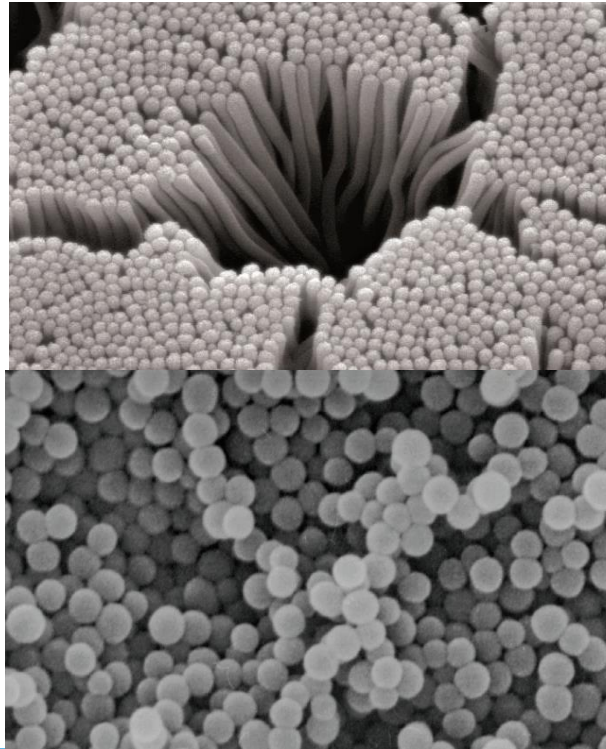


New SPE clean-up method and integrative passive sampler (POCIS) based on Molecularly imprinted Polymers for Glyphosate & AMPA analysis

Jim Fenster



- **HQ in France**
- **14 years experience in Solid Phase Extractions**
- **Manufacture sorbents used in SPE to make sample extractions easier**
- **North American Operations based in Middleton, Wisconsin**

Uniqueness Variety of sorbents to offer customized product



**AFFINIMIP®
SPE**

Selective SPE based on Molecular Imprinted Polymers (MIP) for Glyphosate – AMPA, Bisphenols, Estrogens, Drug residues, antibiotics, Mycotoxins, PAHs,

AttractSPE™

Polymeric phase : HLB, PS-DVB, ion exchange (SAX, SCX, WCX, WAX)

SilactSPE™

Silica-based sorbents (C18, C8, Cyano, Amino, ...)
Broad range of chemically modified silica

Qcleanup™

QuEChERS for multiresidues pesticides analyses

Uniqueness Comprehensive formats to adapt to customers workflow and applications



Different formats providing the flexibility you need to meet any volume requirement.

Open, Reversible, LRC, ASPEC ready Cartridge

Formats: 1mL, 3mL, 6mL, 15mL, 20mL, 60mL

Materials: Polypropylene, glass (6mL)

