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Molecularly imprinted polymer dedicated to the extraction of glyphosate and its metabolite, AMPA, in water

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Glyphosate [(N-phosphonomethyl)glycine] is a non-selective broad-spectrum herbicide which is extensively used in agriculture. This molecule inhibits the plant enzyme which enables the plant to produce amino acids and metabolites that are needed for its growth. The biodegradation of glyphosate (GLY) in the environment leads to aminomethylphosphonic acid (AMPA) and both molecules are included in the DCE 2006/18 circular which define criteria for the good status of groundwater in application of the Water Framework Directive 2000/60/EC (WFD)

According to the data available in ADES data (French National Data base of groundwater), in French groundwater, the average concentrations of GLY and AMPA are about 0.7 and 0.3 µg/L, respectively. Thus, GLY and AMPA monitoring at such low concentrations requires sensitive analytical methods and efficient pre-concentration tools. In the present study, integrative passive samplers (IPS) were assessed as in situ pre-concentration apparatus. However, none of the commercial sorbents usually used in IPS was appropriate to retain very polar and hydrophilic analytes such as GLY and AMPA. For this reason, a molecular imprinted polymer (MIP) was synthesized to directly and specifically rebind the target molecules in underground waters.

Several monomers have been tested in order to obtain imprints able to bind efficiently GLY and AMPA in complex matrices such as natural waters. Since the target analytes are polar and hydrophilic, electrostatic interactions and hydrogen bonds have been favored for the functional monomers selection. The assessment of the MIP has systematically been carried out by comparison of the recoveries obtained with MIP and NIP (Non Imprinted Polymer, synthesized with the same reagents as MIP, but without template) by solid phase extraction (SPE). The selectivity of MIP versus NIP was satisfactory for 3 imprinted polymers with a very straightforward protocol (conditioning of 250 mg of MIP/NIP packed in 3-mL polypropylene cartridges with 3 mL ultra pure water, loading of GLY and

AMPA (5 mg/L) in ultra pure water (15 mL) and elution by 3 mL NH₄OH (10 mM) or by 3 mL HCl (10 mM). Thus, one polymer gave MIP recoveries of GLY and AMPA equal to 105% and 80% respectively against NIP recoveries of GLY and AMPA only equal to 68% and 19% respectively. However, the substitution of ultra pure water by mineral water caused the decrease of MIP recoveries (about 30 % for GLY and 5 % for AMPA), for that, a pretreatment of the sample by ionic exchange resins was set up and succeeded in improving recoveries (about 50% for GLY and 25% for AMPA). For those experiments, the samples, MIP and NIP extractions were systematically analyzed by capillary electrophoresis that is a high throughput analytical method but is not sensitive enough to detect GLY and AMPA in natural groundwaters (concentrations inferior to µg/L).