



# On-line solid-phase extraction method for determination of triazine herbicides and degradation products in seawater by ultra-pressure liquid chromatography–tandem mass spectrometry



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## ABSTRACT

A fast, simple, selective and sensitive method has been developed for the determination of nine triazine herbicides (ametryn, atrazine, cyanazine, prometryn, propazine, simazine, simetryn, terbuthylazine and terbutryn) and eight degradation products (desethyl atrazine, desethyl-desisopropyl atrazine, desethyl 2-hydroxyatrazine, desethyl terbuthylazine, desisopropyl atrazine, desisopropyl 2-hydroxyatrazine, 2-hydroxyatrazine and 2-hydroxyterbuthylazine) in seawater samples. On-line solid-phase extraction coupled with ultra-pressure liquid chromatography–tandem mass spectrometry was employed for simultaneous analysis of all compounds in 11 min. Validation parameters were studied through the estimation of the limits of detection and quantification, calibration curves and precision. Limits of quantification ranged from 0.023 to 0.657  $\mu\text{g L}^{-1}$ . Good linearity was obtained for all compounds with  $R^2 > 0.99$  in all cases. Furthermore, inter-day precision (0–2.1%) and intra-day precision (0–3.9%) were shown to be satisfactory. On-line solid-phase extraction recoveries in spiked unpolluted seawater sample were evaluated and acceptable values (80.3–99.8%) with adequate RSD (0.1–3.1%) were found.

Finally, the proposed method was applied to the analysis of the target compounds in seawater samples collected from seawater nearby a zone of intensive horticulture of Matosinhos (Portugal). The concentrations of the herbicides were below the limit of detection in all cases.

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## 1. Introduction

The occurrence of micropollutants has been highlighted in thousands of publications during the last decade, which have pointed out a growing concern about them. Although there are no discharge limits for most micropollutants, some regulations have been published. Many of these substances, including triazine herbicides, are toxic and hazardous; as an example, atrazine produces genotoxic damage in fish species [1]. Therefore, the chemical pollution of surface water can affect the environment, several effects as chronic toxicity on aquatic organisms, accumulation in the ecosystem, as well as injuries in human health are described. The European Union has included simazine and atrazine in the list of 33 priority substances in the EU Water Framework Directive (2000/60/EC)

by way of Decision 2455/2001/EC [2]. Moreover, the Directive 2008/105/EC [3] sets the Environmental Quality Standards (EQS) for these compounds in surface water. Recently, the Directive 2013/39/EU amending the Directives 2000/60/EC and 2008/105/EC includes terbutryn to the list of priority substances [4]. This Directive establishes a maximum permitted concentration of 0.34, 2 and 4  $\mu\text{g L}^{-1}$  for terbutryn, atrazine and simazine respectively. Furthermore, Directive 2013/39/EU calls the attention on the important role of monitoring emerging pollutants that are not regularly considered in monitoring programs but can have toxicological effects.

In this way, studies examining the concentration of triazines in surface waters have expanded the list of compounds including their main degradation products [5–7]. These degradation products are produced through abiotic and biotic processes in the soil, groundwater and surface water [8]. Because of their mobility in the soil–water environment, the degradation products can reach water bodies more easily than triazines; thus, the impact due to herbicides tends to be underestimated when only the triazines are analysed

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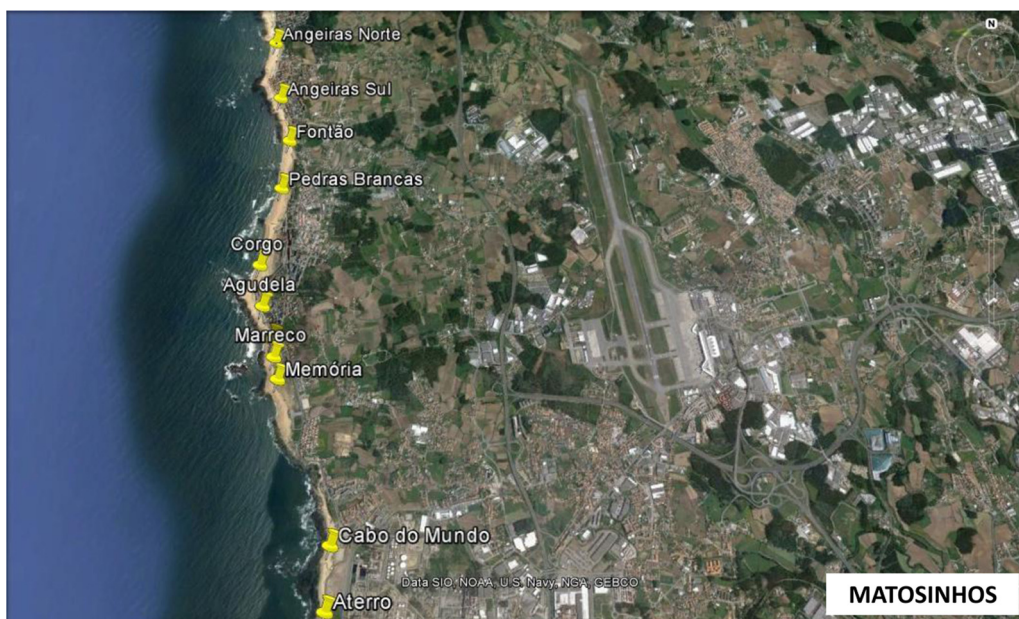


