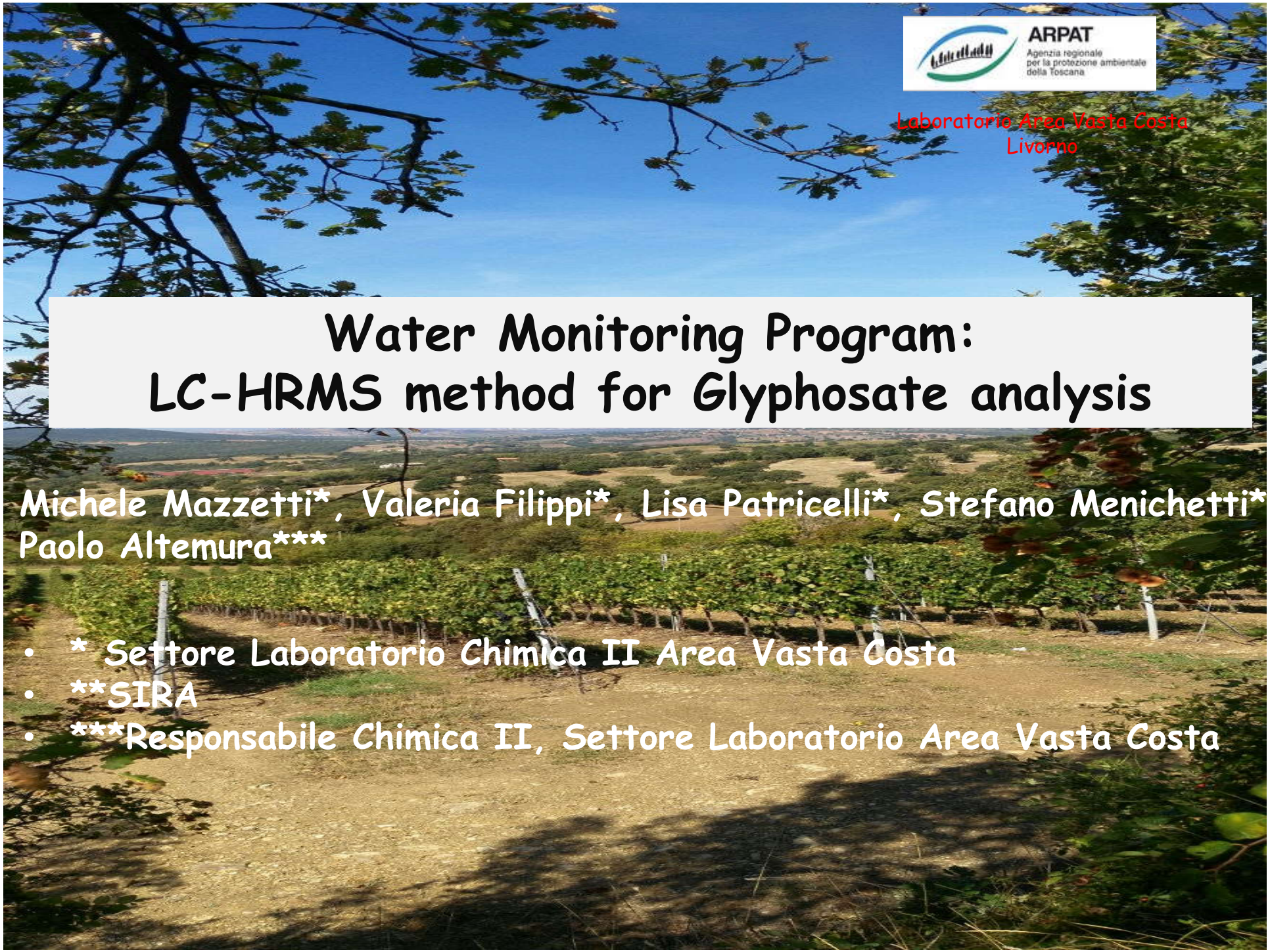


ARPAT
Agenzia regionale per la protezione ambientale della Toscana

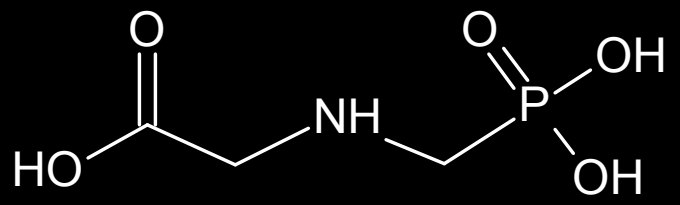
Laboratorio Area Vasta Costa
Livorno

Water Monitoring Program: LC-HRMS method for Glyphosate analysis

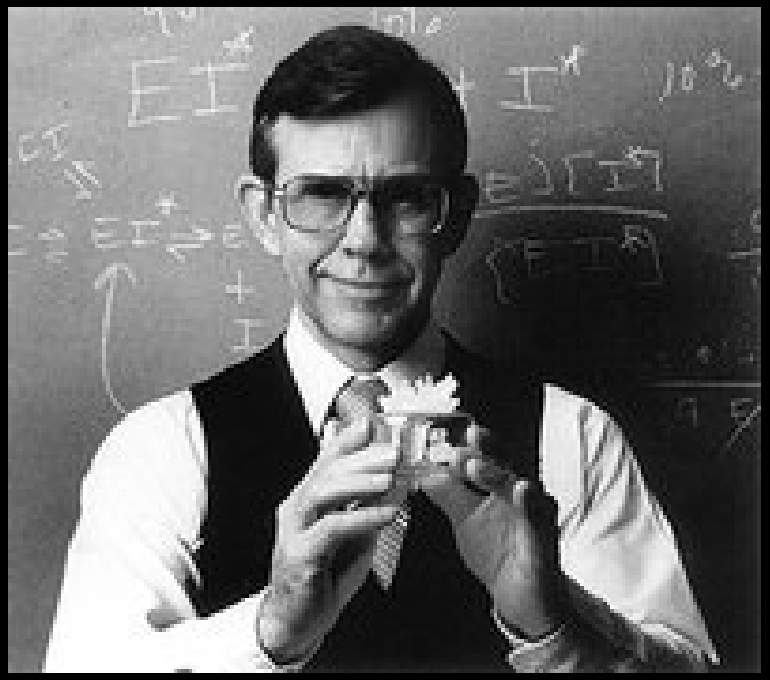
Michele Mazzetti*, Valeria Filippi*, Lisa Patricelli*, Stefano Menichetti*
Paolo Altemura***

- * Settore Laboratorio Chimica II Area Vasta Costa
- **SIRA
- ***Responsabile Chimica II, Settore Laboratorio Area Vasta Costa

A Swiss chemist working for a pharmaceutical company, Dr. Henri Martin, discovered glyphosate [N-(phosphonomethyl) glycine] in 1950. Because no pharmaceutical applications were identifed, the molecule was sold to a series of other companies and samples were tested for a number of possible end uses. A Monsanto chemist, Dr. John Franz, identifed the herbicidal activity of glyphosate in 1970, and a formulated end-use product called Roundup was first sold commercially by Monsanto in 1974. [1]



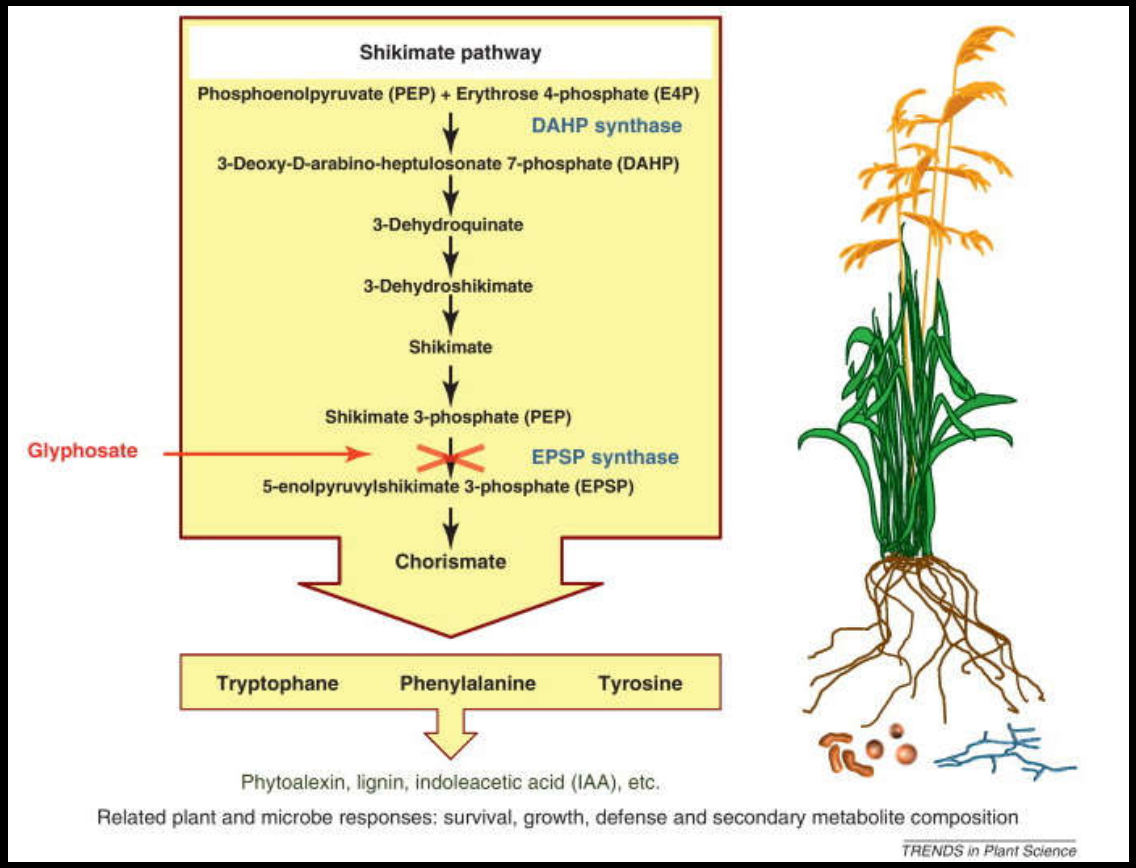
Dr. John Franz



Born: 21/12/1929, Springfield, Illinois (age 86) (1929-12-21)/
Notable awards: National Medal of Technology Carothers Award Perkin Medal (1990)

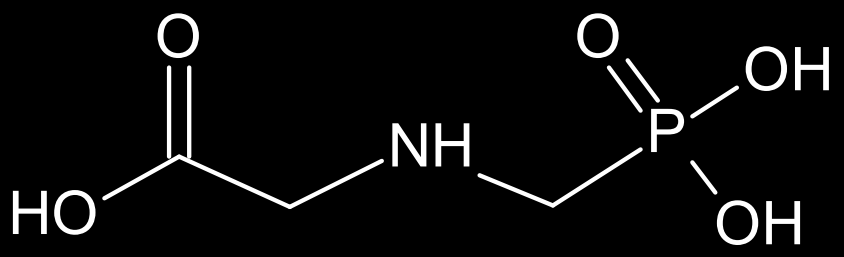
[1] Benbrook Environ Sci Eur (2016) 28:3

Glyphosate, is a broad-spectrum herbicide and, without doubts, is the world's biggest-selling chemical used for weed control in agricultural, silvicultural and urban environments



Glyphosate inhibits the 5-enolpyruvylshikimate-3-phosphate synthase (EPSPS) in the shikimate acid pathway, thereby interfering in the production of proteins and other molecules that require tryptophan, phenylalanine or tyrosine as precursors.Some of the blocked molecules act as growth promoters (e.g., indoleacetic acid, IAA) or defense metabolites (e.g., tannins, anthocyanins, flavonoids and lignin) for the plants. The shikimate pathway can be found in plants and microbes

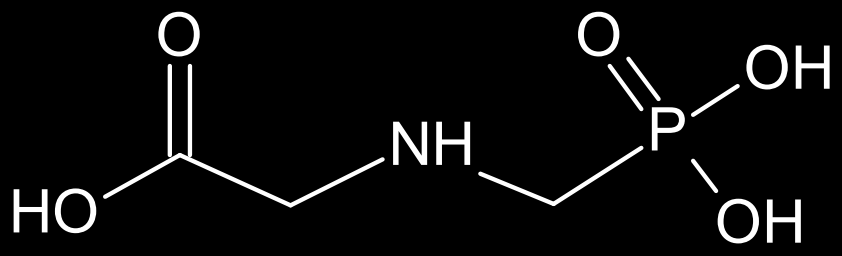
Trends in Plant Science, Volume 17, Issue 10, October 2012, Pages 569–574

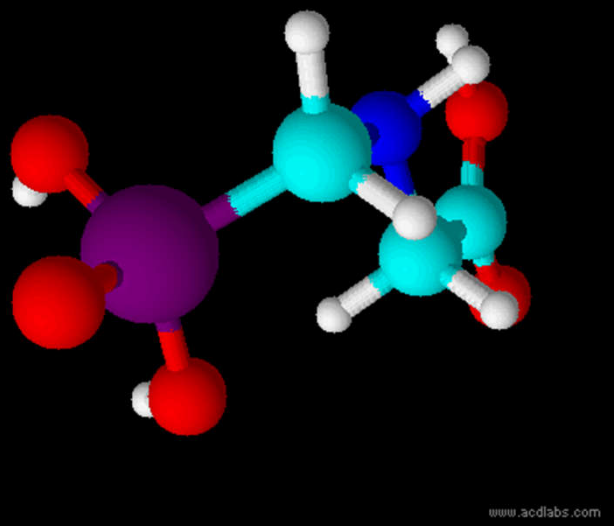


Common Name ISO: GLYPHOSATE

Chemical name IUPAC: N-(phosphonomethyl)-glycin

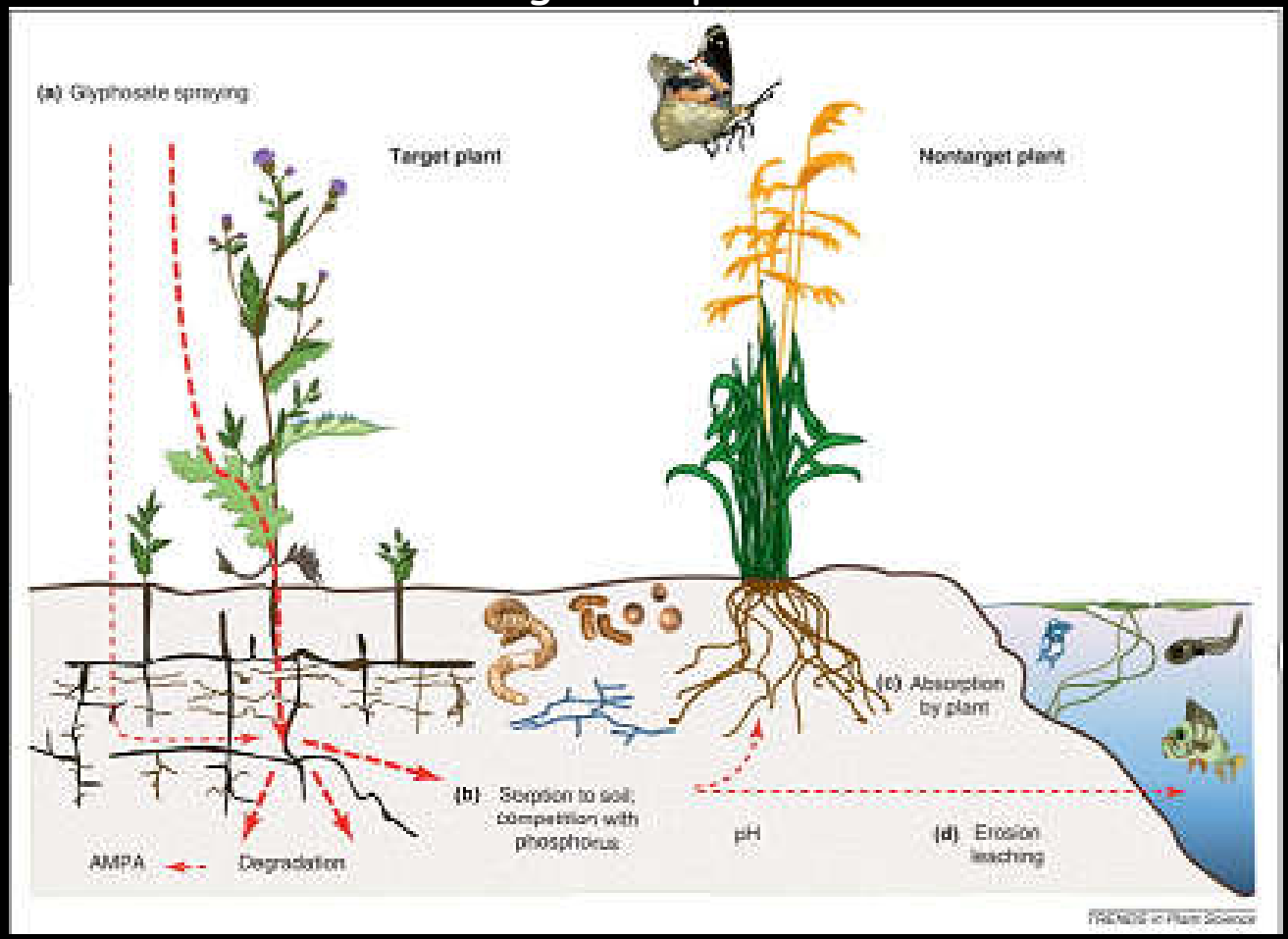
Solvent	Solubility	Solvent	Solubility
Water	**pH 2: 10.5 ± 0.2 g/l 20 °C, 995 g/kg**	Methanol	0.231 g/l
Acetone	0.078 g/l	n-Octanol	0.020 g/l
Dichloromethane	0.233 g/l	Propan-2-ol	0.020 g/l
Ethylacetate	0.012 g/l	Toluene	0.036 g/l
Hexane	0.026 g/l		





