



Development of a multiresidue method for analysis of pesticides in sediments based on isotope dilution and liquid chromatography-electrospray-tandem mass spectrometry



Marianne Köck-Schulmeyer^a, Mar Olmos^a, Miren López de Alda^{a,*}, Damià Barceló^{a,b}

^a Dept. Environmental Chemistry, IDAEA-CSIC, c/ Jordi Girona 18-26, 08034 Barcelona, Spain

^b Catalan Institute for Water Research (ICRA), Emili Grahit, 101, Edifici H2O, Parc Científic i Tecnològic de la, Universitat de Girona, 17003 Girona, Spain

ARTICLE INFO

Article history:

Received 14 March 2013

Received in revised form 1 July 2013

Accepted 9 July 2013

Available online 13 July 2013

Keywords:

Pesticides

Sediment

Analysis

Isotope dilution

LC-MS/MS

ABSTRACT

Because of the complexity of the sediment matrix, selective methods are necessary to identify and quantify different kinds of pesticides at a time. In this context, a multiresidue method based on isotope dilution and final analysis by liquid chromatography-electrospray-tandem mass spectrometry (LC-ESI-MS/MS) was developed for the determination of 26 pesticides and transformation products in sediment. The method developed comprises pressurized liquid extraction (PLE) and further purification of the extract by solid phase extraction (SPE) prior to analysis. In the process of method optimization various SPE cartridges as well as PLE and SPE elution solvents were evaluated. Due to the relatively high volatility of some compounds (e.g., propanil), special attention was paid to the evaporation step. Experiments comparing different pressures and times during solvent evaporation were performed with the aim to improve the recovery of these compounds. Matrix effects were also studied even though they were corrected through the use of 23 deuterated compounds as surrogate standards for quantification. The analytical method developed showed good validation parameters in terms of linearity, sensitivity (limits of detection in the pg g^{-1} or low ng g^{-1} range and limits of determination below 80 ng g^{-1}), accuracy (relative recoveries between 92 and 118%, except for malaoxon (66.5%)), and repeatability (relative standard deviations between 1.5 and 17%, for all compounds except the acidic herbicides). Its main advantage is the simultaneous analysis of pesticides with a large variety of physical-chemical properties, as well as its improved accuracy due to the use of the isotope dilution method. Application of the method to the analysis of 5 real samples from 4 different Spanish rivers revealed the presence of 5 of the 26 target compounds, being chlorpyrifos, diuron and diazinon the most ubiquitous, as expected, due to their high bioaccumulation and low mobility features.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Monitoring of the chemical status of rivers in terms of pesticides pollution has been based in most instances on their analysis in the aqueous compartment. However, sediments are also important and should be included in environmental studies in order to have a more comprehensive picture about the quality status of the rivers since they are the result of the integration of all processes (biological, physical and chemical) that occur in an aquatic ecosystem [1]. In addition, river sediments are unique at providing historical contamination information [2] and identifying pollution episodes [3].

In 2000 the Water Framework Directive (WFD) approved by the European Commission (EC) with the objective to establish a common framework for Community action in the field of water policy [4] addressed for the first time the issue of sediments though no specific environmental quality standards (EQS) were proposed. Four years later, the Working Group on Analysis and Monitoring of Priority Substances (AMPS) considered the technical implications of sediment monitoring and gave technical expert advice to the EC on analysis and monitoring aspects, including the suggestion to monitor some WFD priority substances like alachlor, isoproturon, chlorpyrifos, and chlorfenvinphos in sediment samples [5]. Later on, in 2008 the EC approved the Directive 2008/105/EC that established that Member States should, inter alia, monitor sediment (and biota), as appropriate, at an adequate frequency to provide sufficient data for a reliable long-term trend analysis of those priority substances that tend to accumulate in sediment (and/or biota), and the results of this monitoring should be made available in order

* Corresponding author. Tel.: +34 93 400 6100; fax: +34 93 204 5904.
E-mail address: miaqam@cid.csic.es (M. López de Alda).

