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## Priority organic compounds in wastewater effluents from the Mediterranean and Atlantic basins of Andalusia (Spain)†

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A comprehensive survey of the occurrence of organic compounds in 30 wastewater (WW) effluent samples from 21 urban wastewater treatment plants (WWTPs) from both secondary and tertiary treatments was carried out in the Mediterranean and Atlantic basins of the Andalusia region (south of Spain). For each sample, a total of 226 compounds including pesticides and some transformation products, polycyclic aromatic hydrocarbons (PAHs), phenolic compounds and volatile organic compounds (VOCs) were monitored with the aim of evaluating their occurrence in urban WW effluents. Compounds belonging to each class were detected. Among pesticides, insecticides such as clorfenphos and diazinon as well as herbicides such as diuron, sebutylazine, terbutylazine and terbutylazine desethyl were the most frequently detected. The ubiquity of some compounds such as fluorene, phenanthrene and pyrene was also demonstrated. The compounds evaluated were detected at low concentrations (in general below  $1 \mu\text{g L}^{-1}$ ), except 4-*tert*-octylphenol, which was detected at extremely high concentrations (up to  $443 \mu\text{g L}^{-1}$ ). PAHs and VOCs were the compounds most frequently detected in the assayed samples, and they are the main sources of contamination in WWTPs, as well as some herbicides and transformation products.

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### Environmental impact

Andalusia (south of Spain) represents a semi-arid area with a large agricultural contribution. Bearing in mind the fast growing population and the expanding agricultural sector, looking for alternatives of fresh water resources is necessary. Treated wastewater is a valuable option to alleviate the water demand and therefore, an increasing percentage of irrigated areas are currently using this alternative source of water. However, effluent discharge is regarded as one of the most important sources of contamination in the environment and, as a consequence, the control of residues and contaminants in wastewater effluents, which are used for reutilization, has become one of the most important problems in the environmental field. In this paper, a characterization study of secondary and tertiary effluents from different areas of Andalusia is shown.

### Introduction

The most characteristic feature of the Andalusian climate (south of Spain) is hot and dry summers as well as warm and dry winters. Thus, the shortage of rainfall is quite widespread in this region. In spite of this, there is a large difference between

the Andalusian regions in terms of precipitation, which decreases from the West to the East, showing the uniqueness of having both one of the highest and the lowest rainfall readings of the country.<sup>1</sup> Therefore, Andalusia is a region with very different hydrographic need areas. The scarcity of natural water resources in arid and semiarid areas, as it is the case of the eastern of Andalusia, is causing the depletion and/or deterioration of groundwater resources.<sup>2</sup> In urban areas, the demand for water has been increasing steadily, owing to population growth, industrial development and expansion of irrigated peri-urban agriculture. Because of the increasing difficulties to provide new water resources, reusing reclaimed wastewater (WW) is emerging as an additional source of water.<sup>3</sup> Treated WW effluents can be utilized in industry, for urban uses and environmental water enhancement including groundwater recharge as well as in agriculture, which is a common practice

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in Mediterranean countries.<sup>4,5</sup> Particularly in Andalusia, WW reuse for agriculture represents the large reuse volume.

The presence of pesticide residues in several environmental compartments<sup>6,7</sup> as well as other kinds of organic contaminants, which are commonly found in WW samples, has been widely demonstrated by several studies carried out worldwide. For example, there are studies reporting the presence of emerging contaminants,<sup>8</sup> pharmaceuticals<sup>9</sup> and a wide range of priority pollutants<sup>10,11</sup> in both raw and secondary WW effluents. Taking into account both the high probability that these contaminants reach conventional WWTPs, which are not able to efficiently remove these micro-contaminants,<sup>3</sup> and the subsequent reuse of the treated effluents, WWs represent one of the main sources of environmental contamination.<sup>12</sup> Both the European Union (EU)<sup>13,14</sup> and the Environmental Protection Agency of the United States (EPA)<sup>15</sup> have established lists of priority pollutants, which have been used to select the compounds evaluated in this study, although there is no legislation regarding maximum contamination levels allowed in WW. However, there are maximum concentration levels legislated by the EU in surface water as environmental quality standards,<sup>16</sup> as well as by the EPA in drinking water.<sup>17</sup>

Although the presence of organic pollutants in raw urban WW as well as in treated effluent from municipal WWTPs is a widely studied issue,<sup>8,10–12</sup> the number of compounds simultaneously evaluated is not as extensive as in this survey, in which a comprehensive list of analytes (131 non-polar pesticides, 39 polar pesticides, 24 PAHs, 13 phenolic compounds and 19 VOCs) has been monitored in a high variety of WW effluents from very different areas.

