AUTOMATED SOLID-PHASE EXTRACTION OF PRIORITY AND SUSPECTED ENDOCRINE DISRUPTING PESTICIDES AND METABOLITES. ANALYSIS BY ISOTOPE DILUTION-GC/MS

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Introduction

As a consequence of the amounts of pesticides used, their wide spectrum of applications and their physicochemical properties, these compounds have been found in all the compartments of environment, most of them in surface water samples. Although only 9 pesticides (aldrin, dieldrin, endrin, chlordane, heptachlor, DDT, DDE, mirex and toxaphene) are at present considered as Persistent Organic Pollutants (POPs)[1], many other pesticides and metabolites have been reported as persistent and toxic pollutants in the aquatic environment[2]. In addition, many af these compounds are considered as suspected endocrine disrupting chemicals[3,]

Corrective mesures and legislative prescriptions have been established to control the toxicity and environmental effects of pesticides in drinking and surface water. In 1976, the European Community published the Directive 76/464/EEC with the lists I and II containing respectively compounds and families to be controled[4]. Afterwards, 132 compounds (39 of which are pesticides) were proposed to be included in the list I[5]. Recently, a European Parlament and Council Decision established a list of 33 priority substances (10 of which are pesticides) in the field of water policy[6]. Moreover, in 2000 the Spanish Government fixed quality objectives for 4 pesticides (simazine, atrazine, terbutylazine and metolachlor)[7].

Many techniques have been applied to the extraction and analysis of pesticides in water samples, most of them related to liquid-liquid (LLE) or solid phase extraction (SPE)[8], and GC/MS. Isotope dilution-GC/MS has been reported as a robust method for the analysis of these compounds[9].

In this work, the automatic SPE extraction of 32 pesticides and metabolites with the automated Power-Prep™ system (see table 1) is evaluated for different conditions (type of sorbent, sample flow rate, % of methanol in the sample, and pump material). The optimized method was applied to the analysis of surface warter samples using d_5-atrazine and d_{10}-parathion as internal standards for isotope dilution-GC/MS analysis.

Materials and methods

Pesticide standards were purchased from Ehrenstorfer (Augsburg, Germany). The internal standards d_5-atrazine and d_{10}-parathion were respectively acquired from Ehrenstorfer and Cambridge Isotope Laboratories (Andover, MA, USA). The recovery standard d_{10}-anthracene was from Aldrich (Seelze, Germany).

Table 1. Pesticides and metabolites studied in this work

COMPOUND	European Priority list	Spanish Quality Objectives	Suspected Endocrine Disrupting Effects	Halogenated compounds
3,4-Dichloroaniline				
Desethylatrazine				
Trifluralin				
Simazine				
Atrazine				
Terbutylazine				
Lindane				
Metribuzin				
Alachlor				
Metolachlor				
Chlorpyrifos				
Dicofol				
Chlorfenvinfos				
Procymidone				
Endosulfan-sulphate				
Metoxychlor				
Molinate				
Dimethoate				
Propazine				
Propyzamide				
Diazinon				
Pirimicarb				
Pentachloroaniline				
Chlorpyrifos-methyl				
Terbutryn				
Fenitrothion				
Ethofumesate				
Methidathion				
Imazalil				
Tetradifon				
Azinfos-methyl				
Azinfos-ethyl				

Styrene-divinylbenzene SPE (200mg, ENV+) and sodium sulphate cartridges were from IST (Mid Glamorgan, UK). C_{18} cartridges were from Fluid Management Systems inc. (FMS. Waltham, MA, USA).

The automated Solid Phase Extration system evaluated was the Power-Prep/SPE extraction and clean-up system (FMS, Fluid Management Systems, inc., Waltham, MA, USA). Power-Prep is designed to automate the extraction and clean-up of the toxic compounds such as Pesticides, PAHs, PCBs and Dioxins from environmental, biological and food samples. The system can process up to 6 samples simultaneously. All the wetted parts and tubing made of teflon, as well as the FMS cartridges. In this work two differents pump head materials were studied with the system. The SSY pump material: stainless steel-stainless steel-carbon, and CTC pump material: ceramic-tefzel-ceramic for piston-cylinder case-cylinder liner, respectively. Figure 1 shows the plumbing diagram of the Power-Prep/SPE system.

