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Study of the distribution of 204 organic contaminants between the aqueous phase and the suspended particulate matter in treated wastewater for proper environmental control

Nieves Barco-Bonilla[a], Roberto Romero-González[a], Patricia Plaza-Bolaños[a,b],
Antonia Garrido Frenich[a,*], José L. Martínez Vidal[a], Juan J. Salas[c], Isabel Martín[c]

[a]*Department of Chemistry and Physics (Analytical Chemistry Area), Andalusian Center for the Assessment and Monitoring of Global Change (CAESCG), Agrifood Campus of International Excellence, ceiA3 University of Almería, Almería E-04120, Spain*
Tel. +0034 950015985; Fax: +0034 950015483; email: agarrido@ual.es
[b]*Department of Analytical Chemistry, University of Granada, Granada E-18071, Spain*
[c]*Department of Research and Development, Foundation Center for New Water Technologies (CENTA), Autovía Sevilla-Huelva (A-49), km 28, Carrión de los Céspedes, Seville E-41820, Spain*

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ABSTRACT

A distribution study of 204 organic contaminants, including polar and nonpolar pesticides, polycyclic aromatic hydrocarbons (PAHs), and phenolic compounds, between the two phases composing municipal wastewater (WW) from a small community (aqueous phase and suspended particulate matter (SPM)) has been performed to establish whether the compounds can be more prone to be in the aqueous or in the solid phase, depending on their hydrophobicity. Therefore, a general procedure is proposed to evaluate this issue. This study shows that nonpolar pesticides and PAHs are distributed between the aqueous phase and the SPM (e.g. pyrethroids are mainly found in the SPM), whereas polar pesticides and phenolic compounds are mainly present in the aqueous phase. This fact made clear the relevance of the analysis of both phases in WW samples, bearing in mind that if SPM is discarded, an important fraction of some contaminants is not determined and therefore, it does not assess the total load of pollutants discharged, underestimating the real impact on the environment.

Keywords: Wastewater; Organic contaminants; Aqueous phase; Suspended particulate matter; Distribution

1. Introduction

Nowadays, there is an increasing interest in reusing wastewater (WW) in water-deficient regions. WW treatment plant (WWTP) effluents can be used in several applications such as agricultural irrigation [1,2], municipal and industrial purposes [3], and environmental aims (e.g. recharging of aquifers) or they can be directly discharged into rivers [4,5] or the sea. Certain groups of contaminants (e.g. pesticides, polycyclic aromatic hydrocarbons (PAHs), and phenolic compounds) are listed as priority pollutants by the European Union (EU) [6] and the United States Environmental Protection Agency (US-EPA) [7] because the presence of these compounds in the environment

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*Corresponding author.

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can be harmful to humans and environment, and they have been identified in WWs [8–12]. Consequently, these compounds need to be determined and controlled in WWTP effluents to assure their quality. An important question, which is not usually considered, is that WW is a complex multiphase matrix characterized by the presence of suspended particulate matter (SPM) in different amounts depending on the treatment received. In general, SPM is discarded and not submitted to analysis in WW monitoring and thus, this can have some influence in the determination.

WWTPs consist of a line of WW treatments composed on a pretreatment and consecutive primary, secondary, and tertiary treatments, employing nonconventional, conventional, and modern/recent technologies. Technologies, nonconventional such as maturation pond (MP), anaerobic pond (AP), or conventional as extended aeration (EA), are characterized by a relatively high amount of suspended solids or SPM. Currently, several treatments are being replaced by emerging technologies, such as membrane bioreactors (MBR). However, the high cost of the modern technologies complicate their implementation in small communities and most deprived areas in developing countries, and thus, nonconventional systems must still be taken into account.

Most of the analytical methods found in the literature for the analysis of organic contaminants in WW are only based on the analysis of the aqueous phase obtained after sample filtration, without regarding to the SPM that is retained in the filters [13–16]. However, several studies focused on superficial water samples demonstrate that some organic contaminants (e.g. PAHs) can be associated with SPM depending on their hydrophobicity and the nature and concentration of the particles [17,18]. This can also be observed for other type of organic contaminants, and they can be more or less prone to remain in one phase or another, depending on the hydrophobicity. Therefore, in WW analysis, it is necessary to evaluate the possible distribution of the contaminants between both phases in order to avoid underestimations in the total concentration of these compounds in the samples or to know, depending on the analyzed compound, which phase can be discarded in order to increase sample throughput in routine analysis, considering that the concentration in the discarded phase is negligible.

For that purpose, hydrophobicity is one of the most important physicochemical parameters governing the transport, distribution, and fate of chemicals in the environment. The octanol/water partition coefficient ($\log K_{\mathrm{ow}}$) is a quantitative parameter of the hydrophobicity of organic chemicals that describes the tendency of distribution of a solute from aqueous phase into organic constituents of environmental compartments [19,20]. Therefore, it is frequently used to predict water solubility, and it can be a good indicator of the distribution of a compound between the aqueous phase and SPM.

In this work, a study of the distribution of 204 organic compounds, including pesticides (both polar and nonpolar compounds), PAHs and phenolic compounds, between the aqueous phase and the SPM in different WWTP effluents (AP, MP, EA, and MBR) has been performed. Moreover, a general approach to evaluate this effect is proposed. The selection of the compounds was performed considering current regulations in the EU [6] and relevant lists, such as the EPA list [7].

2. Experimental

A brief summary of the compounds, reagents, solvents, instruments, apparatus, and methods used for the different analyses (sample extraction, instrumental determination, etc.) were provided in Appendix section.

2.1. Treated WW collection

Urban WWTP effluents from four different treatments, namely, MBR, EA, MP, and AP (ordered from low to high SPM content) were collected from the Experimental Plant of Carrión de los Céspedes, Seville, South of Spain. This plant has an area of 45,000 m^2 and currently holds more than 20 WW treatment technologies, both conventional and nonconventional treatments applied to small agglomerations. Treated WW samples were stored at 4°C in the dark and processed within 24 h after the collection.

2.2. Distribution study

2.2.1. Pesticides

The scheme of the procedure carried out during the distribution study is shown in Fig. 1(a). Non-filtered effluent samples were spiked with 4 μg L^{-1} of the target pesticides (Table 1), and then, they were shaken overnight at a rate of 100 oscillations per min to allow a thoroughly interaction between the compounds and the SPM. After this, samples were filtered consecutively using two different pore-size filters (47 mm glass microfibre filters and 0.45 μm HNWP nylon membrane filters) in order to separate and analyze both phases. The aqueous phase was extracted by solid-phase extraction (SPE), whereas for the SPM, a pressurized liquid extraction process was carried out [21]. The distribution of the compounds between the