Frits: Polyethylene, PTFE, Glass fiber



On-line SPE Cartridge

I.D.: 2,1 and 4,6mm

Length: 20mm



Disks



Dispersive SPE & Quechers



Passive Samplers

I.D.: 55mm

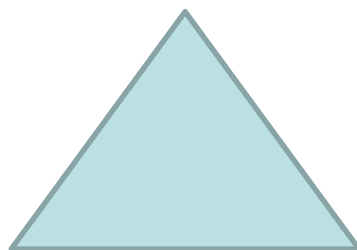
O.D.: 90mm



Objective of the project

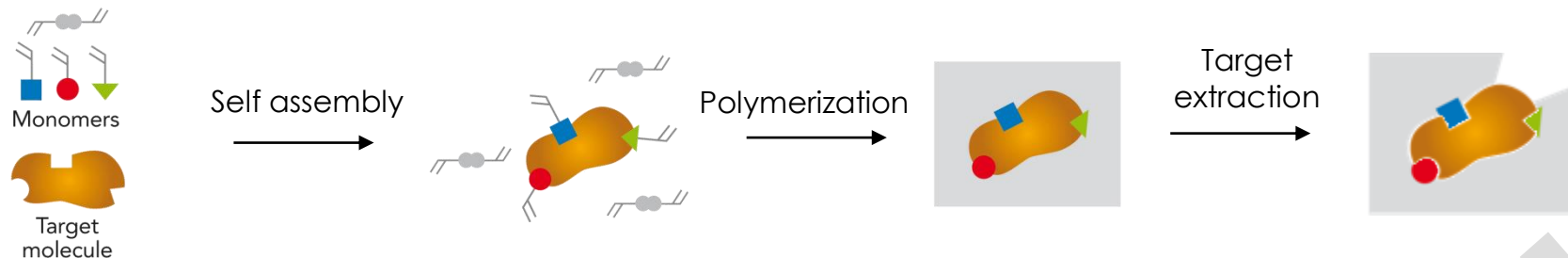


- Could we jointly develop a new MIP sorbent for POCIS to catch Glyphosate and breakdown products:



project called ORIGAMI (ANR project) to develop POCIS studies...

Molecularly Imprinted Polymers



AFFINISEP monomer library : more than 300

- Acrylic monomers
- Vinyls monomers
- ...



Molecular Recognition materials

Physicochemical interactions



- Ionic interactions
- Hydrogen bonding
- π - π stacking
- ...

**High recovery and selectivity
Combining the advantage of
Immunoaffinity and SPE !**

Glyphosate **The existing analytical problem**

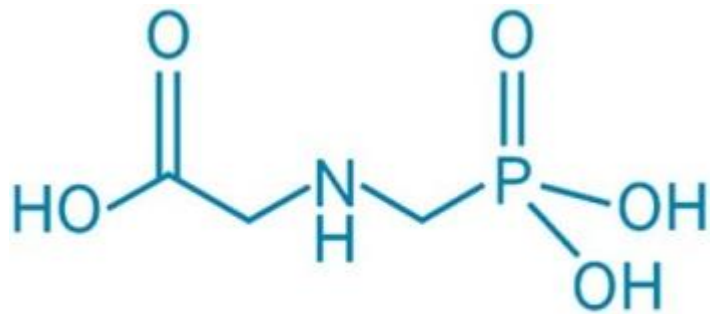


- Glyphosate has been used for years
- Particularly high levels used with GMO crops
- It is ubiquitous

