ELECTRONIC SUPPLEMENTARY MATERIAL to the paper entitled:

Evaluation of soil contamination in intensive agricultural areas by pesticides and organic pollutants: south-eastern Spain as case of study

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This document provides more detailed information to the main paper mentioned above. The following information is included:

Content		Page
Table S1	Selected compounds evaluated in this survey and limits of quantification	2
Table S2	Summary of the analytical methods applied for the analysis of residues and contaminants	4
Figure S1	Ratios observed for the main endosulfan transformation products (TPs) in the studied agricultural soils	5
Figure S2	Contamination pattern of residues and contaminants studied in the different municipalities: (a) Adra; (b) El Ejido; (c) Roquetas de Mar; (d) La Mojonera; (e) Vicar	6
	Apparatus, instruments, solvents and reference standard	7
	Quality control (IQC)	9

Table S1 Selected compounds evaluated in this survey and limits of quantification (LOQs)

Compound	Description	Listed in	LOQ	Compound	Description	Listed in	LOQ	Compound	Descripti	Listed in	LOQ
Pesticides				Metazachlor	HB		3 μg kg^{-1}	PCB 77	IP	POPs	2 μg kg^{-1}
2-Phenylphenol	FUNG		3 μg kg^{-1}	Metobromuron	HB		3 μg kg^{-1}	PCB 81	IP	POPs	2 μg kg^{-1}
Alachlor	HB		3 μg kg^{-1}	Metolachlor	HB		3 μg kg^{-1}	PCB 101	IP	POPs, EPA	2 μg kg^{-1}
Aldrin	INS	EPA[a], POPs[b]	3 μg kg^{-1}	Metoxuron	HB		3 μg kg^{-1}	PCB 105	IP	POPs	2 μg kg^{-1}
Atrazine	HB		3 μg kg^{-1}	Metribucin	HB		3 μg kg^{-1}	PCB 114	IP	POPs	2 μg kg^{-1}
Atrazine desethyl	TP		3 μg kg^{-1}	Mirex	INS	POPs	3 μg kg^{-1}	PCB 118	IP	POPs	2 μg kg^{-1}
Atrazine desisopropyl	TP		3 μg kg^{-1}	Monolinuron	HB		3 μg kg^{-1}	PCB 121	IP	POPs	2 μg kg^{-1}
Azinphos ethyl	INS/ACA		3 μg kg^{-1}	Norflurazon	HB		3 μg kg^{-1}	PCB 123	IP	POPs	2 μg kg^{-1}
Bifenthrin	INS/ACA		3 μg kg^{-1}	*o,p*-DDD	TP		3 μg kg^{-1}	PCB 126	IP	POPs	2 μg kg^{-1}
Bromophos ethyl	INS		3 μg kg^{-1}	*o,p*-DDT	INS	POPs	3 μg kg^{-1}	PCB 128	IP	POPs	2 μg kg^{-1}
Bromophos methyl	INS		3 μg kg^{-1}	Oxadixil	FUNG		3 μg kg^{-1}	PCB136	IP	POPs	2 μg kg^{-1}
Bromopropilate	ACA		3 μg kg^{-1}	*p,p'*-DDD	TP	EPA	3 μg kg^{-1}	PCB137	IP	POPs	2 μg kg^{-1}
Bupirimate	FUNG		3 μg kg^{-1}	*p,p'*-DDE	TP	EPA	3 μg kg^{-1}	PCB 138	IP	POPs, EPA	2 μg kg^{-1}
Carbophenothion	INS/ACA		3 μg kg^{-1}	Parathion ethyl	INS/ACA		3 μg kg^{-1}	PCB 143	IP	POPs	2 μg kg^{-1}