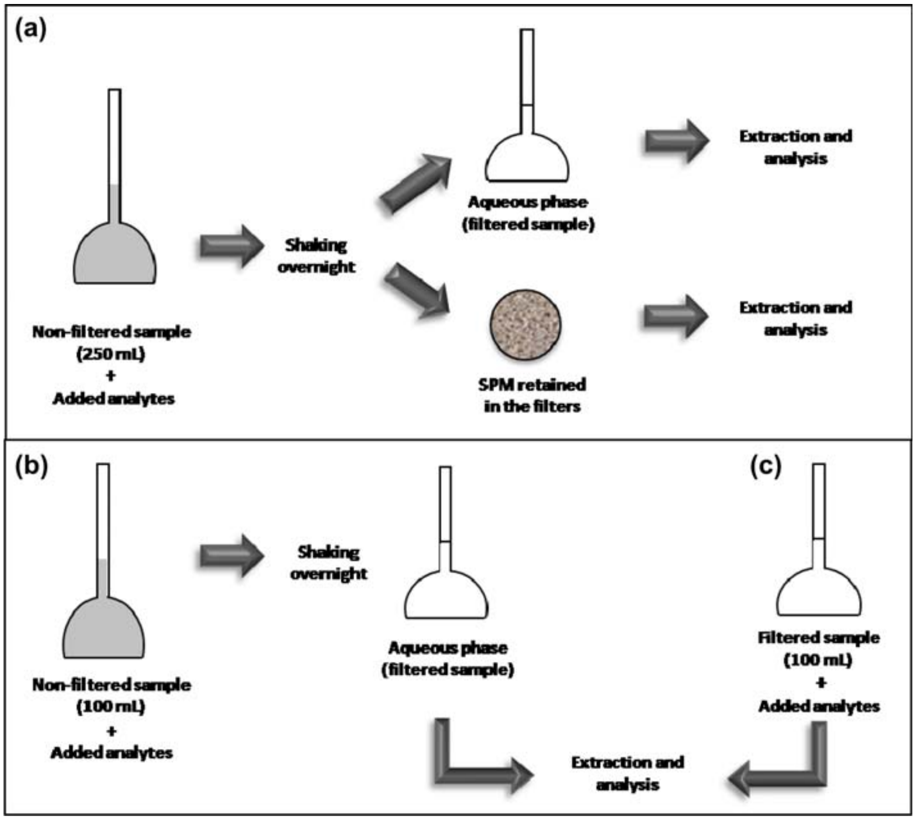

Fig. 1. Scheme of the procedure carried out during the distribution study: (a) pesticides and phenolic compounds and (b, c) PAHs. Abbreviations: SPM: suspended particulate matter.

phases was determined as the percentage of them present in each phase.

2.2.2. PAHs

Nonfiltered-treated WW samples were spiked with the target PAHs (Table 1) at $1\,\mu g\,L^{-1}$ and agitated overnight (horizontal shaker, 100 oscillations per minute). After 24 h, samples were filtered and the aqueous phase was extracted by SPE (Fig. 1(b)) [22]. On the other hand, filtered WW samples were spiked ($1\,\mu g\,L^{-1}$) and analyzed following the same extraction procedure (Fig. 1(c)). The distribution of the PAHs was determined assuming that the difference in the PAH content between both results corresponded to the PAHs retained into the SPM.

2.2.3. Phenolic compounds

Nonfiltered-treated WW effluent samples were spiked at $0.5\,\mu g\,L^{-1}$ of the studied phenolic compounds (Table 1), and then they were agitated overnight at a rate of 100 oscillations per min to allow a thorough interaction between the analytes and both phases of WW (aqueous phase and SPM). After this, samples were filtered to separate and analyze both phases. The aqueous phase was extracted by SPE, whereas for the analysis of the SPM, a solid–liquid extraction-based method previously developed in our laboratory [23] was applied. The distribution of the compounds between both phases was determined as the percentage of them present in each phase as described for pesticides distribution. A brief scheme of the procedure is represented in Fig. 1(a).

3. Results and discussion

The aim of this paper is the evaluation of the distribution of organic contaminants in aqueous phase and SPM. For that purpose, samples were obtained from an Experimental Plant for urban WW treatment, which employs more than 20 different WW treatment technologies that receive the same WW. Four of which were selected as the most representative and interesting technologies, considering their current use and covering a wide range of physicochemical properties. Table 2 shows several parameters of the treated WWs

Table 1
Selected compounds evaluated in this study

Compound	Description	log K_{ow}	Type	Compound	Description	log K_{ow}	Type	Compound	Description	log K_{ow}	Type
Pesticides				Cyproconazole	FUNG	3.1	NP	Isodrin	INS	6.7	NP
2-Phenylphenol	FUNG[a]	2.9	NP	Cyprodinil	FUNG	3.9	NP	Isophenphos	INS	4.0	NP
Acrinathrin	INS/ACA	5.6	NP	Deltamethrin	INS	4.6	NP	Isoproturon	HB	2.5	P
Alachlor	HB	3.1	NP	Diazinon	INS/ACA	3.3	NP	Kresoxim methyl	FUNG	3.4	NP
Aldrin	INS	6.2	NP	Dichlobenil	HB	2.7	NP	α-Lindane	INS	3.5	NP
Atrazine	HB	2.5	P	Dichloran	FUNG	2.8	NP	β-Lindane	INS	3.5	NP
Atrazine desethyl	TP	1.5	P	Dieldrin	INS	4.8	NP	δ-Lindane	INS	3.5	NP
Atrazine desisopropyl	TP	0.4	P	Diethofencarb	FUNG	3.0	NP	γ-Lindane	INS	3.5	NP
Azinphos ethyl	INS/ACA	3.2	NP	Difenoconazole	FUNG	4.4	NP	Lenacil	HB	2.3	P
Azinphos methyl	INS	2.9	NP	Dimetomorph	FUNG	2.6	NP	Linuron	HB	3.0	P
Benalaxyl	FUNG	3.5	NP	Diniconazole	FUNG	4.3	NP	Malathion	INS/ACA	2.7	NP
Benfluralin	HB	5.3	NP	Diuron	HB	2.8	P	Mecarbam	INS/ACA	2.3	NP
Bensulfuron methyl	HB	2.2	P	Endosulfan *α*	INS	4.7	NP	Metalaxyl	FUNG	1.7	NP
Bifenox	HB	4.5	NP	Endosulfan *β*	TP	4.8	NP	Metamitron	HB	0.8	P
Bifenthrin	INS/ACA	6.0	NP	Endosulfan eter	TP	4.0	NP	Metazachlor	HB	2.1	P
Bromophos ethyl	INS	6.1	NP	Endosulfan lactone	TP	4.1	NP	Methidathion	INS/ACA	2.2	NP
Bromophos methyl	INS	5.2	NP	Endosulfan suphate	TP	3.8	NP	Methoxychlor	INS	4.9	NP
Bromopropylate	ACA	5.4	NP	EPN	INS/ACA	4.7	NP	Metobromuron	HB	2.4	P
Bupirimate	FUNG	3.9	NP	Ethion	INS/ACA	4.3	NP	Metolachlor	HB	2.9	P
Buprofezin	INS/ACA	4.3	NP	Ethofumesate	HB	2.7	NP	Metoxuron	HB	1.6	P
Carbophenothion	INS/ACA	4.7	NP	Ethoprophos	INS /NM	3.6	NP	Metribucin	HB	1.6	P
Clodinafop propargyl	HB	3.9	NP	Etrimfos	INS	3.4	NP	Metsulfuron methyl	HB	0.01	P
Chlordane-cis	INS	5.6	NP	Fenamiphos	NEM	3.3	NP	Mevinphos	INS/ACA	0.1	NP
Chlordane-trans	INS	5.6	NP	Fenitrothion	INS	3.4	NP	Mirex	INS	5.3	NP
Chloridazon	HB	1.2	P	Fenoxaprop-P-ethyl	HB	4.6	P	Monolinuron	HB	2.2	P
Chlorfenson	INS	4.5	NP	Fenpropathrin	INS/ACA	6.0	NP	Norflurazon	HB	2.4	NP
Chlorfenvinphos	INS/ACA	3.8	NP	Fenthion	INS	4.8	NP	*o,p*-DDD	TP	5.9	NP
Chlormephos	INS	3.1	NP	Fenarimol	FUNG	3.6	NP	*o,p*-DDT	INS	6.8	NP
Chloropropylate	ACA	4.8	NP	Fipronil	INS	4.0	NP	Oxadixyl	FUNG	0.6–0.8	NP
Chlorpyriphos methyl	INS/ACA	4.2	NP	Fluacipop-butyl	HB	4.5	NP	Oxyfluorfen	HB	4.5	NP
Chlortal dimethyl	HB	4.3	NP	Flucythrinate	INS	4.7	NP	*p,p´*-DDD	TP	6.0	NP
Chlorthion	INS	3.5	NP	Fluorochlorhidrone	HB	3.4	NP	*p,p´*-DDE	TP	6.5	NP
Chlortoluron	HB	2.5	P	Fludioxonil	FUNG	4.1	NP	Parathion ethyl	INS/ACA	3.8	NP

