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Environmental monitoring and risk assessment of pesticide residues in surface waters of the Louros River (N.W. Greece)

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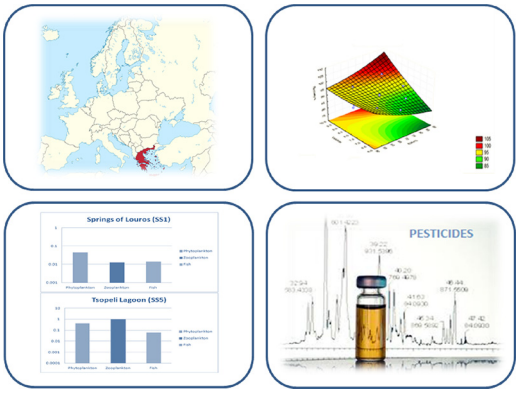
HIGHLIGHTS

- A chemometric approach was used for the extraction optimization.
- Pesticide occurrence was studied with a combination of GC–MS/SPE and LC-ESI-MS/SPE.
- One year monitoring survey was carried out.
- Ecological risk assessment associated with detected pesticides was performed.

GRAPHICAL ABSTRACT



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ABSTRACT

Estuarine environments are being constantly stressed by new sources of pollution (e.g. pesticides) derived from activities of industry and intensive agriculture. The present study aims at quantify pesticides of three different categories (fungicides, herbicides and insecticides) in the Louros River (Epirus region, North-Western Greece). A monitoring study of 34 compounds was carried out in surface river waters from June 2011 until May 2012. Seven water sampling stations were established and 35 water samples were collected. A solid-phase extraction (SPE) method coupled with gas chromatography–mass spectrometry (GC–MS) and liquid chromatography-mass spectrometry (LC-MS), depending on the compound, was developed and validated. During the monitoring study 25 pesticides were detected (13 herbicides, 9 insecticides, 3 fungicides). The most commonly encountered pesticides were quizalofop-ethyl, trifluralin and pendimethaline. Tebufenpyrad was found in all sampling stations and seasons, with the highest concentrations of 0.330 μg/L at Tsopeli Lagoon exceeding the rather low concentrations reported nationwide. Regarding the environmental risk due to the presence of target compounds in surface waters, this was estimated by calculating risk quotients (RQs) for different aquatic organisms (algae, zooplankton and fish). The results denoted a possible threat for the aquatic environment, rendering in this way the RQ method as a useful screening tool. In any case, further extensive study is needed for acetochlor, pirimiphos-methyl, endosulfan-a and azinphos-ethyl in order to better correlate their occurrence and potential toxic effects in aquatic life and humans.

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1. Introduction

A wide variety of pesticides have been used in agriculture and landscape maintenance for controlling insect, bacterial and fungal pests, and for reducing competition from weeds since the middle of the 20th century (Masiá et al., 2014; Wu et al., 2010). Water pollution due to the use of pesticides in agriculture is a priority environmental issue and a cause of major global concern (Herrero-Hernández et al., 2017). Only herbicides represent about 50% of the demand in agricultural chemicals; their prolonged use involves the risk of retention in crops and soils. Besides, because of washing and leaching processes, these substances can pass to the surface and ground waters. Pesticides are primarily transported from agricultural fields to surface waters through surface run-off. The amount lost from fields and transported to surface waters depends on several factors, including soil characteristics, topography, weather, agriculture practices and chemical and environmental properties of individual pesticides (Konstantinou et al., 2006). Chemicals which are sufficiently resistant to degradation and are adequately soluble to be transported on water may reach the sea in significant amounts. Water run-off and river transport are the main processes involved in the land-sea transfer of chemicals (Albanis and Hela, 1998). The uptake of pesticides into watercourses and their propagation through biological chains highlight the importance of monitoring and understanding the fate of herbicides and their degradation products, not only in the areas where they are applied, but also in proximal areas (Tankiewicz et al., 2010; Konstantinou et al., 2006; Wackett, 2007; Gavrilescu, 2005).

Several pesticides are included in the European Union list for priority organic compounds to be monitored from discharges (European Union Directive EC/76/464), while some of them and their transformation products are classified by the IARC (International Agency for Research on Cancer) as potentially carcinogenic to humans (Richardson and Kimura, 2016). In addition a total of 91 pesticides have been listed as confirmed or possible endocrine disruptor (ED) chemicals by the Environment Agency of England and Wales, The German Environment Agency, The European Union Community Strategy for EDs, the Oslo and Paris Commission and the World Wildlife Fund (McKinlay et al., 2008). Causality of detrimental effects on wildlife as a direct consequence of exposure to many ED pesticides is established, and in some cases has been shown to have population level impacts. The European Union has introduced strict directives to protect water quality, such as the REACH Regulation (European Comission, 2006) concerning the Registration, Evaluation, Authorization and Restriction of Chemicals, while Directive 2008/105/EC, on environmental quality standards in the field of water policy, provides a detail of priority substances (33) to be controlled in water, with pesticides making up a third of the list (Herrero-Hernández et al., 2017; Dujaković et al., 2010; EU, 2008). In addition, the EU Regulations for drinking-water quality set a limit in concentration at 0.5 μg/L for the sum of all pesticides and 0.1 μg/L for each individual compound, in order to limit human risks and environmental pollution (Herrero-Hernández et al., 2017; Postigo et al., 2010; Dujaković et al., 2010; Hurtado-Sánchez et al., 2013; EC, 1998).

