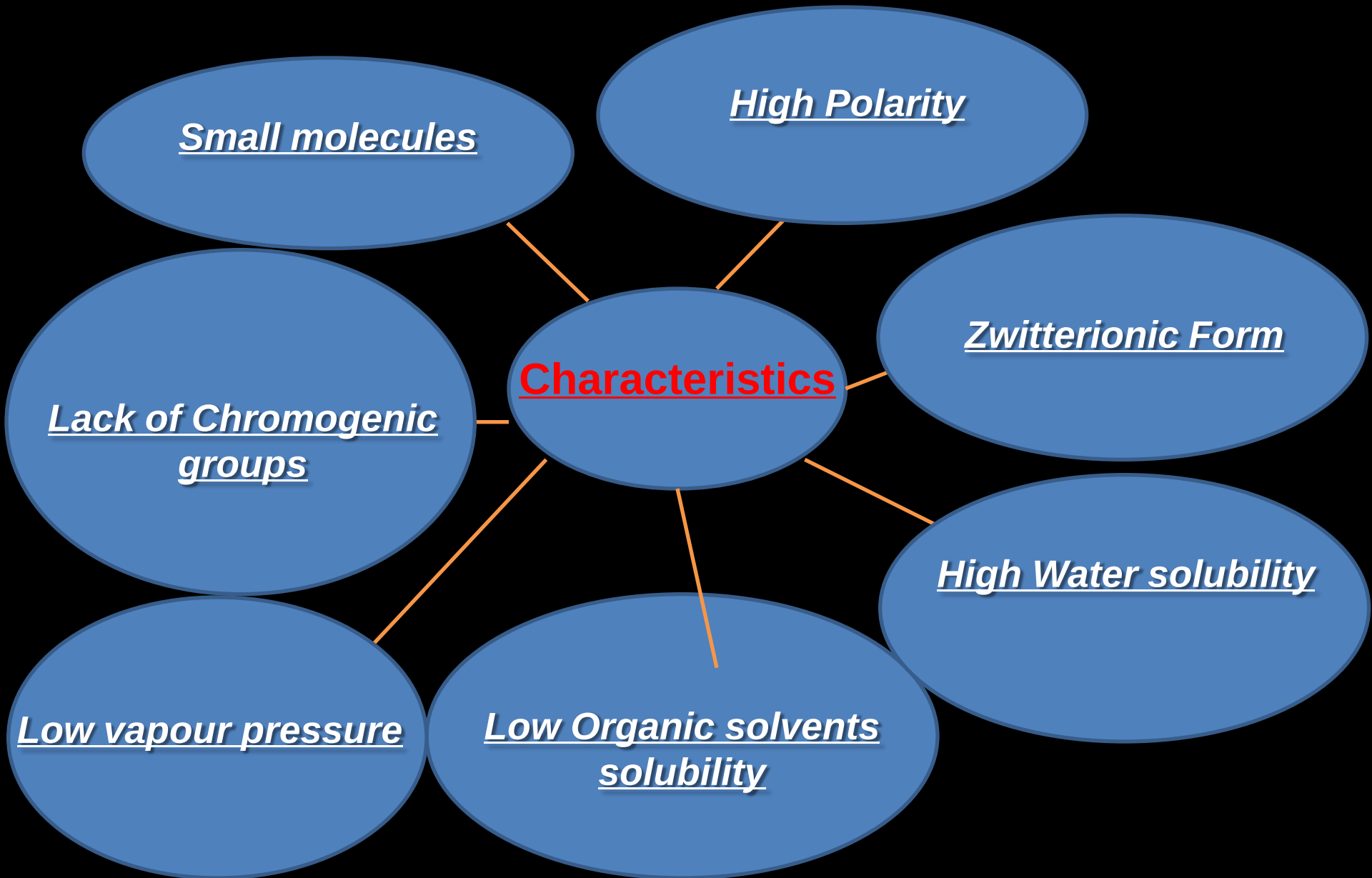
BfR reviews monograph of the International Agency for Cancer Research (IARC) on glyphosate - divergence procedure within the WHO still in progress

Agricoltura | Inquinamenti

Glifosate, in Toscana in un solo anno vendute 100 tonnellate dell'erbicida probabile cancerogeno

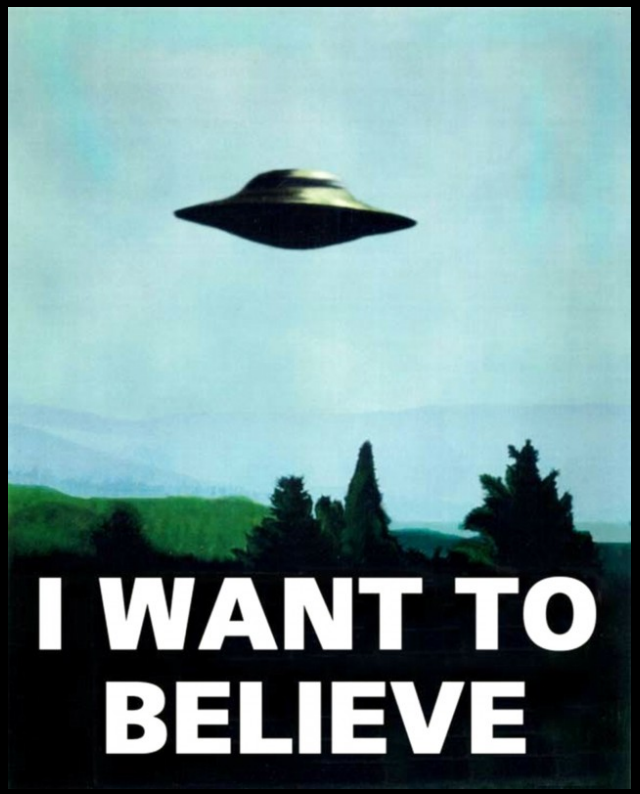
[17 aprile 2015]

Analysis of Glyphosate and AMPA



Direct Analysis of Glyphosate and AMPA ?

Truth or Mith?



CSIC
Consejo Superior de Investigaciones Científicas

Direct analysis of Glyphosate by LC-MS/MS in drinking water samples

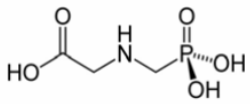
María del Mar Soto[1], Cintia Flores[1], Claudia P.B.Martins[2], Josep Caixach[1]

[1]Mass Spectrometry Laboratory, IDAEA-CSIC, Jordi Girona 18-26, 08034-Barcelona (Spain), e-mail: jcgeco@cid.csic.es

[2] Thermo Fischer Scientific, C/Acero 30-32, plta 2ª, mód.3 Edificio Sertram, 08038-Barcelona (Spain)

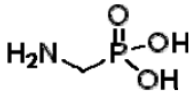
INTRODUCTION

Glyphosate is a nonselective amino-phosphonate acid-type herbicide worldwide used that controls a wide range of weeds, and broadleaf weeds (1). Due to its ionic character, high solubility in water, low volatility and low mass, the sub µg/L determination in water, as required by the European Union Legislation, is very difficult. Consequently, the use of techniques such as mass spectrometry (MS) is necessary in order to achieve an excellent sensitivity and unequivocal confirmation.



GLYPHOSATE
CAS Number:: 1071-83-6
Monoisotopic mass: 169

At the present, most studies for the analysis of glyphosate and its principal degradation product - aminomethylphosphonic acid (AMPA) – make use of derivatization steps (2) or complex eluents like in ion exchange chromatography (3).



AMPA
CAS Number: 1066-51-9
Monoisotopic mass: 112

A fully-automated, rapid, sensitive, selective and robust method without derivatization was carried out for the determination of glyphosate and AMPA in drinking water by on-line solid phase extraction-liquid chromatography tandem mass spectrometry (On-line SPE-LC-MS/MS)