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 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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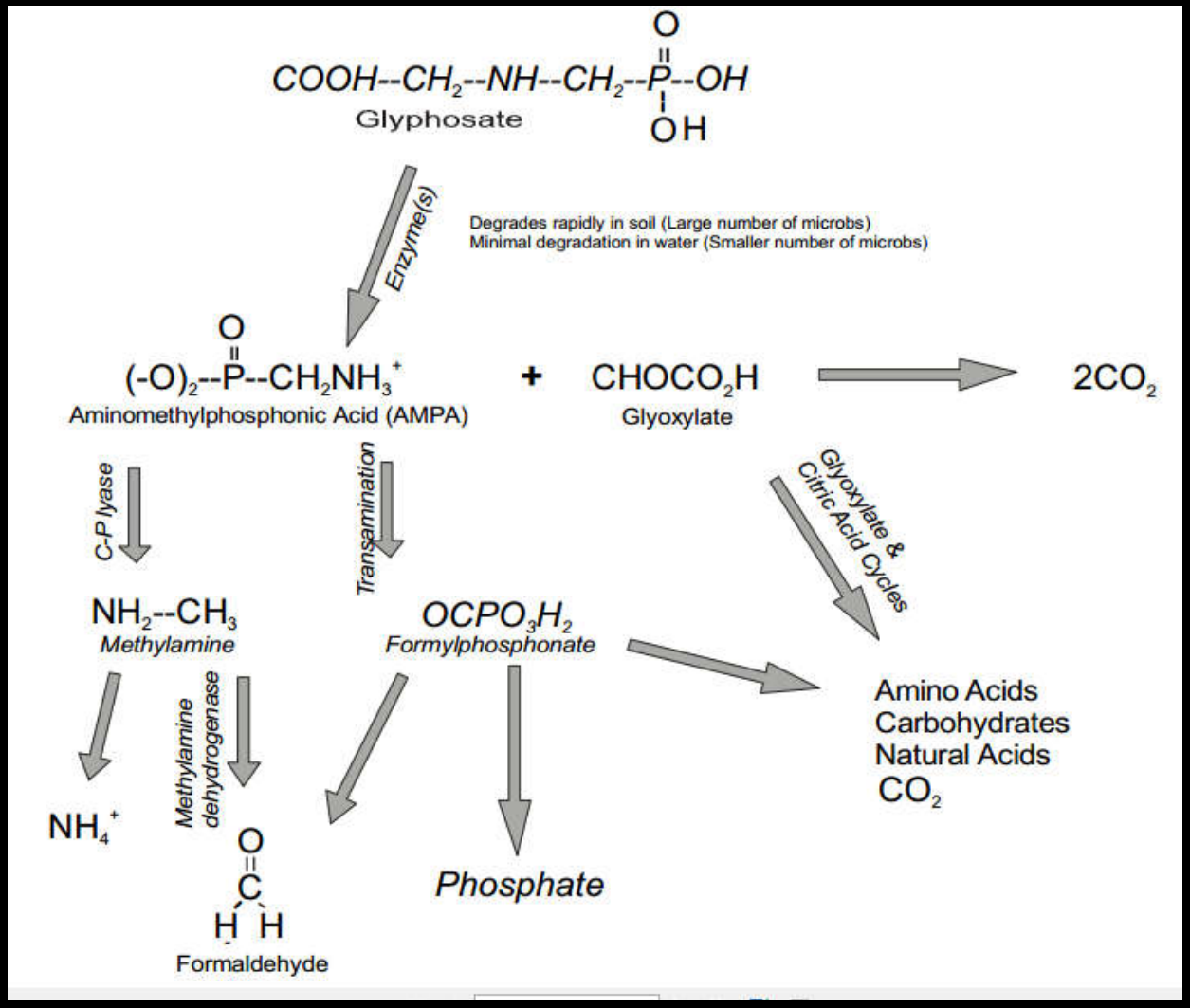
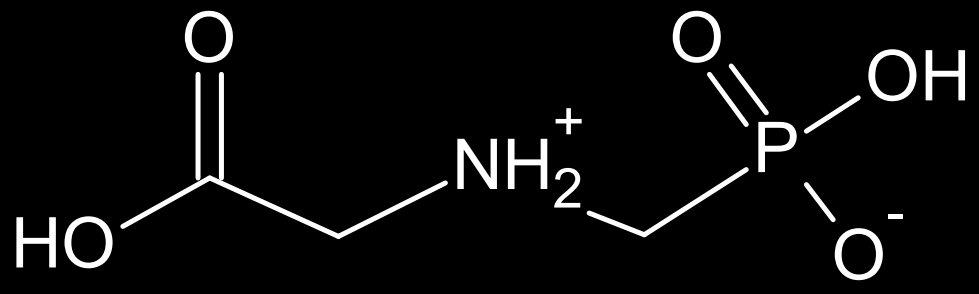


ENVIRONMENTAL FATE OF GLYPHOSATE Jeff Schuette Environmental Monitoring & Pest Management Department of Pesticide Regulation Sacramento, CA 95824-5624 (Revised November 1998)

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

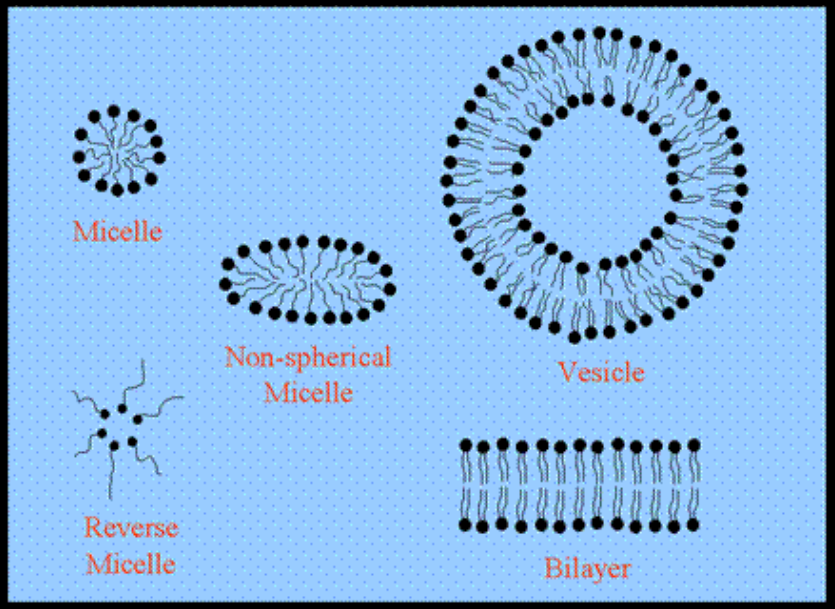


Acid Dissociation Constants of Glyphosate	Value of Dissociation Constant of Glyphosate	Dissociated Proton in Glyphosate
pKa_1	0,8	First phosphonic
pKa_2	2,3	Carboxilate
pKa_3	6,0	Second phosphonic
pKa_4	11,0	Amine

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.

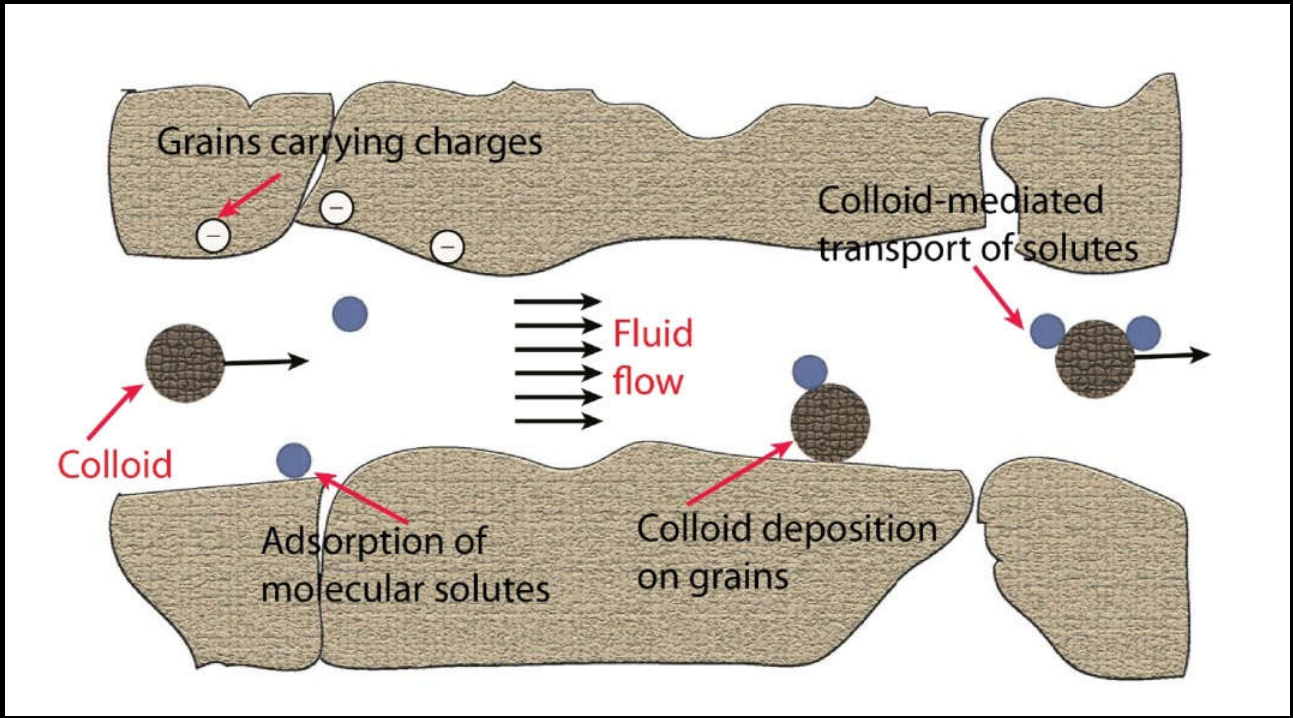
The importance of particulate matter in the transport of pollutants and subsequent deposition is recognized.

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

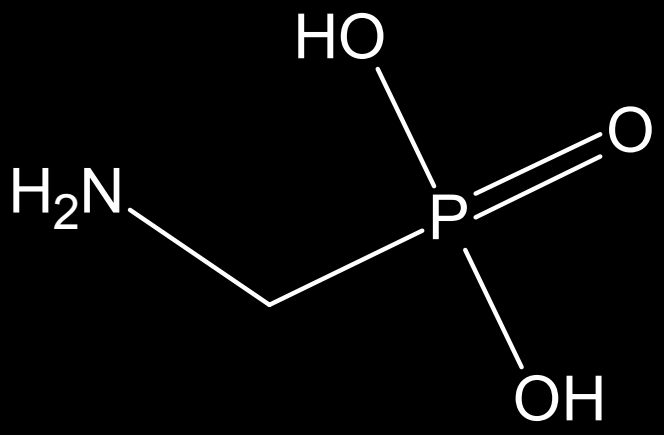
Presence of colloidal matter in natural waters can vary with season. Furthermore, the concentration distribution of the chemical through a water body is not likely to be omogenous. Therefore, the estimated environmental concentrations in water could be overestimated or underestimated at specific sites.

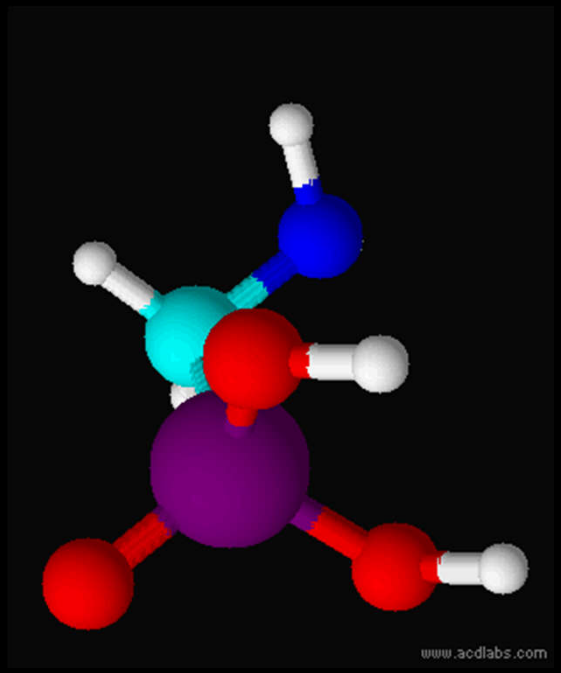


Geological Disposal of Nuclear Waste: Fate and Transport of Radioactive Materials,

By Prabhakar Sharma DOI: 10.5772/50391

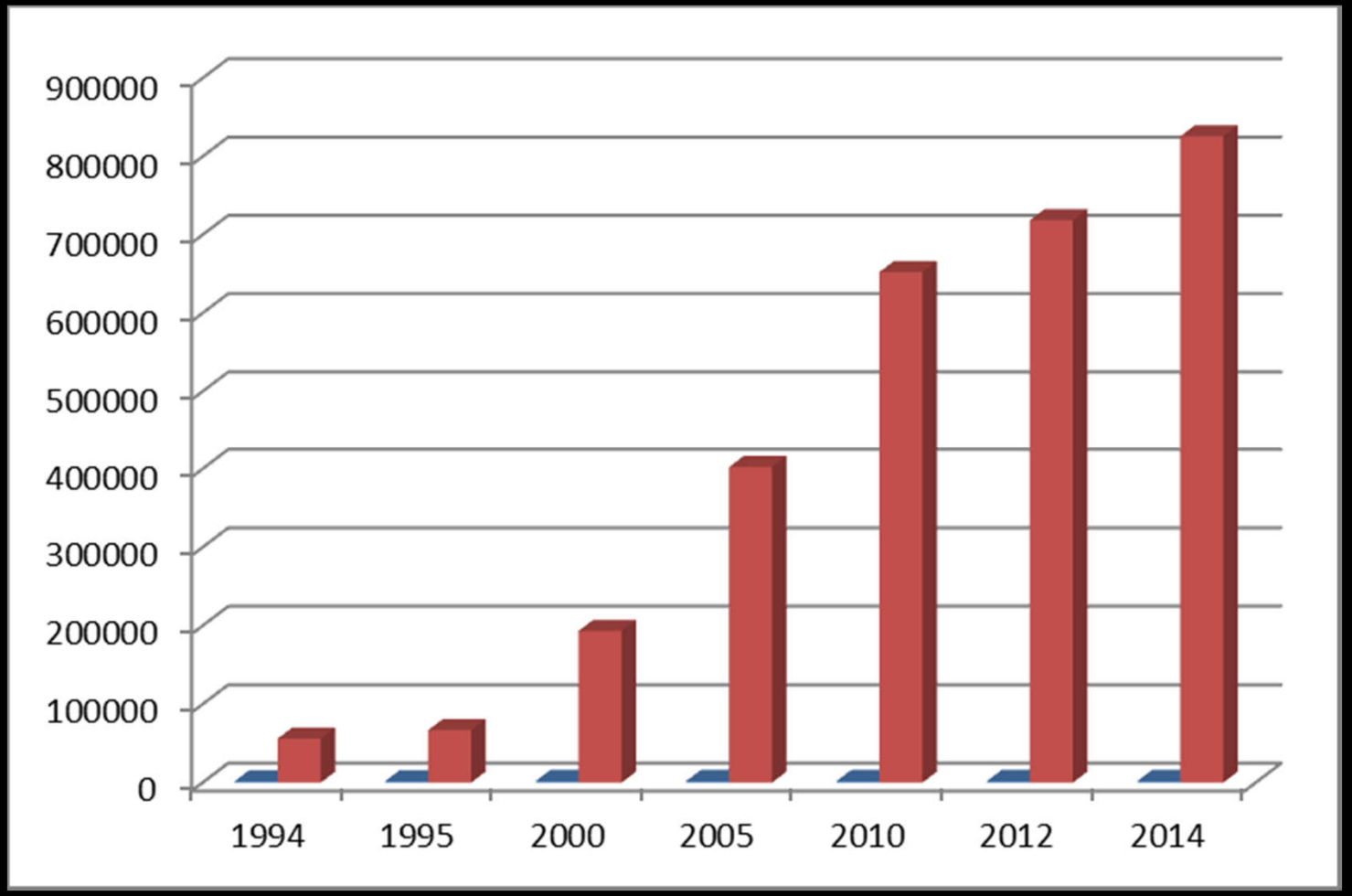
The primary metabolite of glyphosate is aminomethylphosphonic acid (AMPA). Degradation of AMPA is generally slower than that of glyphosate possibly because AMPA may adsorb onto soil particles more strongly than glyphosate and/or because it may be less likely to permeate the cell walls or membranes of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





Aminomethylphosphonic acid (AMPA).

Global agricultural and non-agricultural use of glyphosate: 1994 -2014
tons



Benbrook Environ Sci Eur (2016) 28:3

TUSCANY
Active Substances Sales data
Year 2009
Expressed in 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.