Clodinafop propargyl	HB		3 μg kg^{-1}	Parathion methyl	INS/ACA		3 μg kg^{-1}	PCB 153	IP	POPs, EPA	2 μg kg^{-1}
Chloridazone	HB		3 μg kg^{-1}	Penconazole	FUNG		3 μg kg^{-1}	PCB 156	IP	POPs	2 μg kg^{-1}
Chlormephos	INS		3 μg kg^{-1}	Pendimethalin	HB		3 μg kg^{-1}	PCB 157	IP	POPs	2 μg kg^{-1}
Chloropropylate	ACA		3 μg kg^{-1}	Pentachlorobenzene	FUNG	POPs	3 μg kg^{-1}	PCB 167	IP	POPs	2 μg kg^{-1}
Chlorphenson	INS		3 μg kg^{-1}	Phentoate	INS/ACA		3 μg kg^{-1}	PCB 169	IP	POPs	2 μg kg^{-1}
Chlorphenvinphos	INS/ACA		3 μg kg^{-1}	Pyridaben	INS/ACA		3 μg kg^{-1}	PCB 170	IP	POPs	2 μg kg^{-1}
Chlorpyriphos methyl	INS/ACA		3 μg kg^{-1}	Pirifenox	FUNG		3 μg kg^{-1}	PCB 180	IP	POPs, EPA	2 μg kg^{-1}
Chlortal dimethyl	HB		3 μg kg^{-1}	Pirimicarb	INS		3 μg kg^{-1}	PCB 185	IP	POPs	2 μg kg^{-1}
Chlortion	INS		3 μg kg^{-1}	Pirimiphos ethyl	INS		3 μg kg^{-1}	PCB 189	IP	POPs	2 μg kg^{-1}
Chlortoluron	HB		3 μg kg^{-1}	Pirimiphos methyl	INS/ACA		3 μg kg^{-1}	PCB 194	IP	POPs	2 μg kg^{-1}
Cyanophenphos	INS		3 μg kg^{-1}	Piriproxifen	INS		3 μg kg^{-1}	PCB 206	IP	POPs	2 μg kg^{-1}
Cyproconazole	FUNG		3 μg kg^{-1}	Procymidone	FUNG		3 μg kg^{-1}	PCB 209	IP	POPs	2 μg kg^{-1}
Diazinon	INS/ACA		3 μg kg^{-1}	Propachlor	HB		3 μg kg^{-1}	***PAHs***			
Dichlobenil	HB		3 μg kg^{-1}	Propazine	HB		3 μg kg^{-1}	Acenaphthene	UB	EPA	2 μg kg^{-1}
Dichloran	FUNG		3 μg kg^{-1}	Propiconazole	FUNG		3 μg kg^{-1}	Acenaphthylene	UB	EPA	2 μg kg^{-1}
Dieldrin	INS	EPA, POPs	3 μg kg^{-1}	Propizamide	HB		3 μg kg^{-1}	Anthracene	UB	EPA	2 μg kg^{-1}
Diethofencarb	FUNG		3 μg kg^{-1}	Prometrine	HB		3 μg kg^{-1}	Benz[*a*]anthracene	UB	EPA, REACH[c]	2 μg kg^{-1}
Difeconazole	FUNG		3 μg kg^{-1}	Propoxur	INS		3 μg kg^{-1}	Benzo[*a*]pyrene	UB	REACH	2 μg kg^{-1}
Dimetomorph	FUNG		3 μg kg^{-1}	Pyrazophos	FUNG		3 μg kg^{-1}	Benzo[*b*]fluoranthene	UB	EPA, REACH	2 μg kg^{-1}
Diniconazole	FUNG		3 μg kg^{-1}	Quinalphos	INS/ACA		3 μg kg^{-1}	Benzo[*k*]fluoranthene	UB	REACH	2 μg kg^{-1}
Diuron	HB		3 μg kg^{-1}	Quinoxyfen	FUNG		3 μg kg^{-1}	Benzo[*ghi*]perylene	UB		2 μg kg^{-1}
Endosulfan α	INS	EPA	3 μg kg^{-1}	Quintocene	FUNG		3 μg kg^{-1}	Benzo[*j*]fluoranthene	UB	REACH	2 μg kg^{-1}
Endosulfan β	TP	EPA	3 μg kg^{-1}	S421	INS		3 μg kg^{-1}	2-Bromonaphthylene	UB		2 μg kg^{-1}
Endosulfan eter	TP[a]		3 μg kg^{-1}	Sebutylazine	HB		3 μg kg^{-1}	Chrysene	UB	EPA, REACH	2 μg kg^{-1}