(*Continued*)

Table 1 (*continued*)

Compound	Description	log K_{ow}	Type	Compound	Description	log K_{ow}	Type	Compound	Description	log K_{ow}	Type
Chlozolinate	FUNG	3.1	NP	Fonophos	INS	3.9	NP	Parathion methyl	INS/ACA	3.0	NP
Cycloate	HB	3.9	NP	Formothion	INS	1.5	NP	Penconazole	FUNG	3.7	NP
Cinidon-ethyl	HB	4.5	NP	Furalaxyl	FUNG	2.7	NP	Pendimethalin	HB	5.2	NP
Cinosulfuron	HB	2.0	P	Heptachlor	INS	5.4	NP	Pentachlorobenzene	FUNG	5.2	NP
γ-Cyhalothrin	INS	6.9	NP	Heptachlor epoxide	TP	4.2	NP	Permethrin	INS	6.1	NP
Cyanofenphos	INS	4.2	NP	Heptenophos	INS	2.3	NP	Phenthoate	INS/ACA	3.7	NP
Cycloxydim	HB	1.4	P	Hexachlorobenzene	FUNG	5.7	NP	Phorate	INS/ACA/NEM	3.9	NP
Cyfluthrin	INS	6.0	NP	Hexaconazole	FUNG	3.9	NP	Pyridaben	INS/ACA	6.4	NP
Cypermethrin	INS	6.6	NP	Iodosulfuron-methyl	HB	1.1	P	Pyrifenox	FUNG	3.4	NP
Pirimicarb	INS	1.7	NP	Triasulfuron	HB	1.1	P	4-Tertoctylphenol	IP/TP	4.1	NP
Pirimiphos ethyl	INS	5.0	NP	Vinclozoline	FUNG	3.0	NP				
Pirimiphos methyl	INS/ACA	4.2	NP	*PAHs*							
Pyriproxyfen	INS	5.4	NP	Acenaphthene	UB	4.0	NP				
Procymidone	FUNG	3.1	NP	Acenaphthylene	UB	3.9	NP				
Prometryn	HB	3.1	P	Anthracene	UB	4.5	NP				
Propachlor	HB	2.3	NP	Benz[*a*]anthracene	UB	5.6	NP				
Propazine	HB	2.9	P	Benzo[*a*]pyrene	UB	6.0	NP				
Propiconazole	FUNG	3.7	NP	Benzo[*b*]fluoranthene	UB	6.3	NP				
Propyzamide	HB	3.2	P	Benzo[*k*]fluoranthene	UB	6.4	NP				
Pyrazophos	FUNG	3.8	NP	Benzo[*ghi*]perylene	UB	6.7	NP				
Quinalphos	INS/ACA	4.4	NP	Benzo[*j*]fluoranthene	UB	6.1	NP				
Quinmerac	HB	−1.1	P	2-Bromonaphthalene	UB	4.1	NP				
Quinoxyfen	FUNG	4.7	NP	Chrysene	UB	5.7	NP				
Quintocene	FUNG	5.1	NP	Cyclopenta[*cd*]pyrene	UB	4.9	NP				
S421	INS	5.3	NP	Dibenzo[*a,e*]pyrene	UB	7.4	NP				
Sebuthylazine	HB	3.2	P	Dibenzo[*a,h*]anthracene	UB	6.9	NP				
Sethoxydim	HB	4.5	P	Dibenzo[*a,h*]pyrene	UB	7.4	NP				
Silafluofen	INS	8.2	NP	Dibenzo[*a,i*]pyrene	UB	7.4	NP				
Simazine	HB	2.1	P	Dibenzo[*a,l*]pyrene	UB	7.4	NP				
Sulfotep	INS/ACA	3.9	NP	Fluoranthene	UB	5.1	NP				
Tau fluvalinate	INS/ACA	4.3	NP	Fluorene	UB	4.1	NP				
Tebufenozide	INS	4.2	NP	Indeno[1,2,3-*cd*]pyrene	UB	7.1	NP				
Tebufenpirad	ACA	5.0	NP	5-Methylchrysene	UB	6.3	NP				

(*Continued*)

Table 1 (*continued*)

Compound	Description	log K_{ow}	Type	Compound	Description	log K_{ow}	Type	Compound	Description	log K_{ow}	Type
Tebutam	HB	3.0	P	Naphthalene	UB	3.3	NP				
Tecnazene	FUNG	4.0	NP	Phenanthrene	UB	4.5	NP				
Tepraloxydim	HB	1.5	P	Pyrene	UB	5.1	NP				
Terbumeton	HB	3.0	P	*Phenolic compounds*							
Terbutryn	HB	3.6	NP	2,4,5-Trichlorophenol	IP/TP	3.7	P				
Terbuthylazine	HB	3.2	P	2,4,6-Trichlorophenol	IP/TP	3.7	P				
Terbuthylazine desethyl	TP	1.9	P	2,4-Dimethylphenol	IP/TP	2.3	P				
Tetrachlorvinphos	INS/ACA	3.9	NP	4-Chloro-3-methylphenol	IP/TP	3.1	P				
Tetraconazole	FUNG	3.6	NP	2,4-Dichlorophenol	IP/TP	3.2	P				
Tetradifon	ACA	4.6	NP	2-Chlorophenol	IP/TP	2.1	P				
Tetramethrin	INS	4.6	NP	4-Chlorophenol	IP/TP	2.4	P				
Thiazopyr	HB	3.9	P	2-Nitrophenol	IP/TP	1.8	P				
Thifensulfuron methyl	HB	1.1	P	3-Nitrophenol	IP/TP	2.0	P				
Tolcophos methyl	FUNG	4.6	NP	4-Nitrophenol	IP/TP	1.9	P				
Transfluthrin	INS	5.5	NP	4-n-Nonylphenol	IP/TP	5.7	NP				
Triadimefon	FUNG	3.1	NP	Pentachlorphenol	IP/TP	5.2	NP				

[a] Abbreviations: ACA: Acaricide; FUNG: Fungicide; HB: Herbicide; IN: Industrial product; INS: Insecticide; NEM: Nematicide; TP: Transformation product; UB: Ubiquitous contaminant; NP: nonpolar; P: polar.

