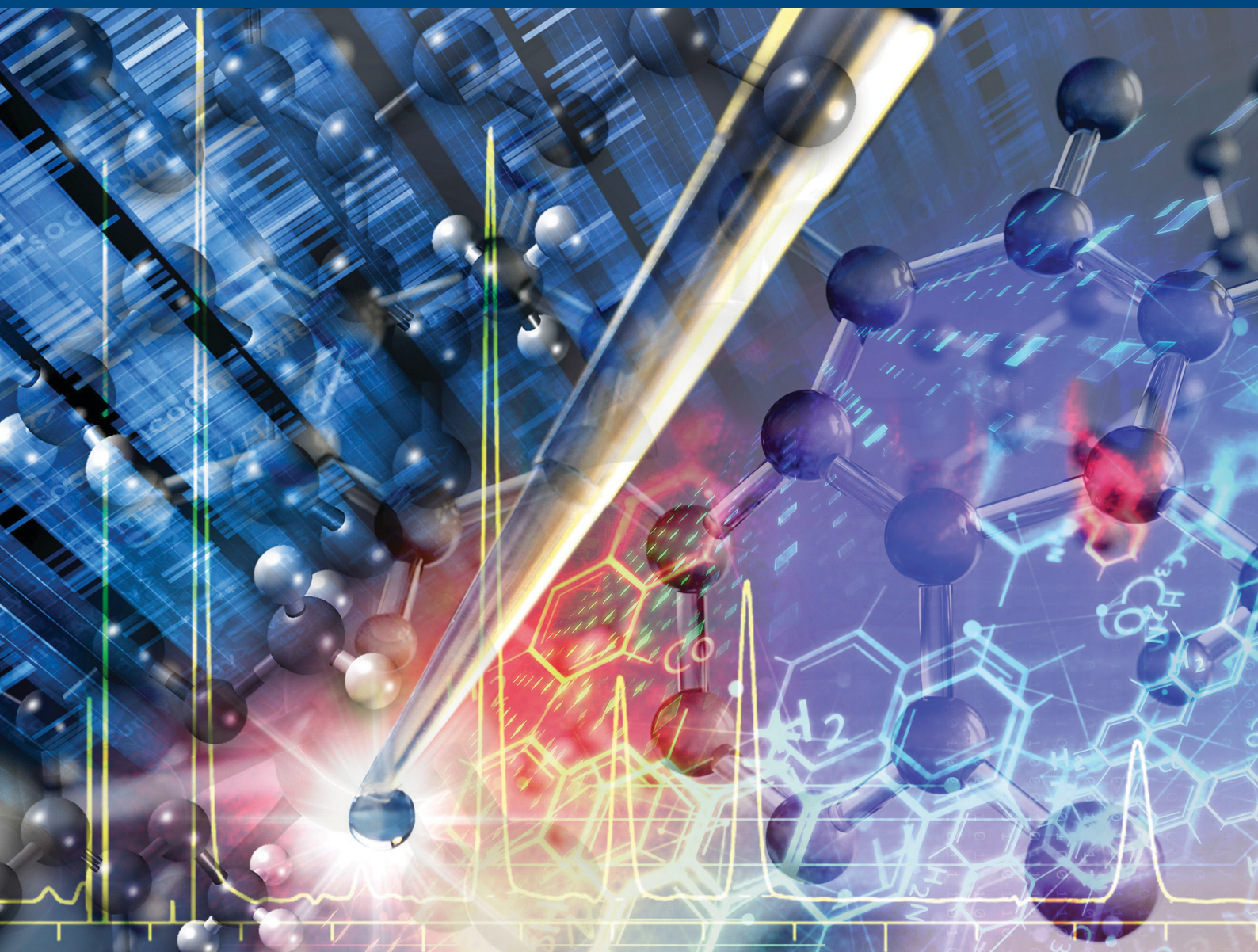


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RESEARCH ARTICLE

Evaluation of 2-hydroxyethyl methacrylate as comonomer in the preparation of water-compatible molecularly imprinted polymers for triazinic herbicides

Myriam Díaz-Álvarez | Antonio Martín-Esteban  | Esther Turiel 

Departamento de Medio Ambiente y Agronomía, INIA-CSIC, Madrid, Spain

Correspondence

Esther Turiel, Departamento de Medio Ambiente y Agronomía, INIA-CSIC, Carretera de A Coruña km 7.5, 28040 Madrid, Spain.
Email: turiel@inia.csic.es