Analysis of Glyphosate and AMPA

Trends in Analytical Chemistry, Vol. 22, No. 11, 2003

Derivatization in the current practice of analytical chemistry

Jack M. Rosenfeld

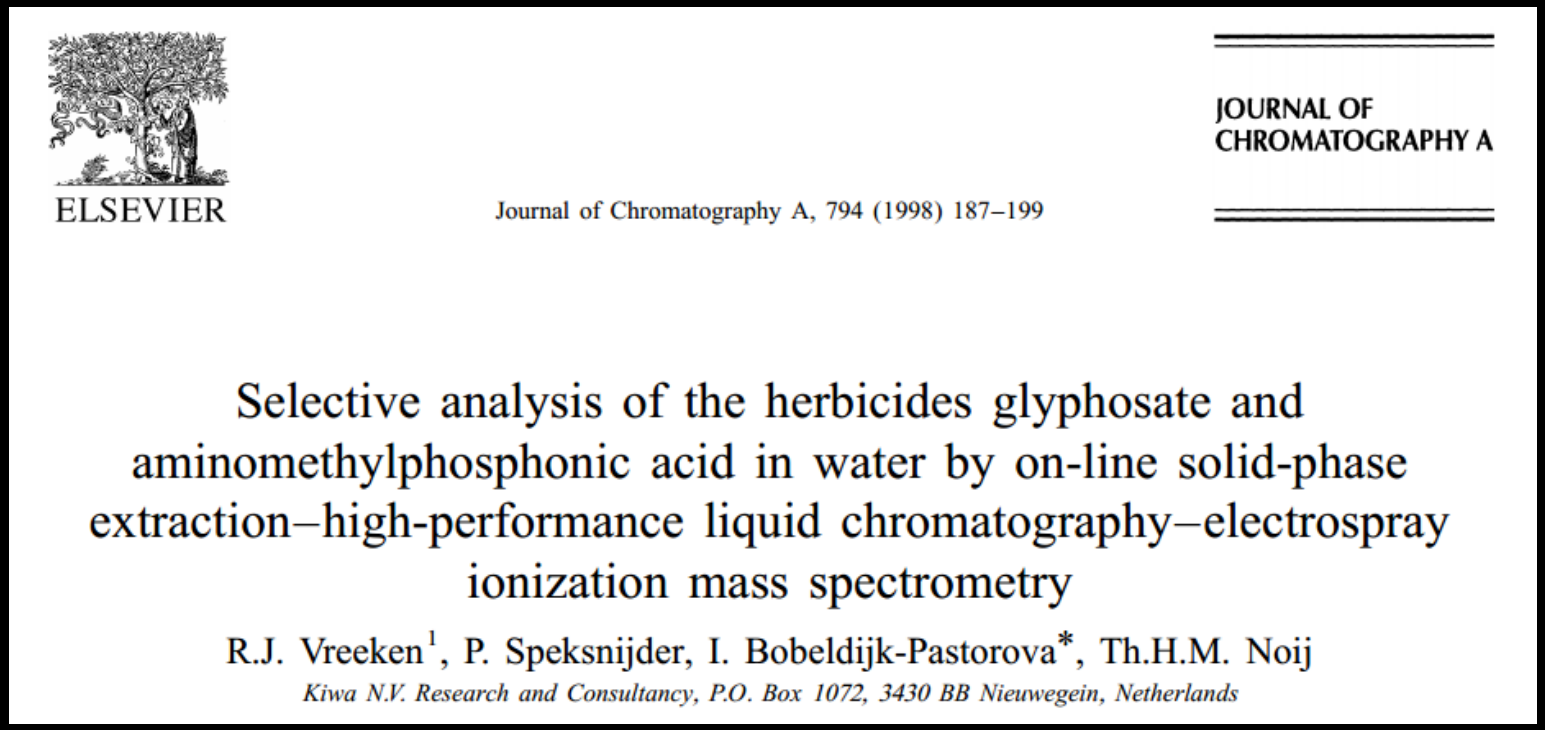
LC

Insertion of Chromogenic group
and/or improvement of chromatographic behaviour

GC

Insertion of group for
enhancement of volatility

Analysis of Glyphosate and AMPA



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Journal of Chromatography A, 794 (1998) 187–199

JOURNAL OF CHROMATOGRAPHY A

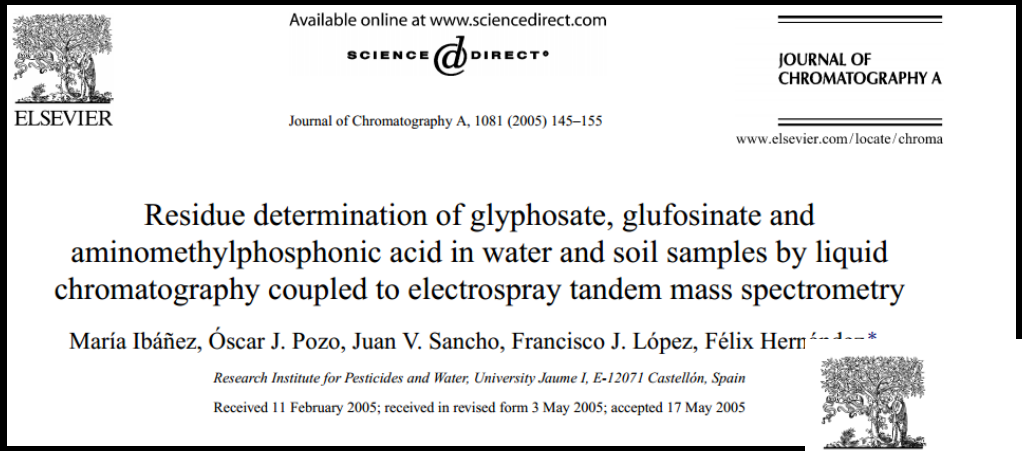
Selective analysis of the herbicides glyphosate and aminomethylphosphonic acid in water by on-line solid-phase extraction–high-performance liquid chromatography–electrospray ionization mass spectrometry

R.J. Vreeken[1], P. Speksnijder, I. Bobeldijk-Pastorova*, Th.H.M. Noij

Kiwa N.V. Research and Consultancy, P.O. Box 1072, 3430 BB Nieuwegein, Netherlands

- ***Derivatization with FMOC-Cl***
- ***SPE off-line clean-up and concentration***
- ***Analysis of the extracts by LC-MS and LC-MSMS negative ionization***

Analysis of Glyphosate and AMPA



Available online at www.sciencedirect.com
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Journal of Chromatography A, 1081 (2005) 145–155
JOURNAL OF CHROMATOGRAPHY A
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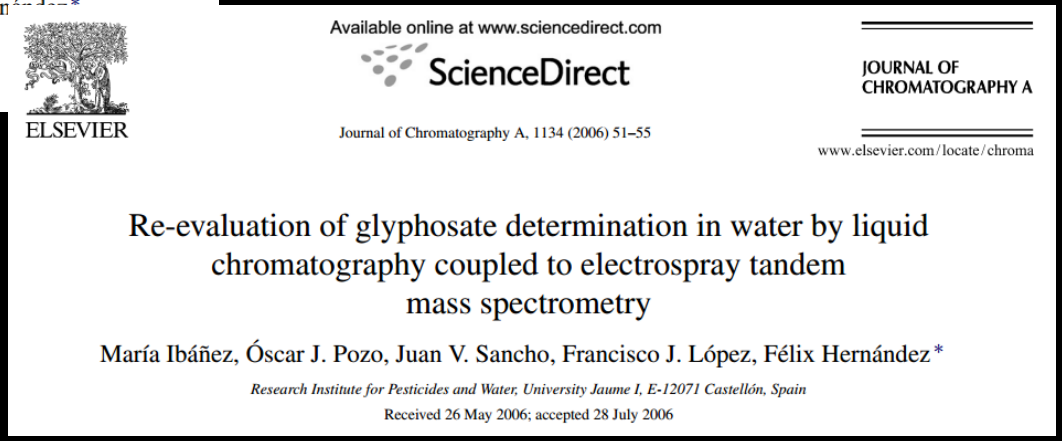
Residue determination of glyphosate, glufosinate and aminomethylphosphonic acid in water and soil samples by liquid chromatography coupled to electrospray tandem mass spectrometry

María Ibáñez, Óscar J. Pozo, Juan V. Sancho, Francisco J. López, Félix Hern[illegible]*

Research Institute for Pesticides and Water, University Jaume I, E-12071 Castellón, Spain

Received 11 February 2005; received in revised form 3 May 2005; accepted 17 May 2005



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Re-evaluation of glyphosate determination in water by liquid chromatography coupled to electrospray tandem mass spectrometry

María Ibáñez, Óscar J. Pozo, Juan V. Sancho, Francisco J. López, Félix Hernández*

Research Institute for Pesticides and Water, University Jaume I, E-12071 Castellón, Spain

Received 26 May 2006; accepted 28 July 2006

- ***Derivatization with FMOC-Cl***
- ***SPE on-line clean-up and concentration***
- ***Analysis of the extracts by LC-MS and LC-MSMS positive ionization***

Analysis of Glyphosate and AMPA

Anal Bioanal Chem (2008) 391:2265–2276
DOI 10.1007/s00216-008-2134-5

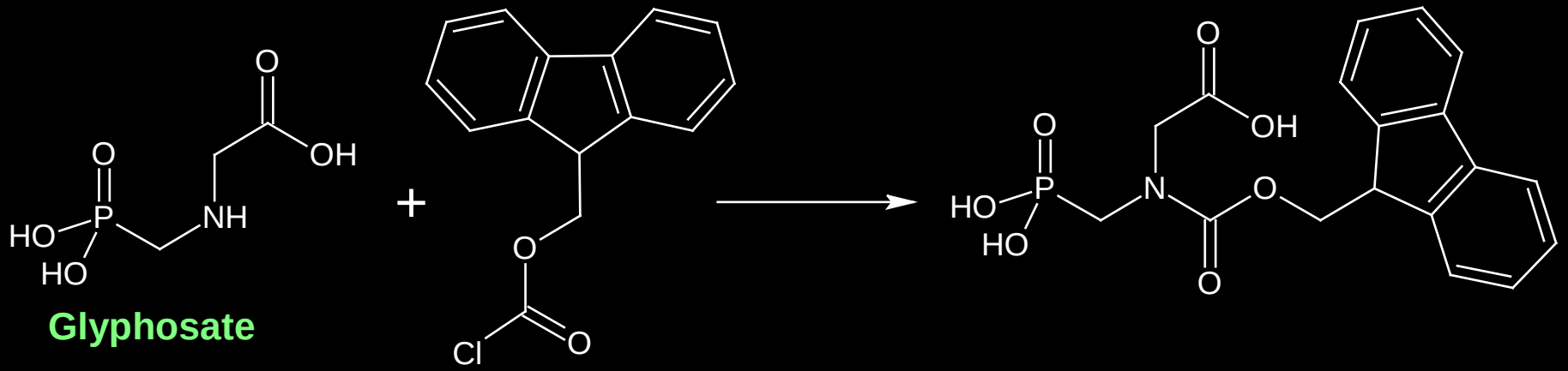
ORIGINAL PAPER

Ultratrace-level determination of glyphosate, aminomethylphosphonic acid and glufosinate in natural waters by solid-phase extraction followed by liquid chromatography–tandem mass spectrometry: performance tuning of derivatization, enrichment and detection