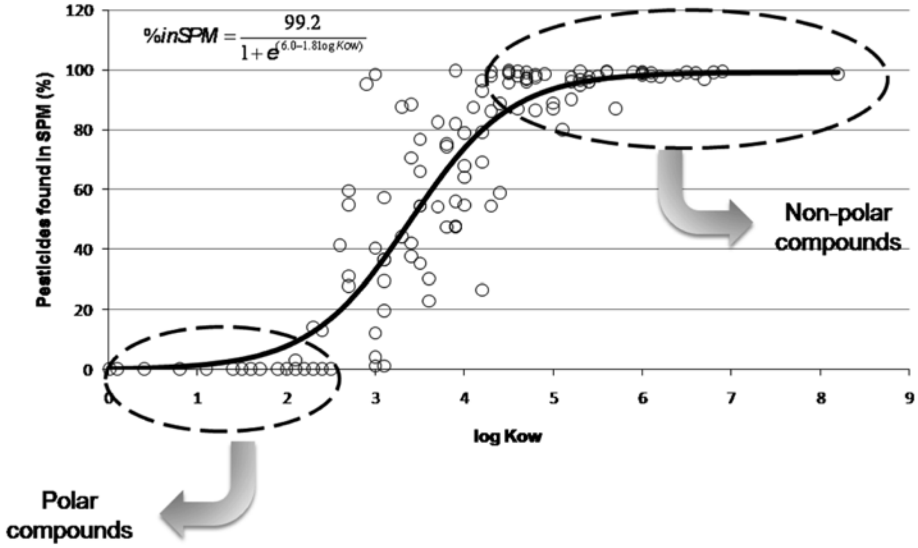

Fig. 2. Percentage of pesticides found in the SPM according to the $\log K_{\mathrm{ow}}$ as a measure of the hydrophobicity of the compounds.

under study and it is important to notice that these outlets present different amounts of SPM, finding that the treatment that generated the effluent with higher amount of SPM was AP ($99\,\mathrm{mg\,L^{-1}}$), followed by MP ($59\,\mathrm{mg\,L^{-1}}$), and EA ($38\,\mathrm{mg\,L^{-1}}$). MBR contained a minimal amount of solids ($9\,\mathrm{mg\,L^{-1}}$).

Due to the difference in the amount of SPM and other physicochemical properties in the evaluated effluents, the distribution study was carried out separately in the four treatments selected in order to establish if the same trend is observed irrespective of the type of effluent, or in contrast, it depends on the treatment received in the Experimental Plant. Repeatability of the experiments was carried out ($n = 4$).

3.1. Distribution study for pesticides

Because of their different physicochemical properties, pesticides can be distributed in the two phases composing WWTP samples: aqueous phase and SPM ("solid phase"). Therefore, a study of their distribution between these phases was carried out to establish if the studied compounds are mostly detected in the aqueous phase or in the SPM, or, on the contrary, they can be detected in both phases. In consequence, this evaluation would indicate which phase(s) should be analyzed to determine the concentration of these organic contaminants in treated WWs.

This study was performed using the procedures described in Sections 3.1, 3.2, and 3.3 of the Appendix. It can be indicated that depending on the hydrophobicity of the compounds, they are mainly distributed in the aqueous phase or SPM. The same trend was observed irrespective of the type of effluent. These results were in accordance to those described previously [21]. As it has been previously commented, the $\log K_{\mathrm{ow}}$ is a quantitative measure of the hydrophobicity, and therefore, it provides an estimation of the tendency of the compounds to remain in the aqueous phase or the SPM. This trend is graphically shown in Fig. 2, and it can be observed that the compounds are more prone to remain in the SPM (the hydrophobicity of the compounds increases) at higher values of $\log K_{\mathrm{ow}}$. Moreover, it is possible to fit the observed sigmoidal curve to a logistic equation, which may be useful to predict the distribution of the pesticide in the SPM according to its $\log K_{\mathrm{ow}}$. Thus, if $\log K_{\mathrm{ow}}$ is < 2.5, the amount of compound detected in SPM is negligible, whereas at higher values the percentage of compound found in the SPM increases. Furthermore, it can be observed that if $\log K_{\mathrm{ow}}$ is > 5, most of the amount of the compound is detected in the SPM ($\% > 50\%$).

Therefore, for nonpolar pesticides, it was observed that most of the compounds were distributed in both the aqueous and the "solid phase" (SPM), except for pyrethroids and organochlorine pesticides (higher $\log K_{\mathrm{ow}}$), which were more prone to remain in the SPM. As it can be seen in Table 1, pyrethroids are the pesticides with higher values of $\log K_{\mathrm{ow}}$ (> 6.0). Therefore, the behavior shown by these compounds was similar to that expected from their hydrophobicity. This fact demonstrates the need for analyzing both phases, the aqueous and the "solid phase", which is normally discarded. Furthermore, as the content of

Table 2
Average value ($n = 23$) of several physicochemical parameters measured during one year for the four effluents evaluated

Treatment	BOD[a] (mg L^{-1} O$_2$)	COD (mg L^{-1} O$_2$)	Ammonium (mg L^{-1} N)	Phosphate (mg L^{-1} P)	Total phosphorus (mg L^{-1} P)	Nitrates (mg L^{-1} N)	Total suspended solids (mg L^{-1})	Dissolved oxygen (mg L^{-1} O$_2$)	Conductivity (µS cm^{-1}, 20°C)	T (°C)	pH
MBR	12	35	5	5	6	34	9	6	1,223	18	7
EA	45	114	34	5	7	7	38	2	1,364	21	7
MP	48	209	25	5	7	7	59	4	1,237	21	8
AP	272	503	50	6	7	8	99	1	1,386	20	7

[a]Abbreviations: AP: anaerobic pond; BOD: biochemical oxygen demand; COD: chemical oxygen demand; EA: extended aeration; MBR: membrane bioreactor; MP: maturation pond.

SPM of the different effluents increased (from MBR to AP), a higher number of compounds mainly retained in the solids were observed, indicating that treated WW samples do not show a unique analytical behavior. Moreover, Table 3 shows that the distribution of the selected pesticides was independent of the amount of SPM in WW, considering that similar distribution was obtained for the four treatments evaluated, except for some compounds such as endosulfan lactone, pyrifenox, tebupenfyrad, and α and ß-lindane. For these compounds, it can be observed that higher percentages of pesticides were detected in WW effluents with higher amount of SPM, such as AP. Therefore, the analysis of SPM in WW effluents from AP treatments is important, considering that this treatment provides higher amount of solids.

On the other hand, in order to cover a wide range of WWTP effluents, only two of them, those that present the higher and lower amount of SPM (AP and MBR, respectively) were evaluated for polar pesticides. In this case, the fraction of analytes bound to particles was negligible, and they were mainly found in the aqueous phase (these compounds present lower $\log K_{\text{ow}}$, in general < 3.0). Thus, more than 86% of the analyzed compounds were detected mainly in the aqueous phase, whereas the rest of the compounds were distributed between the two phases. Therefore, the analysis of SPM was not necessary when polar pesticides are monitored.