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In this work, the preparation and evaluation of water-compatible molecularly imprinted polymers for triazines using 2-hydroxyethyl methacrylate and methacrylic acid as comonomers is described. Four sets of molecularly imprinted and non-imprinted polymers for propazine were prepared at varying monomer molar ratios (from 4:0 to 1:3), and evaluated for the recognition of several triazines directly in aqueous media. The evaluation was performed by loading 1 mL of an aqueous solution containing 500 ng of each selected triazine, washing with 500 μ L of acetonitrile, and eluting with 500 μ L of methanol followed by $2 \times 500 \mu$ L of a solution of methanol containing 10% of acetic acid. Final determinations were performed by high-performance liquid chromatography-ultraviolet detection. Improvement in molecular recognition of triazines in water was obtained on those molecularly imprinted polymers incorporating 2-hydroxyethyl methacrylate in 3:1 or 2:2 molar ratios, being the former selected as optimum providing recoveries for propazine up to 80%. A molecularly imprinted solid-phase extraction protocol was developed to ensure that triazines-selective recognition takes place inside selective binding sites in pure water media. Finally, the developed method was successfully applied to the determination of the selected triazines in environmental waters providing limits of detection from 0.16 and the 0.5 μ g/L concentration range.

KEYWORDS

environmental water samples, solid-phase extraction, triazinic herbicides, water-compatible molecularly imprinted polymers

Article Related Abbreviations: AIMN,

2,2'-azobis-2-methylbutyronitrile; ATZ, atrazine; C18, octadecyl silica; DEA, desethylatrazine; EGDMA, ethylene glycol dimethacrylate; HEMA, 2-hydroxyethyl methacrylate; HOAc, acetic acid; MAA, methacrylic acid; MeOH, methanol; MIP, molecularly imprinted polymer; MISPE, molecularly imprinted solid-phase extraction; NIP, non-imprinted polymer; TER, terbuthylazine.

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1 | INTRODUCTION

During the last decades, a great development in analytical instrumentation has occurred, and nowadays it is possible to determine almost any organic compound in any kind of sample by different chromatographic techniques coupled to UV, fluorescence, MS, or MS/MS detectors. However, in

many cases matrix components can significantly interfere with the detection, preventing direct injection of the obtained extracts. In this regard, sample treatment is still considered a key step in the whole analytical process [1]. A good sample treatment should include the removal of interferences and the preconcentration of the target analytes, among other objectives. In this regard, SPE has been commonly used in laboratories for the extraction and purification of analytes from a wide variety of liquid and solid samples. However, the sorbents typically used for SPE retain compounds in a non-specific manner causing the co-extraction of matrix interferences, making it difficult to meet the strict LODs established by current regulations. To overcome this problem, molecularly imprinted polymers (MIPs) have been proposed as selective sorbents for the extraction and clean-up of compounds of interest in biological, environmental, and food samples [2, 3].

MIPs are custom-made synthetic materials prepared by the copolymerization of a functional monomer with a cross-linker in the presence of a template molecule. After polymerization, the template is removed from the resulting polymer network, leaving free binding sites with shape, size, and functionalities complementary to the template [4]. The combination of molecular imprinting and SPE, so-called molecularly imprinted SPE (MISPE), represents by far the most advanced technical application of MIPs, providing a powerful analytical tool with the features of both technologies: simplicity, flexibility, and selectivity [5, 6]. However, given the simplicity of the process and the availability of numerous functional monomers, most of the MIPs are prepared by non-covalent imprinting, where the monomer-template complex is stabilized mainly through hydrogen bonding and Van der Waals forces. This synthesis procedure provides excellent performance of MIPs in organic solvents but their selective binding capacity in aqueous media is considerably reduced. This represents the major drawback of MIPs as many compounds of interest are found in aqueous media such as body fluids, food, and environmental samples.

Consequently, the development of MIPs showing selective recognition in aqueous media has become an increasingly important research topic, and different strategies for preparing so-called water-compatible MIPs have been described in recent years [7, 8] such as increasing the polarity of the reaction microenvironment by imprinting in polar porogens or using pickering emulsion polymerization [9–12]. Other strategies are based on the use of hydrophilic comonomers and/or cross-linkers such as 2-acrylamido-2-methylpropanesulfonic acid [13] and modified β -cyclodextrin [14, 15]. In particular, 2-hydroxyethyl methacrylate (HEMA) has been used as a co-functional monomer to prepare water-compatible MIPs for the analysis of target pharmaceuticals and hormones in aqueous

and biological samples [16–19]. Also, HEMA has been often used in the modification of hydrophilic polymer brushes on MIPs via reversible addition-fragmentation chain transfer precipitation [20–22]

Hence, this work presents a complete evaluation of the use of HEMA as a co-monomer together with methacrylic acid (MAA) for the preparation of MIPs capable of establishing selective interactions with triazines in aqueous media. Triazine herbicides have been widely used for weed control of several crops and are classified as persistent organic compounds since they resist biological and chemical degradation. In spite of the ban on the use of atrazine (ATZ) by the European Union in 2004 [23], triazines are still the most frequently detected pesticides in environmental waters [24, 25]. In fact, it is still used in several non-European countries or just replaced by terbuthylazine (TER), and thus, both herbicides are included in the list of priority substances in the field of water policy [26].