Fig. 1. Location of sampling sites in Matosinhos (North of Portugal).

in samples. Therefore, the main degradation products should be included in current analytical methods to obtain a better knowledge of water quality regarding herbicides contamination [9].

In order to support the implementation of the Directive 2013/39/EU, simple, selective and sensitive analytical methods are required. Different chromatographic techniques have been used to determine triazines and/or their degradation products in water. Between these techniques, the application of liquid chromatography-tandem mass spectrometry (LC-MS/MS) has provided an increased selectivity and sensitivity [10–16]. The recent development of chromatographic columns using new stationary phases with particle size  $<2\ \mu\text{m}$  for ultra-pressure liquid chromatography (UPLC) allows significantly shorten the analysis time [17]. UPLC-MS/MS can offer not only good sensitivity but also high confidence in the confirmation of compounds detected allowing to achieve more than 3–4 identification points. Thus, UPLC coupled to tandem MS provides an interesting tool for fast determination of these compounds in water samples [18–21].

Regarding extraction procedure, off-line SPE methods usually require high sample volume and are time-consuming [22]. On the other hand, although on-line SPE provides advantages, it also has disadvantages including the complexity of the set-ups of valve-switching, lack of flexibility as compared to off-line SPE and possible interferences from loading the entire extracted sample. Most of these problems have been resolved with advances in automated on-line SPE systems, integrated and flexible software programs and application of tandem spectrometry detectors for better selectivity. On-line SPE offers advantages, such as the minimal amount of solvents required for extraction, fast sample preparation and small sample volumes [23]. For this reason, the use of on-line SPE coupled to liquid chromatography-mass spectrometry has increased and some methods have been published for the analysis of triazines and their degradation products in water [7,13,20]. Nonpolar SPE sorbents are generally selected for extracting triazines from water samples. However, the degradation products, which contain polar functional groups, can be more efficiently extracted by using polar sorbents [24]. For SPE, different solid phases such as Oasis MCX cartridges [25,26], PLRP-s [13,20], Oasis HLB cartridges [15,20], Amberlite XAD-4 resin [27] and Oasis MAX cartridges [16] have been employed for triazines

and their major hydroxy and dealkylated products. Several articles have compared different adsorbents and Oasis HLB has shown to have better ability to retain both non-polar and polar compounds.

The aim of this study was to develop a fast, simple, selective and sensitive analytical method for the quantification and confirmation of 17 compounds (nine triazine herbicides as well as their main degradation products) in seawater. The method developed is based on an on-line solid-phase extraction (OASIS HLB cartridges) followed by UPLC-MS/MS determination. This method enables the determination of these pollutants at the levels required by European Union legislation [4]; consequently, it can be an important tool to control the presence of triazines and their degradation products in seawater samples. To the best of our knowledge, studies using on-line SPE-UPLC-MS/MS have not been done to determine the target compounds in seawater. However, the monitoring of these compounds in marine ecosystems situated close to areas of intensive horticulture is of great interest. Finally, the proposed method was applied to determine the target herbicides in seawater samples from beaches of Matosinhos (Portugal).

## 2. Experimental

### 2.1. Study area and sampling

The studied area is situated in the Portuguese seashore. This area presents some vulnerability due to hydrogeological factors and the interdependence with properties of pesticides what may add higher importance to the groundwater contamination and in this particular case reaching seawater [28]. Fig. 1 shows the study area with the sampling points. Seawater samples were collected from ten beaches susceptible to contamination by triazines during December of 2015. Sampling points are listed below: 1 (Angeiras Norte), 2 (Angeiras Sul), 3 (Fontão), 4 (Pedras Brancas), 5 (Pedras do Corgo), 6 (Agudela), 7 (Marreco), 8 (Memória) 9 (Cabo do Mundo) and 10 (Aterro).

Seawater samples were collected in amber glass bottles and transported to the laboratory under cooled conditions ( $4^\circ\text{C}$ ). At each sampling point, three samples were collected. Upon reception, samples were filtered through a PTFE syringe filter to eliminate

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