3.2. Distribution study of PAHs

PAHs are nonpolar compounds showing high lipophilic character. However, in spite of PAHs show hydrophobic properties, they are also found in water due to their ubiquitous nature. Thus, in order to establish the need for analyzing both phases in treated WWs, it is necessary to evaluate the distribution of these compounds between the aqueous phase and the SPM. For that purpose, PAHs were extracted from samples using the procedures described in Section 3.4 of the Appendix, and the results obtained were evaluated. Table 4 shows the distribution of the target compounds between both phases, expressed as percentage. PAHs were principally retained in the SPM, although it can be noted that higher percentages (> 10%) of light PAHs, such as naphthalene, acenaphthylene, and acenaphthene, were found in the aqueous phase. The PAH content determined in the samples spiked after the filtration step was considerably higher than the content in the nonfiltered-spiked sample. Consequently, it is necessary to analyze both phases when these compounds are determined in

Table 3
Distribution percentages of pesticides between the SPM and the water phase (WP) according to the type of treatment

	MBR[a]		EA		MP		AP	
Compound	%SPM	%WP	%SPM	%WP	%SPM	%WP	%SPM	%WP
2-Phenylphenol	90	10	75	25	74	26	95	5
Achrinatrin	100	0	97	3	98	2	99	1
Alachlor	14	86	5	95	14	86	57	43
Aldrin	81	19	98	2	95	5	98	2
Benfluralin	80	20	92	8	93	7	95	5
Bifenthrin	100	0	97	3	98	2	99	1
Bromacil	66	34	72	28	100	0	86	14
Bromophos ethyl	93	7	96	4	96	4	98	2
Bromophos methyl	76	24	84	16	92	8	96	4
Bromopropylate	63	37	71	29	86	14	96	4
Bupirimate	0	100	0	100	14	86	0	100
Buprofezin	63	37	67	33	81	19	0	100
Butraline	68	32	100	0	100	0	0	0
Carbophenothion	94	6	95	5	96	4	97	3
Chlordane-cis	87	13	98	2	96	4	100	0
Chlorfenson	83	17	80	20	94	6	96	4
Chlorfenvinphos	21	79	15	85	51	49	47	53
Chlormephos	7	93	16	84	18	82	37	63
Chlorpyriphos-methyl	43	57	42	58	73	27	79	21
Chlortal-dimethyl	63	37	54	46	79	21	86	14
Cicloate	23	77	17	83	25	75	56	44
Cinidon-ethyl	97	3	94	6	100	0	99	1
Clodinafop-propargyl	89	11	65	35	100	0	100	0
Cyanophenphos	57	43	62	38	87	13	96	4
Cyfluthrin	100	0	97	3	97	3	98	2
Cypermethrin	100	0	98	2	97	3	99	1
Cyproconazole	0	100	4	96	7	93	19	81
Cyprodinil	15	85	13	87	51	49	82	18
Delta-lindane	7	93	23	77	53	47	77	23
Deltamethrin	100	0	98	2	98	2	99	1
Diazinon	13	87	8	92	23	77	44	56
Dichlobenil	20	80	59	41	30	70	55	45
Dichloran	3	97	8	92	31	69	0	0
Dieldrin	65	35	87	13	92	8	97	3

(*Continued*)

Table 3 (*continued*)

	MBR[a]		EA		MP		AP	
Compound	%SPM	%WP	%SPM	%WP	%SPM	%WP	%SPM	%WP
Difenoconazole	69	31	70	30	77	23	89	11
Dimethomorph	8	92	6	94	24	76	41	59
Dinobuton	65	35	57	43	82	18	100	0
Dinoconazole	7	93	18	82	27	73	54	46
Disulfoton	29	71	47	53	61	39	43	57
Endosulfan ether	14	86	29	71	50	50	79	21
Endosulfan lactone	59	41	11	89	47	53	7	93
Endosulfan sulfate	0	100	59	41	80	20	0	100
Endosulfan α	63	37	78	22	89	11	97	3
Endosulfan β	61	39	74	26	89	11	98	2
EPN	75	25	84	16	92	8	96	4
Ethion	81	19	85	15	92	8	98	2
Ethofumesate	14	86	7	93	23	77	31	69
Ethoprophos	8	92	5	95	13	87	23	77
Etrimfos	13	87	10	90	32	68	42	58
Fenamiphos	64	36	57	43	83	17	88	12
Fenarimol	3	97	8	92	15	85	30	70
Fenitrothion	48	52	40	60	71	29	71	29
Fenpropathrin	100	0	98	2	97	3	99	1
Fenthion	64	36	75	25	91	9	86	14
Fentoate	61	39	33	67	68	32	83	17
Fipronil	2	98	1	99	18	82	68	32
Fluacipop-butyl	95	5	85	15	94	6	100	0
Flucythrinate	100	0	98	2	98	2	99	1
Fludioxonil	5	95	24	76	53	47	87	13
Flurochloridone	28	72	16	84	46	54	38	62
Fonofos	18	82	19	81	42	58	48	52
Furalaxyl	15	85	7	93	1	99	28	72
Gamma-lindane	11	89	22	78	37	63	54	46
Heptachlor	68	32	95	5	94	6	96	4
Heptachlor epoxide	56	44	78	22	94	6	93	7
Heptenophos	4	96	0	100	9	91	14	86
Hexachlorobenzene	53	47	87	13	91	9	87	13
Hexaconazole	0	100	0	100	0	100	0	100
Iprodione	99	1	96	4	97	3	99	1

(*Continued*)

Table 3 (*continued*)

Compound	MBR[a]		EA		MP		AP	
	%SPM	%WP	%SPM	%WP	%SPM	%WP	%SPM	%WP
Isodrin	57	43	97	3	95	5	97	3
Isophenphos	12	88	13	87	36	64	55	45
Kresoxim methyl	21	79	12	88	45	55	0	100
Lambda-cyhalothrin	100	0	98	2	98	2	99	1
Malathion	32	68	18	82	42	58	60	40
Mecarbam	16	84	40	60	61	39	0	100
Metalaxyl	36	64	23	77	68	32	86	14
Methidathion	13	87	23	77	56	44	0	100
Methoxychlor	80	20	90	10	95	5	99	1
Mevinphos	0	100	0	100	0	100	0	100
Mirex	99	1	97	3	98	2	99	1
Norflurazon	2	98	4	96	16	84	13	87
o,p´-DDT + *p,p´*-DDD	95	5	97	3	96	4	99	1
o,p´-DDD	89	11	97	3	95	5	99	1
Oxadixyl	0	100	0	100	0	100	0	100
Oxyfluorfen	95	5	95	5	97	3	99	1
p,p´-DDE	99	1	98	2	97	3	99	1
Parathion ethyl	46	54	36	64	70	30	75	25
Parathion methyl	40	60	32	68	62	38	40	60
Penconazole	0	100	13	87	18	82	0	100
Pendimethalin	81	19	87	13	93	7	98	2
Pentachlorobenzene	42	58	78	22	74	26	90	10
Permethrin	100	0	97	3	96	4	99	1
Phorate	27	73	31	69	58	42	47	53
Pirimicarb	0	100	0	100	0	100	0	100
Procymidone	32	68	15	85	39	61	36	64
Propachlor	0	100	0	100	0	100	0	100
Propargite	98	2	87	13	95	5	97	3
Propiconazole	19	81	11	89	34	66	54	46
Propoxur	19	81	0	100	9	91	0	100
Pyrazophos	37	63	42	58	68	32	74	26
Pyridaben	98	2	96	4	96	4	98	2
Pyrifenox	12	88	56	44	43	57	88	12
Pyrimiphos ethyl	38	62	45	55	70	30	89	11
Pyrimiphos methyl	23	77	23	77	52	48	69	31

(*Continued*)

Table 3 (*continued*)