Up to date, the MISPE procedures that have been developed for these herbicides in environmental waters require two-step MISPE, imprinting on resins, performing drastic solvent exchanges that included exhaustive drying steps, and/or using dual phases to achieve selectivity recognition inside the binding sites [8, 27–30]. For this reason, the objective of this work was to study the potential of HEMA as a co-monomer to achieve true recognition of triazines by the binding sites directly in the aqueous media in order to obtain a real water-compatible MIP material suitable for the determination of triazines in environmental waters.

2 | MATERIALS AND METHODS

2.1 | Chemicals and materials

Desethylatrazine (DEA), desisopropylatrazine, simazine, cyanazine, ATZ, propazine (PPZ), TER, MAA, ethylene glycol dimethacrylate (EGDMA), and 2,2'-azobis-2-methylbutyronitrile (AIMN) were supplied by Sigma-Aldrich (Madrid, Spain). HEMA was purchased from Merck (Darmstadt, Germany). ACN and methanol (MeOH) were from Scharlab (Barcelona, Spain). AIMN was recrystallized in MeOH and EGDMA and MAA were freed from stabilizers by distillation under reduced pressure prior to use. Purified water was obtained from a Milli-Q purification system purchased from Millipore (Madrid, Spain). All other chemicals were of analytical reagent grade and used as received.

2.2 | Preparation of MIPs

MIPs were prepared following a precipitation polymerization protocol previously used in our research group

[27]. Briefly, 0.25 mmol of propazine, 1 mmol of MAA or combinations of MAA with HEMA, and 3 ml of toluene were placed in a 6 ml glass tube. The mixture was left in contact for five minutes and then 5 mmol of EGDMA and 0.35 mmol of AIMN were added. The tube was sealed in a nitrogen atmosphere and placed in a water bath at 60°C to start the polymerization process. After 24 h the polymer particles obtained were air-dried and the template was removed by Soxhlet extraction with a MeOH:acetic acid (MeOH:HOAc) mixture (1:1, v/v) for 18 h. Non-imprinted polymers (NIPs) were prepared following the same procedure but without the addition of the template molecule. The obtained materials (100 mg) were placed in empty SPE cartridges for further evaluation.

2.3 | Molecularly imprinted SPE

For its first use, MIP and NIP cartridges were conditioned with 3 × 5 mL of ACN and 3 × 5 mL purified water. The conditioning step used between samples consisted of 2 × 1 mL of ACN and 2 × 1 mL of purified water. Next, 25 mL of the water sample were loaded, washed with 500 µL of ACN, and the analytes were eluted with 500 µL of MeOH and 2 × 500 µL of a MeOH:HOAc mixture (9:1, v/v). The obtained extracts were evaporated to dryness and redissolved in 250 µL of purified water for HPLC analysis.

2.4 | Environmental water samples

Surface water was collected in Valmayor Dam (Valdemorillo, Spain), and well water from a private plot from Rivas (Madrid). Samples were filtered through nylon filters of 0.45 µm supplied by Filter-Lab (Barcelona, Spain) prior to the MISPE procedure.

2.5 | HPLC analysis

All chromatographic measurements were performed using an Agilent Technologies 1200 Series HPLC instrument equipped with a quaternary high-pressure pump, a vacuum degasser, an autosampler, and a diode-array detector. Separation of triazines was achieved using injection volumes of 100 µL and a kromasil 100 C18 3.0 µm (160 × 4.6 mm i.d.) analytical column. Gradient elution was programmed from 85% water (A) and 15% ACN (B) to 35% A and 65% B in 20 min. Triazines were monitored at 220 nm and quantified by external calibration using peak area measurements.

TABLE 1 Polymerization mixtures composition (mmol) employed in the synthesis of the different molecularly imprinted polymers (MIPs) using 3 mL of toluene as porogen

	MIP1	MIP2	MIP3	MIP4
Propazine	0.25	0.25	0.25	0.25
MAA	1	0.75	0.5	0.25
HEMA	0	0.25	0.5	0.75
EGDMA	5	5	5	5
AIMN	0.35	0.35	0.35	0.35

3 | RESULTS AND DISCUSSION

3.1 | Composition of the polymerization mixture

As aforementioned, the aim of this work was to perform an exhaustive evaluation of the influence of HEMA as a co-monomer on the ability of MIPs to establish selective interactions with triazines in aqueous media. Accordingly, the first experiments were focused on studying the performance of the MIPs prepared with different amounts of HEMA in the polymerization mixtures, by performing rebinding experiments of PPZ solutions in pure water. Table 1 shows the template/monomers/crosslinker molar ratios assayed in the different polymerization mixtures using 3 ml of toluene as porogen, AIMN as initiator, and PPZ as a template. Four MIP materials were obtained (further labeled as MIP1–MIP4) for whose the corresponding NIP materials were also prepared following the same procedure but in absence of a template (NIP1–NIP4).