Endosulfan suphate	TP	EPA	3 μg kg^{-1}	Silafluofen	INS		3 μg kg^{-1}	Cyclopenta[*cd*]pyrene	UB		2 μg kg^{-1}
EPN	INS/ACA		3 μg kg^{-1}	Simazine	HB		3 μg kg^{-1}	Dibenzo[*a,e*]pyrene	UB		2 μg kg^{-1}
Ethion	INS/ACA		3 μg kg^{-1}	Sulfotep	INS/ACA		3 μg kg^{-1}	Dibenzo[*a,h*]anthracene	UB	EPA, REACH	3 μg kg^{-1}
Etofumesate	HB		3 μg kg^{-1}	Tau fluvalinate	INS/ACA		3 μg kg^{-1}	Dibenzo[*a,h*]pyrene	UB		3 μg kg^{-1}
Etoprophos	INS /NM		3 μg kg^{-1}	Tebufenpirad	ACA		3 μg kg^{-1}	Dibenzo[*a,i*]pyrene	UB		3 μg kg^{-1}
Etrimphos	INS		3 μg kg^{-1}	Tebutam	HB		3 μg kg^{-1}	Dibenzo[*a,l*]pyrene	UB		3 μg kg^{-1}
Fenamiphos	NM		3 μg kg^{-1}	Tecnacene	FUNG		3 μg kg^{-1}	Fluoranthene	UB	EPA	3 μg kg^{-1}
Fenitrothion	INS		3 μg kg^{-1}	Terbumetrone	HB		3 μg kg^{-1}	Fluorene	UB	EPA	3 μg kg^{-1}
Fenoxaprop-P-ethyl			3 μg kg^{-1}	Terbuthrin	HB		3 μg kg^{-1}	Indeno[1,2,3-*cd*]pyrene	UB	EPA	3 μg kg^{-1}
Fenpropathrin	INS/ACA		3 μg kg^{-1}	Terbutylazine	HB		3 μg kg^{-1}	5-Methylchrysene	UB		3 μg kg^{-1}
Feranimol	FUNG		3 μg kg^{-1}	Terbutylazine desethyl	TP		3 μg kg^{-1}	Naphthalene	UB	EPA	3 μg kg^{-1}
Fipronil	INS		3 μg kg^{-1}	Tepraloxidim	HB		10 μg kg^{-1}	Phenanthrene	UB	EPA	3 μg kg^{-1}
Flucythrinate	INS		3 μg kg^{-1}	Tetraconazole	FUNG		3 μg kg^{-1}	Pyrene	UB	EPA	3 μg kg^{-1}
Fluchlorhidrone	HB		3 μg kg^{-1}	Tetradiphon	ACA		3 μg kg^{-1}	***Phenolic compounds***			
Fludioxonil	FUNG		3 μg kg^{-1}	Tetramethrin	INS		3 μg kg^{-1}	2,4,5-Trichlorophenol	IP/TP		10 μg kg^{-1}
Fonofos	INS		3 μg kg^{-1}	Tiazopir	HB		3 μg kg^{-1}	2,4,6-Trichlorophenol	IP/TP	EPA	10 μg kg^{-1}
Heptachlor	INS	EPA, POPs	3 μg kg^{-1}	Tolcophos methyl	FUNG		3 μg kg^{-1}	2,4-Dimethylphenol	IP/TP	EPA	10 μg kg^{-1}
Hexachlorbencene	FUNG	EPA, POPs	3 μg kg^{-1}	Transfluthrin	INS		3 μg kg^{-1}	4-Chloro-3-methylphenol	IP/TP		50 μg kg^{-1}
Imidacloprid	INS		3 μg kg^{-1}	Triadimephon	FUNG		3 μg kg^{-1}	2,4-Dichlorophenol	IP/TP	EPA	10 μg kg^{-1}
Isophenphos	INS		3 μg kg^{-1}	Vinclozolin	FUNG	REACH	3 μg kg^{-1}	2-Chlorophenol	IP/TP	EPA	5 μg kg^{-1}
Isoproturon	HB		10 μg kg^{-1}	***PCBs***				4-Chlorophenol	IP/TP		5 μg kg^{-1}
Kresosin methyl	FUNG		3 μg kg^{-1}	PCB 5	IP	POPs	2 μg kg^{-1}	2-Nitrophenol	IP/TP	EPA	50 μg kg^{-1}
α-Lindane	INS	EPA, POPs	3 μg kg^{-1}	PCB 11	IP	POPs	2 μg kg^{-1}	3-Nitrophenol	IP/TP		100 μg kg^{-1}
β-Lindane	INS	EPA, POPs	3 μg kg^{-1}	PCB 18	IP	POPs	2 μg kg^{-1}	4-Nitrophenol	IP/TP	EPA	100 μg kg^{-1}
δ-Lindane	INS	EPA	3 μg kg^{-1}	PCB 28	IP	POPs, EPA	2 μg kg^{-1}	4-n-Nonylphenol	IP/TP	REACH	5 μg kg^{-1}
γ-Lindane	INS	EPA, POPs	3 μg kg^{-1}	PCB29	IP	POPs	2 μg kg^{-1}	Pentachlorphenol	IP/TP	EPA, REACH	1 μg kg^{-1}
Lenacilo	HB		3 μg kg^{-1}	PCB 31	IP	POPs	2 μg kg^{-1}	4-Tertoctylphenol	IP/TP		5 μg kg^{-1}
Linuron	HB		3 μg kg^{-1}	PCB 44	IP	POPs	2 μg kg^{-1}	***Phtalates***			
Malathion	INS/ACA		3 μg kg^{-1}	PCB 47	IP	POPs	2 μg kg^{-1}	DEHP	UB	EPA, REACH	50 μg kg^{-1}
Metalaxyl	FUNG		3 μg kg^{-1}	PCB 52	IP	POPs, EPA	2 μg kg^{-1}				
Metamitrone	HB		3 μg kg^{-1}	PCB 66	IP	POPs	2 μg kg^{-1}				