Irene Hanke · Heinz Singer · Juliane Hollender

- ***Derivatization with FMOC-Cl***
- ***SPE off-line clean-up and concentration***
- ***Analysis of the extracts by LC-MS and LC-MSMS negative ionization***

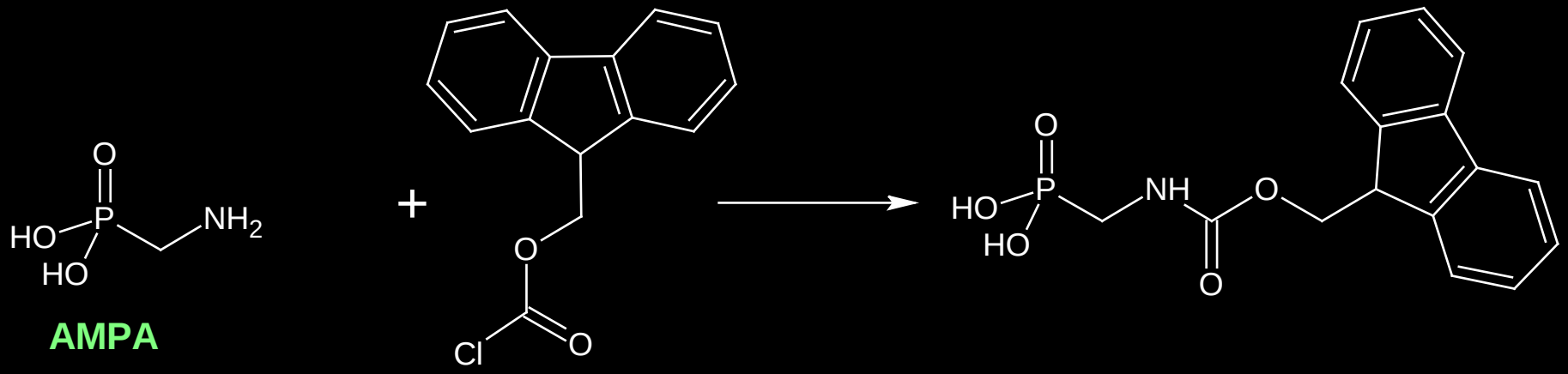
Derivatization of Glyphosate and AMPA with FMOC-Cl



Glyphosate

FMOC-Cl

IUPAC name: Chloroformic acid 9H-fluoren-9-ylmethyl ester
Other names:9-Fluorenylmethyl chloroformate; 9-Fluorenylmethoxycarbonyl chloride;



AMPA

Analysis of Glyphosate and AMPA

Water samples:
Stored frozen in plastic bottle

Thawing

Sub sample of 80 ml
+
1600 µl HCL 6M
after 2 hours
+
1600 µl KOH 6M

80 µl ILSs 100 ng/ml
+
10 ml Borate buffer 5%
+
10 ml FMOC-Cl in CH_3CN 6,5 mM
(daily prepared)

Overnight

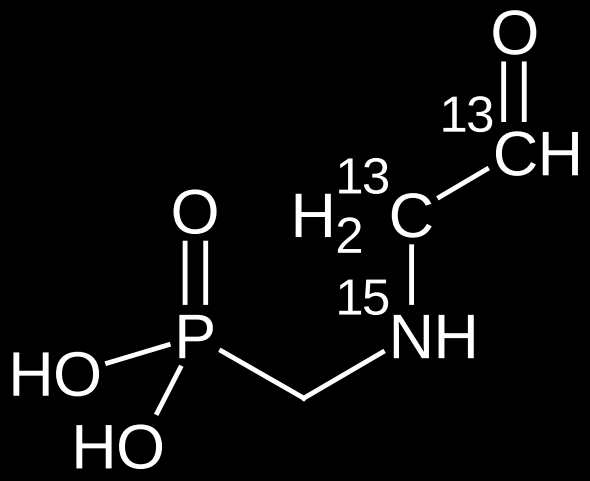
1 ml of HCOOH and filter
+
4 ml EDTA Na_4 1 M
+
100 ml H_2O

SPE

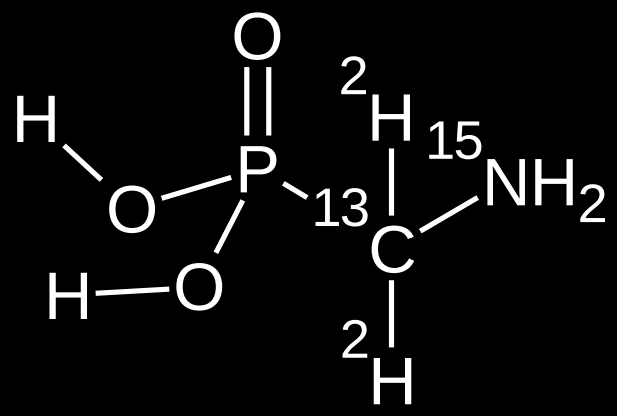
- *9 ml of Methanolic eluate*
- *Evaporate to dryness*
- *Reconstitute with 500 µl of HPLC Mobile Phase*

HPLC-HRMS analysis
Positive ionization

ILSs choice



Glyphosate $^{13}C_2{}^{15}N$



AMPA $^{13}CD_2{}^{15}N$

Positive ionization choice

"Although these compounds have been traditionally recorded in negative ion mode [9,10], in our work the sensitivity in positive ion mode was found to be approximately two times higher. Moreover, the product ions observed in negative ion mode were due to neutral unspecific losses of FMOC, or FMOC plus water. Thus, any isobaric compound that could have been derivatized with FMOC and also presented a water loss, would show the same product ions in its MS/MS spectra, being therefore not very selective. For all these reasons, positive ion mode was selected"

Journal of Chromatography A, 1081 (2005) 145–155

Instrumental Choice

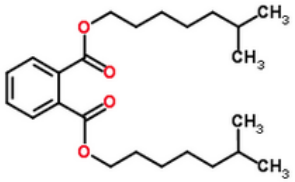
LC-MS-IT

ChemSpider
Search and share chemistry

Simple Structure Advanced History

Found 1 result

Search term: **27554-26-3** (Found by approved synonym)



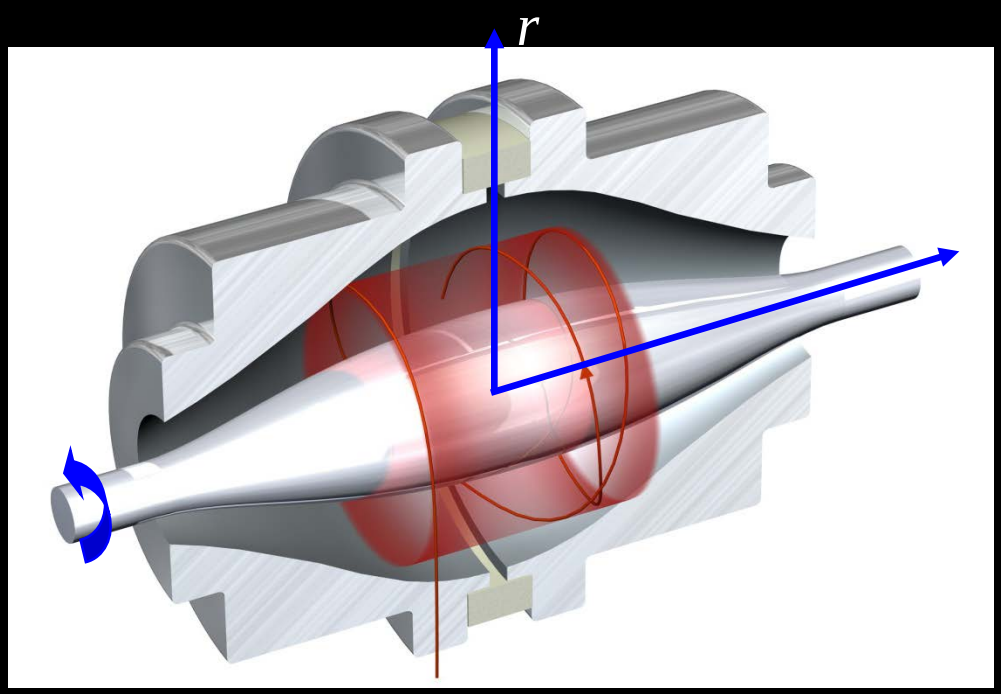
DIISOOCTYL PHTHALATE

Molecular Formula	$C_{24}H_{38}O_4$
Average mass	390.556 Da
Monoisotopic mass	390.277008 Da
ChemSpider ID	31280

Instrumental Choice

Orbitrap Exactive HCD

LC-HRMS: Orbitrap



Hyper-logarithmic potential distribution in the Orbitrap: "ideal Kingdon trap"

$$U(r,z) = \frac{k}{2} \cdot \left\{ z^2 - r^2/2 + R_m^2 \cdot \ln(r/R_m) \right\}$$

•Korsunskii M.I., Basakutsa V.A. *Sov. Physics-Tech. Phys.* 1958; **3**: 1396.

