ANALYSIS OF HALOGENATED AND PRIORITY PESTICIDES AT DIFFERENT CONCENTRATION LEVELS. AUTOMATED SPE EXTRACTION FOLLOWED BY ISOTOPE DILUTION-GC/MS

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Introduction

Pesticides are pollutants of major concern in the aquatic environment due to their common use in agriculture and other applications. A great number of toxic and environmental persistent pesticides[1] including most from the European priority lists are halogenated compounds. In addition, many of these compounds are considered as suspected endocrine disrupting chemicals[2].

In the field of water policy, the old Directive 76/464/CEE[3] has been developed and replaced by the
Water Framework Directive (WFD, 2000/60/CE)[4], which has established a list of 33 priority substances (10 of which are pesticides)[5]. Moreover, in 2000 the Spanish Government fixed a quality objective of 1 µg/L for 4 halogenated pesticides (simazine, atrazine, terbutylazine and metolachlor)[6]. Related to the control of drinking water, the European Union established quality standards of 0.1 and 0.5 µg/L for individual and total pesticide concentration, respectively[7].

Liquid-liquid extraction (LLE) and solid phase extraction (SPE)[8,9] followed by GC/MS have been commonly applied to the analysis of pesticides in water samples. Isotope dilution-GC/MS has been reported as a robust method for the analysis of these compounds[10].

In this work, automatic SPE extraction of 16 pesticides and metabolites (see table 1) with the automated Power-Prep^{TM} system is evaluated at different concentration levels using polymeric (ENV+) and C_{18} sorbent phases. The method was optimised by comparing recoveries obtained using different eluting solvents. The optimised procedure was then applied to spiked water samples at concentration levels of 0.1 µg/L (quality standard for individual pesticides in drinking water) and 0.02 µg/L (close to the detection limit of most pesticides).

Analyses were carried out by GC/MS in SIM mode. Recoveries of pesticides were calculated using d_{10}-anthracene as recovery standard.

Materials and methods

Pesticide standards were purchased from Ehrenstorfer (Augsburg, Germany). The recovery standard d_{10}-anthracene was from Aldrich (Seelze, Germany). Styrene-divinylbenzene SPE (200mg, ENV+) cartridges were acquired from IST (Mid Glamorgan, UK), and C_{18} cartridges were from Fluid Management Systems inc. (FMS. Waltham, MA, USA).

Table 1. Pesticides and metabolites studied in this work

COMPOUND	**PRIORITY LISTS**	**COMPOUND**	**PRIORITY LISTS**
Isoproturon	**EPL.**	Lindane	**EPL., SED,**
Diuron	**EPL. HAL**	Alachlor	**EPL, HAL**
3,4-Dichloroaniline	**EPL., SED, HAL**	Metolachlor	**SQO, HAL**
Desethylatrazine	**EPL., SED, HAL**	Chlorpyriphos	**EPL., SDE,**
Trifluralin	**EPL., SED, HAL**	Chlorfenvinphos	**EPL, HAL**
Simazine	**EPL., SQO., SED,**	Endosulfan-sulphate	**EPL., SDE,**
Atrazine	**EPL., SQO., SED,**	Methoxychlor	**SDE, HAL**
Terbutylazine	**SQO, HAL**	Tetradifon	**HAL**

EPL: European Priority List **SQO: Spanish Quality Objective of 1 µg/L**
SDE: Suspected Endocrine Disrupting chemical **HAL: Halogenated compound**

The automated Solid Phase Extraction system evaluated was the Power-Prep/SPE extraction and clean-up system (FMS, Fluid Management Systems, inc., Waltham, MA, USA).

Firstly, automatic SPE extraction of pesticides was evaluated for ENV+ cartridges by comparing recoveries obtained with different eluting solvents (see table 2).

The optimised method was performed as follows: 50 ng or 10 ng of each pesticide (concentration levels of 0.1 µg/L or 0.02 µg/L) were added to 500 mL of mineral water (Font Vella) containing 1% of methanol. The SPE cartridge was conditionned with ethyl acetate, methanol, and Milli-Q water, and the solution of pesticides was extracted at a flow rate of 5 mL/min. The cartridge was cleaned with Milli-Q water, dried with a nitrogen stream for 18 min, and eluted with the procedure “**Elution 3**” (see table 2). After addition of isooctane, the extract was concentrated under a gentle nitrogen stream. Finally, 50 ng of the recovery standard d_{10}-anthracene were added.