R.it | Ambiente

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"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

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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

LA STAMPA TUTTOGREEN

SEZIONI

"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

LA STAMPA CON TE DOVE E QUANDO VUOI

E-mail

Password

ABBONATI ACCEDI

Recupera password

REGULATION (EC) No 1107/2009

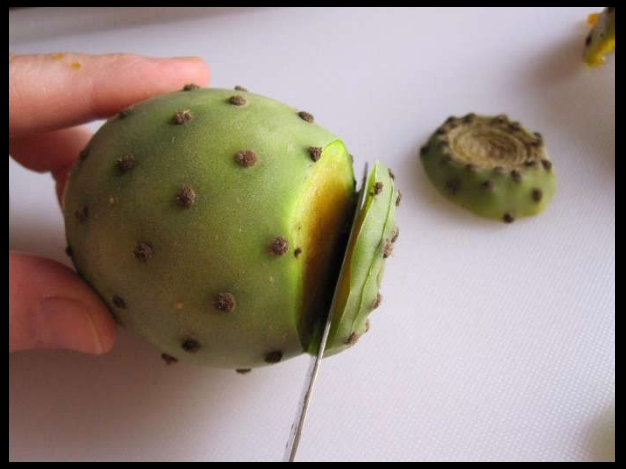
CHAPTER I
GENERAL PROVISIONS
Article 1
Subject matter and purpose

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

20/03/2015

International Agency for Research on Cancer

World Health Organization

Glyphosate monograph is on-line.
The conclusion is that glyphosate is probably carcinogenic to human

30/07/2015

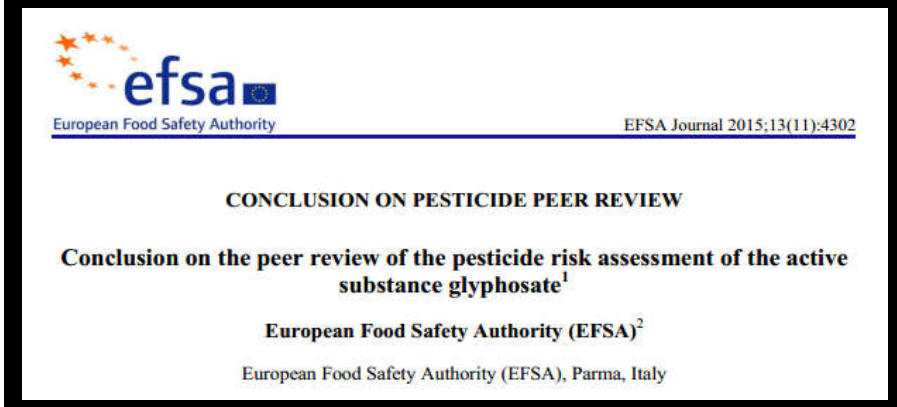
efsa European Food Safety Authority
Committed to ensuring that Europe's food is safe

BfR Bundesinstitut für Risikobewertung

Re-Evaluation

EFSA is to assess the findings of a report by IARC.
Initial draft risk assessment report is produced by an RMS (Rapporteur Member State), in this case, RMS is Germany
The report will be considered as part of EFSA's on-going peer review of the re-evaluation of glyphosate.

12/11/2015


efsa
European Food Safety Authority
EFSA Journal 2015;13(11):4302

CONCLUSION ON PESTICIDE PEER REVIEW

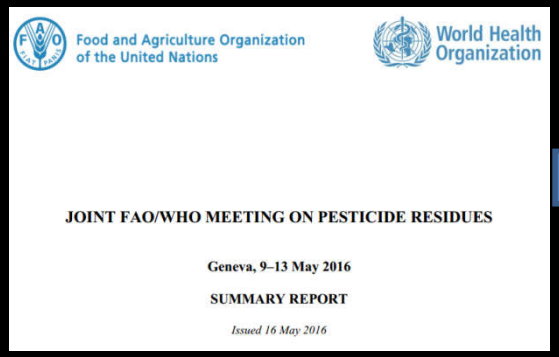
Conclusion on the peer review of the pesticide risk assessment of the active substance glyphosate[1]

European Food Safety Authority (EFSA)[2]

European Food Safety Authority (EFSA), Parma, Italy

...glyphosate is unlikely to pose a carcinogenic hazard to humans and the evidence does not support classification with regard to its carcinogenic potential according to Regulation (EC) No 1272/2008.

16/05/2016


Food and Agriculture Organization of the United Nations

World Health Organization

JOINT FAO/WHO MEETING ON PESTICIDE RESIDUES

Geneva, 9–13 May 2016

SUMMARY REPORT

Issued 16 May 2016

The Meeting concluded that glyphosate is unlikely to be genotoxic at anticipated dietary exposures.

Meeting concluded that glyphosate is unlikely to pose a carcinogenic risk to humans from exposure through the diet.

- ADI 0-1mg/Kg Bodyweight
- No ARfD for glyphosate or its metabolites in view of its low acute toxicity

European Commission

June 2016: No qualified majority from the Member States at either the Standing Committee (6 June) or the Appeal Committee (24 June).

End June 2016: End of the provisional extension at EU level of the active substance glyphosate. Commission extends approval of the substance, under certain conditions. In all, the EU's assessment of glyphosate has taken 3 years, involving public sector scientific experts from EU's agencies (EFSA and ECHA) and national authorities in all 28 Member States.

27 Member States agree with EFSA's conclusion on carcinogenicity (Sweden was in favour of another classification)

The Commission adopted the extension of the current approval of glyphosate for a limited period until the European Chemical Agency (ECHA) has concluded its review.

REGULATION 2016/1313

1. ban a co-formulant called POE-tallowamine from glyphosate based products;
2. minimise the use of the substance in public parks, public playgrounds and gardens;
3. minimise the pre-harvest use of glyphosate

9 August: MINSAN issued a decree which, with effect from 22 August 2016, that include:

- **the revocation of the use** in areas frequented by people (...) such as: parks, gardens, sports fields and recreational areas, playgrounds and green areas within school buildings, children's play areas and adjacent areas to health facilities;
- **prohibition of use in agricultural for the purpose of optimizing the harvest or threshing**;
- **prohibition of non-agricultural use on soils containing a higher percentage of sand to 80%**; areas vulnerable and buffer zones (groundwater protection)

http://europa.eu/rapid/press-release_MEMO-16-2012_en.htm

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Home » News » Agricoltura » Glifosate, in Toscana in un solo anno vendute 100 tonnellate dell'erbicida probabile cancerogeno

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Agricoltura | Inquinamenti

Mi piace 5

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

[17 aprile 2015]

REGIONE TOSCANA

Followed by Resolution 821/2015 of the Regional Government, Tuscany Region has banned the use of Glyphosate in non-agricultural sector

ISPRA
Istituto Superiore per la Protezione e la Ricerca Ambientale

Rapporto nazionale pesticidi nelle acque

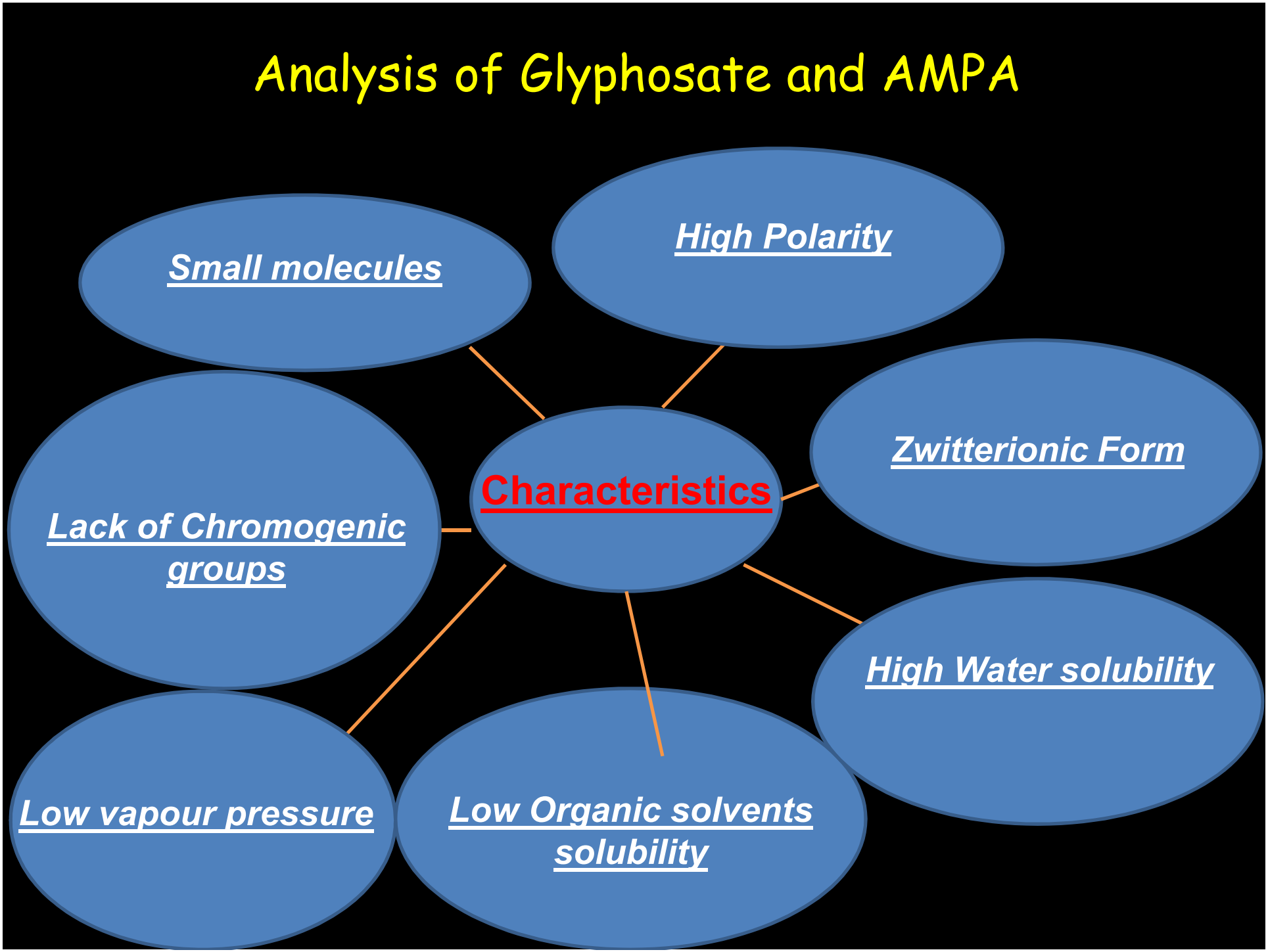
dati 2011-2012

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.

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

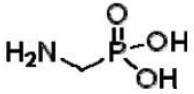
María del Mar Soto[1], Cintia Flores[1], Claudia P.B.Martins[2], Josep Caixach[1]

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

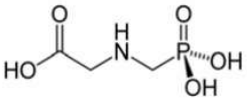
[2] Thermo Fischer Scientific, C/Acero 30-32, plta 2ª, mód.3 Edificio Sertram, 08038-Barcelona (Spain)

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.



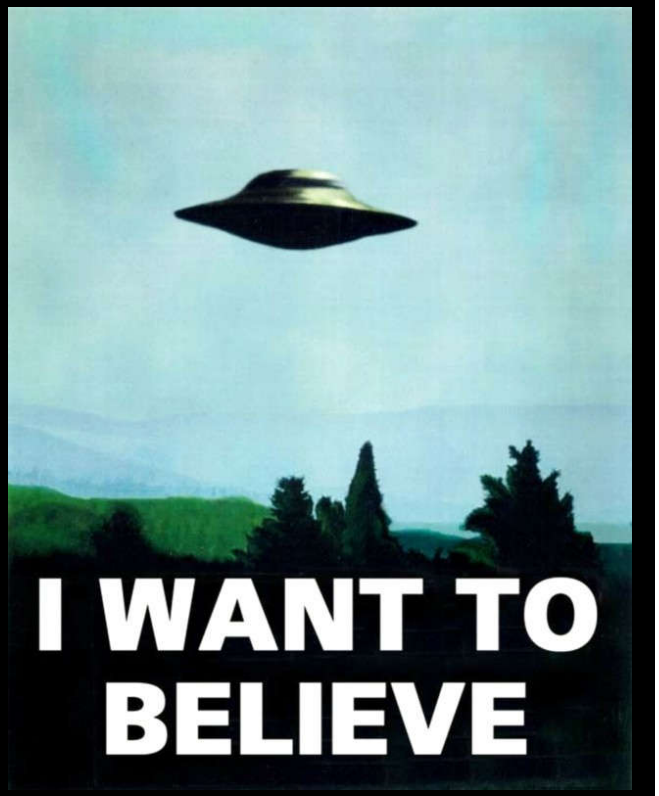
AMPA
CAS Number: 1066-51-9
Monoisotopic mass: 112



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).

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

Microchemical Journal 121 (2015) 99–106

Contents lists available at ScienceDirect

Microchemical Journal

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

Review

The role of derivatization techniques in the analysis of glyphosate and aminomethyl-phosphonic acid by chromatography

T. Arkan, I. Molnár-Perl *

Institute of Chemistry, Department of Analytical Chemistry, L. Eötvös University, H-1117 Budapest, Pázmány Péter sétány 1/A, Hungary

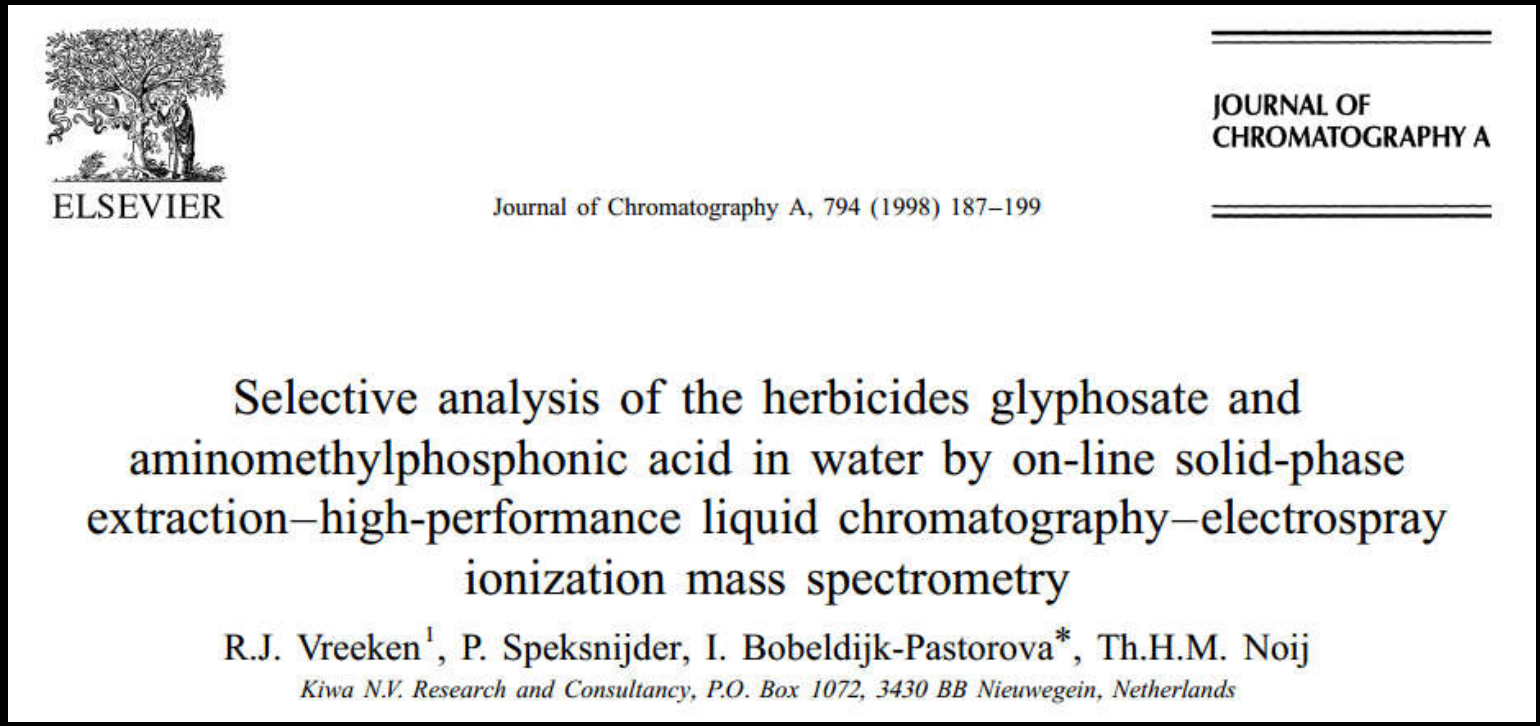
LC

Insertion of Chromogenic group
and/or improvement of chromatographic behaviour

GC

Insertion of group for
enhancement of volatility

Analysis of Glyphosate and AMPA



ELSEVIER

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

ELSEVIER

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

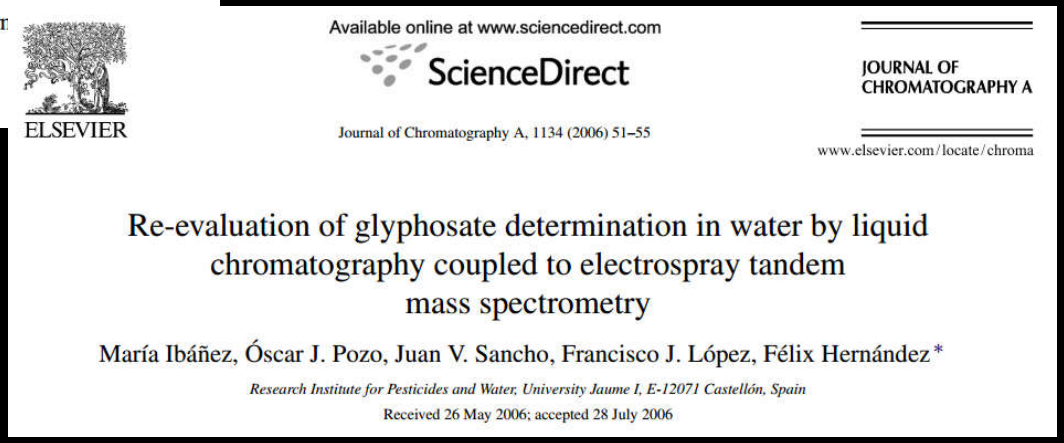
www.elsevier.com/locate/chroma

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 Herr

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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ScienceDirect

