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Coupling passive sampling and time of flight mass spectrometry for a better estimation of polar pesticide freshwater contamination: Simultaneous target quantification and screening analysis

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ABSTRACT

The aim of this study was first to develop and validate an analytical method for the quantification of 35 polar pesticides and 9 metabolites by ultra-high-performance-liquid chromatography combined with a high resolution time-of-flight mass spectrometer detector (UHPLC–(Q)-TOF). Various analytical conditions were investigated (eluent composition and mass parameters) to optimize analyte responses. Analytical performance (linearity, limit of quantification, and accuracy) was then evaluated and interference in the extract of a passive sampler exposed in freshwater (POCIS: Polar Organic Chemical Integrative Sampler) was studied. The proposed quantification method was validated for 43 compounds with variation of calibration slopes below 10% in environmental matrix. For the unvalidated compound DIA (atrazine-desisopropyl: an atrazine metabolite), interference increased the error of concentration determination (50%). The limits of quantification obtained by combining POCIS and UHPLC–(Q)-TOF for 43 target compounds were between 0.1 (terbuthylazine) and 10.7 ng/L (acetochlor). Secondly, the method was successfully applied during a 14-day POCIS river exposure, and gave concentration values similar to a more commonly used triple quadrupole detector regarding concentration, but allowed for the detection of more compounds. Additionally with the targeted compound quantification, the (Q)-TOF mass spectrometer was also used for screening non-target compounds (other pesticides and pharmaceuticals) in POCIS extracts. Moreover, the acquisition of full scan MS data allowed the identification of the polyethylene glycol (PEG) compounds which gave unresolvable interference to DIA, and thus questions the ability of DIA to be used as performance reference compound (PRC) to determine sampling rates *in situ*. This study therefore illustrates the potential, and proposes a pathway, of UHPLC–(Q)-TOF combined with POCIS *in situ* pre-concentration for both quantitative and screening analyses of organic contaminants in water.

1. Introduction

As a result of human activities, a variety of organic compounds are present ubiquitously in the aquatic environment (PAH, PCB, pesticides and emerging substances such as pharmaceuticals). To evaluate freshwater chemical status, Water Framework Directive (WFD) [1,2] appraise the efficiency of remediation strategies and also secure a water supply for humans, thus, it is necessary to accurately determine their presence and concentration ranges. Many multi-residue analytical methods have been developed, in particular, high performance liquid chromatography (HPLC) coupled with a triple quadrupole mass spectrometer (QqQ) is widely used for the determination of polar pesticides in water [3–5]. The triple quadrupole mass spectrometer, operating in a selected reaction monitoring (SRM) mode, has some limitations since the compound list must be constructed before analysis and a post-run qualitative analysis is not possible. Recently, high resolution quadrupole time-of-flight (Q-TOF) mass spectrometry brought new possibilities to water analysis [6]. Indeed, a screening of water samples can be achieved by using a library containing accurate mass data for several families of organic compounds [7–10]. Within the same analysis, a quantitative determination can be performed on a list of target compounds and, additionally, a qualitative analysis can be carried out for other compounds included in a mass

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spectral library. This type of analysis thus appears to be a promising tool for water quality monitoring thanks to the detection of compounds potentially present in the water sample.

Although analytical techniques are now well adapted to quantify trace levels of micropollutants, the question of measurement representativeness remains, especially for grab water samples. Since environmental contaminant concentrations may vary over time, pollution events can be missed with grab water sampling [11,12]. Moreover, when pollutants are present at trace levels, large volumes of water are needed and analytical costs increased. To overcome these difficulties, several passive samplers, adapted for various types of contaminants, can be used [11]. Passive samplers are exposed in the aquatic environment for some days or weeks (generally 14 days) and accumulate compounds during this period. In the linear range of uptake, a time-weighted average concentration can be calculated which improves the representativeness [11,12]. *In situ* pre-concentration of compounds in the sampler allows reduction of limits of quantification (LOQ) and is assumed to reduce risk of contamination during sample treatment or handling [13]. Among passive samplers, the Polar Organic Chemical Integrative Sampler (POCIS) [14] has been used for polar compounds with log *P* values ranging between 0 and 4, in particular for pesticides and pharmaceutical residues [15–17]. To mitigate the effects of environmental parameters (biofouling, variations in flow velocity and temperature), performance reference compounds (PRC) were applied and thus micropollutants more accurately quantified [18].