Table 1
Review of the last 10 years studies analyzing pesticides in sediments and/or soils.

Reference	Year	Analytes	In common ^a	Matrix	Amount (g) ^b	Extraction	Clean-up	Detection	Limits (ng g ⁻¹)
Henriksen et al.	2002	[15] 1 pesticide + 4 metab	None	Soil	30	PLE (ASE)	Filtration (0.45 mm nylon)	LC–MS/MS	LOD: 1.25–12.5
Dagnac et al.	2005	[16] 12 pesticides	9	Soil	15 (<2 mm)	PLE	None	LC–MS and GC–MS/MS	LOQ: 0.5–5
Ibañez et al.	2005	[17] 3 pesticides	None	Soil	5	Shake and cent ^f	Filtration (0.45 mm nylon)	LC(ESI)–MS/MS	LOD: 5
Fuentes et al.	2007	[18] 6 organophosphates	2	Soil	20 (<2 mm)	MAEP	None	GC–FPD and GC–MS/MS	LOD: 4–12
Shen et al.	2007	[19] 5 pesticides	1	Soil	10	MMSPD	None	GC–NPD	LOD: 0.2–2.0
Bermúdez-Couso et al.	2007	[14] 6 fungicides	None	Sed	10 mL	SLE+US	None	GC–MS	LOD: 1–3; LOQ: 4–6
Ghanem et al.	2008	[20] 5 pesticides	4	Sludge	25	Shake	SPE (Florisil)	LC(ESI)–MS/MS	LOD: 0.3–1.5
Hladiz et al.	2008	[21] 1 pesticide + 3 metab	None	Soil/sed	10	USE + filtration	SPE (Oasis HLB 200 g)	GC–MS	LOD: 1–5
Villaverde et al.	2008	[3] 28 pesticides	9	Sed	1 (<100 mm)	PLE (ASE) ^c	None	GC–MS	LOD: <0.04 mg L ⁻¹
Xue et al.	2008	[22] 18 pesticides	3	Sed	20 (wet)	USE	SPE (Oasis HLB 500 mg)	GC–ECD and MS	LOD: 0.00005–0.0015
Lesueur et al.	2008	[23] 24 pesticides	9	Soil	5	PLE (ASE) ^d	filtration (0.45 mm)	GC–MS and LC–MS/MS	LOQ: 0.08–292
Baugros et al.	2009	[24] 12 pesticides	1	Sludge	1.5	PLE (ASE)	SPE (sílica)	LC(ESI)–MS/MS	LOD: 5.2–634
García-Valcarcel et al.	2009	[25] 10 pesticides	2	Sludge	2	USE	DSPE (Bondesil-PSA)	LC(ESI)–MS/MS	LOD: 0.3–4.2
Hutta et al.	2009	[26] 11 pesticides	4	Soil	2.5	USE	ultrafiltration	LVI–HPLC–UV	LOD: 5–6
Hildebrandt et al.	2009	[27] 22 organochlorines, 16PAHs	None	Soil	1 (<120 mm)	PLE (ASE)	None	GC–MS	LOD: 0.19–7.38
Rosales-Conrado et al.	2009	[28] 1 insecticide	None	Soil	10 (<2 mm)	Shake+USE	None	LC(ESI)–MS/MS	LOD: 15–18; LOQ: 50–60
Drozdowski et al.	2009	[29] 4 insecticides	None	Soil	5	QuEchERS	dSPE (cartridges PSA & C18)	UPLC–MS/MS	LOD: 1.8–2.7; LOQ: 6–9
Navarro-Ortega et al.	2010	[30] 69 pollutants (polar pest, PAHs, PPs)	14	Sed	1 (<120 mm)	PLE (ASE)	None	GC–MS	LOD: 0.03–56.33
Ricart et al.	2010	[31] 22 pesticides	22	Sed	5 (<0.125 mm)	PLE (ASE)	SPE (Carbograph)	LC–MS/MS	LOD: 0.02–6.70
Gómez et al.	2011	[2] 19 organochlorine	None	Sed	2 (<63 mm)	MAE	SPE (EPA 3620B)	GC–ECD	LOD: 0.02–0.21; LOQ: 0.11–0.38
Abraham et al.	2011	[32] 44 pesticides (OC, PAHs, PCBs, DDT)	6	Sed	NR ^e	SLE	GPC (EPA 3640)	GC–MS	LOQ: 5