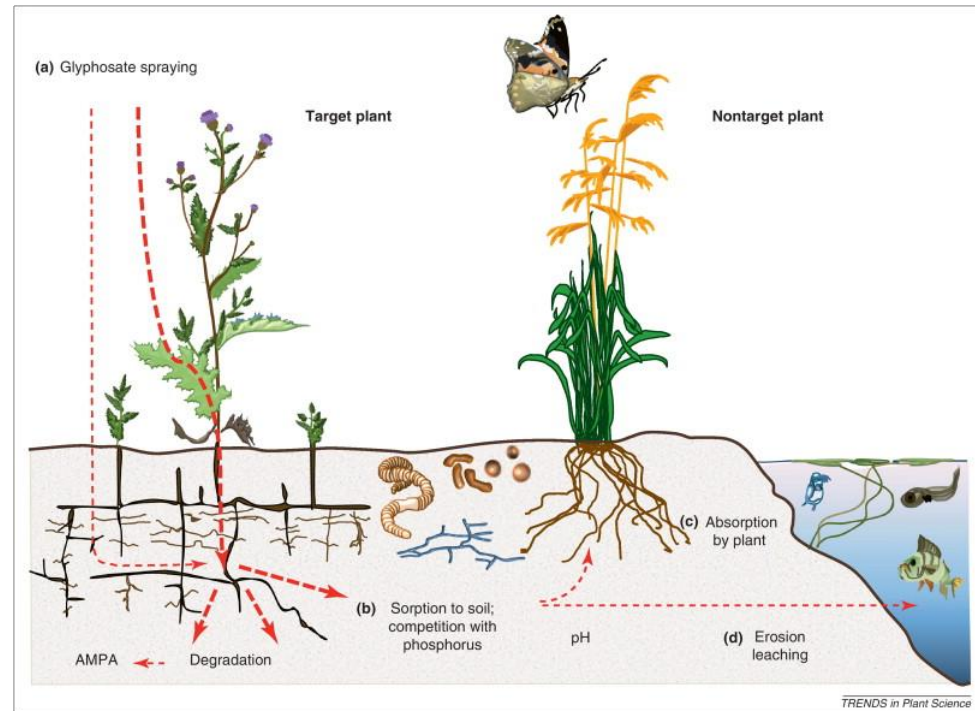


Glyphosate **The existing analytical problem**

- It is quite mobile in plant to soil to water continuum
- Due to its extremely polar nature very difficult to extract from water



Glyphosate

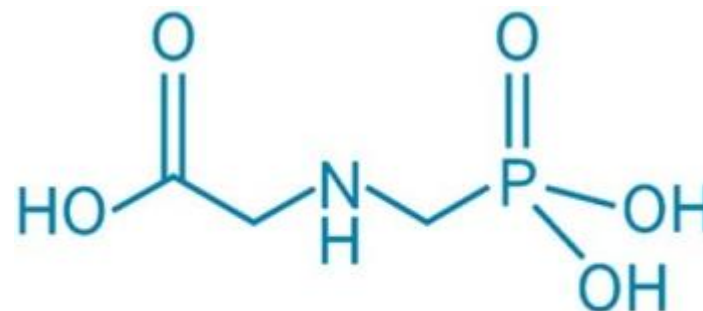


Glyphosate The existing analytical problem



- **Current Methodologies**

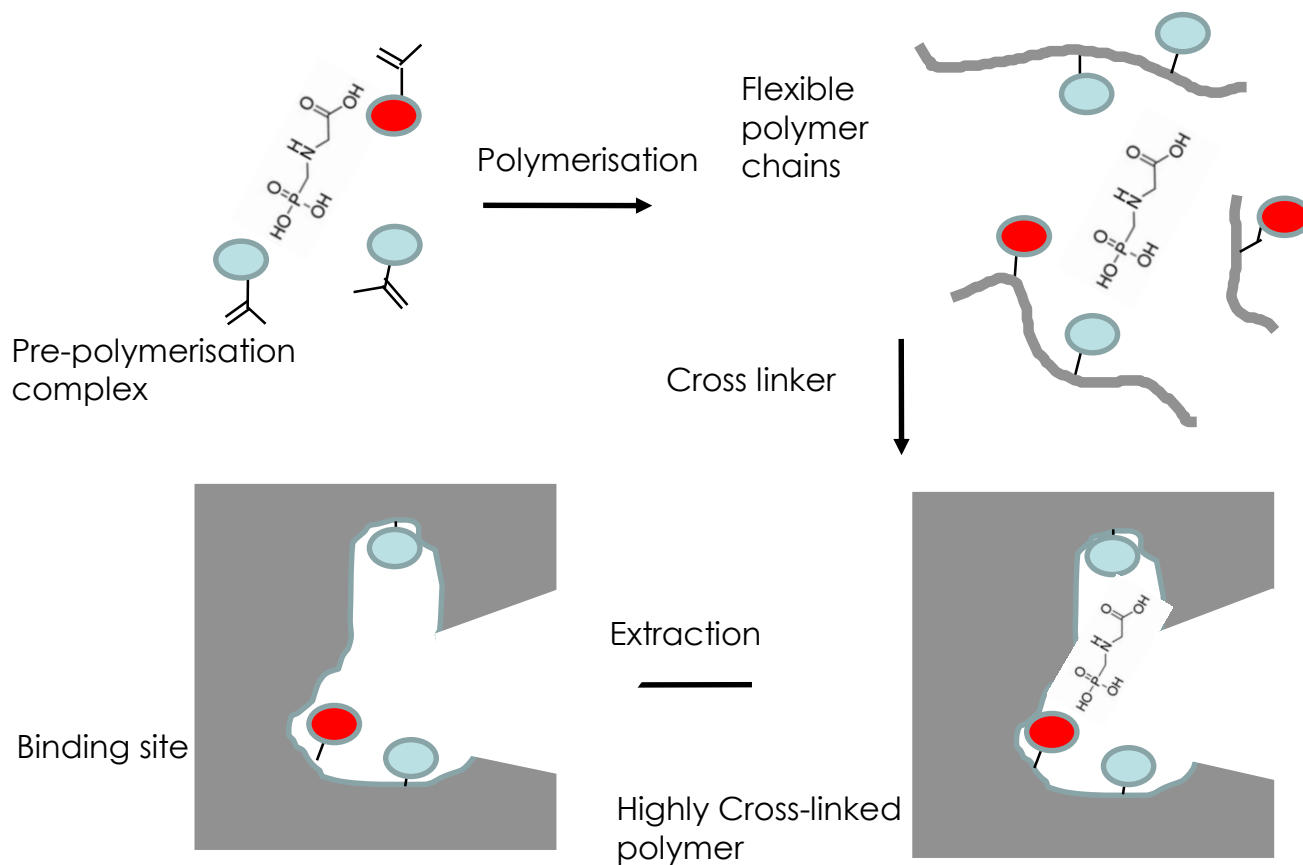
- the derivatization of glyphosate with 9-fluorenylmethyloxycarbonyl chloroformate Fmoc which enables the retention of the product on hydrophobic sorbent phases, again aiming either at cleanup or analyte enrichment. C18 or HLB for SPE and for analytical Column
- Underivatized glyphosate can be extracted by strong anion exchange, immobilized metal affinity.
- Underivatized glyphosate new sorbents affording molecular recognition properties such as those of immunosorbents and molecular imprinted polymers IAC and MIPS