JOURNAL OF CHROMATOGRAPHY A

ELSEVIER

Journal of Chromatography A, 1134 (2006) 51–55

www.elsevier.com/locate/chroma

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

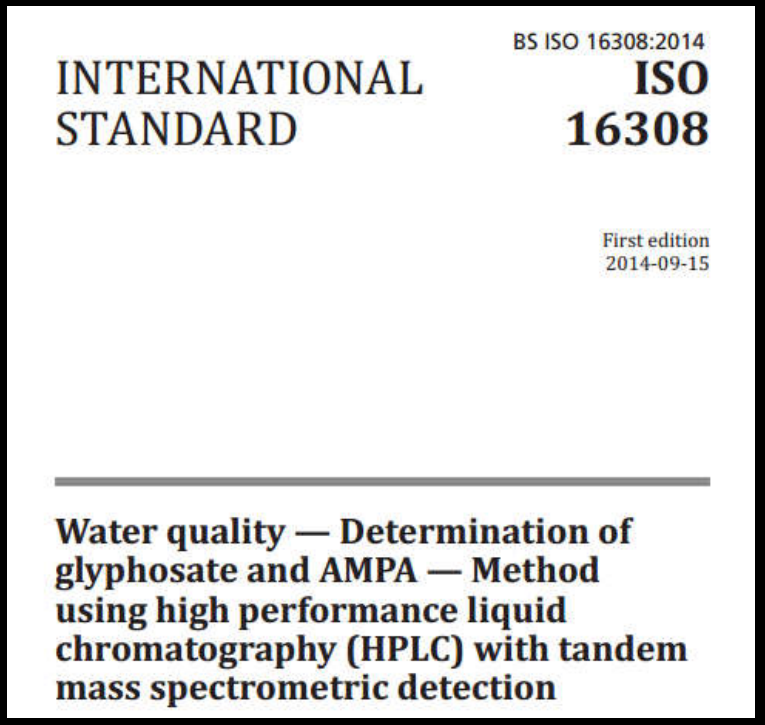
- ***Derivatization with FMOC-Cl***
- ***SPE off-line clean-up and concentration***
- ***Analysis of the extracts by LC-MS and LC-MSMS negative ionization***

Analysis of Glyphosate and AMPA

USGS
science for a changing world

Determination of Glyphosate, its Degradation Product Aminomethylphosphonic Acid, and Glufosinate, in Water by Isotope Dilution and Online Solid-Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry

- ***Derivatization with FMOC-Cl***
- ***Preconcentration-clean-up with SPE (off or on-line) or LLE***
- ***Analysis of the extracts by LC-MS and LC-MSMS negative ionization***


BS ISO 16308:2014

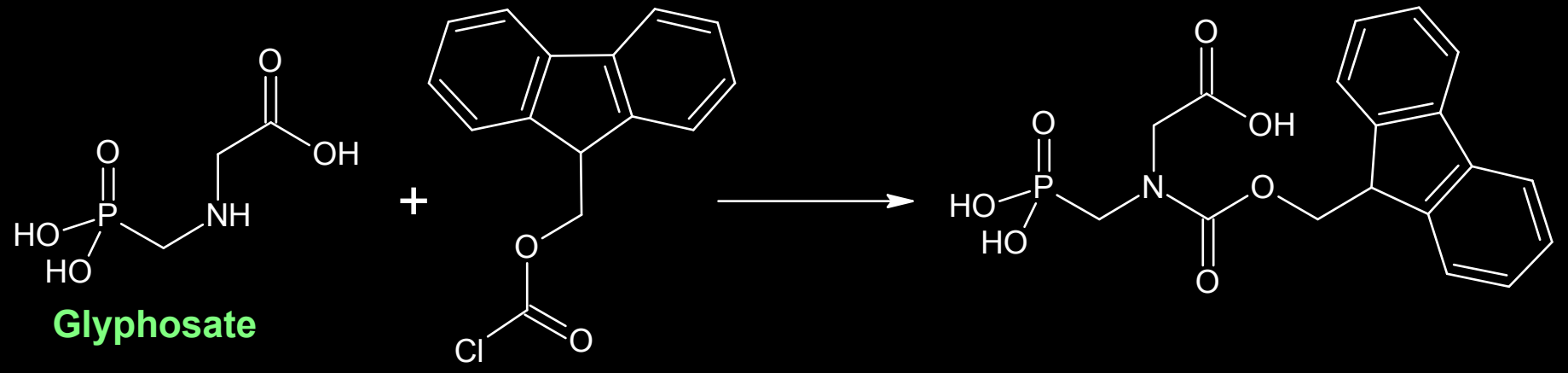
INTERNATIONAL STANDARD

ISO 16308

First edition
2014-09-15

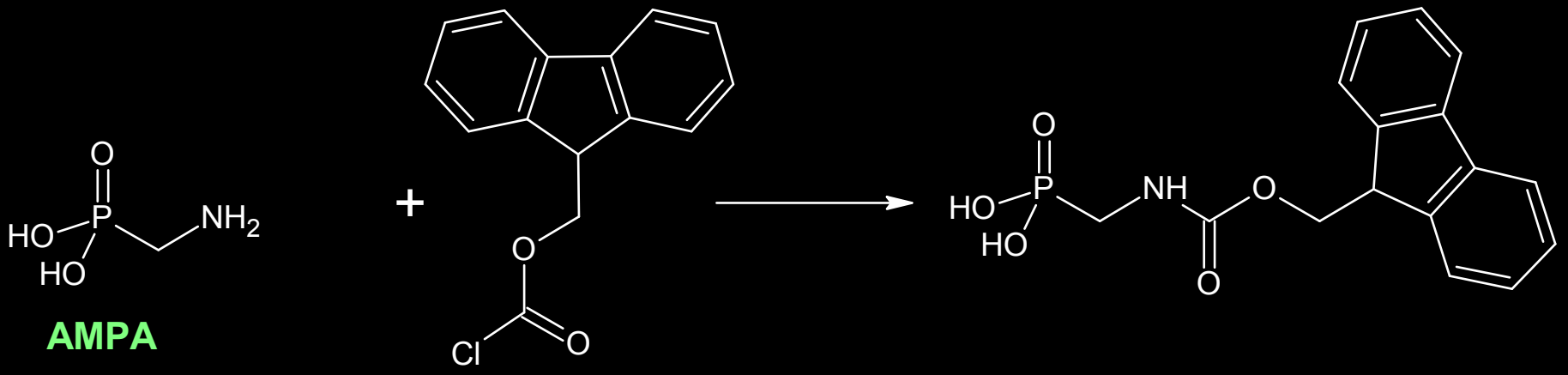
Water quality — Determination of glyphosate and AMPA — Method using high performance liquid chromatography (HPLC) with tandem mass spectrometric detection

Derivatization of Glyphosate and AMPA with FMOC-Cl

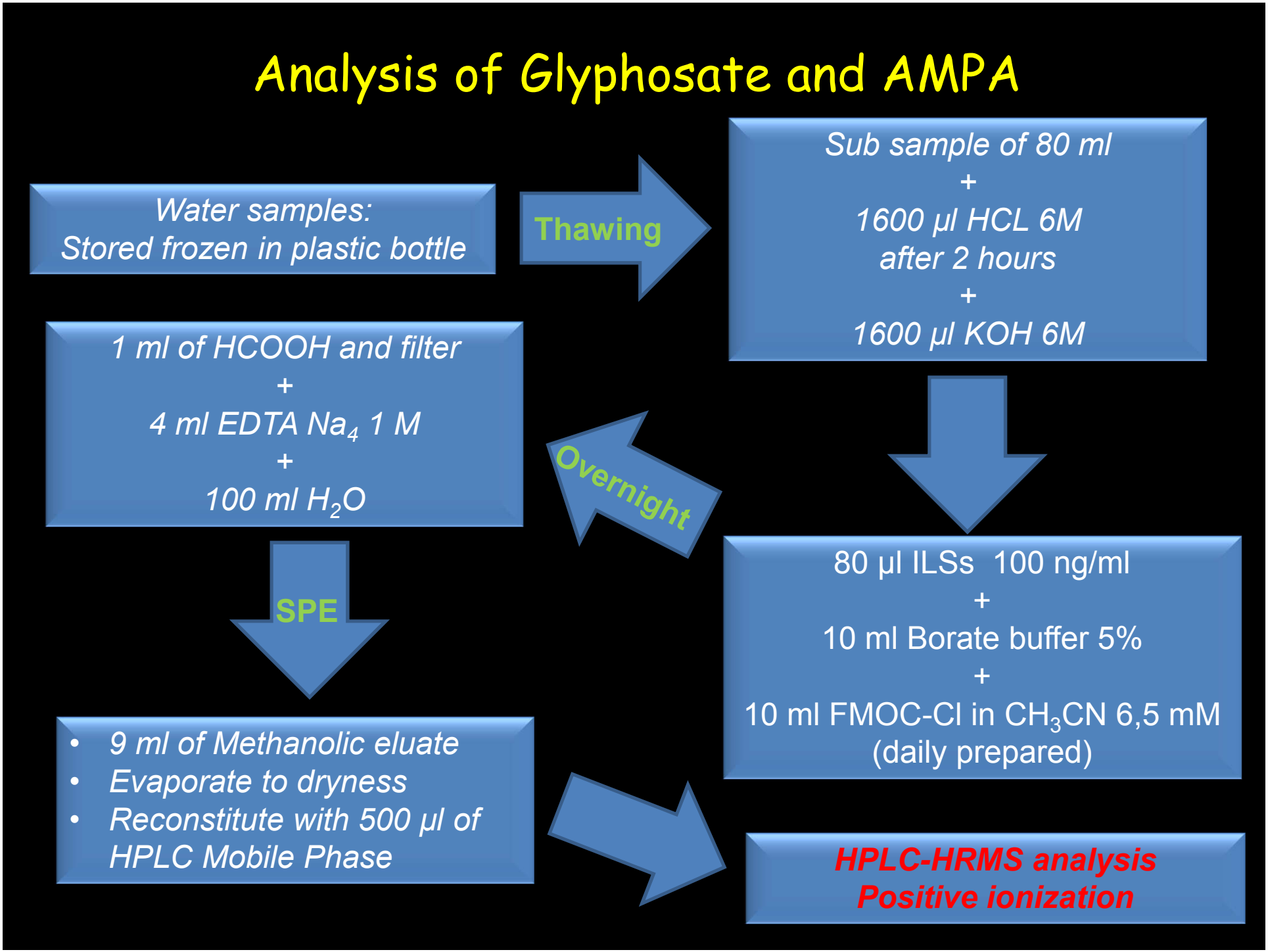


FMOC-Cl

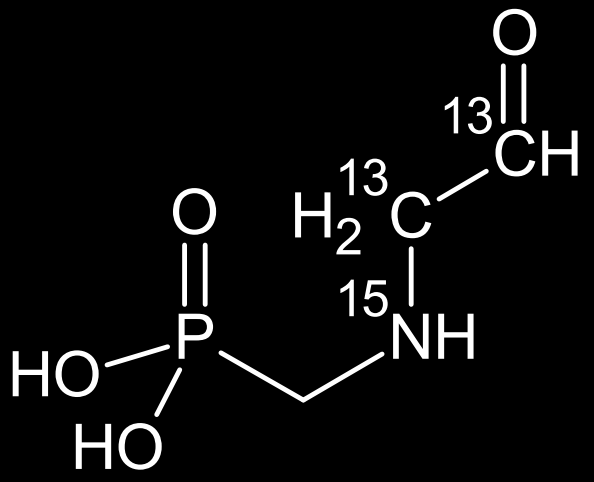
IUPAC name: Chloroformic acid 9H-fluoren-9-ylmethyl ester
Other names:9-Fluorenylmethyl chloroformate; 9-Fluorenylmethoxycarbonyl chloride;



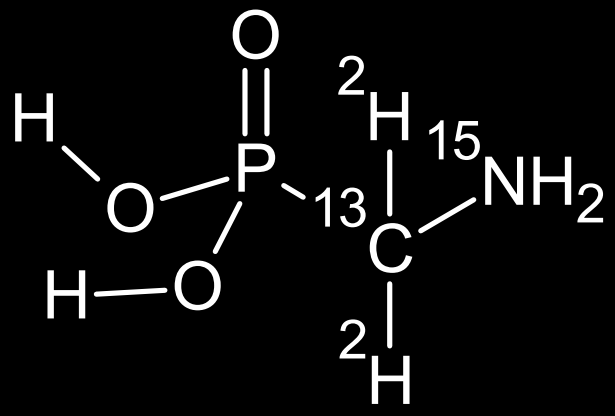
Analysis of Glyphosate and AMPA



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

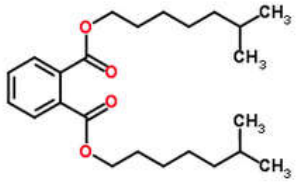
LC-MS-IT

ChemSpider
Search and share chemistry

Simple Structure Advanced History

Found 1 result

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



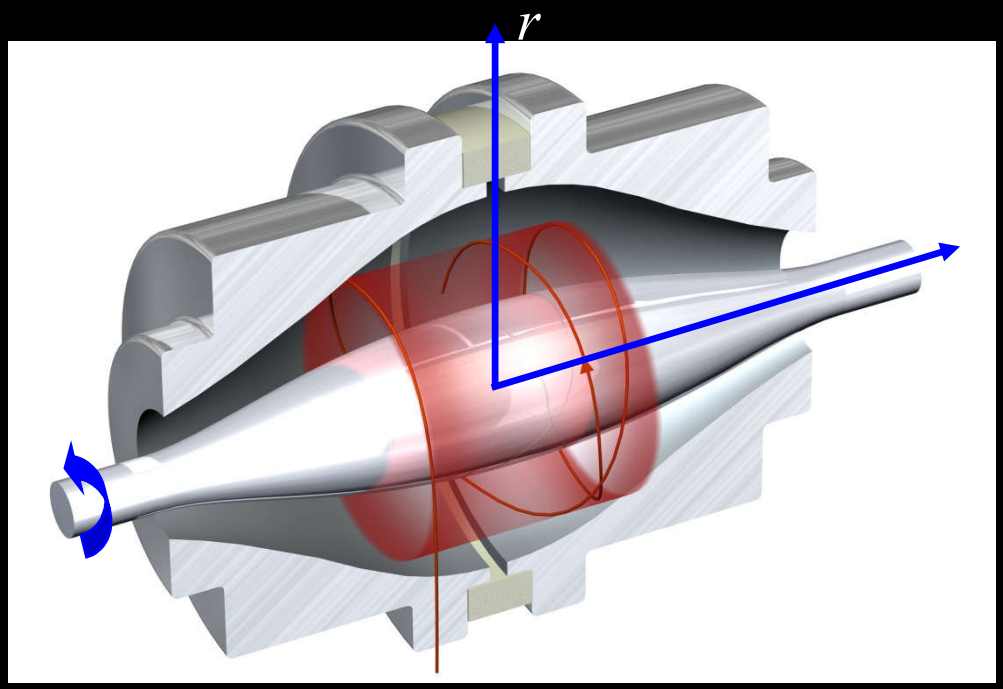
DIISOOCTYL PHTHALATE

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



Characteristic frequencies:
Frequency of rotation ω_φ
Frequency of radial oscillations ω_r
Frequency of axial oscillations ω_z

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

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

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

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

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

•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.