The aim of this study was the evaluation of the occurrence of priority pollutants in WWTP effluents from different areas of Andalusia and, as a consequence, the evaluation of the effectiveness of different secondary and tertiary WW treatment technologies in relation to the removal of such priority organic contaminants. In this sense, PAHs, pesticides, phenolic compounds and VOCs were determined in WWTP effluents

from both secondary and tertiary treatments belonging to very different areas of Andalusia, and consequently the water quality of the studied WWTP effluents in relation to their possible reuse was also evaluated.

## Materials and methods

A brief summary of the compounds, reagents, solvents, instruments, apparatus and methods used for the different analyses (sample extraction, instrumental determination, *etc.*) is provided as ESI.†

### Sample collection

WW effluent samples were obtained from 21 WWTPs distributed throughout the south of Spain (Andalusia region), during the spring period of 2011, showing the sampled points in Fig. 1. In two cases, WWTP6 and WWTP21, several effluent samples were taken from the same WWTP. Hence, from WWTP6 two effluent samples were taken whereas from WWTP21 nine effluents were selected. Thus, a total of 30 WWTP effluent samples were analyzed. The characteristics of the investigated WWTPs and the corresponding effluents are shown in Table 1. WWTP21 is an experimental plant belonging to the Foundation Centre for New Water Technologies (“Centro de las Nuevas Tecnologías del Agua”, CENTA), which is located in Seville, Spain. This WWTP has an area of 41 000 m<sup>2</sup> and it currently holds more than 20 systems with different technologies. The particularity of this WWTP lies in the fact that only one influent enters in the plant, which is divided into different systems. Therefore, the same influent is treated with different technologies, originating as many effluents as technologies applied. Nine of these effluents showing very different characteristics have been selected in this study.

The 30 punctual WWTP effluent samples were collected using a manual sampler and only one sample was taken in each case. All WWTP samples were transferred to 2 L amber glass

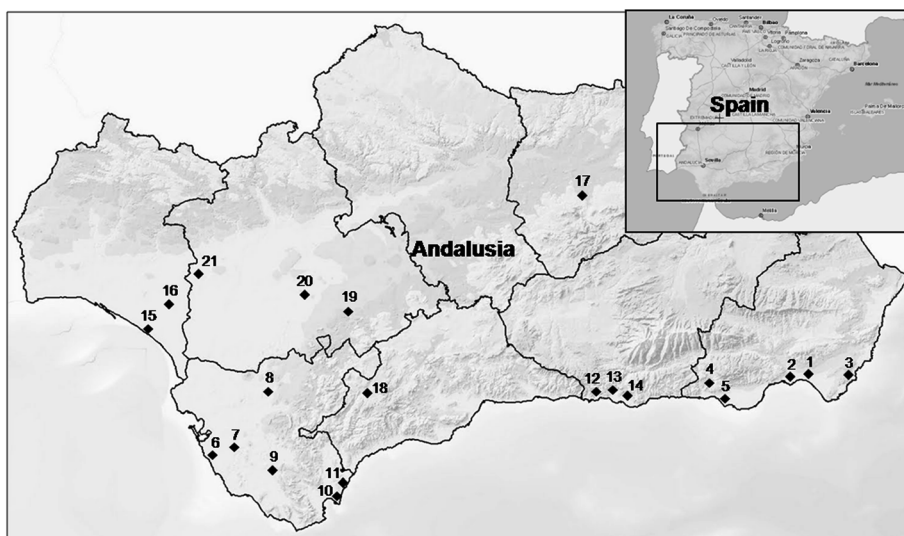


Fig. 1 Location of the WWTP effluents evaluated.