•Knight R.D. *Appl.Phys.Lett*. 1981, **38**: 221.

•Gall L.N.,Golikov Y.K.,Aleksandrov M.L.,Pechalina Y.E.,Holin N.A. *SU Pat. 1247973*, 1986.

Characteristic frequencies:

Frequency of rotation ω_φ

Frequency of radial oscillations ω_r

Frequency of axial oscillations ω_z

$$\omega_\varphi = \frac{\omega_z}{\sqrt{2}} \sqrt{\left(\frac{R_m}{R}\right)^2 - 1}$$

$$\omega_z = \sqrt{\frac{k}{m/q}}$$

Only this frequency does not depend on energy, angle, etc. and is used for mass analysis

Instrumental Method

HPLC Column : Luna Gemini C18-NX, 150 mm, 2 mm, 3 µm
A: Water 98%, ammonium formate 5 mM, methanol, 2%
Fase B: Methanol 85%, Acetonitrile 15%, formiato di ammonio 5 mM,
Flow 400 µl/min

Gradient:

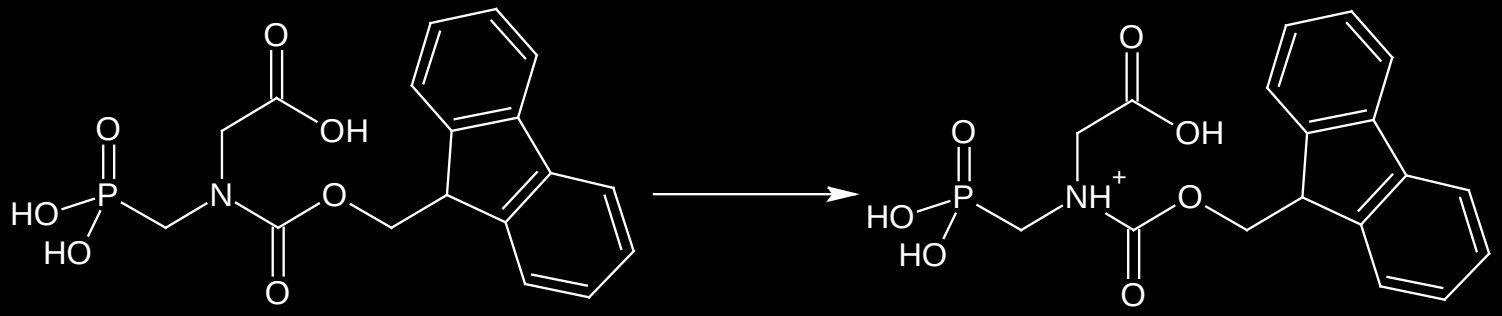
Time	A%	B%
0	95	5
1	95	5
15	29	71
16	5	95
21	5	95
22	95	5
27	95	5

HESI (capillary 275 °C, vaporizer 40 °C)
Positive ionization, Full Scan: resolution 50000.
Fragmentation E HCD= 15V, resolution 50000

LC-HRMS: Full scan

The identification of the analytes is performed in a "full scan" by seeking, for each analyte, the two ions (protonated form) listed below.

In this way, 4 identification points are obtained (DECISION 657/2002, TABLE 5), that are considered to be diagnostic of the presence of the target molecules



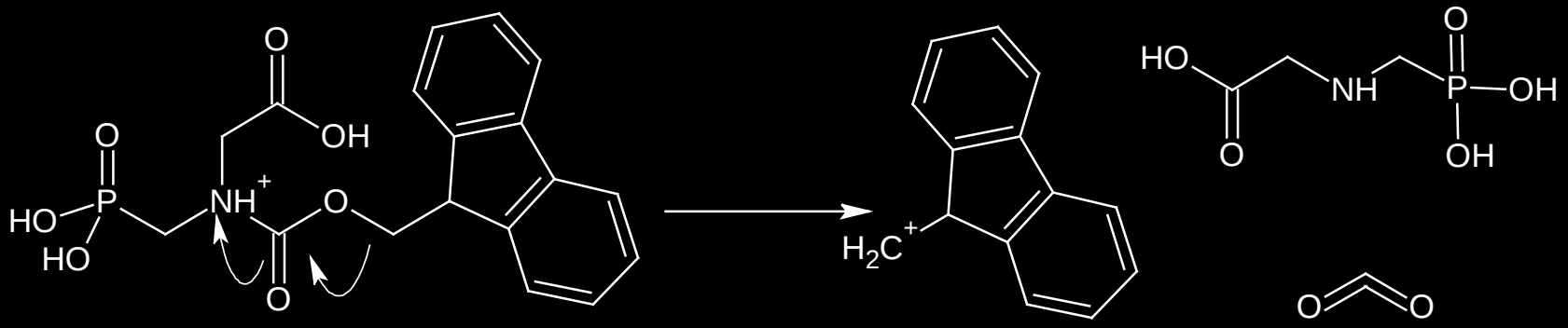
	Formula	Target	Qual.	Ratio Q/Tgt
Glypho-FMOC nat.	$C_{18}H_{18}PNO_7$	392,08936	393,09272	19.47
Glypho-FMOC mark.	$^{13}C_2C_{16}H_{18}P^{15}NO_7$	395,09311	396,09646	17.31
AMPA-FMOC nat.	$C_{16}H_{16}PNO_5$	334.08389	335.08724	17.31
AMPA-FMOC mark.	$^{13}CC_{15}D_2H_{14}P^{15}NO_5$	338.09683	339.10018	16.22

LC-HRMS: HCD fragmentation

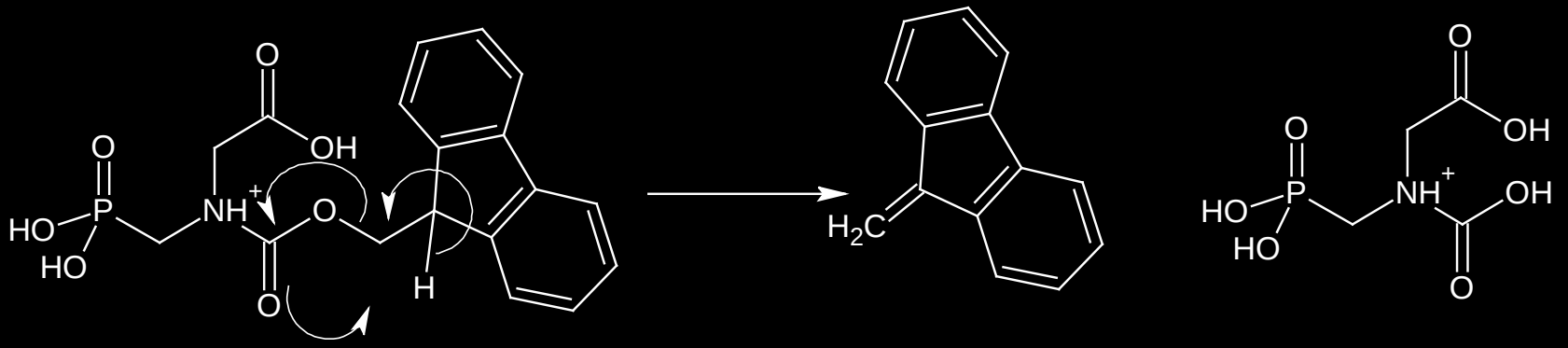
In the event of doubtful situations, we proceed to the analysis of fragments.