Glyphosate

AFFINIMIP® SPE Glyphosate – AMPA is a good

solution



POCIS and Chemcatcher Passive sampler



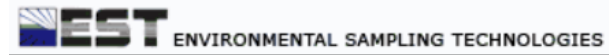
POCIS and Chemcatcher Passive Sampling Technology Enables the monitoring of contaminants in water (surface water, groundwater, coastal water...) for a short (at least 7 days) to long period (with an average field deployment of one month)

Advantages of POCIS or Chemcatcher

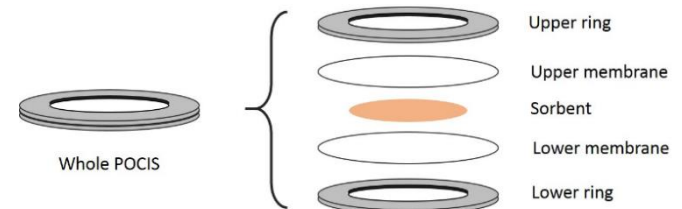
- Can generate a time-weighted average concentration of the contaminants in water
- no power, maintenance and supervision is required.
- Deployable in harsh conditions
- Very simple use



CHEMCATCHER®
COMPONENTS



Description of POCIS



POCIS



AFFINIMIP® POCIS GLYPHOSATE



Sampling Processes using POCIS



AFFINIMIP® POCIS



HOLDER



CANISTER



Teflon carrusel carrying POCIS

Post Sampling Processes



AFFINIMIP® POCIS

Collect of analytes by the POCIS on the field



AFFINIMIP® SPE

Analytes extraction by SPE



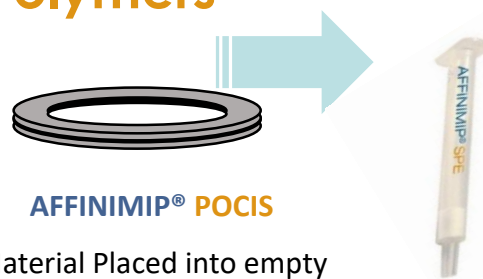
QUANTIFICATION

by HPLC, LCMS or any other analytical method

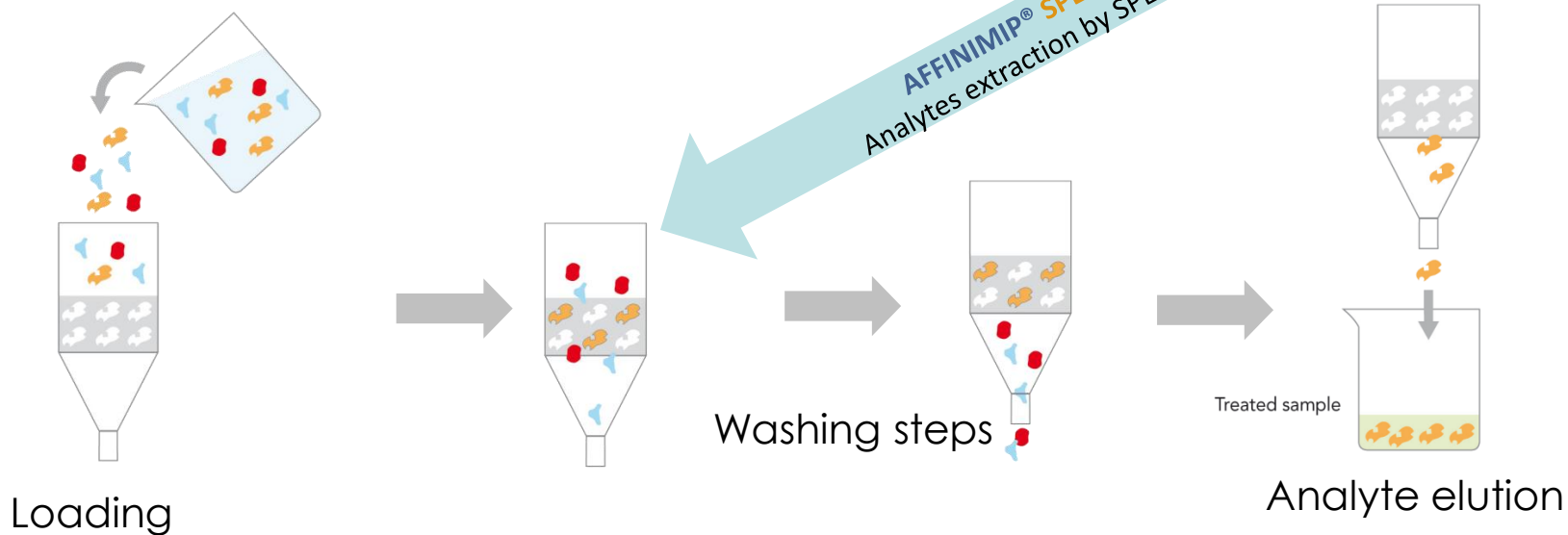
AFFINIMIP® Selective Extraction Cartridges based on Molecularly Imprinted Polymers



Teflon carrousel carrying several POCIS



Material Placed into empty
SPE cartridge



Simulated field sampling



- **Laboratory Sampling Rates Estimation for AMPA and Glyphosate**
- **Apparatus: 100 L Stainless Steel Tank holding 80 L of water carrying the Teflon carousel containing the POCIS connected to electric motor to simulate turbulence.**
- **Solutions : all water samples pH=12 fortified with 500ng/L of AMPA and Glyphosate. Concentrations kept constant during the whole experiment .**
- **Pesticide concentration in the tank, temperature, TOC, and conductivity monitored during the whole experimental sampling period (35 days), to verify the stability of physico-chemical conditions in the water being sampled**