Instrumental Method

HPLC Column : Biphenyl, 150 mm, 2 mm, 3 µm
Phase A: Water 98%, ammonium formate 5 mM, methanol, 2%, Formic Acid 0,01%
Phase B: Methanol: 83%, Isopropanol: 15%, Ammonium formate 5 mM: 2%, Formic Acid 0,01%
Flow 400 µl/min

Gradient:

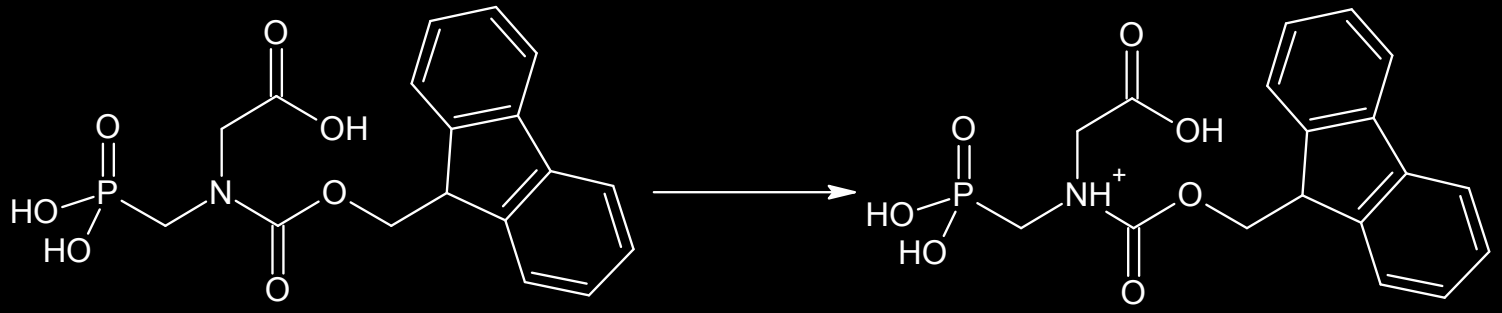
Time	A%	B%
0	95	5
1	95	5
15	29	71
16	5	95
21	5	95
22	95	5
27	95	5

HESI (capillary 350 °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



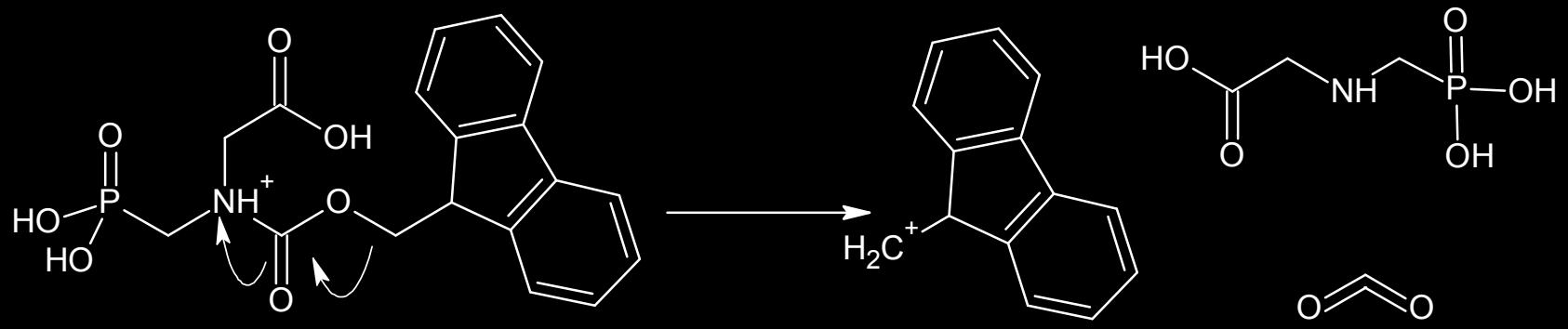
	Formula	Target	Qual.	Ratio Q/Tgt
Glypho-FMOC nat.	$C_{18}H_{18}PNO_7$	392,08936	393,09272	19.47
Glypho-FMOC mark.	$^{13}C_2C_{16}H_{18}P^{15}NO_7$	395,09311	396,09646	17.31
AMPA-FMOC nat.	$C_{16}H_{16}PNO_5$	334.08389	335.08724	17.31
AMPA-FMOC mark.	$^{13}CC_{15}D_2H_{14}P^{15}NO_5$	338.09683	339.10018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

LC-HRMS: HCD fragmentation: Glyphosate

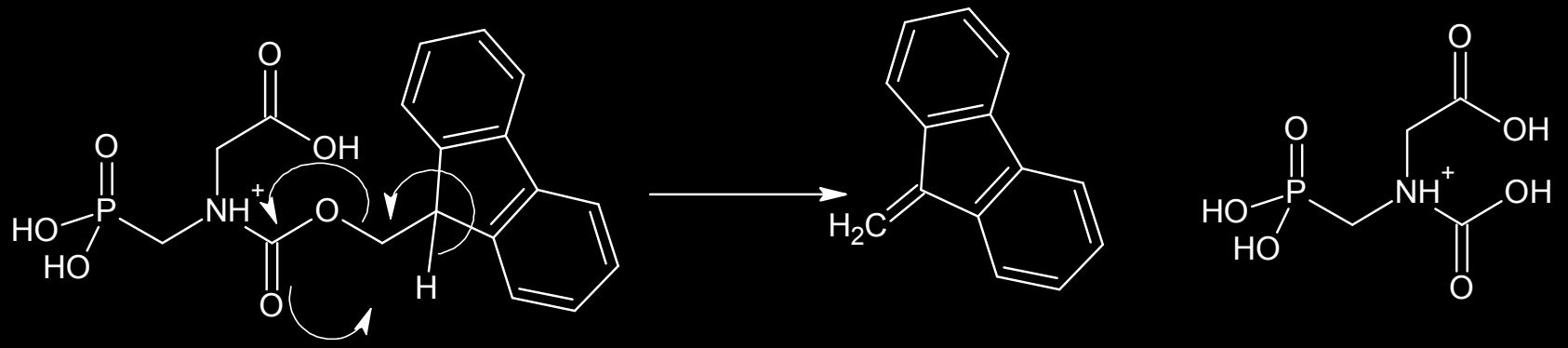
In the event of doubtful situations, we proceed to the analysis of fragments.

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

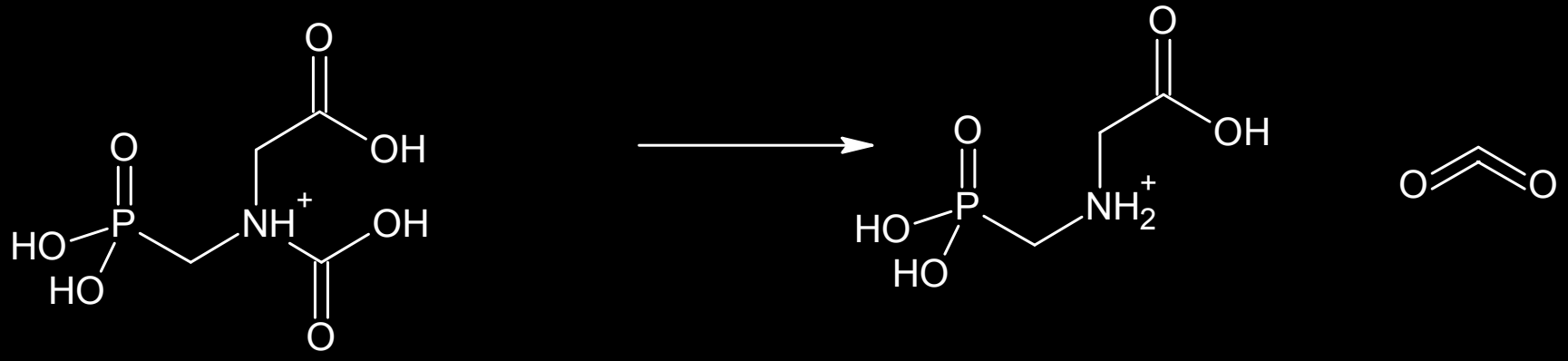
$^{13}C_2C_2H_9P^{15}NO_7$ (protonated adduct)= massa 217.01486

LC-HRMS: HCD fragmentation: Glyphosate

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

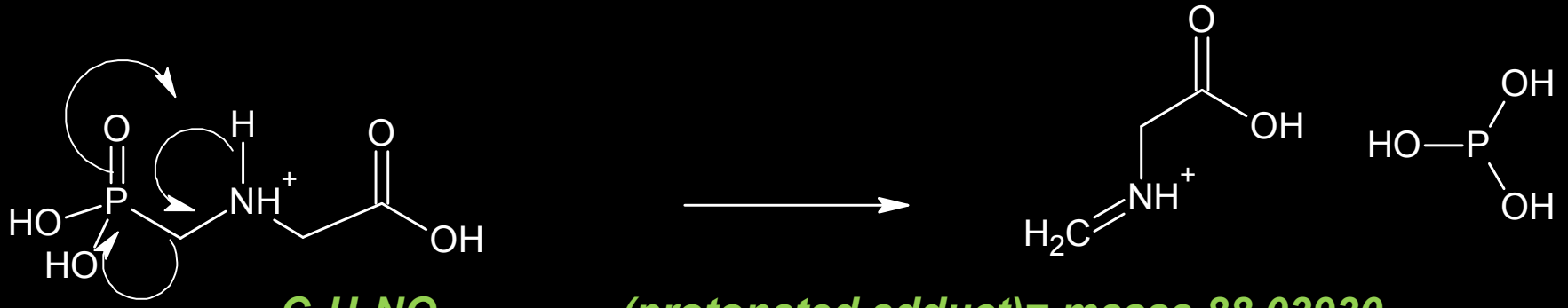
Identification is considered certain if it will prove at least two fragment ions, In this way,

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



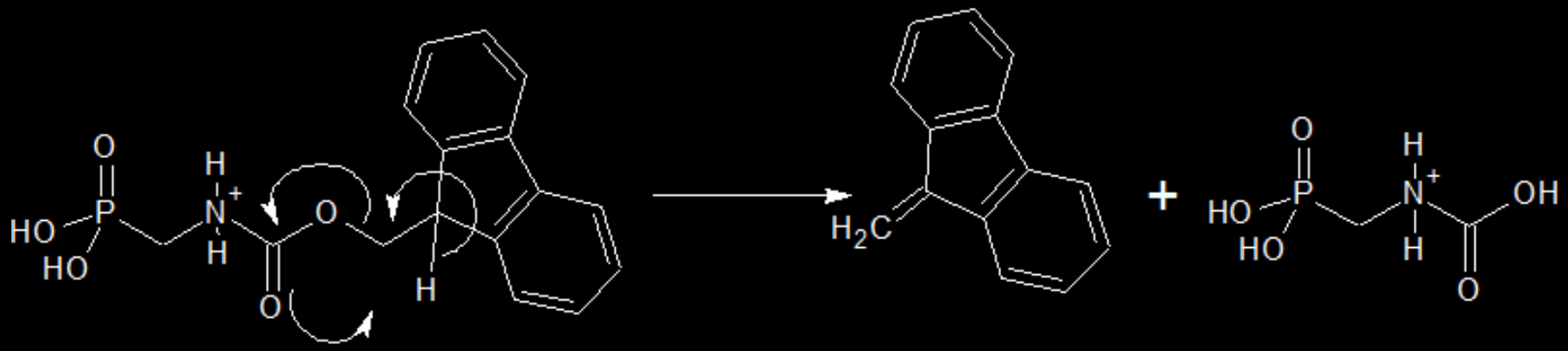
$C_3H_9PNO_5$
$^{13}C_2CH_9P^{15}NO_5$

(protonated adduct)= massa 170.02129
(protonated adduct)= massa 173.02503



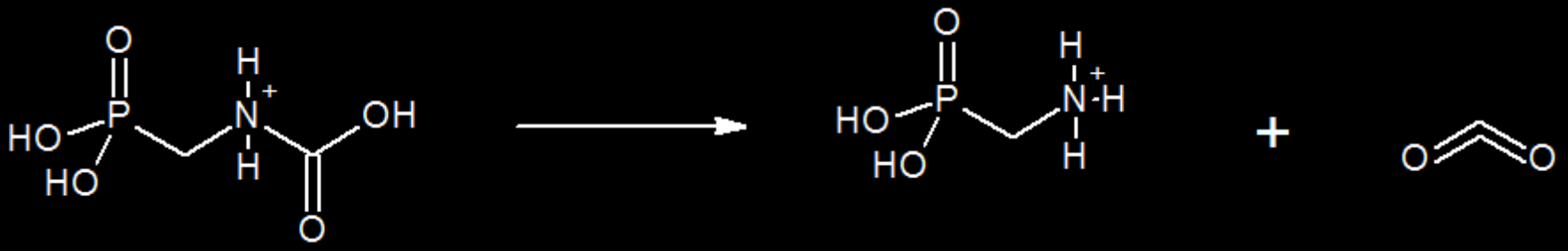
$C_3H_6NO_2$ ***(protonated adduct)= massa 88,03930***
$^{13}C_2CH_6P^{15}NO_2$ ***(protonated adduct)= massa 91,04305***

LC-HRMS: HCD fragmentation
AMPA



$C_2H_5PNO_5$ (protonated adduct)= massa 156,00564

$^{13}CCD_2H_3P^{15}NO_5$ (protonated adduct)= massa 160,01858



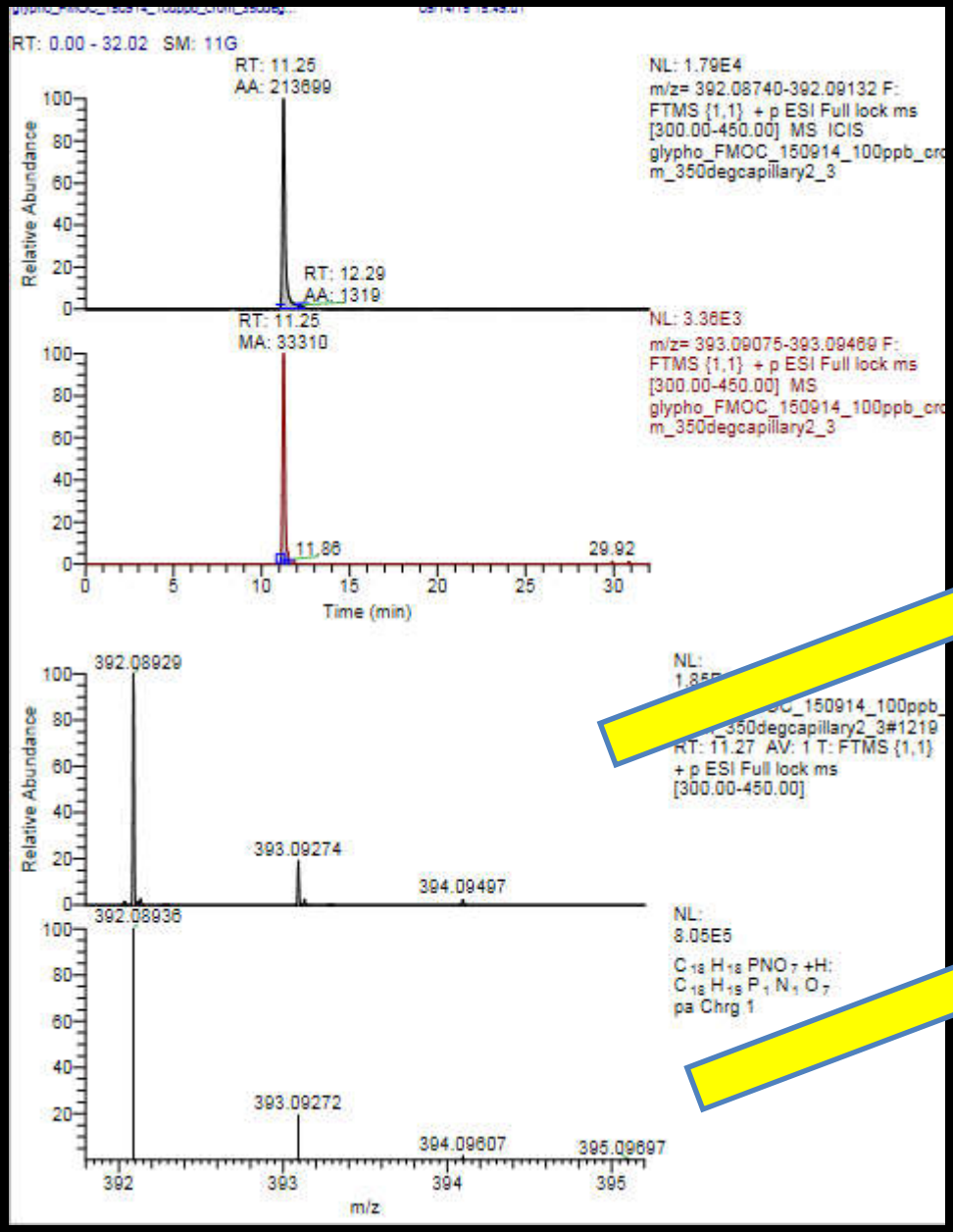
CH_5PNO_3 (protonated adduct)= massa 112.01581

$^{13}CD_2P^{15}NO_3$ (protonated adduct)= massa 116.02875

LC-HRMS: HCD fragmentation

TARGET and FRAGMENT IONS *(HCD 15 eV)*			
	Ion m/z	Ion m/z	Ion m/z
Glyphosate-FMOC	392,08936	214.01111	170.02129
1,2-$^{13}C_2{}^{15}N$ Glyphosate -FMOC.	395,09311	217.01486	173.02503
AMPA-FMOC	334.08389	156.00564	112.01581
$^{13}C^{15}ND_2$ AMPA-FMOC	338.09683	160.01858	116.02875