In a preliminary study, 100 mg of the obtained materials were placed in empty glass SPE cartridges and their ability to selective rebind the template molecule in aqueous media was evaluated. After conditioning the cartridges with 2 × 1 mL ACN and 2 × 1 mL water, 1 mL of a water standard solution containing 0.5 mg/L of PPZ was loaded. Subsequently, cartridges were washed with 0.5 mL of ACN and eluted with 0.5 mL of MeOH and 2 × 0.5 mL of a mixture of MeOH/HOAc (9:1, v/v). The recoveries obtained for MIPs and NIPs are shown in Figure 1. A first comparison of the graphs obtained for each MIP vs its corresponding NIP evidence that, although PPZ is strongly retained in all cases (% of loading fraction is almost zero), very different behavior can be observed during washing and elution steps in the MIPs or their corresponding NIP materials. In all cases, the amount of PPZ that is lost in the washing step is higher in NIPs than in MIPs, confirming the presence of binding sites in all MIP materials capable of selectively rebinding the template molecule.

In the second set of experiments, the recognition of two other more hydrophilic triazines, such as ATZ and DEA, by the different MIPs was also studied. A volume of 1 mL

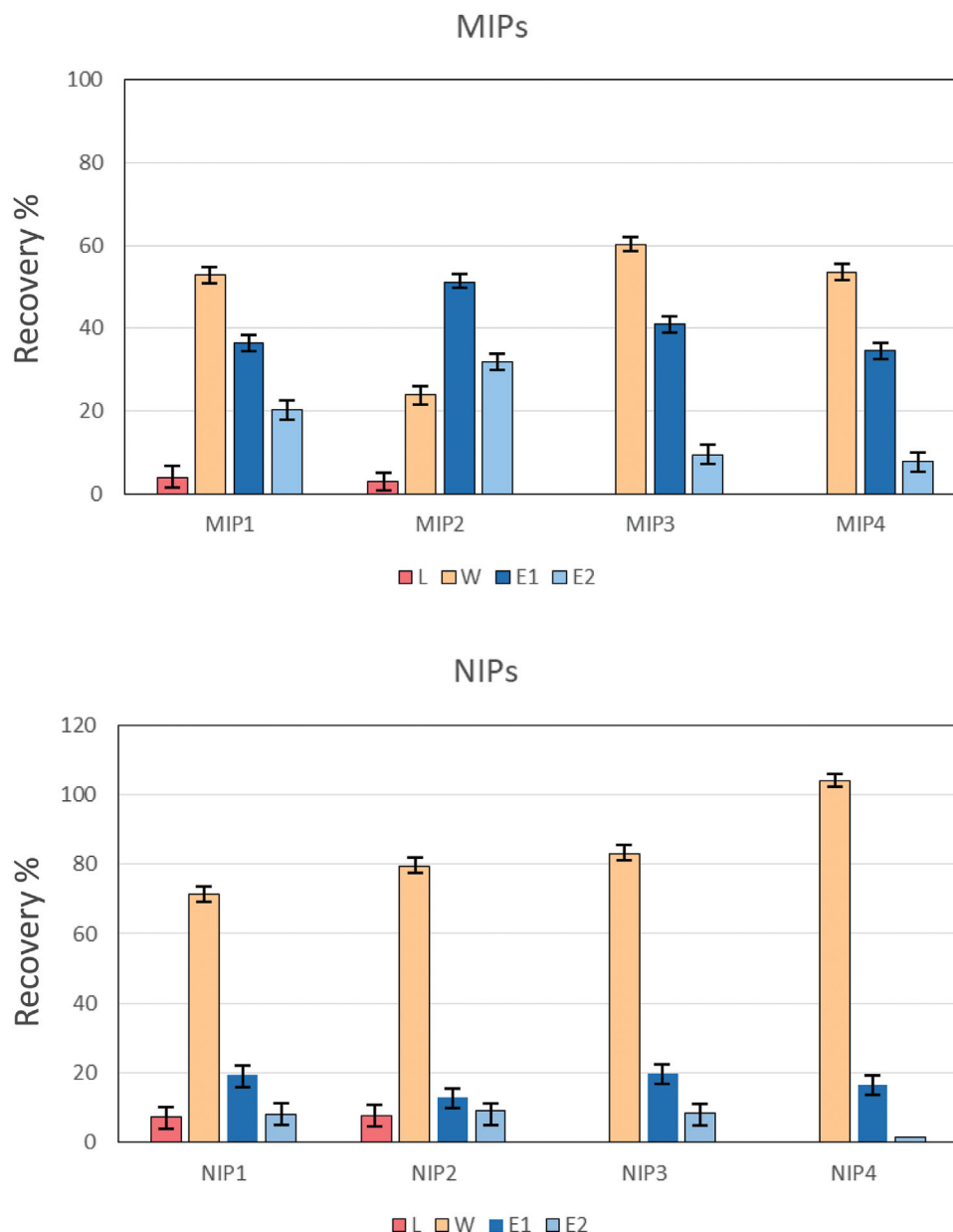


FIGURE 1 Mean recoveries ($n = 3$) obtained for propazine (PPZ) in the loading (L), washing (W), and elution (E1 and E2) fractions, in the different molecularly imprinted polymer (MIP) and non-imprinted polymer (NIP) materials

