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Analysis of pesticides and metabolites in Spanish surface waters by isotope dilution gas chromatography/mass spectrometry with previous automated solid-phase extraction
Estimation of the uncertainty of the analytical results

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Abstract

A method based on isotope dilution gas chromatography/mass spectrometry (GC/MS) with automated solid-phase extraction (SPE) is described for the analysis of 32 pesticides and metabolites in surface waters. This approach consist in the use of nine isotopically labelled representative pesticides as internal standards, which allows high accuracy (trueness and precision) and sensitivity for most analysed compounds, as it is required for isotope dilution-based methods. Uncertainties associated with pesticide determination in real samples were estimated using quality assurance/quality control (QA/QC) data. For most pesticides expanded uncertainty was below 40%, according to the commonly established requirements for analytical results.

Ninety three Spanish surface waters collected in June–July and September–November 2004 were analysed. Concentration and occurrence of pesticides were evaluated. These parameters were higher in the summer than in the autumn period. In summer four pesticides were found in more than 50% of the analysed samples and four compounds were detected above the concentration level of 1 μg/l (atrazine, terbutylazine, 3,4-dichloroaniline and fenitrothion), while in autumn percentage of detection was below 50% for all pesticides and only one compound (terbutylazine) exceeded 1 μg/l.

Keywords: Pesticides; Isotope dilution; Automated SPE; GC/MS; Uncertainty; Surface waters

1. Introduction

According to Eurostat [1], pesticide annual sales in the European Union (EU) increased during the period 1992–2001 from $291,895 \times 10^3$ to 327279.9×10^3 kg. In the same period, pesticide annual usage in the USA declined from 426376.82×10^3 to 402790.02×10^3 kg [2]. In 2001, Spain was the third EU country in pesticide sales ($35,700 \times 10^3$ kg), after France and Italy. Regarding to the type of pesticides, the highest percentage of Spanish sales was for herbicides (34%), followed by insecticides (33%), fungicides (22%) and other pesticides (11%) [1].

As a consequence of the amounts of pesticides used, their wide spectrum of applications and their physicochemical and toxicological properties, these compounds and their metabolites are considered an important problem for environment and human health. In addition, many pesticides have been classified as substances with evidence or potential endocrine disruption [3]. Pesticide contamination mainly affects surface waters, especially in lowland rivers, and also groundwater and rainwater. Pesticide occurrence in Spanish surface waters was studied (samples analysed by GC/MS) in the frame of an agreement between the Ministry of Public Works and our laboratory [4], and several periods of pesticide monitoring in surface waters ordered by the Ministry of Environment have been carried out since 2000.

In the field of water policy, European legislative prescriptions related to pesticides and other contaminant substances have been established. The Water Framework Directive [5] was amended by the Decision 2455/2001/EC [6], which published a list of 33 priority substances, including 10 pesticides, selected on the

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basis of risk to or via the aquatic environment. Moreover, in 2000 the Spanish legislation fixed quality objectives of 1 μg/l for the concentration of four pesticides (simazine, atrazine, terbutylazine and metolachlor) in continental surface waters [7]. Regarding to the water intended for human consumption, European [8] and Spanish [9] authorities fixed quality standards of 0.1 μg/l for pesticide individual concentrations and 0.5 μg/l for the sum of all pesticides.

In the last 10 years, many techniques have been applied to the extraction and analysis of pesticides and their metabolites in environmental samples. Regarding to the extraction of water samples, the most commonly used methods are liquid–liquid extraction (LLE) [10,11], solid-phase extraction (SPE) [10–14] and solid-phase microextraction (SPME) [15]. LLE and SPE can be used to determine a broad range of pesticides in one analysis. SPE methods are rapid, efficient (good recoveries and low detection limits), use less solvent than LLE and consequently have lower laboratory expenses. In addition, SPE methods can be automated by using laboratory robotic systems [11] that do all or part of the sample preparation steps.

The most widely used methods for the analysis of pesticides are based on gas chromatography (GC) [10,11,13,16], liquid chromatography (LC) [16,17] and capillary electrophoresis (CE) [12,18]. For GC and LC, mass spectrometry (MS)-based detection techniques have become powerful instruments for pesticide analysis because of their selectivity and sensitivity. Concretely, GC/MS [10,11,14] is a very efficient technique with a high resolution power for volatile and semivolatile compounds, especially when using the selected-ion monitoring (SIM) mode [14], which eliminates interferences and improves detection limits. The combination of SPE with GC/MS on-line [10] and off-line [11,14] allows the determination in one analysis of a great number of pesticides.

Isotope dilution, based on the addition of labelled internal standards prior to sample extraction, has proven to be a powerful quantitative analytical technique. If thermodynamic equilibrium between native analytes and labelled standards is achieved, errors due to sample preparation are compensated since identical chemical and physical behaviour is highly probable between native and labelled substances [19]. This method, combined with GC/MS, has been widely applied to the analysis of different environmental pollutants [20–22]. However, few references were found related to the isotope dilution GC/MS analysis of pesticides [23,24].

Table 1
Pesticides and metabolites analysed by isotope dilution GC/MS

Compound	Type	Priority list	Endocrine disruption
3,4-Dichloroaniline	Metabolite of diuron[a], linuron and propanil (herbicides)		
Molinate	Herbicide		
Desisopropylatrazine (DIA)	Metabolite of atrazine[a] or simazine[a]	Decision no. 2455/2001/EC[a], RD 995/2000[b]	
Desethylatrazine (DEA)	Metabolite of atrazine[a]	Decision no. 2455/2001/EC[a], RD 995/2000[b]	
Trifluralin	Herbicide	Decision no. 2455/2001/EC[a]	SEC (2004) 1372[c]
Dimethoate	Insecticide		
Simazine	Herbicide	Decision no. 2455/2001/EC[a], RD 995/2000[b]	
Atrazine	Herbicide	Decision no. 2455/2001/EC[a], RD 995/2000[b]	
Propazine	Herbicide		
Terbutylazine	Herbicide	RD 995/2000[b]	
Lindane	Insecticide	Decision no. 2455/2001/EC[a]	SEC (2004) 1372[c]
Propyzamide	Herbicide		
Diazinon	Insecticide		
Pirimicarb	Insecticide		
Pentachloroaniline	Metabolite of quintozene (fungicide)		
Metribuzin	Herbicide		SEC (2004) 1372[c]
Chlorpyriphos-methyl	Insecticide		
Alachlor	Herbicide	Decision no. 2455/2001/EC[a]	
Terbutryn	Herbicide		SEC (2004) 1372[c]
Fenitrothion	Insecticide		SEC (2004) 1372[c]
Ethofumesate	Herbicide		
Thiobencarb	Herbicide		
Metolachlor	Herbicide	RD 995/2000[b]	
Chlorpyriphos	Insecticide	Decision no. 2455/2001/EC[a]	
Chlorfenvinphos	Insecticide	Decision no. 2455/2001/EC[a]	SEC (2004) 1372[c]
Procymidone	Fungicide		SEC (2004) 1372[c]
Metidathion	Insecticide		
Endosulfan-sulfate	Metabolite of endosulfan[a] (insecticide)	Decision no. 2455/2001/EC[a]	
Methoxychlor	Insecticide		SEC (2004) 1372[c]
Tetradifon	Acaricide		
Azinphos-methyl	Insecticide		
Azinphos-ethyl	Insecticide		

[a] European priority list [6].
[b] Spanish legislation [7].
[c] Pesticides with evidence or potential endocrine disruption [3].