	MBR[a]		EA		MP		AP	
Compound	%SPM	%WP	%SPM	%WP	%SPM	%WP	%SPM	%WP
Pyriproxyfen	87	13	91	9	92	8	97	3
Quinalphos	32	68	28	72	54	46	59	41
Quinoxyfen	0	100	89	11	95	5	0	100
Quintozene	45	55	58	42	83	17	80	20
S421	87	13	67	33	94	6	97	3
Silafluofen	98	2	95	5	98	2	99	1
Sulfotep	23	77	16	84	39	61	48	52
Tau-fluvalinate	99	1	96	4	98	2	99	1
Tebufenozide	0	100	0	100	10	90	27	73
Tebufenpyrad	47	53	42	58	67	33	87	13
Tecnazene	31	69	39	61	59	41	64	36
Terbutryn	0	100	0	100	0	100	0	100
Tetrachlorvinphos	0	100	25	75	49	51	0	100
Tetraconazole	18	82	13	87	30	70	0	100
Tetradifon	89	11	89	11	95	5	98	2
Thiometon	32	68	34	66	77	23	43	57
Tolclofos methyl	54	46	50	50	78	22	87	13
Transfluthrin	91	9	94	6	96	4	98	2
Triadimefon	14	86	9	91	21	79	29	71
Vinclozoline	96	4	48	52	84	16	98	2
α-Lindane	21	79	18	82	16	84	66	34
β-Lindane	0	100	34	66	43	57	54	46

[a] Abbreviations: AP: anaerobic pond; EA: extended aeration; MBR: membrane bioreactor; MP: maturation pond; SPM: suspended particulate matter; WP: water phase.

Table 4
Distribution of PAHs between the aqueous phase and the SPM

Compound	Abbreviation	PAHs in aqueous phase (%)	PAHs in SPM (%)
Acenaphthene	ACP	9.7	90.3
Acenaphthylene	ACY	16.7	83.3
Anthracene	ANT	8.2	91.8
Benz[*a*]anthracene	BaA	7.3	92.7
Benzo[*a*]pyrene	BaP	3.8	96.2
Benzo[*b*]fluoranthene	BbFA	2.7	97.3
Benzo[*ghi*]perylene	BghiP	2.2	97.8
Benzo[*j*]fluoranthene	BjFA	2.5	97.5
Benzo[*k*]fluoranthene	BkFA	2.2	97.8
2-Bromonaphthylene	BrNPH	30.2	69.8
Chrysene	CHR	3.2	96.8
Cyclopenta[*cd*]pyrene	CPcdP	2.8	97.2
Dibenzo[*a,e*]pyrene	DBahA	3.4	96.6
Dibenzo[*a,h*]anthracene	DBaeP	2.8	97.2
Dibenzo[*a,h*]pyrene	DBahP	3.9	96.1
Dibenzo[*a,i*]pyrene	DBaiP	3.6	96.4
Dibenzo[*a,l*]pyrene	DBalP	6.0	94.0
Fluoranthene	FA	3.9	96.1
Fluorene	FLR	7.0	93.0
Indeno[1,2,3-*cd*]pyrene	IP	8.2	91.8
5-Methylchrysene	MCHR	20.4	79.6
Naphthalene	NPH	10.9	89.1
Phenanthrene	PHE	4.4	95.6
Pyrene	PYR	6.2	93.8

treated WW samples. In this sense, and in order to increase sample throughput, instead of analyzing both phases separately, only one extraction can be applied and for that purpose it was observed that the application of stir bar sorptive extraction (SBSE) can be used [22]. Thus, SBSE procedure can be applied to raw WW effluent (nonfiltered) for the simultaneous extraction of PAHs from both phases.

3.3. Distribution study of phenolic compounds

Although phenolic compounds show polar nature, and theoretically must be present in the aqueous phase, it is necessary to verify whether the compounds are also present in the SPM. If they are present quantitatively in the SPM, the analysis of WWTP effluents should not be limited to the aqueous phase. The distribution study was therefore carried out, applying the procedure described in Section 3.5 of the Appendix. As it is observed for polar pesticides, only MBR and AP were analyzed since they can be considered as representative WW effluents with low and high SPM. It can be noted that the phenolic compounds were mainly found in the aqueous phase, although those compounds with high $\log K_{\mathrm{ow}}$ (4-*n*-nonylphenol, 4-tert-octylphenol, and pentachlorophenol) were also found in the SPM, but at negligible percentages ($< 5\%$). This study revealed that when phenolic compounds are analyzed in treated WW samples, it is possible to limit the analysis to the aqueous phase, discarding the SPM.

3.4. Analysis of real samples

Finally, the aqueous phase and the SPM of 6 WWTP effluents from different treatments, namely rotating biological contactor (RBC), MP, horizontal subsurface-flow constructed wetland (SSF), Imhoff tank, AP, and a combination of EA + sand filters + UV, were analyzed. An internal quality control was carried out in order to guarantee that the measurement process was under statistical control. WW samples were previously analyzed to check the occurrence of the compounds under study. This sample eliminated possible false positives produced by contamination. In

Table 5
Analysis of nonpolar pesticides in WW effluents

Treatment	Concentration	Compound										
		2-Phenylphenol	Alachlor	Chlorfenvinphos	Chlormephos	Cyfluthrin	Cyproconazole	Diazinon	Ethoprophos	Isodrin	Mevinphos	Pirimicarb
RBC	AqP[a]	N.D.[d]	N.D.	N.D.	N.D.	N.D.	N.D.	0.11	N.D.	N.D.	N.D.	N.D.
	SPM[b]	21	37	N.D.	8	179	N.D.	<LOQ	N.D.	N.D.	176	8
	Total[c]	0.08	0.15	–	0.03	0.72	–	0.11	–	–	0.70	0.03
MP	AqP	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.12	N.D.	N.D.	N.D.	N.D.
	SPM	47	N.D.	N.D.	N.D.	96	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Total	0.19	–	–	–	0.38	–	0.12	–	–	–	–
SSF	AqP	N.D.	N.D.	0.20	N.D.	N.D.	0.09	0.07	N.D.	0.05	N.D.	N.D.
	SPM	2065	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Total	8.26	–	0.20	–	–	0.09	0.07	–	0.05	–	–
EA + sand filters + UV	AqP	N.D.	N.D.	<LOQ[e]	N.D.	N.D.	N.D.	0.92	0.02	N.D.	N.D.	N.D.
	SPM	21	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Total	0.08	–	<LOQ	–	–	–	0.92	0.02	–	–	–
Imhoff tank	AqP	N.D.	N.D.	0.02	N.D.	N.D.	N.D.	N.D.	0.14	N.D.	N.D.	N.D.
	SPM	73	N.D.	14	N.D.	725	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Total	0.29	–	0.08	–	2.90	–	–	0.14	–	–	–
AP	AqP	0.70	N.D.	0.15	N.D.	N.D.	N.D.	N.D.	0.36	N.D.	N.D.	N.D.
	SPM	66	N.D.	17	N.D.	407	N.D.	17	N.D.	N.D.	N.D.	<LOQ
	Total	0.96	–	0.22	–	1.63	–	0.07	–	–	–	<LOQ

Abbreviations: RBC: rotating biological contactor; MP: maturation pond; SSF: horizontal subsurface-flow constructed wetland; EA: extended aeration; UV: ultraviolet; AP: anaerobic pond.

[a] Concentration obtained in the aqueous phase (AqP) expressed in μg L^{-1}.

[b] Amount detected in the SPM obtained from 250 mL of WW effluent, expressed as ng.

[c] Total concentration detected considering both phases (expressed in μg L^{-1}).

[d] N.D.: not detected.

[e] LOQ: limit of quantification.