of a water solution containing 0.5 mg/L of each triazine was loaded independently onto each pair of MIP and NIP cartridges, conveniently washed with ACN, and then, the elution fractions were collected together and further analyzed. Figure 2 shows the recoveries obtained for each triazine in each cartridge. As a derived conclusion of both sets of experiments, it can be stated that the presence of HEMA as a co-monomer significantly improves the recognition of triazines of different polarity by the MIPs in aqueous media. This increase in selective recognition inside the binding sites might be attributed to the summation of two positive effects of adding HEMA up to a certain extent on the properties of the final MIP materials obtained (see

Supporting Information). As was proposed by Dirion et al [31], the inclusion of a hydrophilic monomer could contribute to defining the imprinted site in addition to creating a more hydrophilic polymer matrix, which would finally reduce the hydrophobic and $\pi-\pi^*$ non-specific interactions. In the present case, this double effect can explain the increase in the recovery obtained for the three triazines using MIP2 and MIP3 materials versus the decrease observed using the corresponding NIPs. According to the results obtained for the pair MIP4/NIP4, it seems that too much HEMA might affect negatively the interaction of triazines with MAA inside the binding sites, which is governed by hydrogen bond and van der Waals interactions.

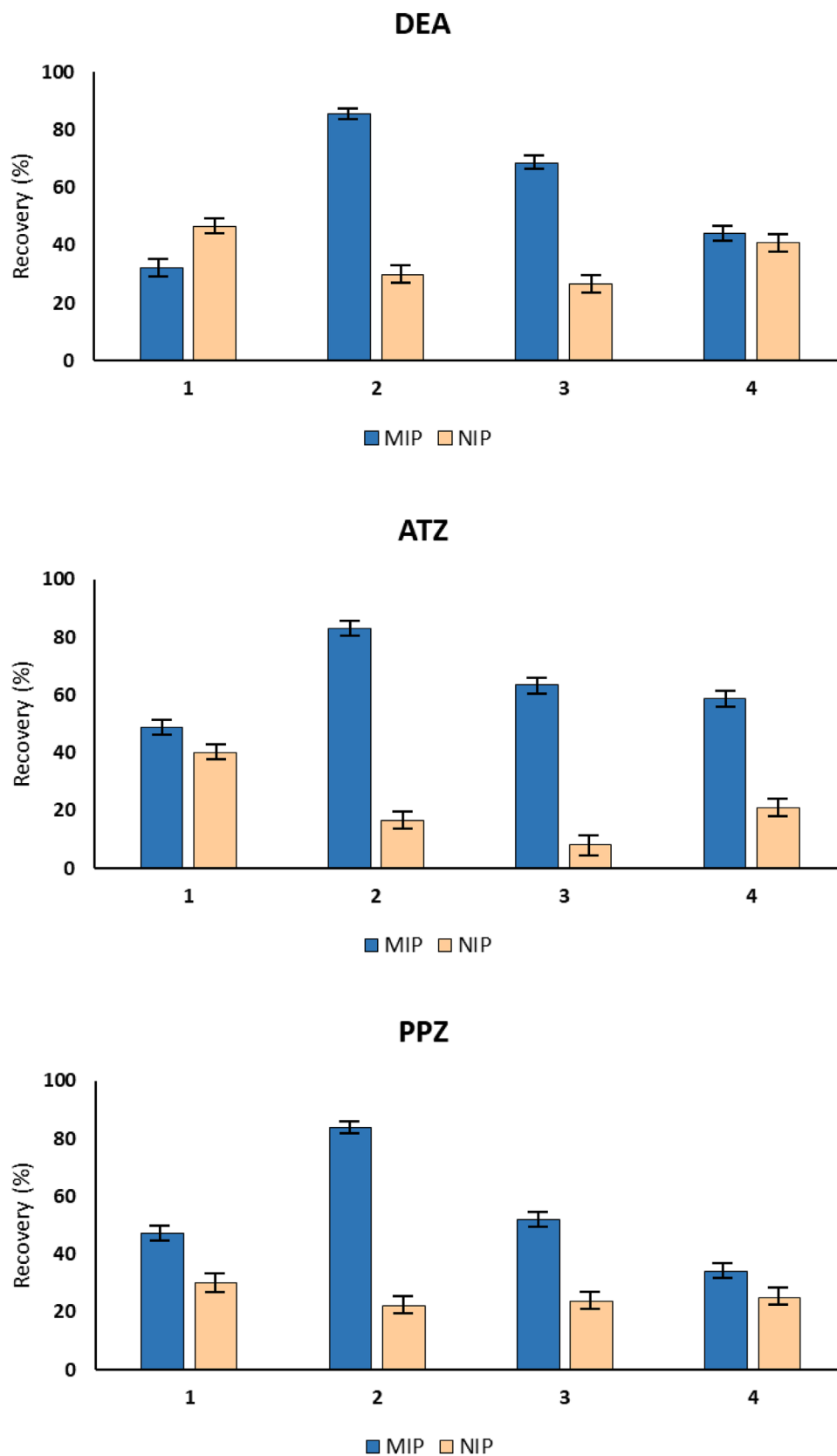


FIGURE 2 Mean recoveries ($n = 3$) desethylatrazine (DEA), atrazine (ATZ), and propazine (PPZ) after SPE onto the different molecularly imprinted polymer (MIP)/non-imprinted polymer (NIP) pairs

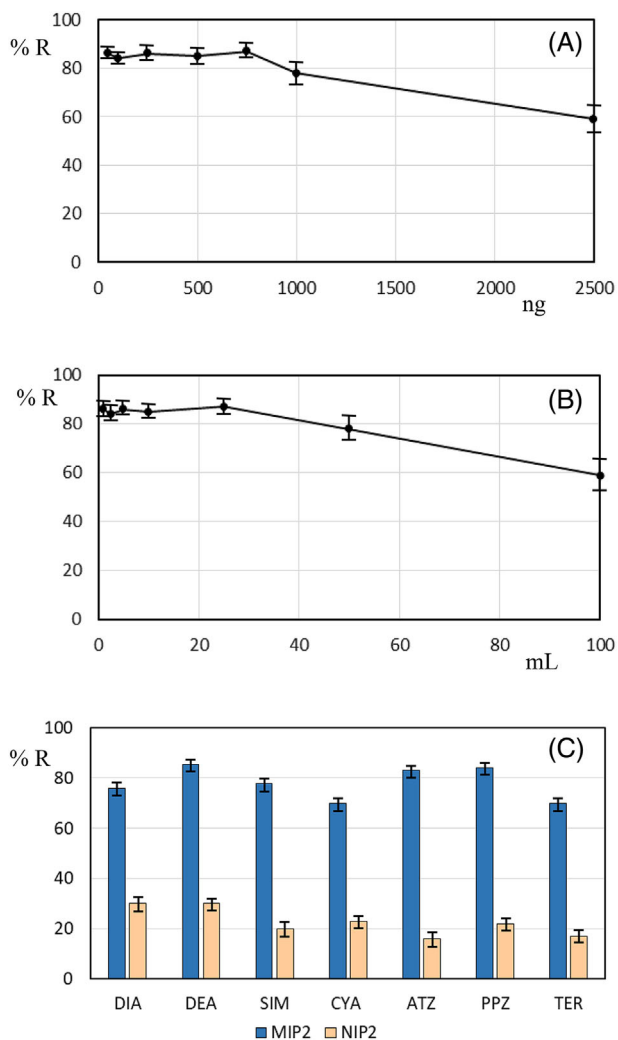


FIGURE 3 Breakthrough volume (A) and capacity study (B) for MIP2. Mean recoveries ($n = 3$) obtained for seven selected triazines in MIP2 and NIP2 (c)

As a conclusion, and taking into account all the results shown in Figures 1 and 2, it can be concluded that the best specific versus non-specific interaction ratio was obtained using the pair MIP2/NIP2, corresponding to polymerization mixture number 2 in Table 1, and thus it was selected for further experiments (Figure 3).

3.2 | Capacity and breakthrough volume studies