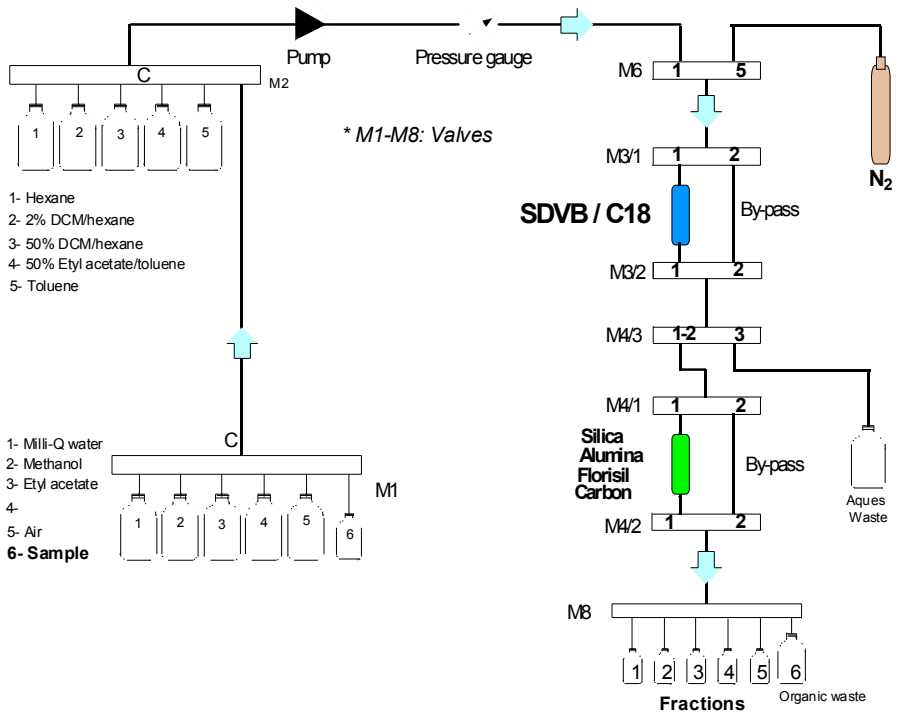

Figure 1. Plumbing diagram of the Power-Prep/SPE Extraction & Cleanup system.

The optimized method for the extraction of pesticides was performed as follows: 50ng of each pesticide were dissolved in 500mL 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 5mL/min. The cartridge was cleaned with Milli-Q water, dried with a nitrogen stream for 15min, and eluted with 20 mL of ethyl acetate. 10mL of isoctane were added to the extract, and it was concentrated under a gentle nitrogen stream. Finally, 50ng of the internal standards d_5-atrazine and d_{10}-parathion were added.

The developed analytical procedure was applied to the extraction of 12 real water samples. d_5-Atrazine and d_{10}-parathion were as internal standards and they were spiked into the samples before extraction. d_{10}-Anthracene was added to the final extract as recovery standard.

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

Results and discussion

Extraction of pesticides included in table 1 was studied with regard to the sorbent phase (styrene-divinylbenzene and C_{18}), the sample extraction flow rate (5 and 10mL/min), the % of methanol in the sample (0, 1 and 2%), and the pump material (SSY and CTC).

The highest recoveries were obtained for the styrene-divinylbenzene cartridge, with 1% of methanol at a flow rate of 5mL/min, and using a SSY pump. The results related to 16 priority and suspected endocrine disrupting pesticides are summarized in figure 2.

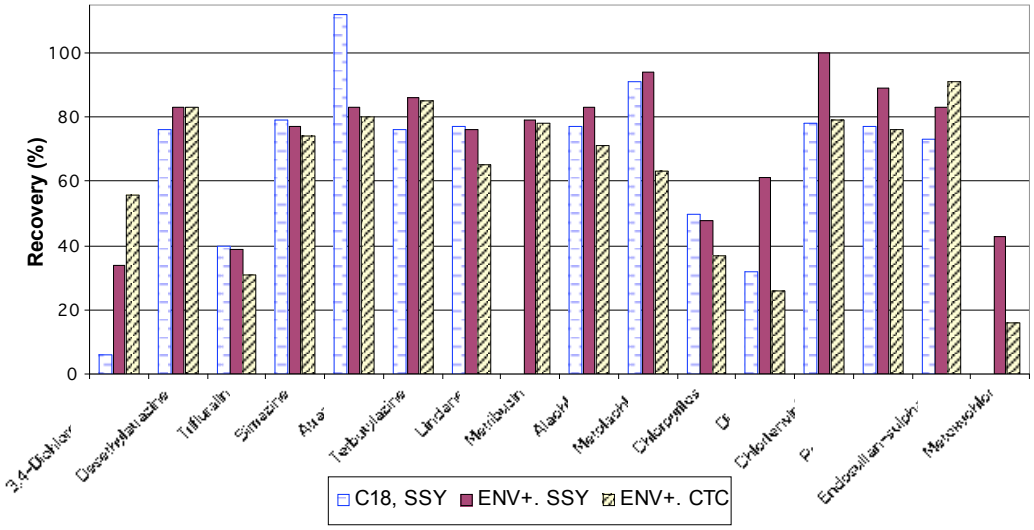

Figure 2. Automatic SPE extraction: Sorbent phase and Pump material.

For the 12 surface water samples extracted with the optimized procedure, the average recovery for the internal standards d_5-atrazine and d_{10}-parathion was 99%, with respective standard deviations of 10% and 11%.

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References
1.World Wildlife Fund. Persistent organic pollutants: Criteria and procedures for adding new substances to the global POPs treaty. Washington, 1999.
2. Royal Society of Chemistry. The agrochemicals handbook (2nd edn.). Cambridge, 1990.
3. European Parliament. Endocrine disrupting chemicals: A challenge for the EU?, March, 1998.
4. 76/464/EEC Council Directive (OJ L 129 of 18 May 1976).
5. List of substances proposed for inclusion in the list I from the Directive 76/464/EEC (OJ L 176 of 14 July 1982).
6. 2455/2001/CE European Parliament and Council Decision establishing the list of priority substances in the field of water policy. Brussels, 2001.
7. Real Decreto 995/2000 establishing quality objectives for specific pollutants. Madrid, 2000.
8. Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory. U.S. Geological Survey, Open-File Report 95-181 Denver, CO, 1995.
9. USEPA Method 1625 (1989) Semivolatile organic compounds by isotope dilution GC/MS.