Lazartigues et al.	2011	[33] 13 pesticides	1	Soil/sed	4	SLE	None	LC–MS/MS	LOQ: 0.1–57.7
Wasswa et al.	2011	[34] 16 organochlorines	None	Sed	200	Solid dispersion method	GPC	GC–ECD and GC–MS	LOD: 0.0014–0.0082
Brondi et al.	2011	[1] 3 pesticides	1	Sed	10	QuEchERS	dSPE	GC–MS (SIM)	LOD: 3–20; LOQ: 10–50
Sánchez-Ávila et al.	2011	[35] 53 org. micropollutants	None	Sed	1 (<120 mm)	USE	SPE	GC(EI)–MS/MS	LOD: 1–150
Kvicalova et al.	2012	[36] 9 pesticides	None	Sed	4 (<1 mm)	QuEchERS	None	LC–MS/MS	LOD: 0.1–2; LOQ: 1–6
Van Ael et al.	2012	[37] 58 org. pollutants	None	Sed	3	soxhlet	SPE (8 g sílica)	GC–MS	LOQ: 1–4
Liu et al.	2012	[38] 21 organochlorines	None	Sed	10	USE	SPE (sílica)	GC–MS	LOD: 0.2–100 pg g ⁻¹
Nomen et al.	2012	[39] 10 OC/organophosphates	None	Sed/soil	10	Shake-flask	dSPE (20 g gel sephadex)	GC–ECD and FPD	LOQ: 18–46.6
Hellar-Kihampa et al.	2013	[40] 18 pesticides	None	Sed	2	Soxhlet	Silica	GC–ECD	LOQ: 0.1
Quinete et al.	2013	[41] 3 pesticides	None	Sed/soil	20	QuEchERS	C18	LC(APCI)–MS/MS	LOD: 1–16
Toan et al.	2013	[42] 13 pesticides	1	Sed	20 (<2 mm)	SLE (Shake) and LLE	SPE (C18)	GC–MS	NR ^e
Yang et al.	2013	[43] 10 organochlorines	None	Sed	10	Soxhlet	Alumina/silica	GC–ECD	NR ^e
Zhao et al.	2013	[44] 21 organochlorines	None	Soil	10	PLE (ASE)	Alumina/silica	GC–ECD	LOD: 0.01–1.07

dSPE, dispersive solid phase extraction; EPA, Environmental Protection Agency; GC, gas chromatography; GPC, gel permeation chromatography; LC, liquid chromatography; LOD, limit of detection; LOQ, limit of quantification; LVI, large volume injection; MAE, microwave assisted extraction; MAEP, microwave assisted extraction and partitioning; MMSPD, modified matrix solid-phase dispersion; OC, organochlorine compound; PAHs, polycyclic aromatic hydrocarbons; PCBs, polychlorinated biphenyls; PLE, pressurized liquid extraction; PPs, polar pesticides; PSA, primary secondary amine; QuEchERS, Quick Easy Cheap Effective Rugged and Safe; sed, sediment; SLE, solid-liquid extraction; SPE, solid phase extraction; USE, ultrasonic solvent extraction.

^a Number of pesticides in common with this work.

^b Sieving pore size between parenthesis.

^c Soxhlet and USE were also tested

^d USE, Shake-flask and QuEchERS were also tested.

^e NR, not reported.

^f Centrifugation.

Download English Version:

<https://daneshyari.com/en/article/7614209>

Download Persian Version:

<https://daneshyari.com/article/7614209>

[Daneshyari.com](https://daneshyari.com)