Capacity and breakthrough volume studies were carried out using 100 mg of MIP material per cartridge. To determine the maximum capacity of the MIP cartridge for triazines, MISPEs of 1 mL of a water solution containing different amounts of ATZ (50–5000 ng) were performed following the experimental procedure above described. Figure 3A plots the recoveries obtained as a function of

the amount of ATZ loaded. As it can be seen, recovery of ATZ remains quantitative up to 1000 ng, however, a certain decrease in the recovery and some increase in the RSD was obtained for this point with respect to the formers. Accordingly, the capacity of the cartridge was fixed at 750 ng to ensure maintaining the best recovery and precision of the developed procedure.

The breakthrough volume study was then carried out by fixing the amount of ATZ added to the cartridge but varying the volume of water solution loaded on it. The results obtained (Figure 3B) showed that quantitative recoveries can be achieved by percolating up to 50 mL of an aqueous solution, but as well as it occurred in the previous capacity study, RSD for this volume was not so satisfactory, and thus breakthrough volume was fixed in 25 mL. Finally, since breakthrough volume is dependent on the polarity of the analyte, the last study was performed by percolating 25 mL of seven commonly used triazines and degradation products containing 100 ng of each analyte to ensure working below the maximum capacity of the cartridges. In this study, and in other to increase the preconcentration factor, the eluates were evaporated to dryness and redissolved in 250 μ L of pure water before chromatographic analysis. The results obtained in both MIP2 and NIP2 cartridges are shown in Figure 3C. According to all the studies carried out in this section, it can be concluded that both the experimentally determined capacity and breakthrough volumes using 100 mg of MIP2 allow the preconcentration of triazines of different polarities in aqueous media in a very selective way, obtaining quantitative recoveries for all the target analytes. It is important to point out that, by using MIP2, the preconcentration of triazines is based on its molecular recognition directly in the aqueous media (preconcentration takes place inside the binding sites of the MIP material), and not by a first non-specific preconcentration and further solvent exchange to allow analytes to reach binding sites, which is the procedure usually required to perform selective MISPE for these herbicides in water samples.