[a]List of the 129 priority pollutants by United States Environmental Protection Agency (U.S. EPA). Appendix A to part 423 (available on http://www.epa.gov/waterscience/methods/pollutants.htm, last accessed December 2011)
[b] Stockholm Convention Persistent Organic Pollutants, Secretary-General of the United Nations, 22 May 2001. http://www.pops.int. (Last acceded December 2010)
[c] E.P. Council, Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC, Off. J. Eur. Union (2006) 850
Abbreviations: ACA: Acaricide; FUNG: Fungicide; HB: Herbicide; IN: Industrial product; INS: Insecticide; NEM: Nematicide; TP: Transformation product; UB: Ubiquitous contaminant

Table S2 Summary of the analytical methods applied for the analysis of residues and contaminants.

Compound	Extraction method	Determination technique	Injection	Column	Program	Analyzer	Parameters	Recovery (%)	Precision[b]	Ref.
Polar and non-polar pesticides	PLE (AcOEt/MeOH, 3:1 v/v, 75 ºC)	UHPLC (Polar pesticides) GC (non-polar pesticides)	**Polar pesticides**: 5 µL **Non-polar pesticides**: 10 µL, LVI+PTV (Carbofrit)	**Polar pesticides**: C_{18} (100mm×2.1mm,1.7µm) **Non-polar pesticides**: Varian FactorFour VF-5ms (30 m × 0.25 mm × 0.25µm)	**Polar pesticides**: A (MeOH), B (Water, 0.01% HCOOH) 10% A→90% (5 min, kept 2 min)→25% A (over 1.5 min), flow (0.35 ml/min), column (35 ºC) **Non-polar pesticides**: 70 ºC (0.5 min)→310 ºC (100 ºC min^{-1}, 10 min) 70 ºC (3.5 min) →180 ºC (35 ºC min^{-1})→300 ºC (10 ºC min^{-1}, 7 min)	QqQ	**Polar pesticides**: ESI+, capillary (3.5 kV), extractor (5 V), source (110 ºC), desolvation (350 ºC), cone gas (80 L h^{-1}), desolvation gas (600 L h^{-1}) **Non-polar pesticides**: EI (70eV), transfer line (300 ºC), manifold (40 ºC), source (280 ºC)	72-121	Intra-day: < 27 Inter-day: < 36	(1)
PAHs and PCBs	PLE (acetone/hexane, 1:1, v/v, 125 ºC)	GC	10 µL, LVI+PTV (Carbofrit)	Varian FactorFour VF-5ms (30 m × 0.25 mm × 0.25µm)	70 ºC (4 min)→300 ºC (20ºC min^{-1}, 15 min) 70 ºC (0.4 min) →325 ºC (200 ºC min^{-1}, 28 min)	QqQ	EI (70eV), transfer line (300 ºC), manifold (40 ºC), source (280 ºC)	49-110	Intra-day: < 16 Inter-day: < 23	(4)
Phenols	QuEChERS method: SLE (ACN); vortex; induced partition ($MgSO_4$ + CH_3COONa + NaCl); centrifugation	GC	10 µL, LVI+PTV	Varian FactorFour VF-5ms (30 m × 0.25 mm × 0.25 µm)	70 ºC (0.5 min)→310 ºC (100 ºC min^{-1}, 10 min) 70 ºC (3.5 min) →300 ºC (20 ºC min^{-1}, 7 min)	QqQ	EI (70eV), transfer line (300 ºC), manifold (40 ºC), source (265 ºC)	69-103	Intra-day: < 17 Inter-day: < 25	(5)
DEHP	PLE (acetone/hexane, 1:1, v/v)	HPLC	10 µl	Waters 5 µm Atlantis (dC_{18} 150 mm x 2 mm i.d.)	A (MeOH), B (Water) 75% A (kept 5 min) → 100% (in 4 min, kept 2 min) → 75% (1 min, kept 2 min)	Q	ESI+, capillary (3.5 kV), source (120 ºC), desolvation (350 ºC), cone gas (50 L h^{-1}), desolvation gas (250 L h^{-1})	99.8	Intra-day: 4 Inter-day: 8	(6)