The optimised procedure was applied to the analysis of spiked water samples at different concentration levels (0.1 and 0.02 µg/L) using ENV+ and C_{18} sorbent phases (4 experiments, 3 replicates for each experiment).

GC/MS analyses were carried out on integrated quadrupole MD-800 from ThermoFinnigan. Acquisition was performed in SIR mode, monitoring 2 ions for each compound, and using the sum of both for calculations.

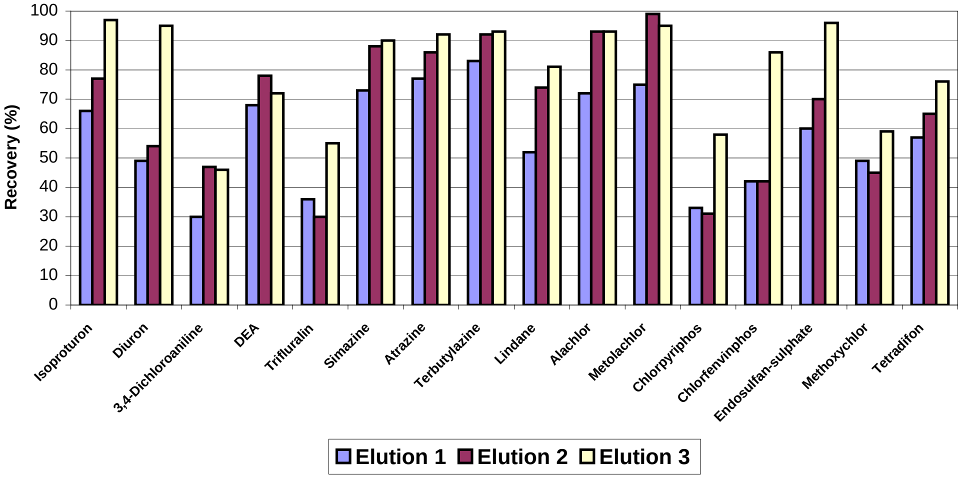
Table 2. Eluting solvents evaluated for the automatic SPE extraction of pesticides

ELUTION 1	ELUTION 2	ELUTION 3
- 5mL Acetone:Hexane (80:20) **- 5mL Acetone:Hexane (50:50)** **- 5mL Acetone:Hexane (20:80)**	**- 3mL Acetone** **- 5mL Ethyl acetate** **- 5mL Hexane**	**- 3mL Acetone:Ethyl acetate (80:20)** **- 5mL Ethyl acetate:Hexane (80:20)** **- 5mL Ethyl acetate:Hexane (50:50)** **- 5mL Ethyl acetate:Hexane (20:80)**

Results and discussion

Automatic SPE extraction of pesticides was optimised with regard to the eluting solvent (using ENV+ cartridges). Results are shown in figure 1. The highest recoveries were obtained when using elution 3, described in table 2.

Figure 1. Automatic SPE extraction of pesticides. Recoveries with different eluting solvents



The optimised method mentioned above (using elution 3) was applied to the analysis of spiked water samples. Results obtained for different concentration levels and sorbent phases are shown in table 3. Each spike recovery is an average ± standard deviation from using n=3 samples.

Table 3. Analysis of spiked water samples. Spike recoveries

PESTICIDES	**Conc. Level=100 ng/L**		**Conc. Level=20 ng/L**	
	ENV+	**C_{18}**	**ENV+**	**C_{18}**
Isoproturon	97±6	86±3	95±1	87±4
Diuron	95±7	74±4	82±2	80±3
3,4-Dichloroaniline	46±6	30±1	33±7	16±3
Desethylatrazine (DEA)	72±2	50±5	50±7	31±8
Trifluralin	55±4	53±2	61±5	65±4
Simazine	90±3	98±1	80±2	87±1
Atrazine	92±2	99±2	88±3	95±2
Terbutylazine	93±2	96±2	86±3	89±2
Lindane	81±3	84±4	71±3	78±4
Alachlor	93±3	96±4	81±3	85±2
Metolachlor	95±1	92±3	82±2	88±2
Chlorpyriphos	58±1	57±2	56±1	64±2
Chlorfenvinphos	86±5	105±5	70±3	92±2
Endosulfan-sulphate	96±1	92±3	86±2	89±8
Methoxychlor	59±4	68±4	64±4	64±2
Tetradifon	76±4	83±2	75±3	75±7

Figure 2 compares recoveries obtained at the concentration level of 100 ng/L when using ENV+ and C_{18} sorbent phases. Figure 3 shows results when spiked water samples at both concentration levels (100 ng/L and 20 ng/L) were extracted with ENV+ cartridges.