LC-HRMS: Full scan

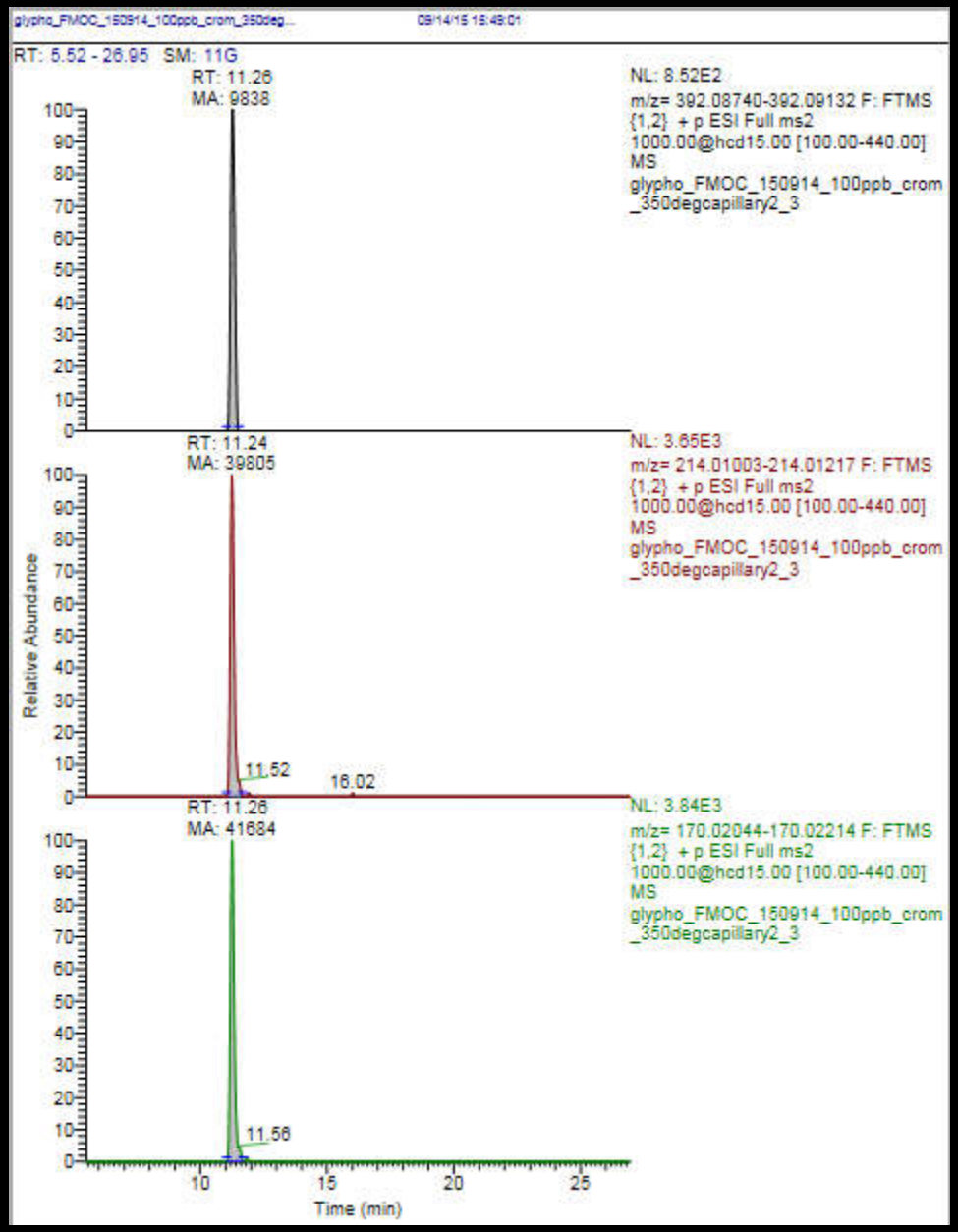


GLY-FMOC
Injection of 15 µl at 100ng/ml

Acquired spectra

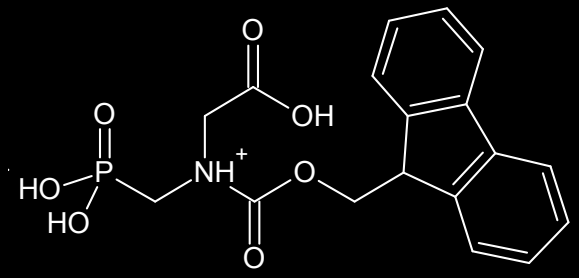
Simulated spectra

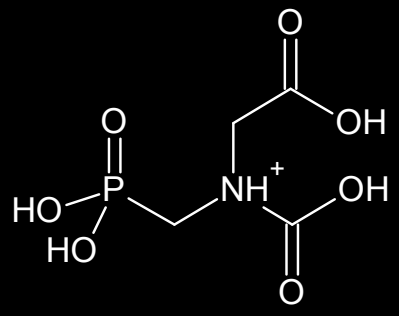
LC-HRMS: HCD Fragmentation

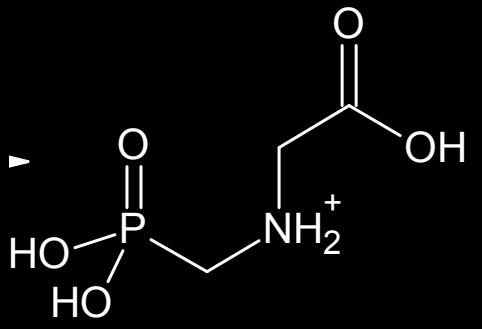


GLY-FMOC

Injection of 15 µl at 100ng/ml

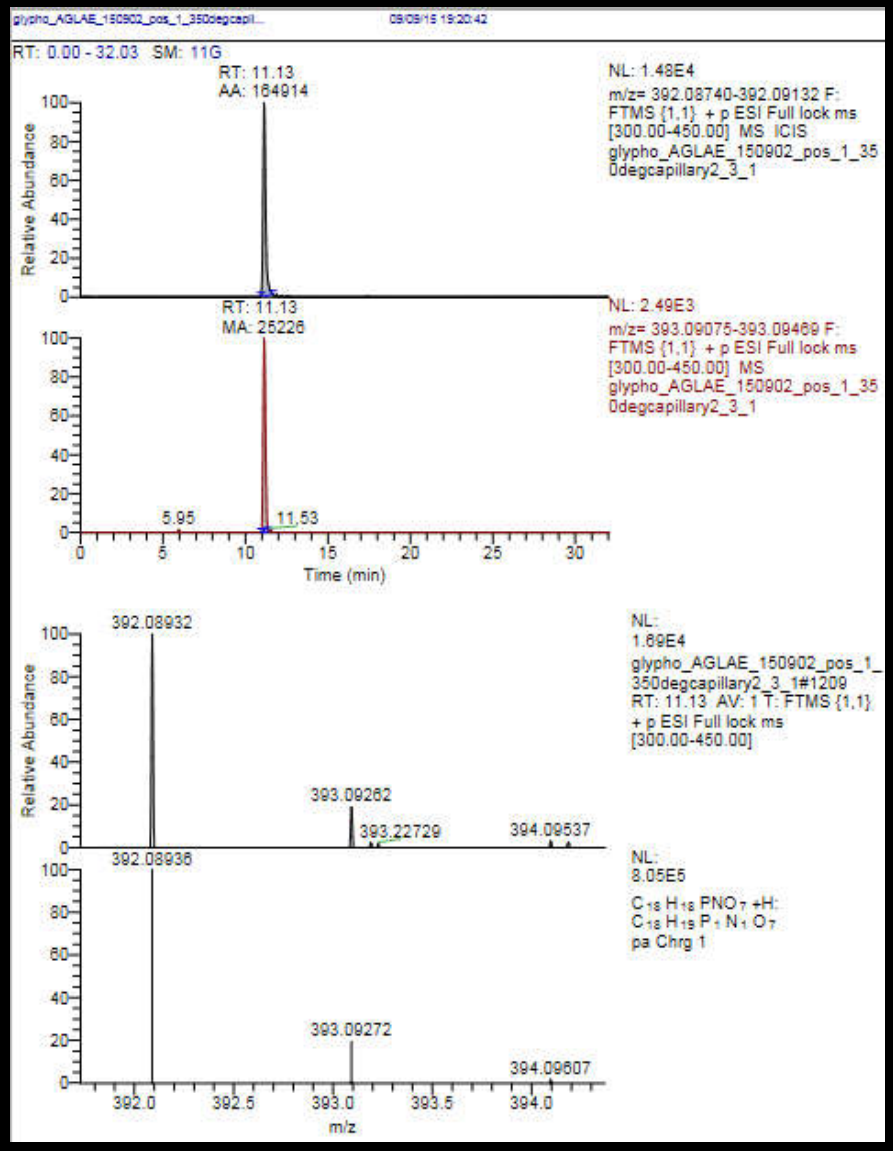


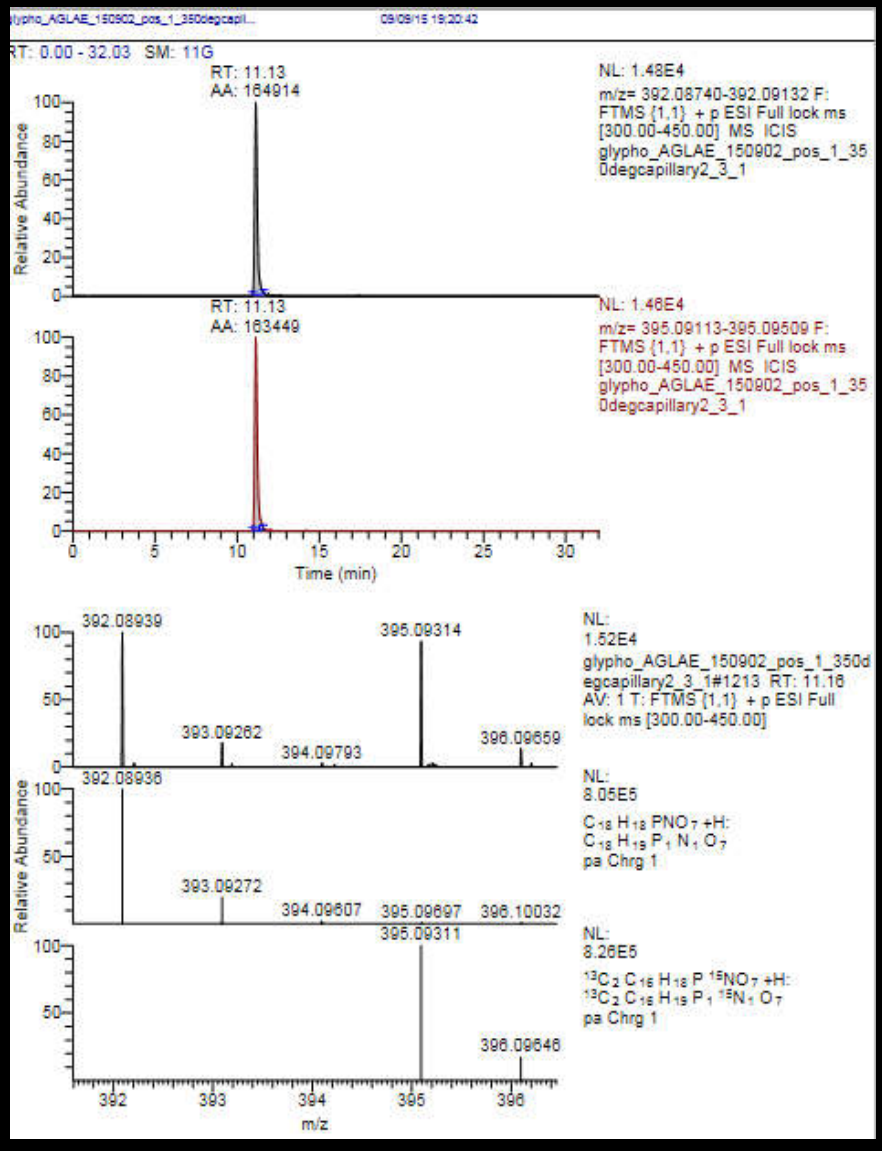




LC-HRMS: Full scan

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





Calculation of results

Isotopic dilution

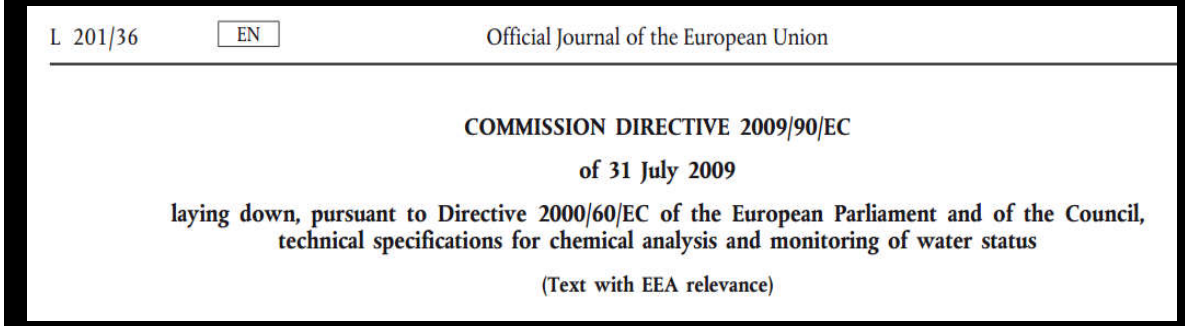
$$F_{x/xILS} = \frac{A_x}{A_{xILS}} = \frac{k_x}{k_{xILS}}$$

$$C_x = (A_x / A_{xILS}) \times C_{xILS} \times \frac{1}{F_{x/xILS}}$$

	F Glyphosate/Glyphosate/1,2-$^{13}C_2{}^{15}N$	F AMPA/AMPA/$^{13}C_2{}^{15}ND_2$
Average	1.018862	1.064397

Quantitation Range

The quantitation range for the method is from 0.02 to 5.0 µg/L



L 201/36 EN Official Journal of the European Union

COMMISSION DIRECTIVE 2009/90/EC

of 31 July 2009

laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status

(Text with EEA relevance)

ART.4

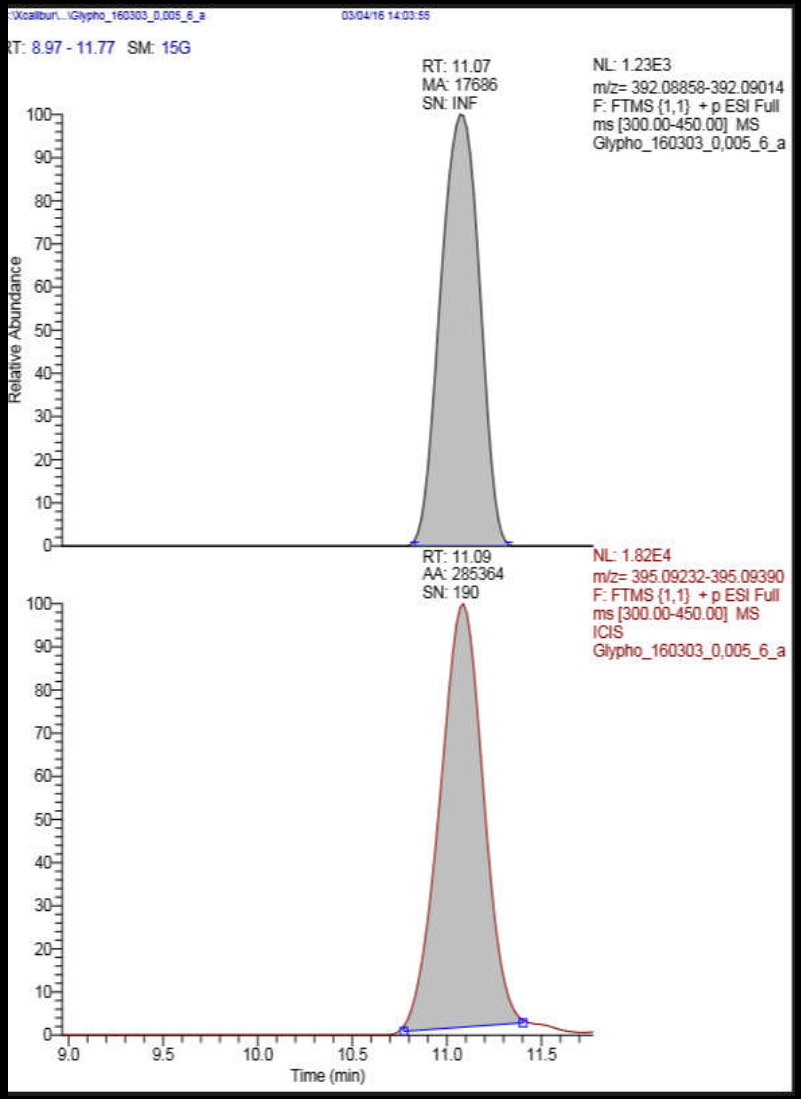
.....a limit of quantification equal or below a value of 30% of the relevant environmental quality standards.

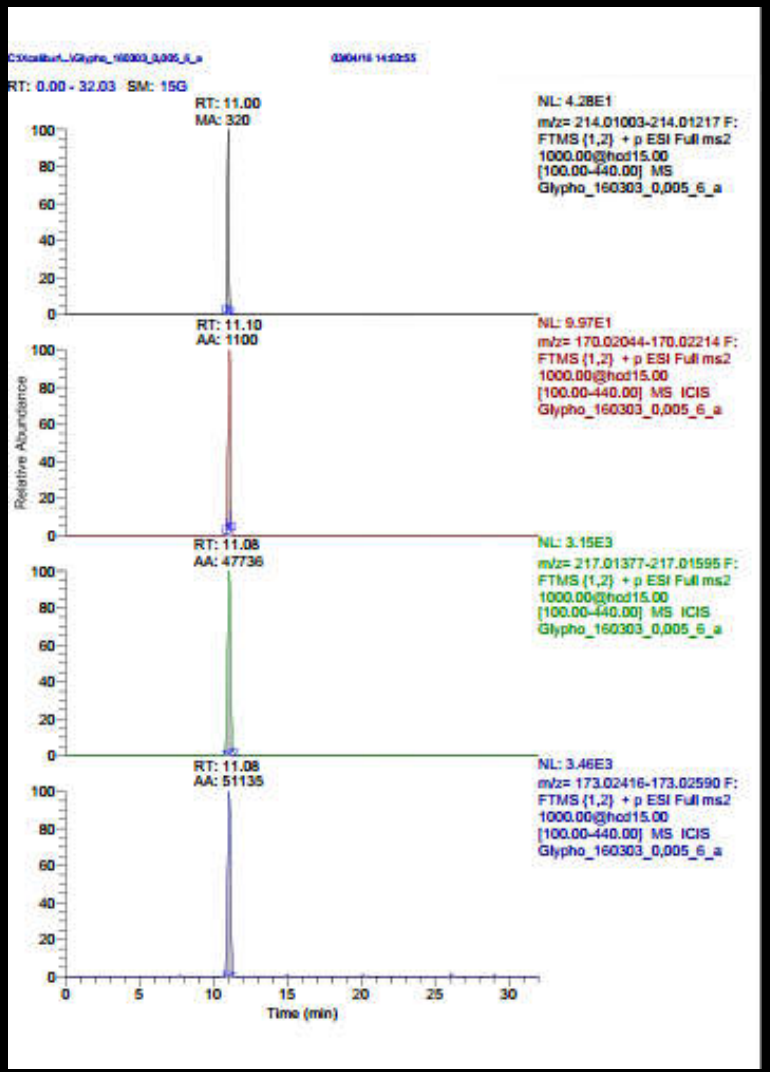
According to the principle of "analogia legis", we use the limit reported in DLGS 31 (0,1 µg/L) for pesticide, so a value of 30% of the Is limit is 0,03µg/L quality standards.

The quantitation range for the method is compliance to Directive 2009/90.