[a] Abreviations: ACN: Acetonitrile; AcOEt: Ethyl acetate; ESI: Electrospray ionization; GC: Gas chromatography; HPLC: High Performance Liquid Chromatography; LVI: Large volumen injection; MeOH: Methanol; PLE: Pressurized Liquid Extraction; PTV: Pressure temperature Vaporization; RSD: Relative standard deviation; SLE: Solid-liquid extraction; UHPLC: Ultra high pressure liquid chromatography

[b] Expressed as Relative Standard Deviation (%).

Fig. S1 Ratios observed for the main endosulfan transformation products (TPs) in the studied agricultural soils

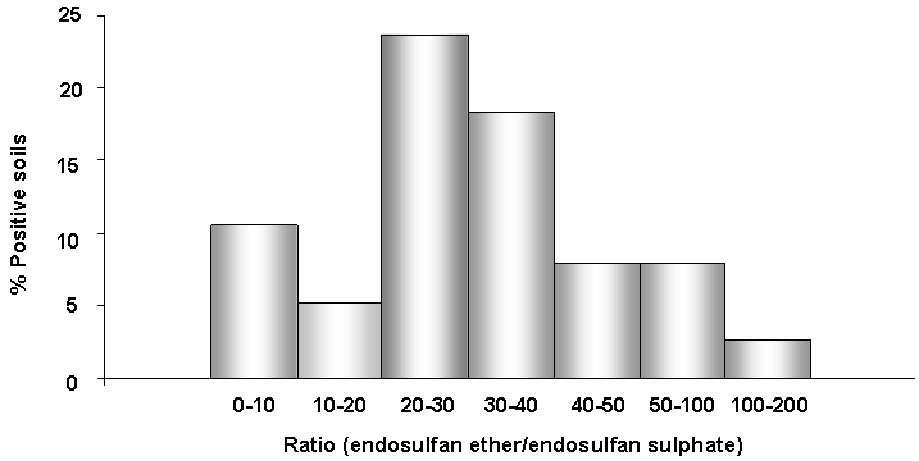
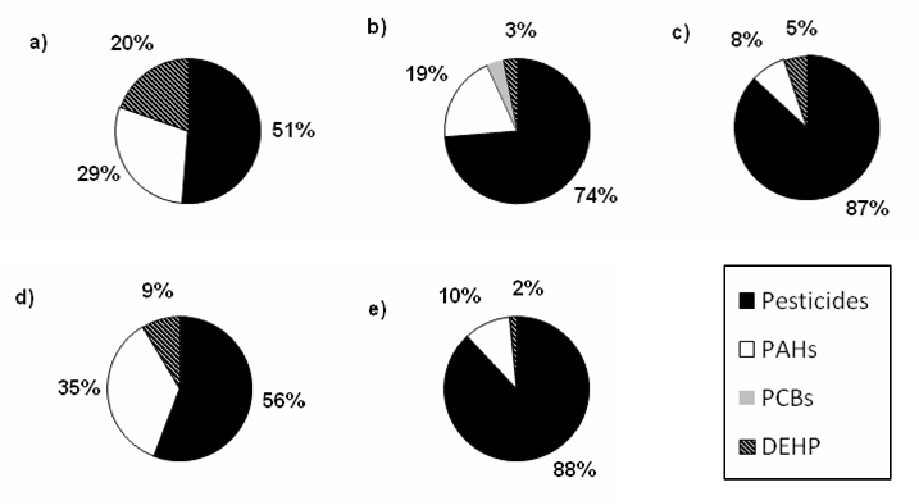


Fig. S2 Contamination pattern of residues and contaminants studied in the different municipalities: (a) Adra; (b) El Ejido; (c) Roquetas de Mar; (d) La Mojonera; (e) Vicar.