Table 6
Analysis of polar pesticides, PAHs, and phenolic compounds in WW effluents

Compound	RBC	MP	SSF	EA + sand filters + UV	Imhoff tank	AP
Polar pesticides ($\mu g\, L^{-1}$)						
Diuron	0.05	0.06	0.06	0.09	N.D.[a]	0.05
Sebuthylazine + terbuthylazine	<LOQ[b]	<LOQ	<LOQ	0.01	N.D.	0.03
Phenolic compounds ($\mu g\, L^{-1}$)						
2,4,6-Trichlorophenol	0.11	N.D.	0.14	0.12	N.D.	N.D.
2,4,5-Trichlorophenol	0.15	0.16	N.D.	N.D.	N.D.	N.D.
4-Tertoctylphenol	0.10	0.09	0.11	0.18	73.45	83.71
Pentachlorophenol	0.04	N.D.	N.D.	N.D.	N.D.	N.D.
PAHs ($\mu g\, L^{-1}$)						
Fluoranthene	0.01	0.01	0.01	0.01	N.D.	<LOQ
Fluorene	0.11	0.09	0.11	0.07	0.03	0.03
Phenanthrene + anthracene	0.04	0.03	0.05	0.03	0.03	0.03
Pyrene	0.01	0.01	0.01	0.01	0.01	0.01

Abbreviations: RBC: rotating biological contactor; MP: maturation pond; SSF: horizontal subsurface-flow constructed wetland; EA: extended aeration; UV: ultraviolet; AP: anaerobic pond.

[a] N.D.: not detected.

[b] LOQ: limit of quantification.

positive samples, the presence of compounds was taken into account in the quantification stage by subtracting the blank area. Only 23 out of the 204 evaluated compounds were detected including 11 nonpolar pesticides, 3 polar pesticides, 4 phenolic compounds, and 5 PAHs.

Table 5 shows the obtained results for nonpolar pesticides and it can be observed that the most detected pesticides in the aqueous phase were chlorfenvinphos, diazinon, and ethoprophos, whereas in SPM, 2-phenylphenol ($\log K_{ow}$ 2.9) and cyfluthrin ($\log K_{ow}$ 6.0) were the most frequently detected. In these cases, the removal of the SPM would imply that the final concentration of the compounds in treated water would have been significantly different, indicating the relevance of the analysis of both phases. In general, the obtained results are in accordance with those obtained for nonpolar pesticides in other reports [9,10,12,24,25], indicating that these compounds are usually found in WW but at low concentrations. Due to no legislation establishing maximum concentration levels of organic contaminants is set in WW, the results obtained were compared with the limits established in surface and drinking water. Considering EU legislation for surface water [26] concentrations above these maximum concentrations were only reported for chlorfenvinphos ($0.20\,\mu g/L > 0.1\,\mu g/L$) and isodrin ($0.05\,\mu g/L > 0.005\,\mu g/L$). In contrast, concentrations above the maximum established by the EPA in drinking water [27] were not reported. Finally, it is important to highlight that the ratios between the concentration found in SPM and water phase were similar to those shown in Table 3.

In Table 6, the concentrations determined for polar pesticides, phenolic compounds, and PAHs are shown. It is important to notice that SPM was not submitted to analysis of polar pesticides and phenolic compounds because according to the distribution study, these analytes are mainly found in the aqueous phase. On the contrary, for PAHs, SPM was simultaneously analyzed with the aqueous phase, using a single method. It must be indicated that herbicides such as diuron and transformation products of atrazine were the compounds most frequently found in the samples. Among PAHs, fluorene, pyrene, and the sum of phenanthrene and anthracene were detected in all the samples, fact that highlights the ubiquity of these compounds. Regarding phenolic compounds, 4-tertoctilphenol was the compound showing higher concentration. The obtained results were in accordance with those reported in the literature where it is demonstrated that the compounds found in this study are the most commonly detected in WW samples [8,10–12,28]. Concentrations of these compounds were always below the maximum established by both the EU in surface water [26] and the EPA in drinking water [27], except for 4-tertoctylphenol, which was found at concentrations slightly higher.

4. Conclusions

A distribution study of a variety of organic contaminants between the two phases composing treated WW samples, aqueous phase and SPM, has been carried out. Although the SPM is not usually analyzed, the study of the distribution between the aqueous phase and the SPM has revealed that for some contaminants it is necessary to analyze both phases to consider the total concentration in the sample and properly assess the possible effects of such pollutants on the environment. Thus, for the analysis of nonpolar pesticides and PAHs, both phases should be submitted to analysis due to these compounds are more prone to remain in the SPM. However, for polar pesticides and phenolic compounds, this analysis does not provide significant information because this type of compounds is mainly found in the aqueous phase. The same trend was observed for all the compounds despite of the type of treatment that WW had undergone. However, according to the chemical oxygen demand (COD) of the WWTPs effluents evaluated, colloidal phase should be significant. Thus, the description of the partitioning of the target compounds based not only on K_{ow} but also considering the colloidal phase should be object of further studies.

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Appendix

1. Chemicals and materials

Pesticide analytical standards were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany), as well as the isotopically labeled pesticides parathion ethyl-d_{10} and simazine-d_5, which were employed as internal standards (ISs) for nonpolar and polar pesticides, respectively.

A mix solution ($200\,\mathrm{mg\,L^{-1}}$) of 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), pyrene (PYR), and 2-bromonaphthalene (BrNPH) (purities $\geqslant 96.6\%$) in dichloromethane was provided by Supelco (Bellefonte, PA, USA). 5-Methylchrysene (MCHR) (99.6% purity), benzo[*j*]fluoranthene (BjFA) (98.6% purity), benzo[*k*]fluoranthene BkFA (99.5% purity), and fluoranthene-d_{10} (FA-d_{10}), which was used as IS, were also obtained from Supelco. Dibenzo[*a,e*]pyrene (DBaeP), dibenzo[*a,i*]pyrene (DBaiP), dibenzo[*a,h*] pyrene (DBahP), dibenzo[*a,l*]pyrene (DBalP), and cyclopenta[*c,d*]pyrene (CPcdP) (purities $\geqslant 99\%$) were obtained from Dr. Ehrenstorfer.

Phenolic compounds standards, 2-nitrophenol (2-NTP), 4-nitrophenol (4-NTP), 2,4-dimethylphenol (2,4-DMP), 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-diCP), 2,4,5-trichlorophenol (2,4,5-triCP), 2,4,6-trichlorophenol (2,4,6-triCP), and 4-n-nonylphenol (4-n-NP) were obtained from Fluka (Steinheim, Germany). On the other hand, 3-nitrophenol (3-NTP), 4-chloro-3-methylphenol (4-C-3-MP), 4-tertoctylphenol (4-tertOP), and pentachlorophenol (PCP) were supplied by Supelco. Purities were always > 97%. Isotopically labeled PCP ($[^{13}C_6]$-PCP) was used as IS and it was obtained from Dr. Ehrenstorfer.

Ethyl acetate (EtOAc), acetonitrile (ACN) and methanol (MeOH) were supplied by J.T. Baker (Deventer, Holland). Acetone was purchased from Fluka and dichloromethane (DCM) was obtained from Riedel-de Haën (Seelze, Germany). All organic solvents were of analytical grade. Ultrapure water was obtained from a Milli-Q Gradient water system (Millipore, Bedford, MA, USA). Formic acid (purity > 98%) and magnesium sulfate anhydrous ($MgSO_4$) were purchased from Panreac (Barcelona, Spain). Sodium chloride (NaCl) and hydrochloric acid (HCl, purity 37–38%) were obtained from J.T. Baker. Anhydride acetic acid (AAA) (purity 99.9%), and pyridine (Py) (purity 99.8%) were purchased from Sigma–Aldrich (Madrid, Spain).