Pesticides ecological risk assessment is given as a function of environmental exposure and ecotoxicological effects. This is usually expressed as the ratio of the predicted environmental concentration (PEC) to predicted no-effect concentration (PNEC). PEC values are calculated using several models taking into consideration application rates, persistence, leaching, sorption and compound bioaccumulation or directly from monitoring data while PNEC values are usually calculated on the basis of critical concentrations, e.g. EC_{50}, LC_{50} and NOEC (Vryzas et al., 2009).

Several sample preparation techniques, mainly liquid liquid extraction (LLE) (Tankiewicz et al., 2010; Wu et al., 2010; Farajzadeh et al., 2014), solid-phase extraction (SPE) (Andrade-Eiroa et al., 2016a; Kuster et al., 2008; Cruzeiro et al., 2017; Bonansea et al., 2013), solid-phase micro-extraction (SPME) (Souza-Silva et al., 2015; Bonansea et al., 2013; Li et al., 2015), liquid phase micro-extraction (LPME) (Tankiewicz et al., 2010; Pinto et al., 2010; Heftmann et al., 2007; Ahmad et al., 2015) and many more, have been used for the preparation of pesticides from water and other sample matrices. Several Environmental Protection Agency (EPA) methodologies include SPE as the procedure recommended for pretreatment of organic pollutants (EPA Method 1699, 2007). SPE is the most widely used method for the extraction, changing of solvents, cleanup, concentration, fractionation of organic compounds from number of samples, but also cleaning up interferences, thus improving detection sensitivity and reducing matrix effects in Mass Spectrometry (MS) (Andrade-Eiroa et al., 2016b).

MS is recognized as a highly sensitive and specific technique suitable for use in environmental organic analysis (Cacho et al., 2017; Masiá et al., 2014; Robert et al., 2016). Gas Chromatography (GC) (Yang et al., 2010; Domínguez et al., 2016) is often used for the determination of pesticides because of its high resolution and high detector sensitivity. However, some of the pesticides cannot be analyzed via GC methods, due to their thermo-instability (poor volatility and high polarity) (Alder et al., 2006; Kuster et al., 2008). As an alternative, liquid chromatography (LC) (Dujaković et al., 2010; Hurtado-Sánchez et al., 2013; Caldas et al., 2016) equipped with ultra-violet (UV) (Polati et al., 2006; Irace-Guigand et al., 2004), fluorescence (FLD) (Fu et al., 2009; Pinto et al., 2010) and MS (Masiá et al., 2014; Caldas et al., 2016; Hao et al., 2016) detectors provide simple and rapid techniques for analysis.

The present work uses a combination of SPE and GC–MS/ LC-MS as an analytical tool for the screening of 34 pesticides residues in surface waters, including river, lake and sea water. The objectives of this study were: (1) to establish a single extraction procedure using SPE that will allow the multi-residue determination of selected compounds belonging to different chemicals groups in surface waters; (2) to combine this sample preparation step with the use of GC–MS/ LC-MS using the selected ion-monitoring mode (SIM) for the qualification and quantification of the target analytes; (3) to apply the methodology developed for the routine analysis of natural water samples in the framework of an extended water quality monitoring survey that included 7 different sampling stations at Louros River basin (North-Western Greece), during a period of one year; and (4) to assess the ecotoxicological risk in Louros River for three taxonomic groups (algae, zooplankton, fish). The novelty of this work lies, on the one hand, in the chemometric approach used for the optimization of the SPE method by means of experimental design and response surface methodology. On the other hand, the study of 34 pesticides of different action groups simultaneously determined was enlightening for the Epirus region. To the best of our knowledge, this is the first study reporting the occurrence of pesticides in the aquatic region of Epirus and especially in the River Louros, in such an extensive and comprehensive manner. In addition, the collection of a year data (survey monitoring) is essential for the assessment of changes in the fluvial system of Louros River. This area is intensely subjected to anthropogenic activity and the aim of this work has been to provide a better understanding of the fate of pesticides in the environment.

2. Experimental

2.1. Chemicals and reagents

Pesticides were obtained from Sigma-Aldrich (St. Louis, Missouri, USA), and were of high purity grade (>96%), with the only exception that of ethoprophos (93.1%). Acetone and methanol were supplied by Carlo Erba (Milan Italy), methanol (LC-MS grade), water (LC-MS grade) and dichloromethane were purchased by Fisher Scientific (Leicestershire, UK), and ethyl acetate was supplied by Pestiscan (Labscan, Ltd., Dublin, Ireland). All solvents and reagents were analytical