Physico-chemical

properties of tested waters

Salt concentrations (mg/L) and

pH of analyzed solutions

	Ca	Na	Mg	K	HCO3	Cl	NO3	SO4	Fe	pH
Groundwater	15,7	11,3	4,9	1,3	76	9,7	<0,5	1,2	7,5	7,1
Groundwater	22,3	105,7	17	4,7	136	159	8,9	15,8	0,17	6,4
Groundwater	104,1	13,9	6,9	1,8	203	28,1	113,7	33		7,1
Geothermal water	799	5163,5	189,5	71,9		9759,7		702,2	3,2	
Mineral water	80	6,5	24	1	360	3,8	3,7	12,6		7,2

SPE method to extract Glyphosate and AMPA

Step	Solvent
Loading	Using POCIS over several days
Washing	3mL Ultrapure Water
Elution	3mL HCl solution (100mM)
Analysis	Derivatization with FMOC (if required) before analysis

AFFINIMIP® SPE Glyphosate - AMPA



Analyte	<ul style="list-style-type: none"> • Glyphosate , AMPA
Tested matrices	<ul style="list-style-type: none"> • Water, Geothermal, mineral, river, underground water
Detection method	<ul style="list-style-type: none"> • LC-MS / Fluo, on line SPE/UPLC/MS/MS
Recovery yield	<ul style="list-style-type: none"> • Higher than 85% - High CAPACITY



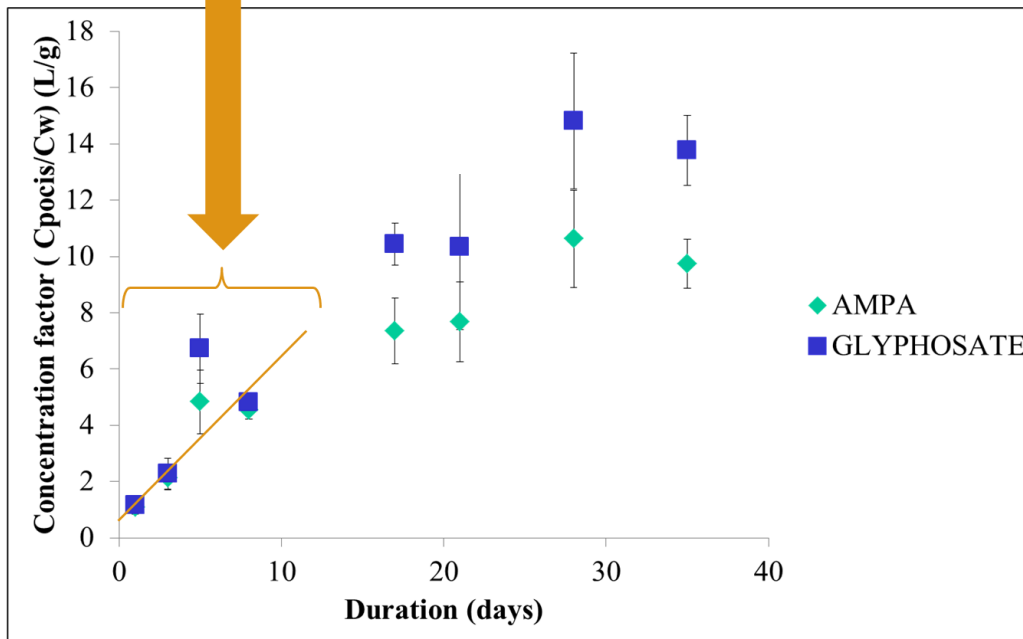
Analyte	Wide variety of water tested by UPLC-MS/MS detection		Capacity testing by fluorescence detection		
	[] range	Recoveries %	[]	Recoveries %	%RSD _R
Glyphosate	50 to 450ng/L	>70%	160ng/mL	87%	6%
AMPA	50 to 550ng/L	>75%	78ng/mL	90%	4%

AFFINIMIP® POCIS GLYPHOSATE



Kinetic accumulation of both molecules in POCIS MIP Very good accumulation in AFFINIMIP® POCIS for both molecules

Sampling rates: 130mL/day/200mg MIP in agreement with other pesticides in classical POCIS.