Identification is considered certain if it will prove at least two fragment ions, In this way,

from four to five identification points are obtained (DECISION 657/2002, TABLE 5)



Aspecific fragmentation: common ion with ILSs



$C_4H_9PNO_7$ (protonated adduct)= massa 214.01111

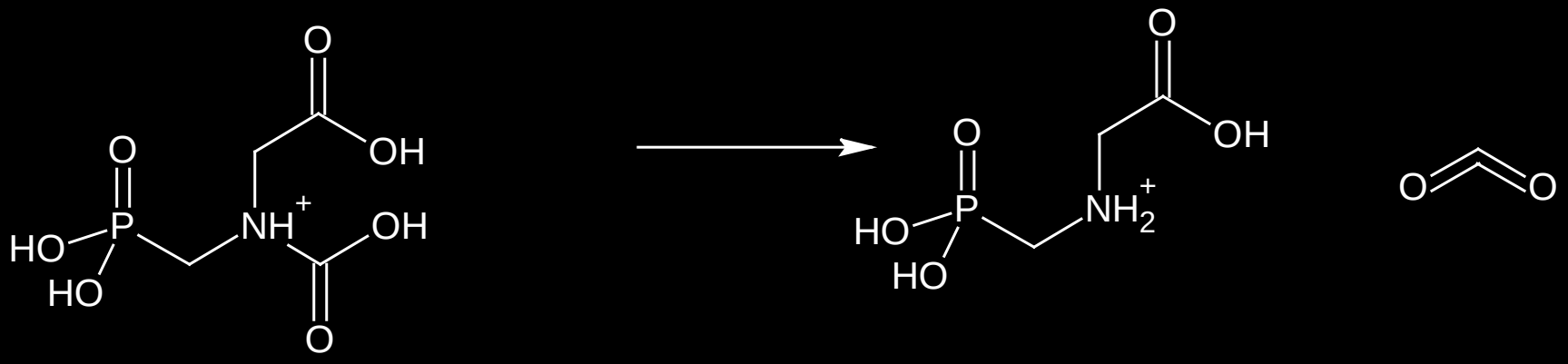
$^{13}C_2C_2H_9P^{15}NO_7$ (protonated adduct)= massa 217.01486

LC-HRMS: HCD fragmentation

In the event of doubtful situations, we proceed to the analysis of fragments.

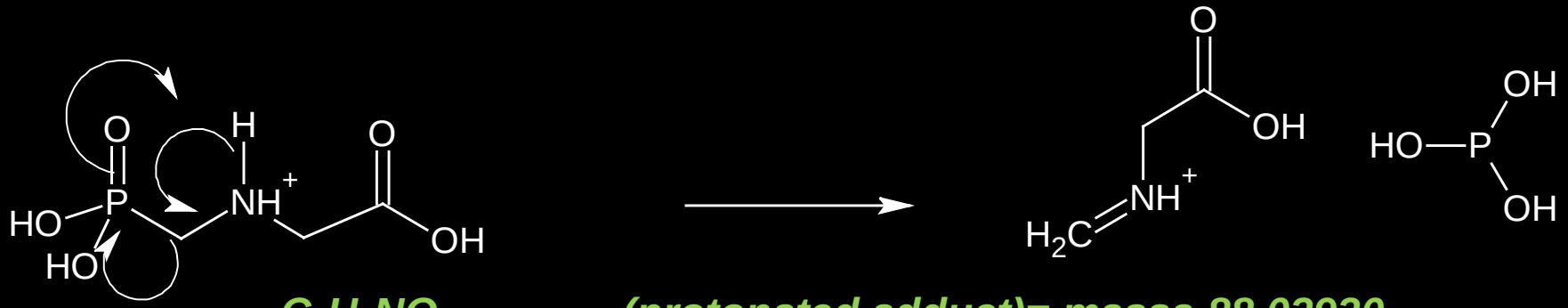
Identification is considered certain if it will prove at least two fragment ions, In this way,

from four to five identification points are obtained (DECISION 657/2002, TABLE 5)



$C_3H_9PNO_5$ ***(protonated adduct)= massa 170.02129***

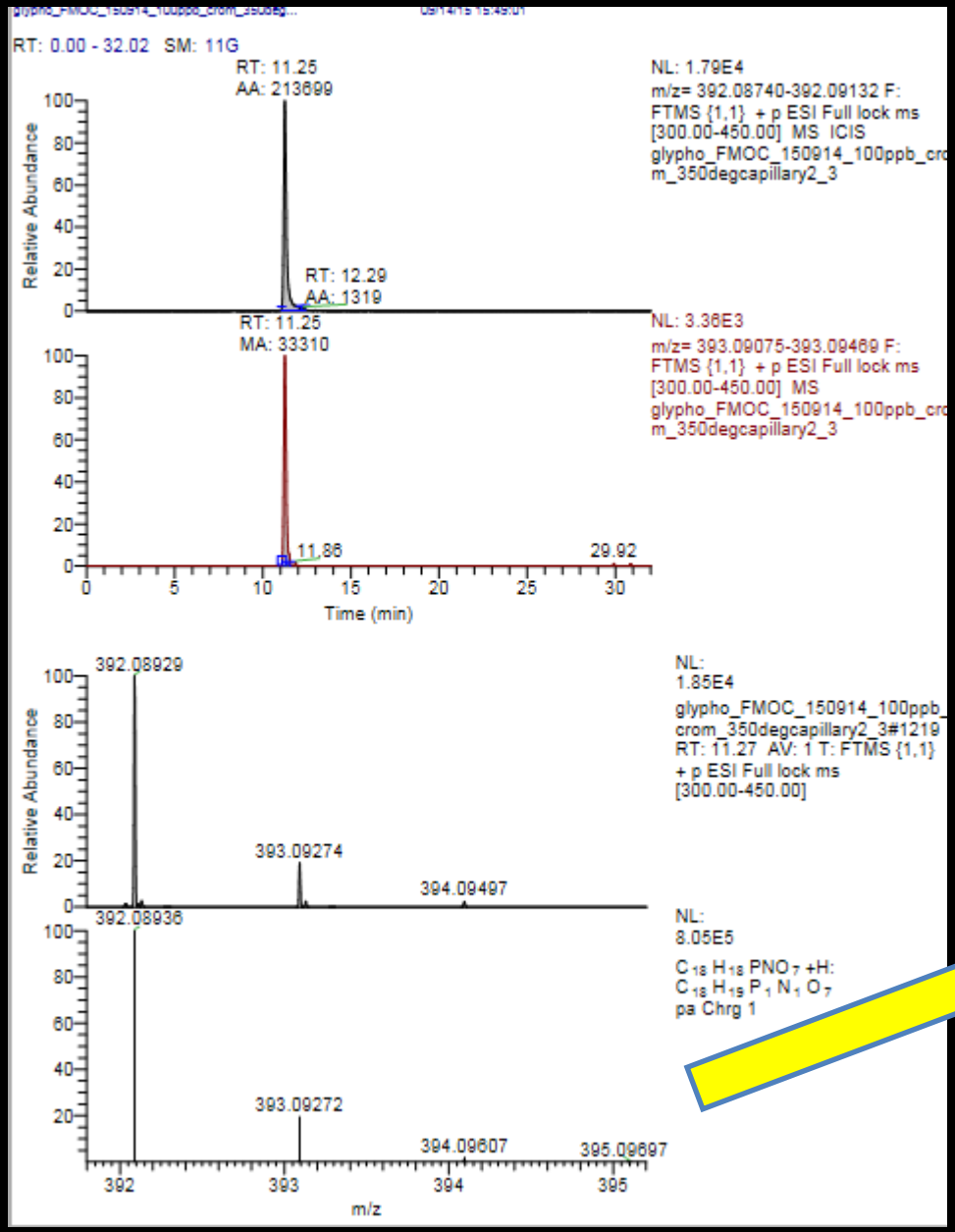
$^{13}C_2CH_9P^{15}NO_5$ ***(protonated adduct)= massa 173.02503***