3.3 | Analytical performance and application to environmental water samples

Calibration curves for each analyte were carried out by triplicate, by percolation of 25 mL of spiked water samples in the concentration range of 0.05–5 μ g/L onto 100 mg of MIP2. Calibrations showed good linearity, and the regression coefficients obtained were higher than 0.996. The precision and repeatability of the developed water-compatible MISPE procedure were studied in terms of recoveries and RSDs at two different spiking concentration levels (1 and

TABLE 2 Analytical performance of the developed method in the determination of triazines in environmental water samples. Recoveries (%R), RSD, and LODs^b

	Well water sample			Surface water sample		
	R (%)	RSD (<i>n</i> = 3)	LOD (µg/L) ^a	R (%)	RSD (<i>n</i> = 3)	LOD (µg/L) ^a
DIA	83.2	9.2	0.16	72.3	10.6	0.19
DEA	85.1	8.5	0.25	86.7	7.7	0.22
SIM	80.2	9.9	0.5	78.6	10.2	0.5
CYA	78.4	9.5	0.27	75.6	9.1	0.26
ATR	83.7	9.4	0.19	81.2	7.8	0.18
PPZ	84.0	8.7	0.4	89.0	8.2	0.35
TER	70.5	10.5	0.43	72.4	10.1	0.44

^aSample volume: 25 ml. MIP amount: 100 mg.

^bCalculated as three times the signal of the noise.

2.5 µg/L) and using three different MIP2 cartridges. All mean recoveries were over 78 % at both concentration levels with RSDs lower than 11% proving the good precision and repeatability of the proposed method.

Water-compatible MIP2 cartridges (100 mg) were then applied to the analysis of selected triazines in environmental waters (25 ml). Surface and well waters were selected for this study and spiked with 1 µg/L of each triazine in order to evaluate the feasibility of the developed procedure for the determination of these herbicides at real environmental concentration levels. All samples were prepared as described in the Experimental section, including the respective non-spiked samples (blank samples), where none of the selected triazines were detected. The obtained results were compared with those that can be obtained by preconcentration and analysis of the same water samples using conventional octadecyl silica (C18) cartridges.

Figure 4 shows the HPLC-UV chromatograms obtained after MISPE for surface and well water samples and, for comparison purposes, the chromatogram obtained for well water samples using C18 has been also included. A summary of the analytical parameters obtained is shown in Table 2. As it can be observed, all selected triazines can be determined at this low concentration level thanks to the highly selective preconcentration performed onto the MIP2 cartridges, which leads to UV chromatograms almost free of interferences and well-defined peaks for the seven triazines selected. In both cases, quantitative recoveries with RSDs lower than 11% were obtained for all the triazines studied. On the contrary, chromatograms obtained using C18 cartridges showed a big hump of interferences that completely prevents performing neither accurate nor selective determination of the selected triazines in these samples, demonstrating once again the high level of selectivity provided by the developed water-compatible MIPs.

Finally, limits of detection were calculated as three times the average signal of the background noise obtained in the analysis of the blank surface and well water samples at the corresponding retention time for each triazine. The obtained values (also included in Table 2) were within the 0.16–0.50 µg/L concentration range, which is low enough for the detection of the selected herbicides in environmental waters at realistic concentration levels.

4 | CONCLUDING REMARKS

In this work, the successful preparation of water-compatible MIPs for the selective extraction of triazinic herbicides has been achieved, based on the use of HEMA as a comonomer together with MAA. After careful optimization of the polymerization mixture, the selected MIP material (MIP2) was proven to be able to recognize simultaneously several triazines and degradation compounds in aqueous media. The use of MIP2 allowed the direct recognition of triazines in environmental water samples using sample volumes up to 25 ml, with recoveries ranging from 71 to 89% for realistic concentration levels and achieving LODs lower than 0.5 µg/L.

