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Assessment of two extraction methods to determine pesticides in soils, sediments and sludges. Application to the Túria River Basin

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ABSTRACT

Pressurized liquid extraction (PLE) and Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) extraction methods were optimized for the simultaneous determination of 50 pesticides in sediment, soils and sewage sludge. For QuEChERS development, several buffers and dispersive solid-phase extraction clean-up (dSPE) sorbents were tested. In the PLE method, several parameters affecting the extraction efficiency, such as organic solvent, amount of sample, cell size, temperature, pressure, static time, number of cycles and % of flush, as well as sorbent used for the on-line clean up, were also evaluated. PLE and QuEChERS were assessed and compared in obtained recoveries (33–89% versus 25–120%), number of pesticides for which recoveries are in the range of 80–100% (up to 13 versus up to 35) and cost of the approach. QuEChERS procedure was faster, cheaper and easier to perform. Recoveries were around 80% (at 50 ng g^{-1} d.w.) and the matrix effect was less than −20% using matrix-matched standard calibration curve for most of the analytes. The limits of quantification were between 0.1 and 10 ng g^{-1} (d.w.) except for alachlor and acetochlor. Repeatability and reproducibility were lower than 28% (%RSD, $n = 5$). Soil, sediment and sludge samples, taken from the Túria River Basin, were analyzed by QuEChERS to determine pesticides. Chlorpyrifos (up to 65.3 ng g^{-1} d.w.) was the most frequent and at higher concentrations. Thiabendazole, imazalil, diazinon, pyriproxyfen, hexythiazox, carbofuran, isoproturon, terbuthylazine and terbumeton were also found in some samples.

1. Introduction

Pesticides include a large group of organic compounds belonging to different chemical families, which play an important role in increasing agricultural productivity [1]. However, they are environmental hazards due to their stability, persistence and toxicity and they pose a tremendous danger to wildlife [2,3]. Monitoring programs have focused mainly on their analysis in the aqueous compartment. The information available on their determination and occurrence in sediments, soil or sludges – these last coming from the waste water treatment plants (WWTPs) [4,5] are focused, predominantly, on organochlorine pesticides [1,3,6–11] that were banned more than 30 years ago. These matrices are reservoirs of pollution and should be included in the environmental studies in order to have a more comprehensive picture about the environmental quality status [5]. The low number of publications reporting currently pesticides in sediments, soil or sludges is influenced by the historical lack of Environmental Quality Standards (EQS) for organic pollutants in these matrices [5].

Only the Directive 2008/105/EC [12] established that Member states should monitor sediment and introduce EQS of those priority substances that tend to accumulate in them. However, the last proposals are still pending of approval and currently EQS for pesticides in sediments, soil or sludges are not included in any directive [5], even though the need to do it is recognized by the EU [12].

Sample preparation still remains a critical step, due to the strong interactions between the analytes and the different constituents of these matrices, particularly, the organic matter [13,14]. Traditionally, time and solvent consuming techniques, such as Soxhlet extraction were used to the analysis of pesticides in sediments. With current trends toward miniaturization of sample preparation, Soxhlet was replaced by more environmental friendly procedures that are in agreement with modern green chemistry and analytical principles. Table 1 reviews the most representative extraction procedures used in the last 5 years (2010–2014) for the analysis of pesticides (except organochlorine) in sediments, soils and sludges.

Currently-used technologies are based on new sources of energy, being PLE [5,20,21,25,27,30,33] and UAE [2,22,24,28,29,34]

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Table 1
Extraction procedures used in the last five years (2010–2014) for the analysis of pesticides (except organochlorines) in sediment, soil and sludge.

