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# Multi-residue analysis of pesticides in surface water by liquid chromatography quadrupole-Orbitrap high resolution tandem mass spectrometry

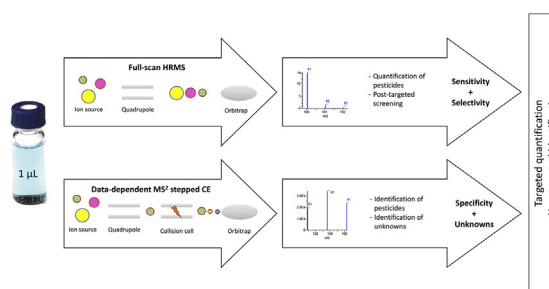
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## HIGHLIGHTS

- LC-Q-Orbitrap-MS method fully optimised and validated for a total of 252 pesticides in surface water.
- Target quantification of pesticides and broader qualitative screening in one single injection.
- Limits of quantification below  $5 \text{ ng L}^{-1}$  for most of the pesticides.
- Application of the method to the analysis of river water samples from England.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A quantitative targeted screening method for the determination of residues of a broad group of more than 250 pesticides in surface water samples was developed and validated. Substances were isolated from the sample matrix by solid-phase extraction (SPE), using hydrophilic-lipophilic balanced polymeric sorbents (HLB), and analysed by reversed-phase liquid chromatography (LC) - Orbitrap high-resolution mass spectrometry (HRMS). Compounds were quantified in full scan acquisition mode, while accurate data dependant  $\text{MS}^2$  analysis was simultaneously triggered for the unambiguous identification of the targeted substances.

This analytical protocol combines simplicity and robustness, with quantitative recoveries for 215 of the pesticides, negligible matrix effects during electrospray ionisation (ESI) and limits of quantification (LOQs) below  $5 \text{ ng L}^{-1}$  for 204 of the analysed compounds. Method capabilities were checked at qualitative and quantitative levels, analysing a set of four river water samples from rural areas in the Southwest of England. A total of 33 different pesticides were found in these samples with MCPA present at the highest concentration, in excess of  $130 \text{ ng L}^{-1}$ .

Retrospective examination of the LC-HRMS chromatograms permitted the identification of an additional pesticide and a group of nine antimicrobials and veterinary drugs that were also present in the processed samples.

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## 1. Introduction

Pesticides are widely used in agriculture and livestock production to control insect, plant and fungal pests and diseases [1].

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During the past 50 years the human population and global agricultural production have both more than doubled, with productive arable areas increasing by some 10% [2]. The use of pesticide products is massive and continues to grow, with an estimated more than 2.5 million metric tons applied every year worldwide [3], 40% of this being herbicides.

Pesticides can be classified according to their chemical structure in these main groups: organophosphates, carbamates, neonicotinoids, chloroacetamides, pyrethroids, azoles, strobins, anilides, ureas, triazines and pyrimidines.

Concerns about the presence of pesticides in different waterbodies has increased markedly in the past 25 years, after some of them were found in groundwater intended for human consumption in the USA [4]. Since then, numerous monitoring campaigns have shown the potential of pesticides to contaminate surface water [5–10], sediments [8,11], groundwater [6] and drinking water [12].

The reason for the presence of pesticides in all these waterbodies is that, after application on agricultural fields [13], the pesticides can be transported by surface runoff into inland surface waters, and can leach through soil into groundwater [14,15]. The fate of individual pesticides depends on the water solubility and the stability of each substance [16,17]. Pesticides are designed to be toxic to living organisms and may also display carcinogenic and mutagenic properties in humans and other animals. Taken together, the potential effects of many pesticides, their persistence and the fact that they are regularly applied in large quantities, these compounds comprise a major risk to people and to the wider environment [18].

By the end of the 20th century the EU had set legal limits for different parameters in water intended for human consumption, aimed at the protection of human health, including a limit of  $0.1 \mu\text{g L}^{-1}$  per individual pesticide and  $0.5 \mu\text{g L}^{-1}$  for the sum of all pesticides [19,20]. In parallel, the Directive 2000/60/EC, amended by Directives (2008)/105/EC and 2013/39/EU, set limits for 45 different substances in different continental waterbodies, inland surface waters, transitional waters, coastal waters and groundwater [21–23]. Among the controlled substances there are several pesticides: alachlor ( $0.7 \mu\text{g L}^{-1}$ ), aclonifen ( $0.012 \mu\text{g L}^{-1}$ ), atrazine ( $2 \mu\text{g L}^{-1}$ ), bifenoxy ( $0.004 \mu\text{g L}^{-1}$ ), chlorfenvinphos ( $0.3 \mu\text{g L}^{-1}$ ), chlorpyrifos ( $0.1 \mu\text{g L}^{-1}$ ), cybutrine ( $0.016 \mu\text{g L}^{-1}$ ), cypermethrin ( $6 \times 10^{-5} \mu\text{g L}^{-1}$ ), dichlorvos ( $7 \times 10^{-5} \mu\text{g L}^{-1}$ ), diuron ( $1.8 \mu\text{g L}^{-1}$ ), endosulfan ( $0.004 \mu\text{g L}^{-1}$ ), heptachlor ( $3 \times 10^{-3} \mu\text{g L}^{-1}$ ), isoproturon ( $1 \mu\text{g L}^{-1}$ ), quinoxifen ( $0.54 \mu\text{g L}^{-1}$ ), simazine ( $4 \mu\text{g L}^{-1}$ ) and terbutryn ( $0.034 \mu\text{g L}^{-1}$ ).