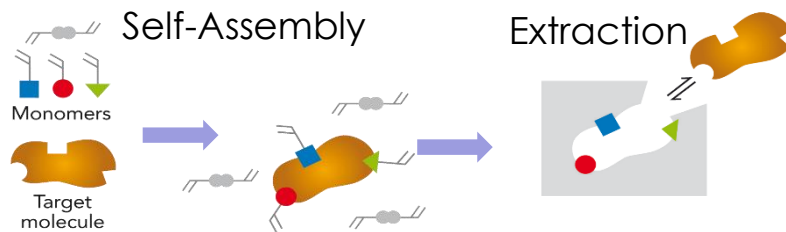


Mixing 2 Technologies for higher Performance



AFFINIMIP® SPE

Based on Molecular Imprinted Polymer



AttractSPE™ Disks

Innovative dense and thin SPE disks giving high interactions with analytes and a maximal flow rates

- ✓ C18, C8, anion exchange, cation exchange, DVB, RPS AND HLB, ...
- ✓ Diameter of 25mm, 47mm, 90mm and custom-made



Mixing 2 Technologies for higher Performance



AFFINIMIP®SPE
Glyphosate



+

AttractSPE™Disks HLB



=

NEW Mixed-mode
HLB and MIP
Glyphosate



NEW Mixed-mode SPE Disks HLB/ AFFINIMIP® Glyphosate



Advantages

- High flow rate more than 1L
- High selectivity for Glyphosate
- Other pesticides for a multianalysis SPE disk

Molecule	Recoveries for SPE	Recoveries for Disks
Glyphosate	108.5%	90.9%
AMPA	78.1%	66.1%
Glufosinate	81.3%	73.1%

Step	Operations for Disks
Conditioning	20 mL Methanol/Water 50/50 2x 50 mL ultrapure water
Loading	1 L of the loading solution
Washing	20 mL ultrapure water
Elution	20 mL HCl solution (100mM)

Analysis LC-MS-MS
No derivatization using an acclaim trinity Q1 Column from thermo



Conclusions



- Results with the Glyphosate MIPS have shown a good ability of this designed sorbent to catch both Molecules (Glyphosate and AMPA) with good recoveries for SPE extractions and this Passive sampling experiment with POCIS
- SPE were carried out with 5 real water matrices without any influence of salts without any affects in performance
- Affinimips for Glyphosate and AMPA will work in any Passive sampling system POCIS or Chemcatcher
- New formulations exist of Affinimips in Disk format for Glyphosate and mixed Mode (Glyphosate plus HLB) can catch Glyphosate and other polar SVOC's from water
- Affinimips are available for many other specific analytes
 - Mycotoxins in foods, environmental pollutants, other specific analytes

Acknowledgments



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Université d'Orléans, Orléans; FRANCE
- **3- BRGM Service Métrologie, Monitoring et Analyse, Unité Chimie Environnementale, 45060 Orléans, FRANCE**
- **French ANR project ORIGAMI (ANR ECOTECH 2011 ORIGAMI 11 ECOT 003)**

Reference Articles cited in this work



Anal Bioanal Chem
DOI 10.1007/s00216-016-0150-4



RESEARCH PAPER

Laboratory calibration of a POCIS-like sampler based on molecularly imprinted polymers for glyphosate and AMPA sampling in water

Catherine Berho¹ · Bérengère Claude² · Emeline Coisy¹ · Anne Togola¹ · Sami Bayoukh³ · Philippe Morin² · Laurence Amalric¹

Environ Sci Pollut Res
DOI 10.1007/s11356-017-8844-5



RESEARCH ARTICLE

Preliminary recovery study of a commercial molecularly imprinted polymer for the extraction of glyphosate and AMPA in different environmental waters using MS

Bérengère Claude¹ · Catherine Berho² · Sami Bayoukh³ · Laurence Amalric² · Emeline Coisy² · Reine Nehmé¹ · Philippe Morin¹

Thank you for your attention !



BE SELECTIVE