LC-HRMS: Full scan and HCD

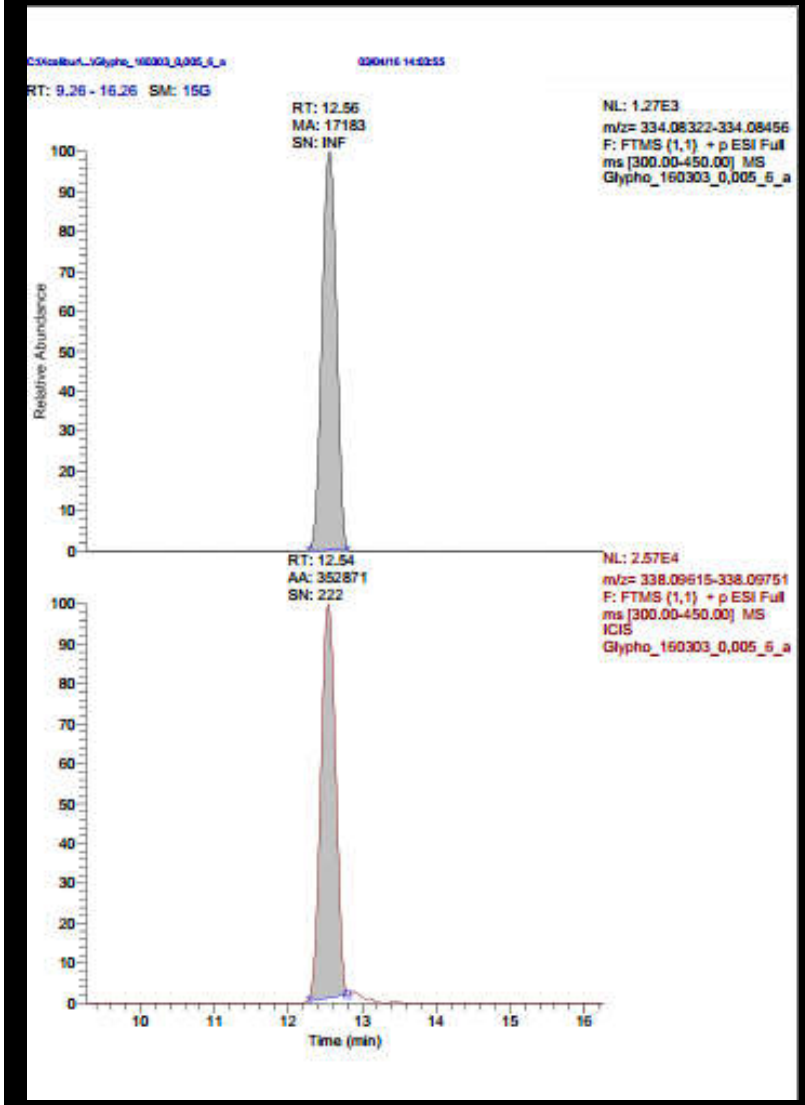
Mineral water spiked with
Glyphosate /Glyphosate ILS
0,005 µg/l/0,1µg/L

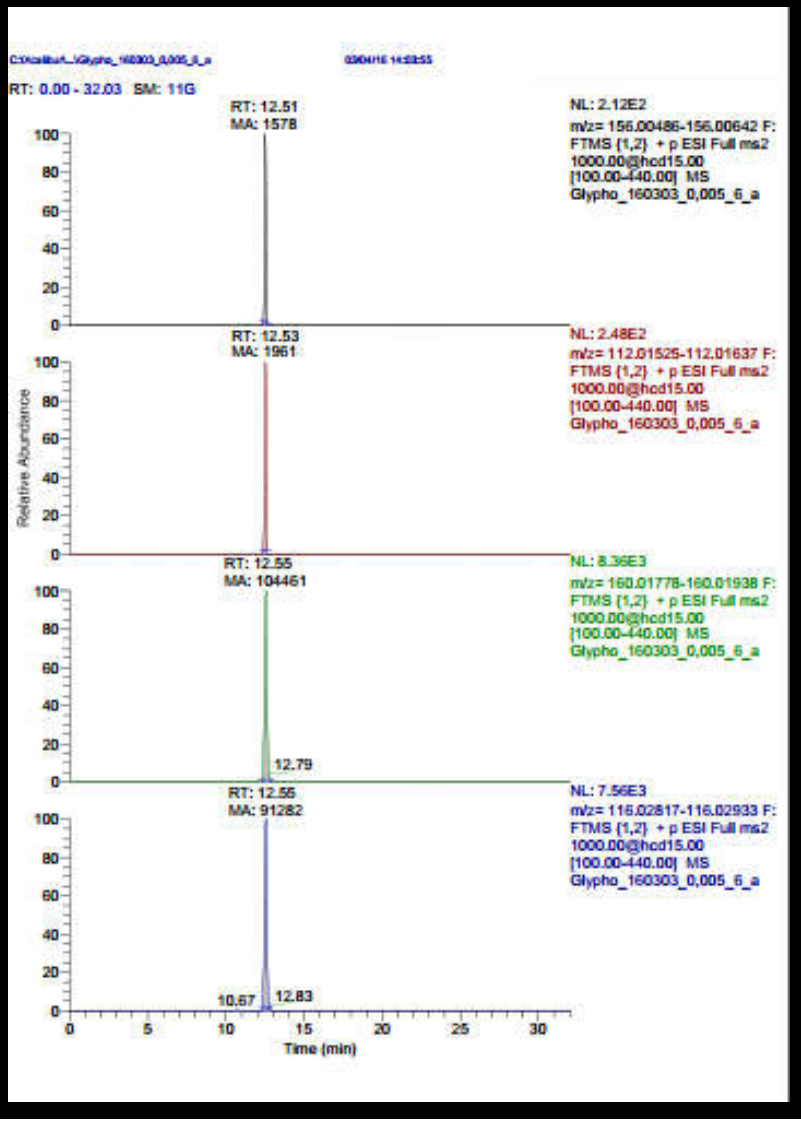




LC-HRMS: Full scan and HCD

Mineral water spiked with
AMPA /AMPA ILS
0,005 µg/l/0,1µg/L





Determination of Statistical parameters

Limit of repeatibility

	Limit of repeatibility Glyphosate	Limit of repeatibility AMPA
Average	Less than 15% at 0,1 µg/L	Less than 15% at 0,1 µg/L

Recovery

According to
«Guidance document on analytical quality control and procedures for pesticide residues analysis in food and feed. SANCO/12571/19November 2013 AL2013 rev. 0" «

" The recovery test may be omitted when the standard addition approach is used or when using the isotope-dilution approach with the isotope-labelled internal standard being added to the analytical portion prior to extraction"

Determination of Statistical parameters

Trueness
(Proficiency Tests)

	Trueness Glyphosate	Trueness AMPA
Average	From 76 to 87%	From 74 to 110%

Uncertainty
(Proficiency Tests)

$$S_{pt}x = S_R x$$

$$u_e x = k \times S_R x$$

All CV%'s were less than 50%, so we have considered a fixed uncertainty of this value accordin g to Directive 2009/90

$$CV\% = (u_e x)/(R_x) \times 100$$

LC-HRMS: Full scan

Proficiency AGLAE 16M55.2

Friday 16/09/2016-

Glyphosate provisional Z-score	**=**	***+0,06***
AMPA provisional Z-score	**=**	***+0,87***

Tuscany: may 2015

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	% 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

Tuscany: may 2015

Analyzed samples 08/08/2016	Average concentration of Glyphosate µg/l	Average concentration of AMPA µg/l
234	1,17	3,68

Analyzed samples 08/08/2016	Maximum concentration of Glyphosate µg/l	Maximum concentration of AMPA µg/l
234	23,99	65,85

Analyzed samples 08/08/2016	Concentration of Glyphosate Median µg/l	Concentration of AMPA Median µg/l
234	0,1	0,32

Tuscany: July 2016

Analyzed samples 08/08/2016	% of samples with Glyphosate concentration higher than 0,005 µg/l	% of samples with AMPA concentration higher than 0,005 µg/l
234	45	60

Analyzed samples 08/08/2016	Maximum concentration of Glyphosate µg/l	Maximum concentration of AMPA µg/l
234	23,99	65,85

Analyzed samples 08/08/2016	Average concentration of Glyphosate µg/l	Average concentration of AMPA µg/l
234	1,17	3,68

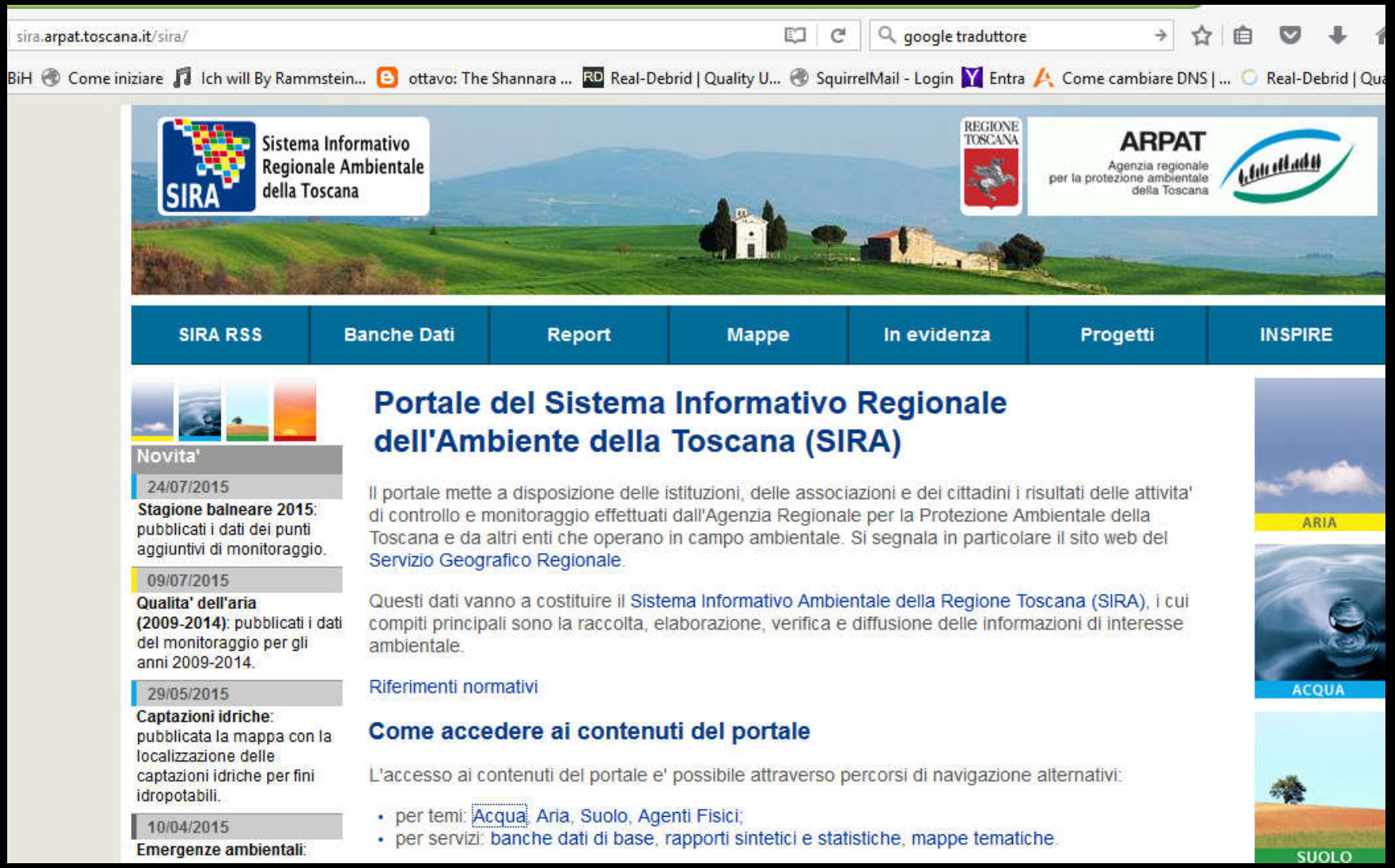
Tuscany: July 2016

Analyzed samples 08/08/2016	% of samples with Glyphosate concentration higher than 0,005 µg/l	% of samples with AMPA concentration higher than 0,005 µg/l
234	45	60

Analyzed samples 08/08/2016	% of samples with Glyphosate concentration higher than 0,1 µg/l	% of samples with AMPA concentration higher than 0,1 µg/l
234	23	39

Analyzed samples 08/08/2016	% of samples with Glyphosate concentration higher than 1 µg/l	% of samples with AMPA concentration higher than 1 µg/l
234	9	21

ARPAT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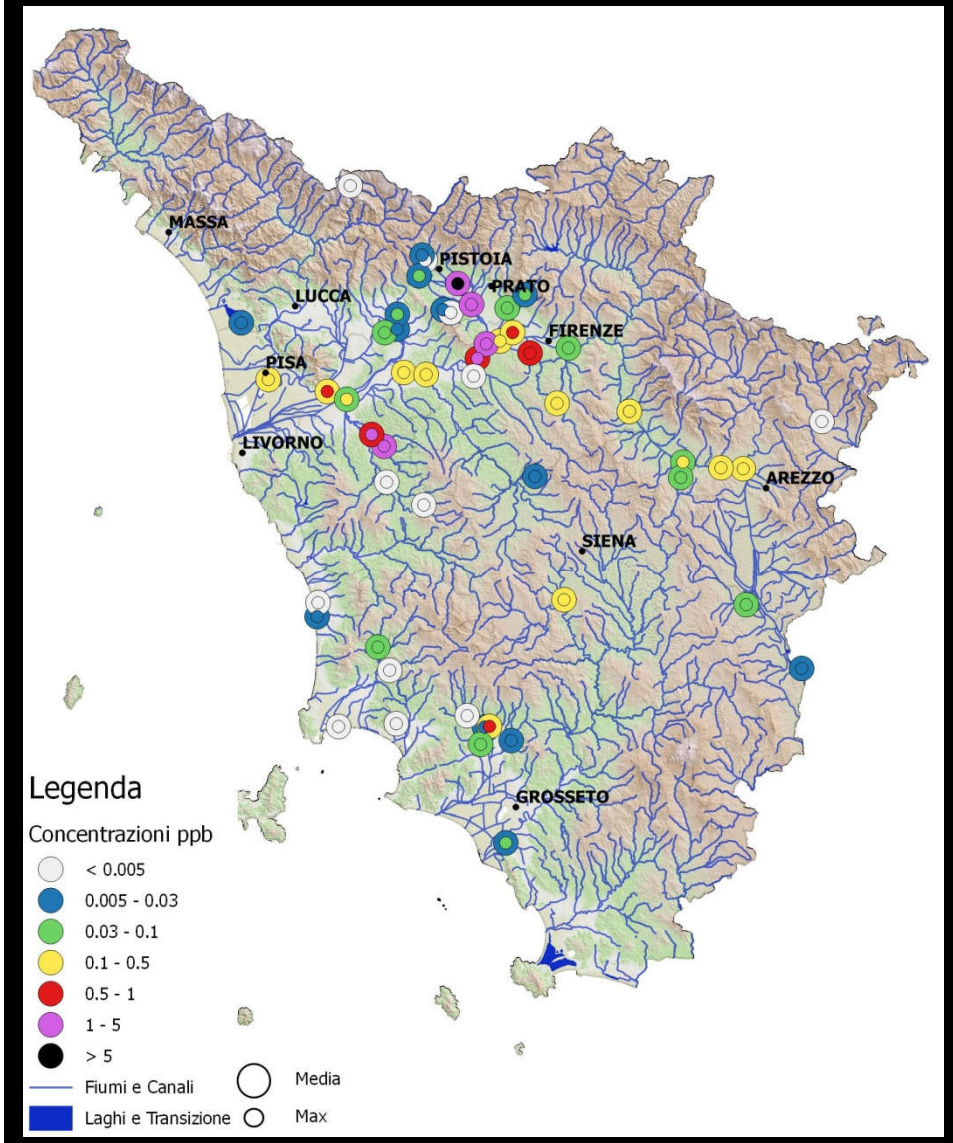
google traduttore
Sistema Informativo Regionale Ambientale della Toscana
SIRA
REGIONE TOSCANA
ARPAT
Agenzia regionale per la protezione ambientale della Toscana
SIRA RSS
Banche Dati
Report
Mappe
In evidenza
Progetti
INSPIRE
Novita'
24/07/2015
Stagione balneare 2015: pubblicati i dati dei punti aggiuntivi di monitoraggio.
09/07/2015
Qualita' dell'aria (2009-2014): pubblicati i dati del monitoraggio per gli anni 2009-2014.
29/05/2015
Captazioni idriche: pubblicata la mappa con la localizzazione delle captazioni idriche per fini idropotabili.
10/04/2015
Emergenze ambientali:
Portale del Sistema Informativo Regionale dell'Ambiente della Toscana (SIRA)
Il portale mette a disposizione delle istituzioni, delle associazioni e dei cittadini i risultati delle attivita' di controllo e monitoraggio effettuati dall'Agenzia Regionale per la Protezione Ambientale della Toscana e da altri enti che operano in campo ambientale. Si segnala in particolare il sito web del Servizio Geografico Regionale.
Questi dati vanno a costituire il Sistema Informativo Ambientale della Regione Toscana (SIRA), i cui compiti principali sono la raccolta, elaborazione, verifica e diffusione delle informazioni di interesse ambientale.
Riferimenti normativi
Come accedere ai contenuti del portale
L'accesso ai contenuti del portale e' possibile attraverso percorsi di navigazione alternativi:
per temi: Acqua, Aria, Suolo, Agenti Fisici;
per servizi: banche dati di base, rapporti sintetici e statistiche, mappe tematiche.
ARIA
ACQUA
SUOLO