Apparatus, instruments, solvents and standards used in the different analytical procedures carried out for the agricultural soils analysis.

Laboratory apparatus-. Pressurized liquid extraction **(**PLE) was performed using an ASE 100 accelerated solvent extraction system (Dionex, Sunnyvale, CA, USA) equipped with 34-mL stainless steel extraction cells. An analytical balance AB204-S from Mettler Toledo (Greifensee, Switzerland) and a rotary evaporator R-114 (Büchi, Flawil, Switzerland) were used during extraction and standards preparation. A Reax-2 rotary agitator from Heidolph (Schwabach, Germany) was used. Centrifugations were performed in a high-volume centrifuge from Centronic (Barcelona, Spain).

Analytical instruments-. Chromatographic analyses were carried out using a GC system Varian 3800 (Varian instruments, Sunnyvale, CA, USA), equipped with electronic flow control (EFC) and interfaced to a 1200L triple quadrupole mass spectrometer (QqQ). Samples were injected into an SPI/1079 split/splitless programmed-temperature injector with a Combi Pal (CTC Analytics AG, Zwingen, Switzerland) autosampler using a 100-µL syringe. The glass liner was equipped with a plug of Carbofrit (Resteck, Bellefonte, PA, USA). A fused-silica untreated capillary column (2 m × 0.25 mm i.d.) from Supelco (Bellefonte, PA, USA), was used as pre-column connected to a Factor Four Capillary Column VF-5ms (30 m × 0.25 mm i.d. × 0.25 µm film thickness) purchased from Varian. The carrier gas was helium (99.9999 %) at a constant flow rate of 1 mL min^{-1}. Argon (99.9999 %) was used as collision gas. The mass spectrometer was operated in electron ionization (EI) at 70 eV. The mass spectrometer was calibrated weekly with perfluorotributylamine. Varian Workstation (version 6.9) was used for instrument control and data analysis.

An ultra high pressure liquid chromatograph (UHPLC) Acquity UPLC™ system (Waters, Milford, MS, USA) was used and separations were achieved using an Acquity UPLC™ BEH C_{18} column (100 mm × 2.1 mm, 1.7 µm particle size) from Waters. MS/MS detection was performed using an Acquity TQD QqQ mass spectrometer (Waters, Manchester, UK). The instrument was operated using an electrospray (ESI) source in positive mode. Data acquisition was performed using MassLynx software (version 4.1) with QuanLynx program (Waters).

A high performance liquid chromatography (HPLC) was utilized using an Alliance 2695 equipped with autosampler, degasser and heated column purchased by Waters. HPLC separation was achieved using a 5 µm Atlantis dC18 150 x 2.0 mm id column

obtained from Waters. The MS system was a ZQ 2000 single quadrupole from Waters-Micromass (Manchester, UK).

Solvents. Several solvents were used for extraction and analysis procedures. Acetone and cyclohexane was purchased from Fluka (Seelze, Germany), *n*-hexane was obtained from J. T. Baker, methanol (MeOH, HPLC grade solvent) was purchased from Sigma (St. Louis, MO, USA), ethyl acetate (EtAc, residue grade analysis) was supplied by Riedel-de-Haën and acetonitrile (AcN) was purchased from Merck (Darmstadt, Germany). Ultrapure water was obtained from a Milli-Q Gradient water system (Millipore, Bedford, MA, USA).

Standards.

Pesticides. 97 non-polar pesticides and 29 polar pesticides (a total of 126) of different families were analyzed. Pesticide standards were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The complete list of the 124 pesticides analyzed can be seen in Table-S1. The method applied for the determination of these compounds has been previously developed in our lab and it allows for simultaneous extraction of non-polar and polar pesticides (1) and the analysis method was based on those previously developed for non-polar (2) and polar pesticides (3).