Figure 2. Automatic SPE extraction of spiked water samples at 100 ng/L. Comparison of ENV+ and C_{18} sorbent phases

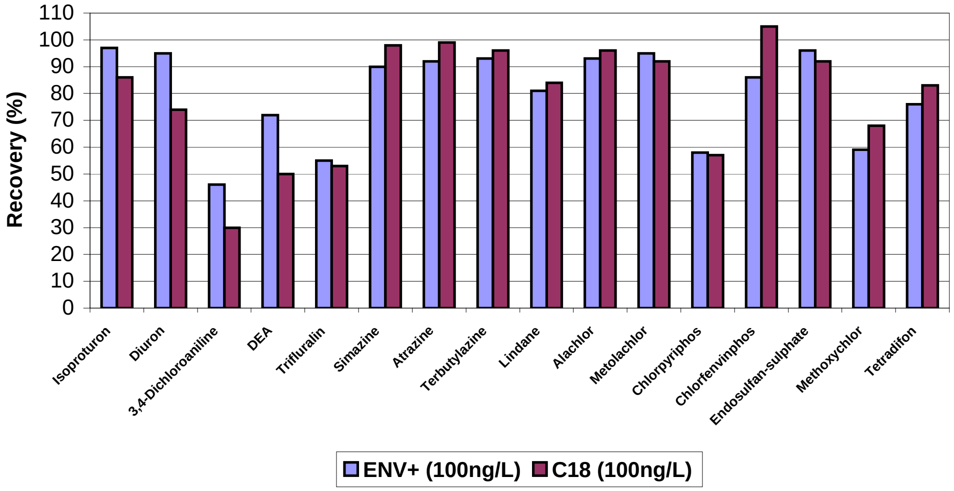
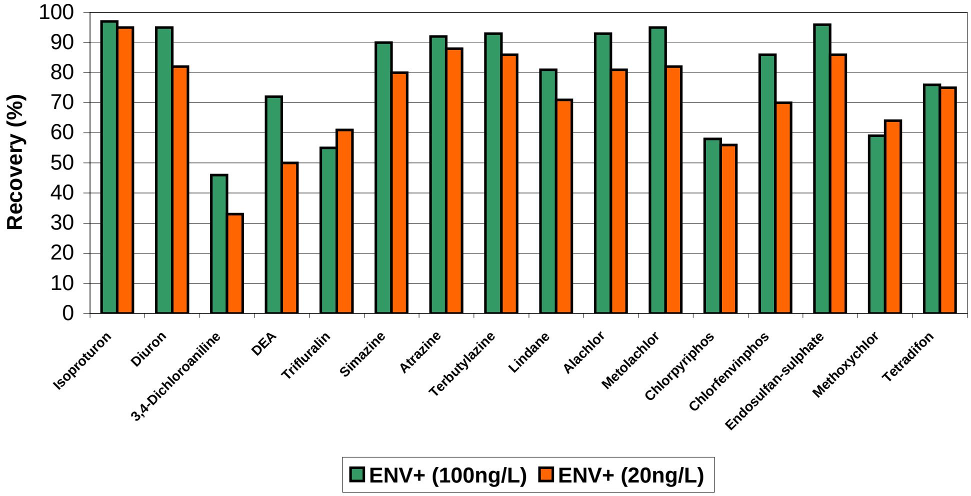


Figure 3. Automatic SPE extraction of spiked water samples at 100 ng/L and 20 ng/L using ENV+ cartridges



Recoveries obtained when using ENV+ and C_{18} sorbent phases (figure 2) were quite similar for most pesticides. In general, hydrophobic pesticides (i.e. chlorfenvinphos, methoxychlor, tetradifon) recovered better with C_{18} cartridges, while metabolites and polar pesticides (isoproturon, diuron, 3,4-dichloroaniline, DEA) showed higher recoveries when the polymeric (ENV+) sorbent phase were used.

On the other hand, recoveries of most pesticides were lower when low-spiked water samples (20 ng/L) were extracted (see figure 3). This fact can be explained by losses during the extraction process, which decrease recoveries when low amounts of pesticides are spiked.

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