$C_3H_6NO_2$ ***(protonated adduct)= massa 88,03930***

$^{13}C_2CH_6P^{15}NO_2$ ***(protonated adduct)= massa 91,04305***

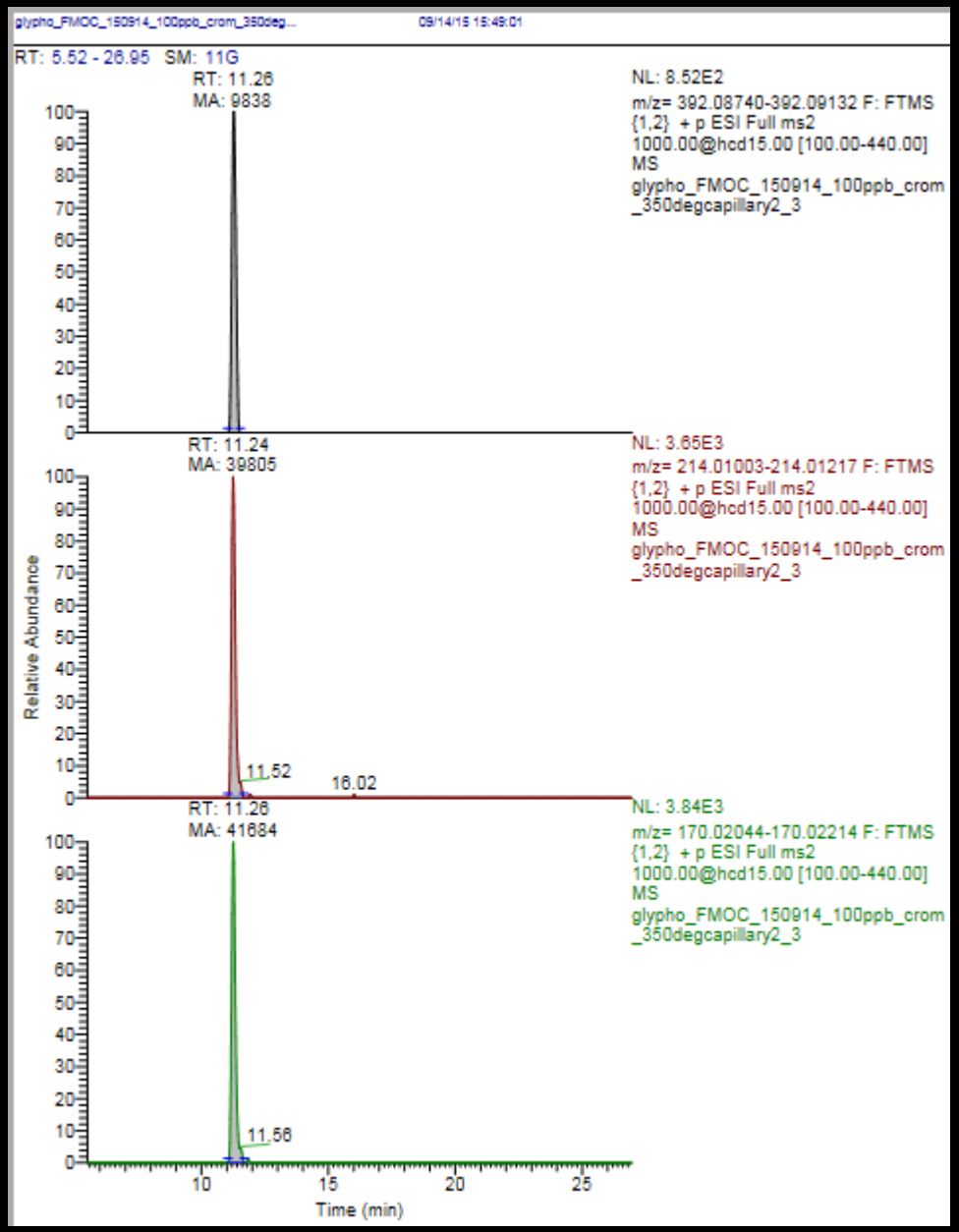
LC-HRMS: Full scan



GLY-FMOC
Injection of 15 µl at 100ng/ml

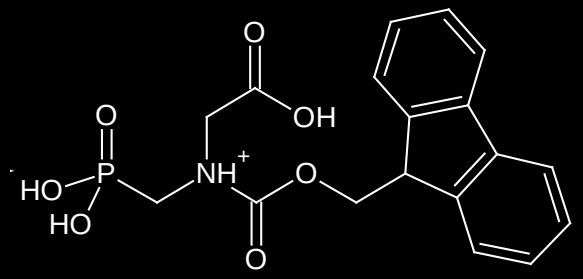
Simulated spectra

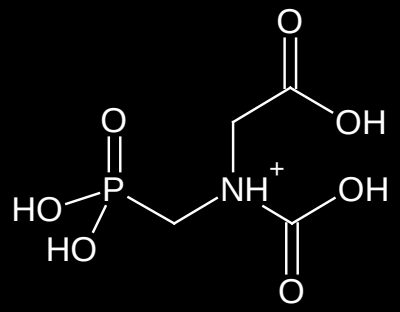
LC-HRMS: HCD Fragmentation

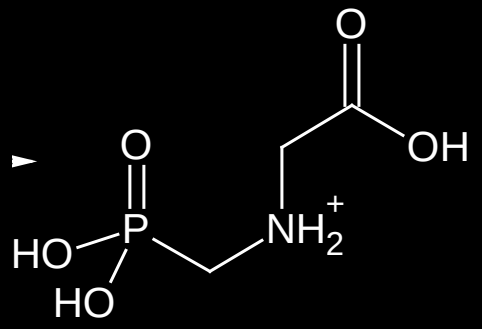


GLY-FMOC

Injection of 15 µl at 100ng/ml

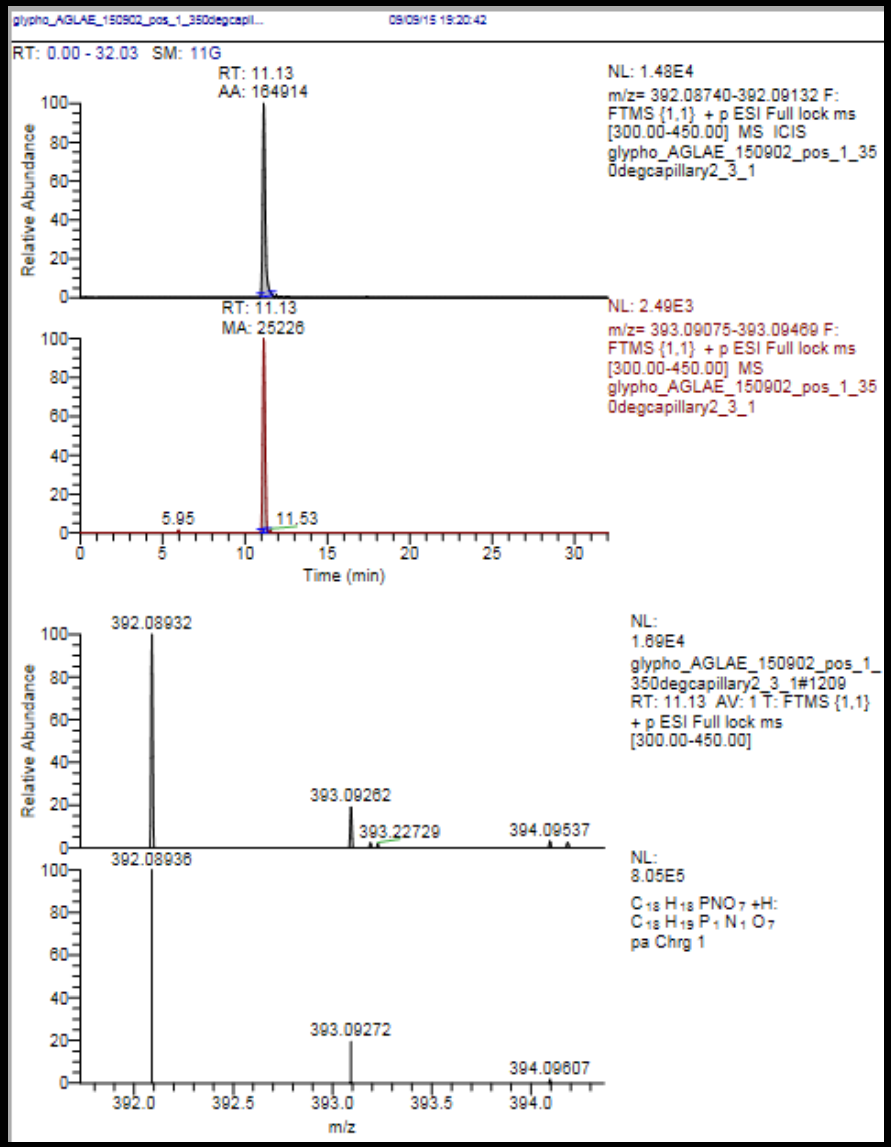


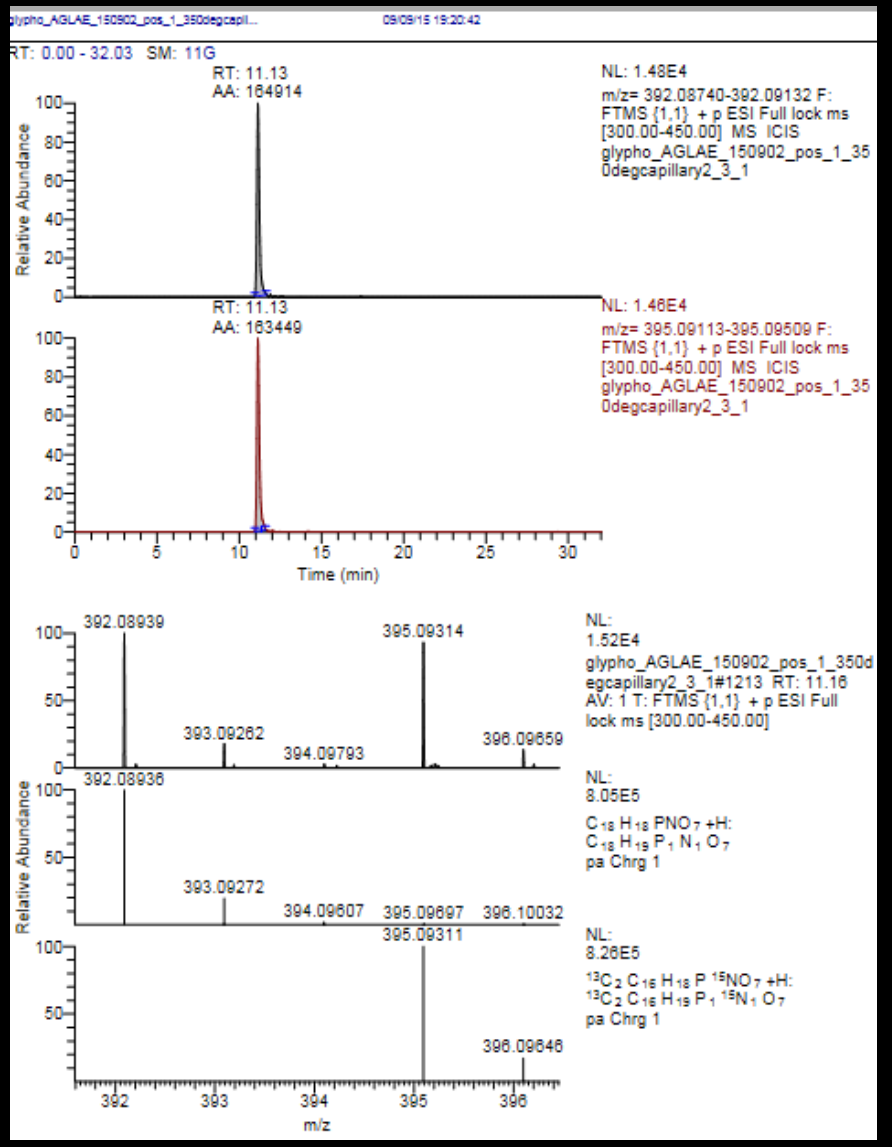




LC-HRMS: Full scan

Mineral water spiked with Glyphosate /Glyphosate ILS
0,2 µg/l e.a.