There are hundreds of papers in the literature reporting diverse liquid chromatography – mass spectrometry (LC-MS) methodologies for the analysis of all the different classes of pesticides [24]. The multi-residue quantitative methods for the analysis of environmental water samples developed in the past 10 years usually rely on tandem mass spectrometry (MS/MS) with triple quadrupole mass analysers (QqQ), after solid-phase extraction (SPE) of the water with reversed-phase sorbents [9,18,25–29].

In the same period of time, the popularity of high-resolution mass spectrometry (HRMS) instruments has importantly grown mainly due to the availability of time-of-flight (TOF) and Orbitrap systems at affordable costs. The major advantage of these mass spectrometers is the possibility of acquiring full-scan spectra at high resolution, whereas QqQ techniques only register selected or multiple reaction monitoring (SRM or MRM) data defined by the user before the analysis [30]. This implies that with LC-QqQ systems all the sample data not specified beforehand is discarded; however, with LC-HRMS techniques it is possible to identify every substance that ionises in the source [31], making the retrospective analysis of other substances feasible and even the qualitative screening of compounds

without reference standards possible [32,33]. Another important advantage of the HRMS over QqQ instruments is the reduction of chances in giving a false positive identification, especially when dealing with complex matrices, even though the sensitivity of QqQ mass analysers is higher. The introduction of this kind of instrumentation has changed the overview of Analytical Chemistry in the recent years, bringing new challenges.

According to Krauss et al. [34], three different approaches can be adopted when working with LC coupled to HRMS: 1) quantitative targeted analysis of pre-selected substances with reference standards; 2) suspects screening of pre-selected substances without reference standards but with predicted MS/MS fragmentation matching; and 3) non-targeted screening of unknowns with peak detection, formula fit and predicted MS/MS fragmentation matching as well. To these three workflows we could add the post-targeted screening, which is the search for additional substances in already acquired chromatograms.

Some methods based on LC-HRMS for the screening of organic micropollutants multi-residues in water, including pesticides, have been developed in the last decade. Most of them adopted the suspects screening strategy at qualitative level [31,33,35], in some cases followed by quantification with LC-QqQ, and in others at semiquantitative level [36,37]. In other cases, post-targeted [32] and non-targeted [38] approaches have been employed with TOF, QTOF and Orbitrap mass analysers. HRMS quantitative target screening methodologies have also been developed [24,30]. Nurmi et al. [30] quantified 84 pesticides and pharmaceuticals in water samples with a Micromass LC-TOF and Ferrer et al. [24] quantified 101 pesticides in food and water samples with an Agilent LC-TOF.

The objective of the present work was to develop and validate a targeted screening method for 275 pesticides and metabolites residues in water (252 of these compounds were finally included) by off-line SPE and LC-Orbitrap-HRMS, with competitive quantitative capabilities for all of them, at the same time as their unambiguous identification was ensured. This method can also be applied to suspect screening of other pesticides and micropollutants, and offers the possibility for screening a huge number of contaminants in post-targeted approaches, once samples have been analysed.

This is possible due to the combination of the high resolution data acquired by the Orbitrap mass analyser, with the collection of MS<sup>2</sup> data, feasible thanks to the presence of a quadrupole mass filter and a HCD collision cell before the high-resolution mass analyser on the hybrid Orbitrap Q Exactive Focus system. This instrument, which was recently introduced by Thermo Fisher Scientific, permits different acquisition workflows to be chosen depending on the objective pursued. In this study we chose the full-scan with data-dependent MS<sup>2</sup> (dd-MS<sup>2</sup>) confirmation mode. In this method, the user predefines an inclusion list containing the ion mass and the retention time of the target substances. During the acquisition, full scan data is collected in a continuous mass range and when any of the rules stated in the inclusion list is accomplished, a single MS<sup>2</sup> scan, sum of all the ions trapped in the C-trap, is collected. This way, sensitive quantification can be carried out with the data registered in full scan, while the selective MS<sup>2</sup> input is used for identification purposes [39].

## 2. Experimental

### 2.1. Standards, solvents, sorbents and samples

High purity standards for the 275 substances in the preliminary list of targets were obtained from Lab Instruments (Castellana Grotte, Italy). The pesticides present in this list were chosen on the basis of the priority list of pollutants of the EU and the US

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