Extraction procedure	Description	Determination	Recovery (%)	Sensitivity ($\mu g\,kg^{-1}$ dw)	Ref
MAE[a]	3 g dry sediment + 8 g Na_2SO_4 + 25 mL of ACE[b]-hexane (1:1) at 100 psi, 1600 W and 60 °C for 10 min	LC–MS/MS	67–123	LOD 0.003–0.024 LOQ 0.009–0.072	[15]
QuEChERS	1 g sediment + 10 mL AcN[c] + 6 g $MgSO_4$, 1.5 g NaCl, 1.5 g (Na_3Cit)[d] + 0.75 g (Na_2HCit sequ)[e]. Then, d-SPE of 1 mL with 50 mg PSA[f], 150 mg $MgSO_4$ and 50 mg C_{18}	LC–MS/MS	40–105	LOD 0.03–1.67 LOQ 0.10–5.00	[16]
QuEChERS	2 g sediment + 10 mL AcN + Acetate buffer (1.5 g NaOAc[g], 6 g $MgSO_4$ (pH = 4.8). Then, d-SPE of 1 mL with PSA/GCB[h] (900 mg $MgSO_4$, 150 mg PSA, 15 mg GCB)	LC–MS/MS	40–98	LOQ 0.5–20	[17]
UAE/SBSE (clean-up)	10 g sediments + 10 mL UAE[i] for 30 min at 35 kHz, 60% of intensity and 80 °C. Then, addition of 85 mL H_2O *SBSE*[j] with a PDMS[k] stir bar for 16 h at 300 rpm and desorption with 2 mL n-hexane:ACE (9:1) for 30 min at 200 rpm	GC–MS	70–111	LOD 0.3–4.4* LOQ 0.8–14 *	[18]
PLE[l]/SPE[m] (purification)	5 g sediment + 6 g alumina/sand, extracted with ACE:DCM, (1:1) with HCOOH[n] 1% at 100 °C and 100 bar in 2 cycles of 5 min. Then, the extract are solvent exchanged to MeOH[ñ]:H_2O, and cleaned up through SPE with Oasis HLB. The analytes are eluted again with MeOH:DCM (1:1)	LC–MS/MS	92–118	LOD 0.02–16.98 Ldet 0.13–76.60 LOD 2.3–17	[19]
PLE	5 g sediment + sand, extracted with: (a) 3% ACE in hexane, (b) 0.02% TFA in ACE, (c) MeOH at 100 °C and 100 bar in 3 cycles of 5 min	GC–MS	–	–	[20]
PLE/QuEChERS (clean-up)	4–6 g sediments + 250 mg diatomaceous earth, extracted with EtAc: ACE (70:30) at 80 °C. The extract is evaporated to dryness and dissolved in H_2O + 5 mL AcN + 1.6 g $MgSO_4$ + 0.4 g NH_4Cl	LC-ESI-HRMS/MS LC-ESI-APCI/MS	57–139	LOD 0.010–4 LOQ 0.030–14	[21]
Triple ultrason-ication	2 g sediments + 3 × 8 mL ACE sonication for 20 min	GC–MS	70–114	LOD 50–100 LOQ 300–500	[22]
QuEChERS	4 g sediments + 10 mL acetonitrile + 2 g NaCl + 2 g $MgSO_4$ for 10 min	LC–MS/MS	<1–159	LOD 0.1–2 LOQ 1–6	[5]
Luke	4 g sediments + 10 mL ACE:Hexane: DCM (1:1:1) + 15 g Na_2SO_4 for 1 h	LC–MS/MS	<1–116	LOD 0.1–2 LOQ 1–6	[5]
Method using basic conditions	4 g sediment + 10 mL AcN:H_2O:25% NH_4+ (80:20:1) for 1 h	LC–MS/MS	<1–102	LOD 0.1–2 LOQ 1–6	[5]
Single solid–liquid extraction	4 g sediments + 10 mL AcN/H_2O (50:50) + 4 g $MgSO_4$ for 10 min. Acetonitrile extract was cleaned up with Et.Acet/AcN and then with Et. Act./cyclohexane	LC–MS/MS	35–125	LOQ 0.1–49.0 $ng\,g^{-1}$	[23]
UAE/heated-copper (clean-up)	5 g sediments + 20 mL ACE/methylene chloride (1:1, v/v) + 5 g Na_2SO_4 at 50–60 Hz for 15 min. Then, 12 g cooper incubation at 60 °C, evaporation and reconstitution in 6 mL MTBE and pass through Florisil cartridge (pre-washed with 6 mL MTBE[o])	GC-ECD	94–120	LOD 0.22–3.72 $\mu g\,kg^{-1}$	[24]
PLE/SBSE	10.0 g sediment at 80 °C, 1000 psi for 3 cycles of 10 min with 15 mL of methanol. *SBSE with* 10 mL of the methanolic extract +200 mL H_2O + 60 g NaCl for 12 h	TD-GC–MS/MS	63–119	LOD 0.001–0.3 LOQ 0.002–0.99	[25]
SFE[p]/DLLME[q]	1.2 g sediment extracted with CO_2 flow-rate of 0.5mL min^{-1} for 10 min (static) and 30 min (dynamic) at 150 bar and 60 °C, pesticides collected 1 mL ACN *DLLME*: 7.0 μL Cl_4C	GC-FID	44.4–95.4	LOD 1–9	[26]
QuEChERS	10 g sediment + 10 mL ACN + 4 g $MgSO_4$ + 1 g NaCl. Then. d-SPE: 330 mg PSA + 330 mg C18 + 1 cm layer $MgSO_4$	GC–MS	48–115	LOD 3–20 LOQ 10–50	[27]
LDMHLLE[r]	Amount of sample: 5.0 g of homogenized sed. Extraction solvent: 0.5 mL n-hexane (solvent of lower density than water Time: 30 min	GC–MS	–	LOD 0.13–0.26	[28]
UAME[s]/SPE	20 g sediment + 100 mL hexane/ACE (1:1) at 100 W of microwave and 50 W ultrasounds for 3.6 and 9 min, respectively. Extract passed through a *PSA/GCB SPE* and pesticide eluted with 7 m L DCM:hexane (3:7)	GC–MS	65.2–141	LOD 0.31–0.70	[29]
PLE/SPE (clean-up)	5 g sed + 10 g Na_2SO_4, + 10 g sand extracted with DCM/ACE (1:1) at 100 °C and 2000 psi for 2 cycles of 5 min. Extract passed through a *PSA/GCB SPE* and pesticide eluted with 7 mL DCM:hexane (3:7)	GC–MS	65.7–118.8	LOD 0.68–1.43	[30]