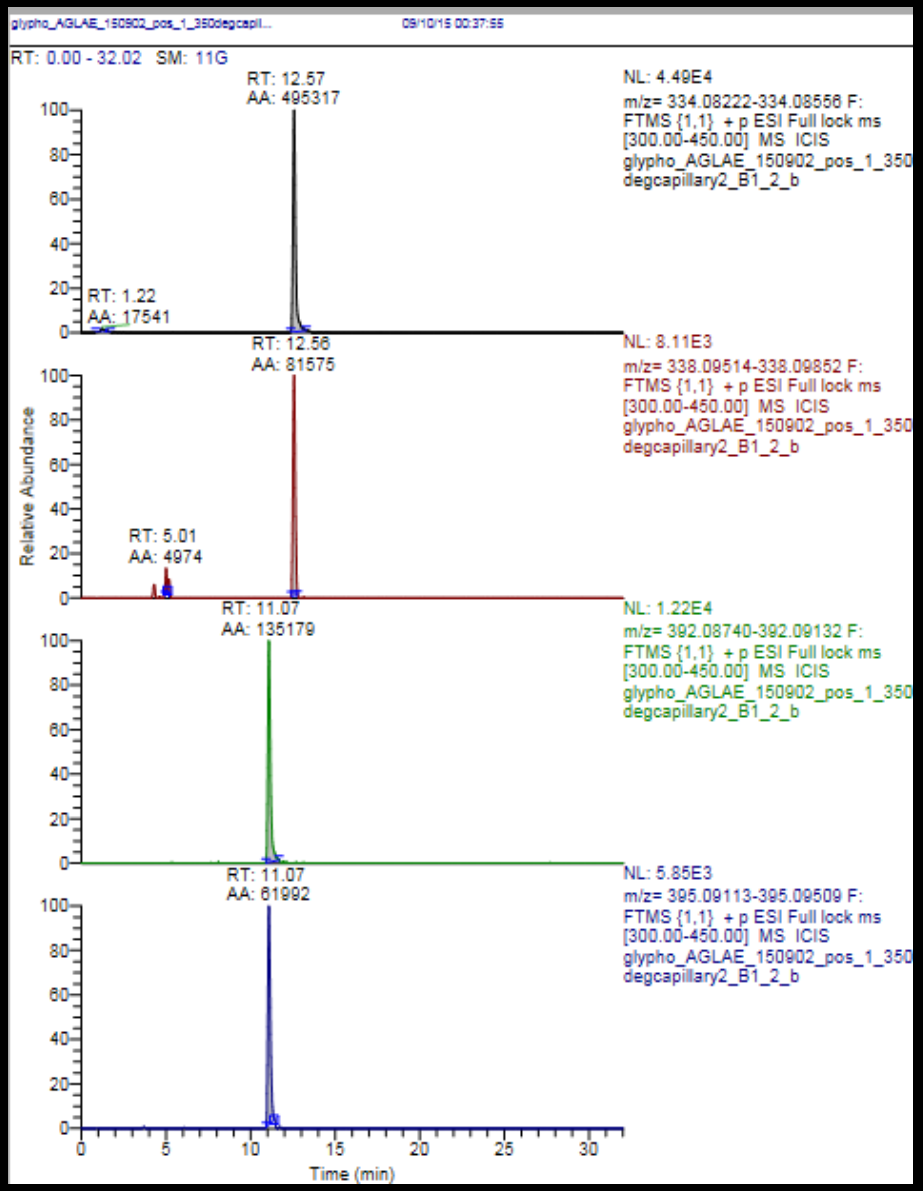
LC-HRMS: Full scan

Mineral water spiked with Glyphosate /Glyphosate ILS 0,2 µg/l e.a, AMPA/AMPA ILS 0,6 µg/l. 10 indipendent analysis

	Cv% Tgt	CV% Qual	Qual/Tgt	RF
AMPA_FMOC	5	5	16	0,978
AMPA_FMOC_mark	5	5	17	
Gly_FMOC	5	9	17	1,00
Gly_FMOC_mark	7	9	17	

LC-HRMS: Full scan

Proficiency Test 29/04/2015



AGLAE

Improve the quality of your analyses

PROFICIENCY TESTING SCHEME
15M55.1

GLYPHOSATE, AMPA AND AMINOTRIAZOLE IN CLEAN WATERS

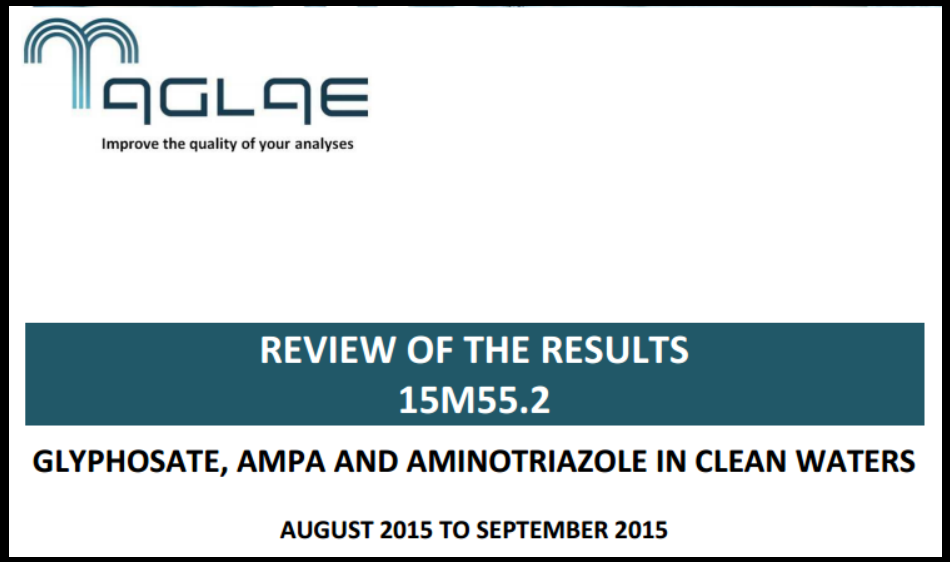
The table below summarises your test results for each parameter.

Your laboratory code for this test: 24

Mean of your results	Reference value (consensus)	Standard deviation for proficiency assessment	Z-score	Accuracy ranking
		glyphosate (µg/L)		
0,1738	0,2263	0,0303	-1,74	A
		AMPA (µg/L)		
0,2920	0,3822	0,0601	-1,50	A*