For filtration stages, 47 mm glass microfibre filters from Whatman (Maidstone, England, UK) and 0.45 μm HNWP nylon membrane filters from Millipore (Carrigtwohill, County Cork, Ireland) were used.

For solid-phase extraction (SPE), C_{18} Sep-Pak cartridges (500 mg, 6 cc) as well as Oasis HLB (200 mg, 6 cc) cartridges, obtained from Waters (Milford, MA, USA), were employed. 30 mm cellulose filters (Whatman) and Hydromatrix (Varian) were used for pressurized liquid extraction (PLE).

2. Apparatus

Nonpolar pesticide, PAHs and phenolic compounds analyses were carried out using a GC system Varian 3800 (Varian Instruments, Sunnyvale, CA, USA) equipped with electronic flow control (EFC). Samples were injected into an SPI/1079 split/splitless programmed-temperature injector, utilizing the large volume injection (LVI) technique and 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 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). The carrier gas was helium (99.9999%) at a constant flow rate of 1 mL min^{-1}. The GC was interfaced to a 1200 L QqQ mass spectrometer (Varian Instruments) operating in electron ionization (EI) at 70 eV. Argon (99.999%) was used as collision gas. The mass spectrometer was calibrated every four days with perfluorotributylamine. Varian Workstation software was used for instrument control and data analysis.

Polar pesticide analyses were performed in an Acquity UPLC system using an Acquity UPLC BEH C_{18} column (100 mm × 2.1 mm), with a 1.7 μm particle size (both from Waters). Chromatographic separations were carried out using gradient elution with eluent A, being MeOH, and eluent B, consisting of an aqueous solution of formic acid (0.01%, v/v). MS analysis was carried out using a Waters Acquity TQD QqQ mass spectrometer (Waters, Manchester, UK). The instrument was operated using positive electrospray ionization (ESI+). Data acquisition was performed using MassLynx 4.0 and QuanLynx software (Waters).

The horizontal shaker used in the distribution study was obtained from P-Selecta (Selecta, Barcelona, Spain). PLE was performed using an ASE 100 Accelerated Solvent Extraction system (Dionex, Sunnyvale, CA, USA) equipped with 34 mL stainless steel extraction cells. A Reax-2 rotary agitator from Heidolph (Schwabach, Germany) was used for agitation of the derivatization mixture for phenolic compounds. An analytical balance AB204-S from Mettler Toledo (Greifensee, Switzerland) and a rotary evaporator R-114 (Büchi, Flawil, Switzerland) were also used.

3. Extraction procedures

Due to the difficulty of finding real blank WW samples, during the distribution study nonspiked WW samples were always used as ''blank'' samples in order to check possible looses or contamination of the analytes during the procedure. In positive samples, the presence of the compounds was taken into account in the quantification stage by subtracting the blank area.

3.1. Extraction of the aqueous phase by SPE for nonpolar pesticides

Filtered water samples (250 mL) were adjusted to pH 3.0 with 2 M HCl (all samples showed pH > 7), and 2.5 g of NaCl was added in order to adjust the conductivity to 50 mS. An organic modifier (MeOH) was added (1%, v/v) before performing the SPE procedure in order to avoid possible analyte adsorptions in the glass material. The C_{18} cartridges were previously conditioned with 3 mL of EtOAc, followed by 3 mL of MeOH, and 3 mL of ultrapure water without allowing the cartridges to dry out. Then, the WW samples were passed through the cartridges under vacuum at a flow rate of 10 mL min^{-1}. The cartridges were dried for 3 h and the pesticides were eluted with 5 mL of EtOAc. The extracts were evaporated with a vacuum rotary evaporator at 45°C, and the residues were redissolved adding 25 μL of parathion ethyl-d_{10} (500 μg L^{-1}) and EtOAc (final volume: 2 mL) before chromatographic analysis.

3.2. Extraction of the aqueous phase by SPE for polar pesticides

Conductivity and pH adjustments were performed to 250 mL of each filtered WW sample as described for the analysis of nonpolar pesticides. Depending on the type of WW effluent, two conditioning/elution conditions were utilized. Oasis HLB cartridges were conditioned with 5 mL of EtOAc (for MBR, EA, and MP effluents) or DCM (for AP samples) followed by 5 mL of MeOH and 5 mL of ultrapure water. The cartridges were dried for 3 h after passing the sample and the pesticides were eluted with 5 mL of MeOH, followed by 5 mL of EtOAc (MBR, EA, and MP) or DCM (AP). The extracts were evaporated with a vacuum rotary evaporator at 45°C, and the residues were redissolved adding 25 μL of simazine-d_5 (500 μg L^{-1}) and a mixture of MeOH/aqueous solution of formic acid 0.01% (50:50, v/v) to a final volume of 2 mL before chromatographic analysis.

3.3. Extraction of nonpolar pesticides from the SPM by PLE

The filters containing the SPM were dried and submitted to the PLE extraction. Briefly, a cellulose filter was placed at the bottom of a 34 mL stainless steel extraction cell. Filters with the SPM were cut into small pieces and placed into the cell mixed with Hydromatrix up to filling it. The extraction was performed using EtOAc:MeOH (3:1, *v/v*) under the PLE conditions described by Martínez-Vidal et al. [1] for the extraction of pesticides in agricultural soils. The extracts were then evaporated and redissolved as explained for the SPE samples.

3.4. Extraction of the aqueous phase by SPE for PAHs

The C_{18} cartridges were previously conditioned with 5 mL of ACN followed by 10 mL of ultrapure water without allowing the cartridges to dry out. Then, WW samples (100 mL WW + 30 mL ACN) were passed through the cartridges under vacuum at a flow rate of 10 mL/min. The glass material containing the samples was washed with 20 mL of a mixture of ACN/water (30:100, v/v), and the solution was subsequently passed through the cartridges. These were dried for 3 h and the elution was performed with 5 mL of *n*-hexane. All the extracts were evaporated with a vacuum rotary evaporator at 40°C and finally the residues were reconstituted adding 25 μL of fluoranthene-d_{10} (final concentration: 500 $\mu g L^{-1}$) and EtOAc to a final volume of 2 mL before chromatographic analysis.

3.5. Extraction of the aqueous phase by SPE for phenolic compounds

As the filtered WW effluents showed pH values between 7.7 and 8.3, then pH was adjusted to 2.5–2.7 with HCl (2 M) to ensure the protonated form of the phenolic compounds, facilitating the absorption into the solid phase, and an adequate preservation of the samples. The Oasis HLB cartridges were conditioned with 5 mL of acetone followed by 5 mL of MeOH and 3 × 5 mL of ultrapure water without allowing the cartridges to dry out. Then, the filtered WW sample (250 mL) was passed through the cartridges under vacuum at a flow rate of 10 mL min^{-1}. The cartridges were dried for 2 h and the phenolic compounds were eluted sequentially with 3 mL of acetone and 2 mL of DCM. The extracts were collected into 5 mL volumetric flasks, adjusting the total volume with DCM, without any evaporation step. Then, the derivatization stage was performed according to the procedure described by Padilla-Sánchez et al. [2]. Briefly, 860 μL of the extract was transferred to a 2 mL vial and 20 μL of [$^{13}C_6$]-PCP (IS), 20 μL of Py and 100 μL of AAA were added to carry out the derivatization reaction. The mixture was shaking in a rotary agitator for 2 min before chromatographic analysis.

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