PAHs and PCBs. A total of 24 PAHs have been monitored, including low and high molecular mass compounds (also known as light and heavy PAHs). Acenaphthene (ACP), acenaphthylene (ACY), anthracene (ANT), benz[*a*]anthracene (BaA), benzo[*a*]pyrene (BaP), benzo[*b*]fluoranthene (BbFA), benzo[*ghi*]perylene (BghiP), chrysene (CHR), dibenz[*a,h*]anthracene (DBahA), fluoranthene (FA), fluorene (FLR), indeno[1,2,3-*cd*]pyrene (IP), naphthalene (NPH), phenanthrene (PHE), and 2-bromonaphthalene (BNPH) at a concentration of 2 mg L^{-1} in methylene chloride were obtained from Supelco (Bellefonte, PA, USA) as well as 5-methylchrysene (MCH, 99.6% purity), benzo[*j*]fluoranthene (BjFA, 98.6% purity), benzo[*k*]fluoranthene (BkFA 99.5% purity), and fluoranthene-d10 (FA d10, 99.2% purity), which was used as internal standard. Dibenzo[*a,e*]pyrene (99% purity), dibenzo[*a,i*]pyrene (99.9% purity), dibenzo[*a,h*]pyrene (99% purity), dibenzo[*a,l*]pyrene (99.5% purity), and cyclopenta[*cd*]pyrene (99% purity) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany).

A total of 36 PCBs were monitored in this survey. PCBs standards (5, 11, 18, 28, 29, 31, 44, 47, 52, 66, 77, 81, 101, 105, 114, 118, 121, 123, 126, 128, 136, 137, 138, 143, 153, 156, 157, 167, 169, 170, 180, 185, 189, 194, 206 and 209) were obtained from Dr.

Ehrenstorfer GmbH. Both PAHs and PCBs were extracted and analyzed applying the methodology developed by Martinez Vidal et al (4).

Phenolic compounds and DEHP. Phenolic compounds (12 compounds) belonging to different families, such as chlorophenols (CPs), nitrophenols (NTPs), alkylphenols (Aps) and cresols, were studied in this work. 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-diCP) 2,4-dimethylphenol, 2-nitrophenol (2-NTP), 4-nitrophenol, 2,4,5-trichlorophenol (2,4,5-triCP), 2,4,6-trichlorophenol (2,4,6-triCP), 4-n-nonylphenol (4-n-NP) and [13C6]- pentachlorophenol (PCP), used as IS, were supplied by Fluka (Buchs, Switzerland). 3-nitrophenol, 4-chloro-3-methylphenol, 4-tertoctylphenol (4-tertOP) and PCP were purchased from Supelco (Belle- fonte, PA, USA). DEHP purity higher than 99%, was obtained from Sigma-Aldrich (Steinheim, Germany). The simultaneous extraction and analysis of phenolic compounds (5) and the procedure for the analysis of DEHP were carried out using methodologies previously developed (6). It must be noticed that, for the analysis of DEHP, the use of plastic materials was avoided as far as possible since it can be found, for instance, in tips, peek tubing and similar labware. Then, glass material was rinsed thoroughly with acetone and heated at 350 ºC for 3 h, to reduce phthalate contamination.

Quality control (IQC)

An internal quality control (IQC) was carried out during the different analysis in order to guarantee that the measurement process was under statistical control. Analyte free agricultural soil samples were obtained from University of Almeria. These samples were checked by our laboratory to ensure the absence of any target compound and they were used for the IQC. The IQC was based on the use of a blank extract, which eliminated false positives caused by a contamination in the extraction procedure or by the presence of a interference; a reagent blank (obtained by performing the whole procedure without sample), which removed any possibility of false positive due to contamination in the instruments or reagents employed; two spiked blank samples with concentrations depending on the compounds analyzed, which were used to assess the extraction efficiency (in terms of recovery); and a calibration curve to check linearity and sensitivity.

In relation to the spiked blank samples used to check the recovery in every batch of samples, concentration was equal to the first or second calibration point and calibration curves were constructed with different concentrations according to the linearity of each

analyte. Consequently, the concentrations used in the IQC spiked samples depend on the group of analytes, but always relatively low concentrations (e.g. 10 µg/kg).

For the analysis of DEHP, the use of plastic material was avoided as far as possible due to an important background noise was observed in the instrument. Then, glass material was rinsed thoroughly with acetone and heated at 350 ºC for 3 h, to reduce phthalate contamination.

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