LC-HRMS: Full scan

Proficiency Test 19/09/2015



Friday 18/09/2015

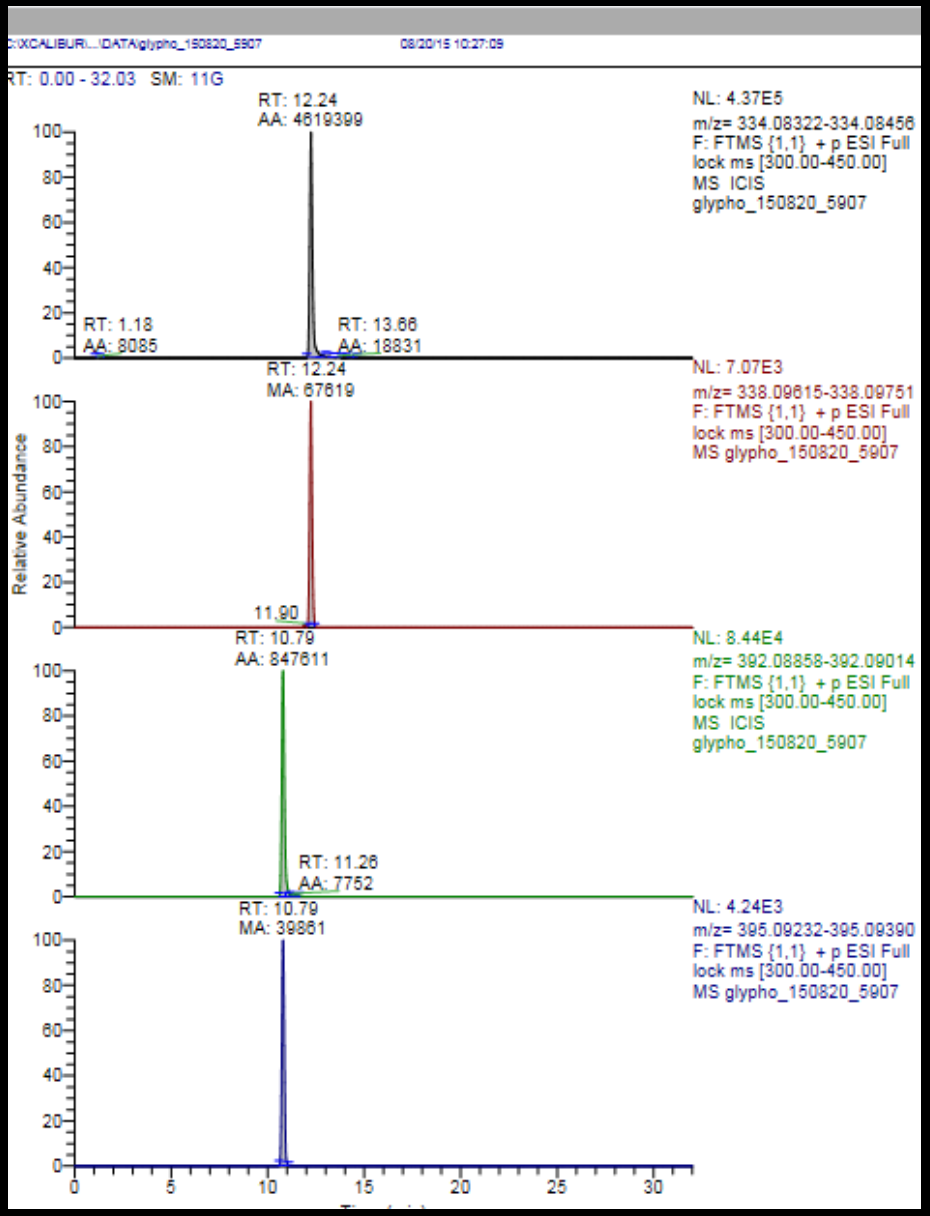
Our Lab Code is 13

Glyphosate provisional Z-score = -0,99

AMPA provisional Z-score = +0,87

LC-HRMS: Full scan

Real samples



Real samples

Analyzed samples 30/05/2015	% of samples with Glyphosate concentration higher than 0,005 µg/l	% of samples with AMPA concentration higher than 0,005 µg/l
130	65	68

Analyzed samples 30/05/2015	Maximum concentration of Glyphosate µg/l	Maximum concentration of AMPA µg/l
130	20,73	13,72

Analyzed samples 30/05/2015	Average concentration of Glyphosate µg/l	Average concentration of AMPA µg/l
130	0,61	1,48

Real samples

Analyzed samples 30/05/2015	% of samples with Glyphosate concentration higher than 0,1 µg/l	% of samples with AMPA concentration higher than 0,1 µg/l
130	25	42

Analyzed samples 30/05/2015	% of samples with Glyphosate concentration higher than 1 µg/l	% of samples with AMPA concentration higher than 1 µg/l
130	9	15

Analyzed samples 30/05/2015	Concentration of Glyphosate Median µg/l	Concentration of AMPA Median µg/l
130	0,07	0,21

ISPRA
Istituto Superiore per la Protezione e la Ricerca Ambientale

Rapporto nazionale pesticidi nelle acque

dati 2011-2012

Nel 2012 nelle acque superficiali, glifosate e il suo metabolita AMPA, cercati solo in Lombardia, sono presenti con frequenze rispettive del 18% e del 47%; gli erbicidi terbutilazina, terbutilazina-desetil,

Glifosate

Il glifosate è un erbicida non selettivo impiegato sia su colture arboree che erbacee e aree non destinate alle colture agrarie (industriali, civili, argini, scoline, ecc.). È una delle sostanze più vendute a livello nazionale e la sua presenza nelle acque è ampiamente confermata anche da dati internazionali[6], ma il suo monitoraggio è tuttora effettuato solo in Lombardia, dove la sostanza è presente nel 31,8% dei punti di monitoraggio delle acque superficiali e il suo metabolita, AMPA, nel 56,6%.
Glifosate e AMPA sono fra le sostanze che più determinano il superamento degli SQA nelle acque superficiali: AMPA in 155 punti (56,6% del totale), glifosate in 85 punti (31% del totale). Meno frequente è la presenza nelle acque sotterranee, dove il glifosate è presente oltre il limite in 2 pozzi e l'AMPA in 5 pozzi.


Technical Difficulties
Please "Hang" Around!

PERSPECTIVES

Surfactants

The role of a surfactant in a herbicide product is to improve wettablility of the hydrophobic surface of plants for maximum coverage and aid penetration through the plant surface. A surfactant can be a pesticide inactive ingredient ("inert") in a formulated end-use product, which is classified as Confidential Business Information (CBI). A surfactant is usually added as an adjuvant to a tank mix.

Surfactants are not usually a single chemical of defined composition, but structurally related compounds of varying number of carbons in the hydrophobic tail. A very important property of surfactants is the formation of micelles , which are ordered assemblages (structured) of disorder surfactant molecules. The concentration at which micelles start forming is known as the Critical Micelle Concentration (CMC). The CMC also depends of the characteristics of the medium, such as pH, temperature, and ionic strength. Each type of surfactants has a different CMC, which also depends on the length and structure of the hydrophobic tail

Surfactants

Alkyl poly(ethylene) oxide (PEO) is the generic name for some nonionic surfactants, which vary among them in the number of carbons in the alkyl chain and the number of ethylene oxide groups. Although the name and composition of the surfactant in the formulated end-use product is CBI, the labels of glyphosate recommend the use of nonspecific nonionic surfactants in the tank mix. The surfactant POEA has been associated with glyphosate formulations and/or adjuvant. The name POEA is used for "Polyethoxylated tallow amine". Unlike the nonionic PEO, POEA is a cationic surfactant derived from quaternary amine cations. The uncertainty in the chemical nature of surfactant in the formulated end-use product makes difficult to ascertain which is more toxic, the surfactant or the glyphosatesurfactant. Furthermore, the role of CMC in the overall behavior of a formulated end-use product in a tank mix with an adjuvant is not known and makes difficult to interpret the effects of different formulations/adjuvant combinations.

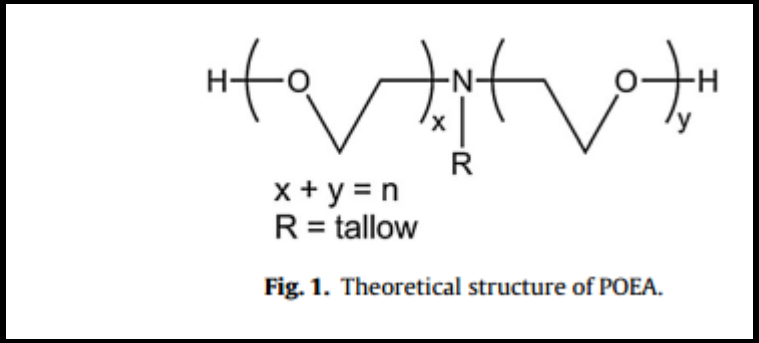


Fig. 1. Theoretical structure of POEA.

Surfactants

Alkyl poly(ethylene) oxide (PEO) is the generic name for some nonionic surfactants, which vary among them in the number of carbons in the alkyl chain and the number of ethylene oxide groups. Although the name and composition of the surfactant in the formulated end-use product is CBI, the labels of glyphosate recommend the use of nonspecific nonionic surfactants in the tank mix. The surfactant POEA has been associated with glyphosate formulations and/or adjuvant. The name POEA is used for "Polyethoxylated tallow amine". Unlike the nonionic PEO, POEA is a cationic surfactant derived from quaternary amine cations. The uncertainty in the chemical nature of surfactant in the formulated end-use product makes difficult to ascertain which is more toxic, the surfactant or the glyphosatesurfactant. Furthermore, the role of CMC in the overall behavior of a formulated end-use product in a tank mix with an adjuvant is not known and makes difficult to interpret the effects of different formulations/adjuvant combinations.

Conclusions:

A major uncertainty remains on the nature of the surfactant used in the formulated enduse product and the plausible enhanced effect with the adjuvant.

Surfactants

G Model
TOX-51062; No. of Pages 7
ARTICLE IN PRESS

Toxicology xxx (2012) xxx–xxx

Contents lists available at SciVerse ScienceDirect

Toxicology

journal homepage: www.elsevier.com/locate/toxicol

Ethoxylated adjuvants of glyphosate-based herbicides are active principles of human cell toxicity

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Journal of Chromatography A, 1319 (2013) 80–87

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Characterization of polyoxyethylene tallow amine surfactants in technical mixtures and glyphosate formulations using ultra-high performance liquid chromatography and triple quadrupole mass spectrometry

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[b] Department of Chemistry, University of Kansas, 1251 Wescoe Hall Drive, Lawrence, KS 66045, USA

Aknowledgments

To all fantastic members of Organic Micropollutants Group

Elisa Banti
Sara DelRio
Valeria Filippi
Alessandra Iarrobino
Lisa Patricelli

Thanks