Using conventional MIPs (i.e., without the presence of HEMA), target analytes (and matrix components) in aqueous media are retained by non-specific interactions onto polymer matrix, which behaves like a reverse-phase sorbent. Then, a washing solvent able to remove matrix components and to re-distribute non-specifically bound analytes to the selective imprints is introduced. In this sense, it is remarkable the behavior of MIPs incorporating HEMA to the polymer matrix, as proposed in the present paper, since it allows the direct selective recognition of target analytes by the binding sites in aqueous media. The results presented in this paper demonstrate the suitability of HEMA in the development of successful water-compatible MIPs,

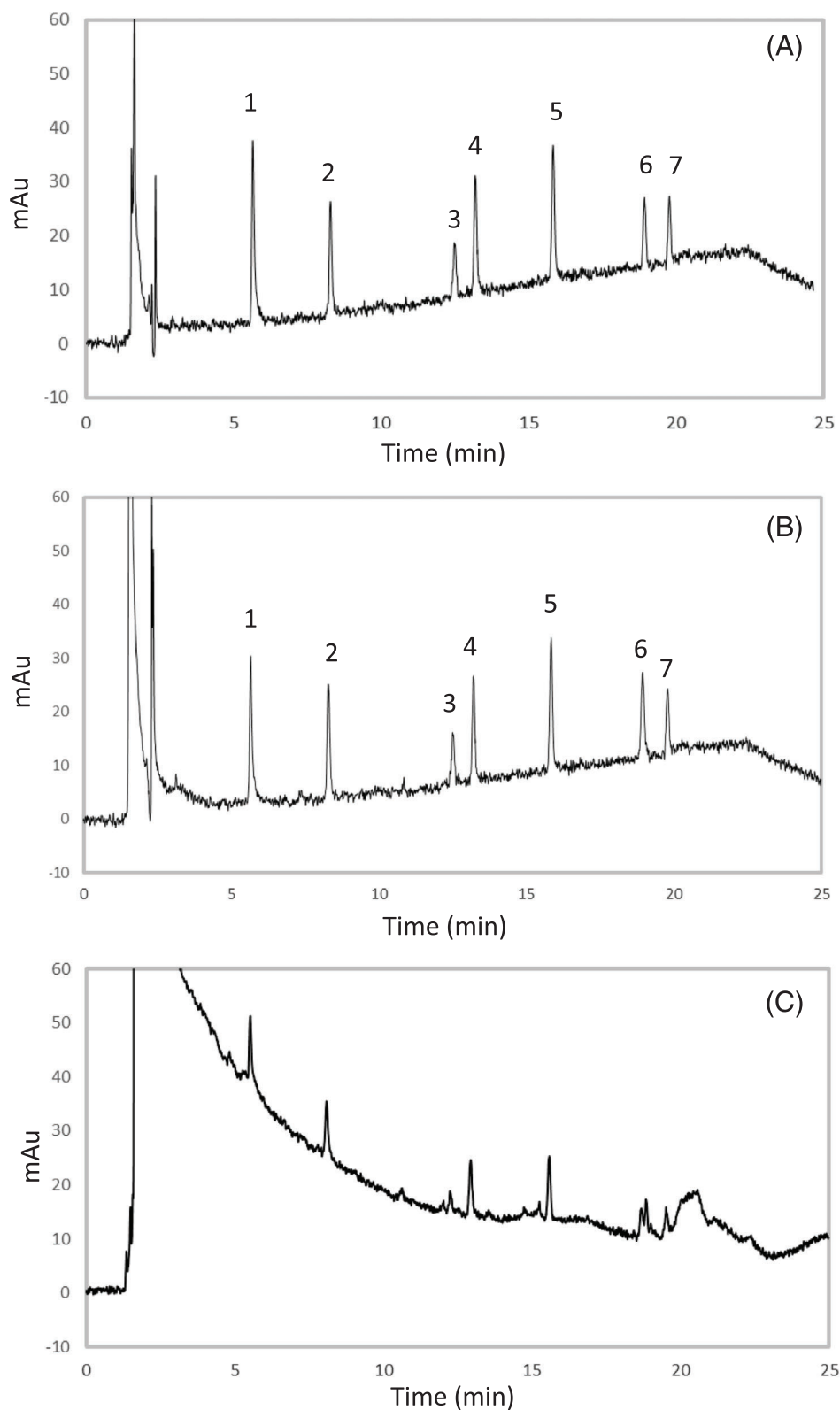


FIGURE 4 UV-Vis chromatograms obtained at 220 nm for well (A) and surface (B) water samples spiked at 1 $\mu\text{g/L}$ concentration level after molecularly imprinted SPE (MISPE) onto MIP2, and for well water samples spiked at the same level after SPE in conventional C18 cartridge (C). Peak assignment: (1) desisopropylatrazine (DIA); (2) desethylatrazine (DEA); (3) simazine (SIM); (4) cyanazine (CYA); (5) atrazine (ATZ); (6) propazine (PPZ); (7) terbutylazine (TER)

thus eliminating the traditional MIP drawback of lack of selective recognition in water samples.

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CONFLICT OF INTEREST

The authors have declared no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ORCID

Antonio Martín-Esteban  <https://orcid.org/0000-0003-0498-5153>

Esther Turiel  <https://orcid.org/0000-0001-5942-2433>

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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