Superficial Water

Glyphosate



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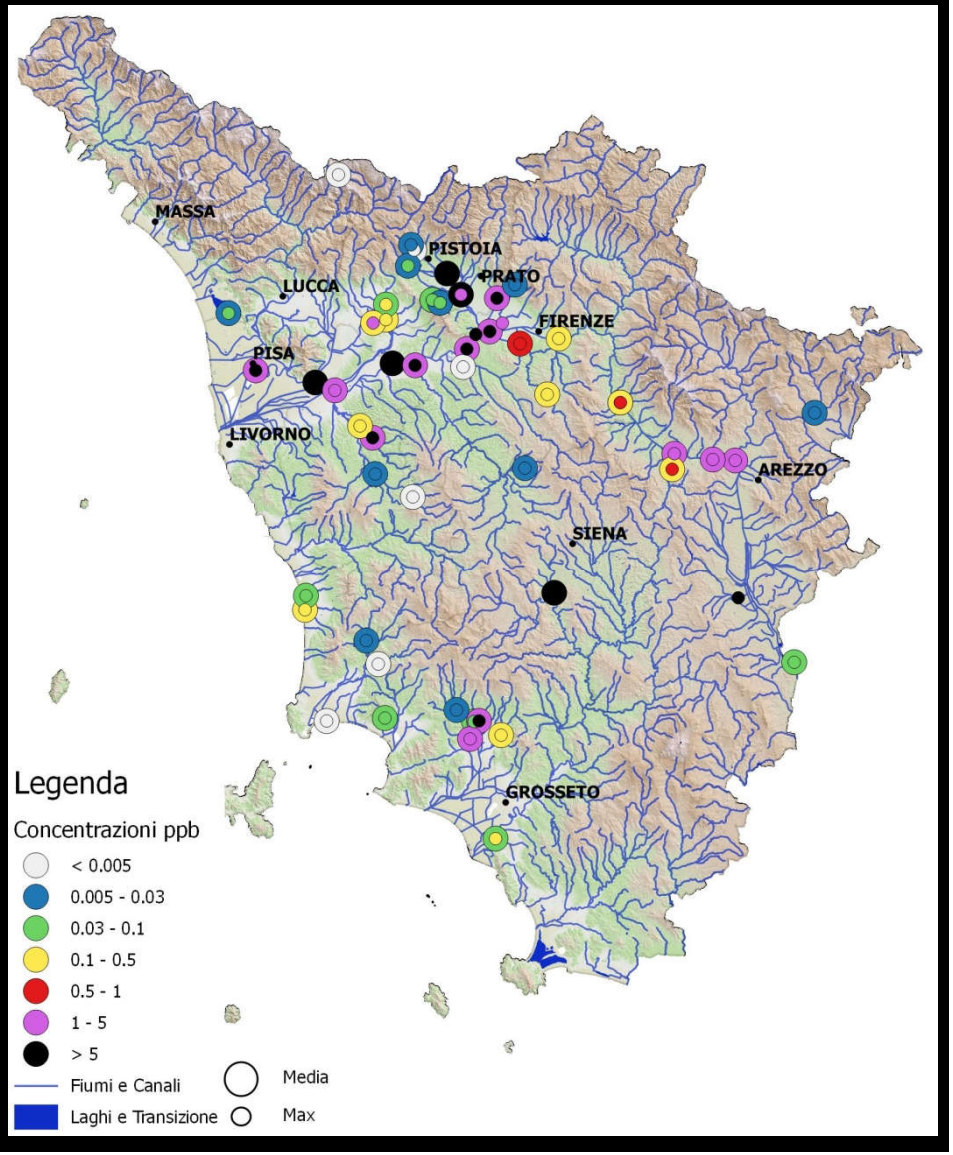
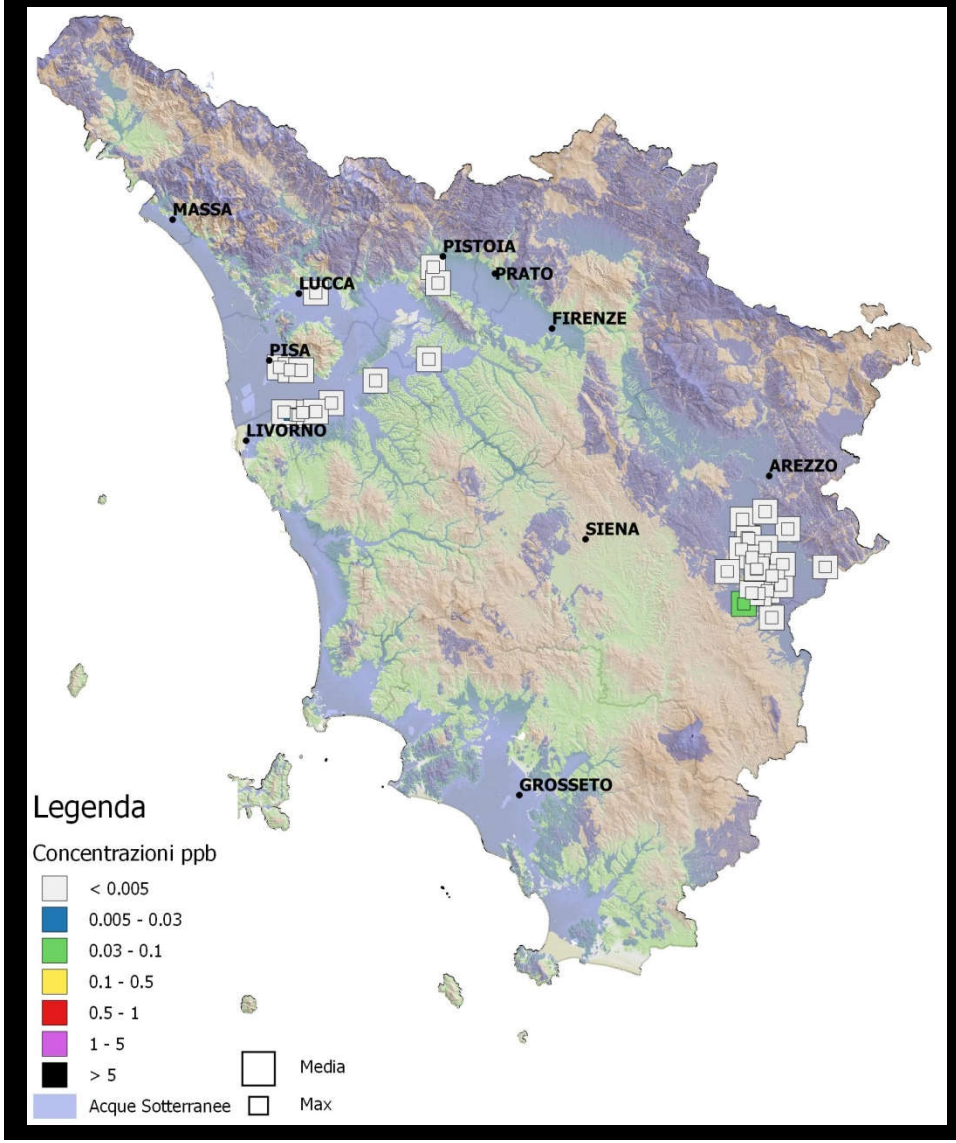


Groundwater

Glyphosate



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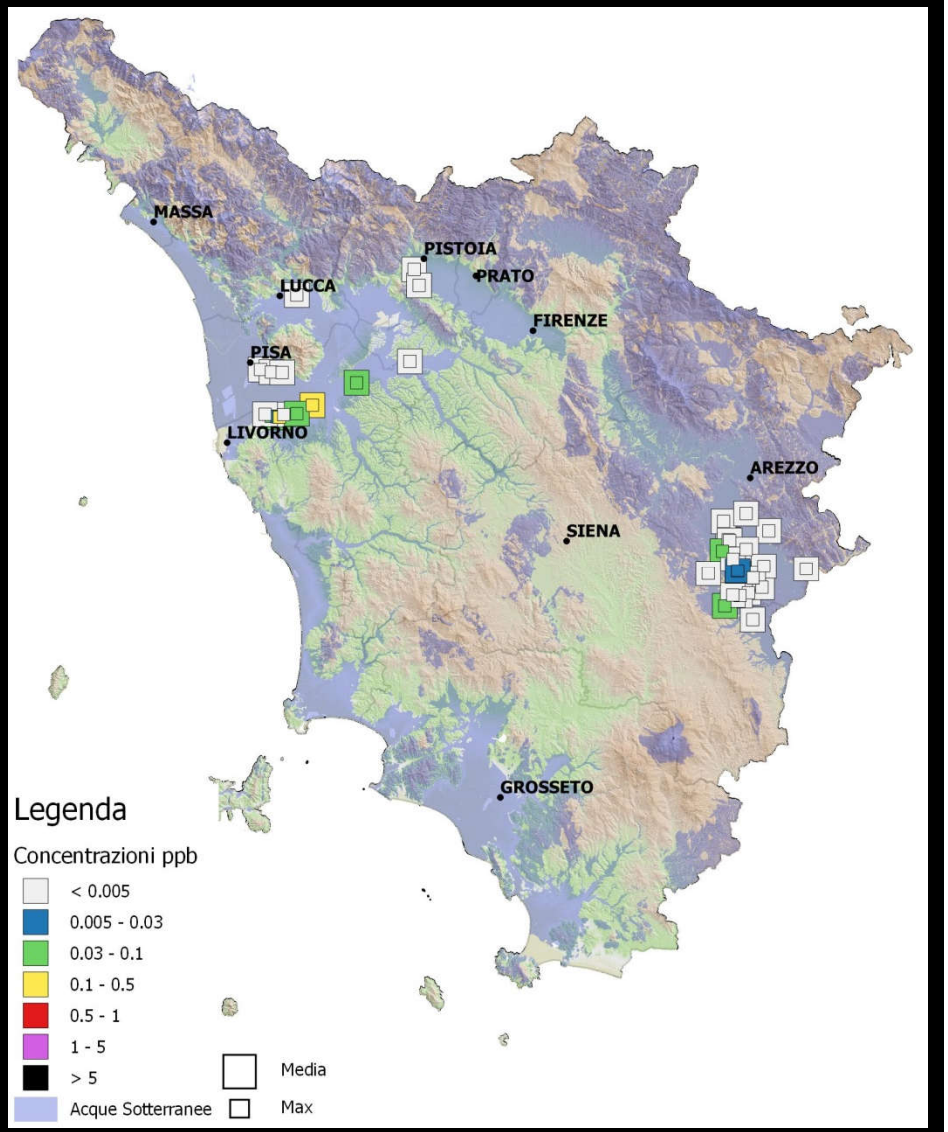
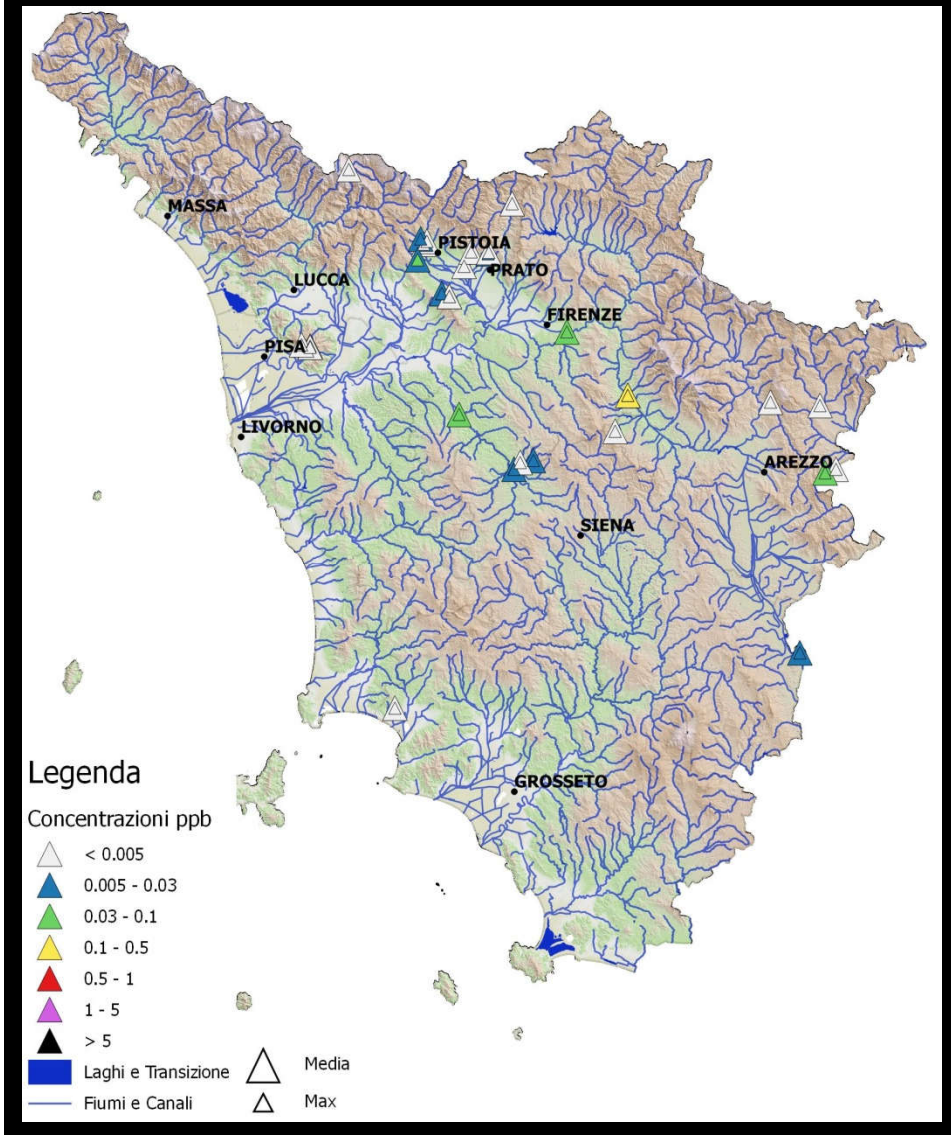


Superficial Catchment points for drinking water production

Glyphosate



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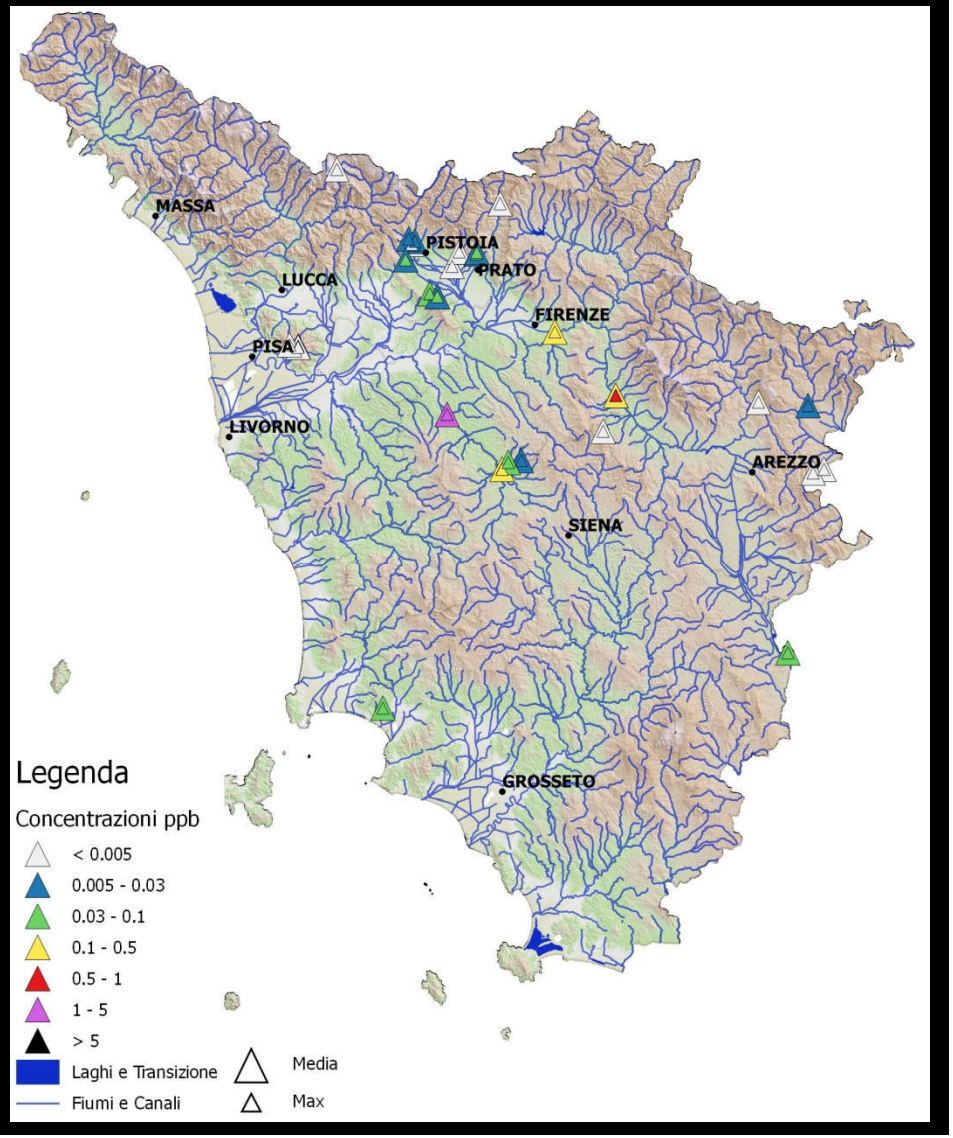

Aknowledgments

To all fantastic members of
Organic Micropollutants Group

Elisa Banti
Sara DelRio
Alessandra Iarrobino

Thanks