Gravell et al. [8] previously pointed out the power of coupling passive samplers with high resolution techniques for pollutant screening in grab water samples. Zendong et al. [19] used passive samplers (POCIS, low density polyethylene, polydimethylsiloxane, etc.) combined with a (Q)-TOF for the analysis of marine toxins. Moreover, the HPLC-(Q)-TOF analytical technique has already been validated for the quantification of pesticides and pharmaceutical residues in surface water, effluents or food samples [20,21]. The present work is, to the best of our knowledge, the first report of a validation procedure for the combined use of passive sampling (POCIS exposed in freshwater) with an HPLC-(Q)-TOF analytical technique. Firstly, this article describes development and validation of the analytical method for quantification of 35 polar pesticides and 9 metabolites. Secondly, this paper compares the performance of the Q-TOF against the QqQ to quantify the 43 pesticides and metabolites validated from POCIS extracts. Finally, benefits of passive sampling coupled to Q-TOF detector for more accurate quantification and screening analysis are discussed.

2. Materials and methods

2.1. Reagents and standards

Ultrapure water (UPW) was produced by a Gradient A10 Milli-Q system from Millipore (Bellerica, MA, USA). UHPLC solvents (methanol and acetonitrile) were obtained from J.T. Baker (Deventer, Netherlands) and were all UHPLC–MS quality. Reagents added to eluents (formic acid and ammonium formate) were obtained from Agilent (Santa Clara, CA, USA) (purity 99%). Ethyl acetate, 99.5% purity, used for Solid Phase Extraction (SPE) elution, was purchased from Sigma–Aldrich (Steinheim, Germany).

The list of pesticides selected for the study is presented in supplementary materials (Table S1), which also includes pesticide properties. All pesticides (35), metabolites (9) and deuterated pesticides were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) with a purity higher than 97% for 40 targeted pesticides (purity between 94 and 96.5% for the four others). Pesticides with purity above 98% were used for screening investigations (isoxaben and methacrifos) and were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany).

Stock pesticide solutions at a concentration of 100 mg/L, except for norflurazon-desmethyl (1 mg/L), were prepared in acetonitrile and stored at −18 °C for no more than 6 months. The stock solution of internal standards (deuterated pesticides at a concentration of 1 mg/L) was prepared in acetonitrile and stored in the same conditions. Calibration solutions containing pesticide standards (concentrations 1 μg/L, 5 μg/L, 10 μg/L, 25 μg/L and 100 μg/L) and internal standards (concentration 100 μg/L) were prepared in a mixture of UPW/methanol (90/10, v/v).

2.2. Ultra high performance liquid chromatography (UHPLC) and electrospray ionization source (jet stream) tandem quadrupole time-of-flight (Q-TOF)

2.2.1. Chromatography

Chromatographic separation was performed with a UHPLC 1290 Infinity apparatus from Agilent (Santa Clara, CA, USA). An analytical gradient of 20 min was used with UPW and methanol with 5 mM ammonium formate and formic acid (0.1%) (supplementary material Table S2a). The injected sample volume was 5 μL. Chromatographic separation was performed with a Zorbax Eclipse Plus C18 Rapid Resolution High Definition column (2.1 mm × 150 mm, 1.8 μm) from Agilent. Column and autosampler temperatures were maintained at 30 °C and 5 °C, respectively.

Although several chromatographic conditions were investigated (gradient, column temperature), an optimized UHPLC separation of acetochlor from alachlor (isomeric compounds) could not be achieved. A proper separation of all other analytes and internal standards was obtained (see Table S3 in supplementary material for the retention times and corresponding internal standards).

2.2.2. Detector

The detector was a tandem mass spectrometer composed of a quadrupole combined with a time-of-flight (Accurate Mass LC/MS 6540 Agilent). It was equipped with an Agilent Jet Stream electrospray ionization source (ESI) operating in the positive ionization mode. Mass acquisition was performed in the "All-ions" mode. In this MS scan mode, ions are not filtered by the quadrupole and are transferred to the collision cell where they are all fragmented simultaneously at various collision energies: 0 V, 10 V, 20 V and 40 V. Optimized source parameters and other TOF-MS parameters are shown in supplementary material Table S2b.

The mass axis was calibrated using the mixture provided by Agilent (from the lowest mass 118.0863 *m/z* to the highest 2721.8948 *m/z*). A reference solution was also employed for continuous calibration using the reference mass 922.0098 *m/z*. Data acquisition was performed in the Extended Dynamic Range 2 GHz over the *m/z* 100–1700 range. The Agilent 6540 is also capable of running at 4 GHz (high resolution mode). Recorded data were processed with the MassHunter Qualitative and Quantitative software from Agilent (versions B.06.00 Build 6.0.633.10 and B.06.00 Build 6.0.388.1, respectively). TOF-MS accurate mass spectra were compared to a library (Agilent Pesticides Database) to confirm the presence of the compounds and avoid any false positives. The mass error was systematically below 0.22 ppm.

2.3. Method validation procedure

Several solutions were prepared to validate the method, *i.e.* to study 4 parameters: calibration – linearity, limit of quantification, accuracy and interference (as indicated in the French standard NF T90-210 [22]). Solution preparation and sample analysis were performed in two different conditions.