**Table 1** Characteristics of the 21 WWTPs investigated

WWTP	Effluent no.	Type of wastewater treated	Treatment	Maximum treatment level	Treated flow (m <sup>3</sup> per year)	Treated flow (PE)
WWTP1	1	Urban	Extended oxidation + sand filters + ozone + chloration	Tertiary	1 265 746	19 651
WWTP2	2	Urban	Activated sludge	Secondary	8 794 659	173 484
WWTP3	3	Urban	Lagooning	Secondary	127 413	1827
WWTP4	4	Urban	Extended aeration	Secondary	840 742	17 276
WWTP5	5	Urban	Extended aeration	Secondary	514 532	9985
WWTP6	6a	Urban	Activated sludge	Secondary	2 617 710	35 740
	6b	Urban	Physicochemical + biofilters	Secondary	2 617 710	35 740
WWTP7	7	Urban	Activated sludge	Secondary	3 735 826	61 752
WWTP8	8	Urban	Activated sludge + material filters + UV	Tertiary	2 289 223	41 812
WWTP9	9	Urban	Extended aeration + material filters + UV	Secondary	885 439	13 383
WWTP10	10	Urban	Activated sludge	Secondary	3 677 610	40 471
WWTP11	11	Urban	Extended aeration + physicochemical + decantation + sand filters + UV	Tertiary	267 320	2051
WWTP12	12	Urban	Extended aeration	Secondary	640 428	8042
WWTP13	13	Urban	Extended aeration	Secondary	1 826 441	39 865
WWTP14	14	Urban	Activated sludge	Secondary	5 604 883	78 315
WWTP15	15	Urban	First and second step physicochemical + ultra filtration	Tertiary	1 213 846	13 358
WWTP16	16	Urban	Extended aeration + phosphorus removal iron salt	Secondary	535 359	9240
WWTP17	17	Urban	Activated sludge	Secondary	8 284 997	219 420
WWTP18	18	Urban	Activated sludge	Secondary	2 770 371	79 822
WWTP19	19	Urban	Extended aeration	Secondary	503 643	6301
WWTP20	20	Urban	Extended aeration	Secondary	1 058 237	11 452
WWTP21	21a	Urban	Vertical subsurface-flow constructed wetland	Secondary	103 985	1527
	21b	Urban	Horizontal subsurface-flow constructed wetland	Secondary	103 985	1527
	21c	Urban	Vertical subsurface-flow constructed wetland	Secondary	103 985	1527
	21d	Urban	Free water surface constructed wetland	Secondary	103 985	1527
	21e	Urban	Horizontal subsurface-flow constructed wetland	Secondary	103 985	1527
	21f	Urban	Horizontal subsurface-flow constructed wetland with <i>Phragmites australis</i>	Secondary	103 985	1527
	21g	Urban	Extended aeration + sand filters + UV	Tertiary	103 985	1527
	21h	Urban	Intensive green filter	Secondary	103 985	1527
	21i	Urban	Maturation pond	Secondary	103 985	1527

bottles, which were filled up to the top to prevent that some analysis could be affected by aeration (e.g. analysis of VOCs). The samples were stored at 4 °C until extraction.

### Analytical methods

The analytical methods employed for the measurement of non-polar and polar pesticides,<sup>18</sup> PAHs,<sup>19</sup> phenolic compounds<sup>20</sup> and VOCs<sup>21</sup> in WW samples were previously developed in our research group. A list of the target compounds with the legislation involved is described in Table S-1,<sup>†</sup> while a summary of the aforementioned methods is shown in Table S-2 (both provided as ESI<sup>†</sup>).

### Data treatment

Univariate descriptive statistics (minimum, maximum, mean, median, standard deviation (SD) and frequency of detection (FD)) of each variable were calculated. Furthermore, correlation

between variables was performed using Spearman coefficients in order to check relationships between the analytes included in this study.

Then, multivariate analysis was carried out applying unsupervised methods such as cluster analysis and principal component analysis (PCA). For that, values below the detection limit (LOD) were assumed to be equal to half the LOD, whereas values below the quantification limit (LOQ) were assumed to be equal to half the LOQ. Autoscaling was used to pretreat all the data before multivariate analysis.

Statistical analyses were carried out with IBM SPSS Statistic for Windows version 19 (SPSS Inc. IL, USA).

## Results and discussion

FDs, SDs, average, median, minimum and maximum values were estimated for each detected pollutant and a summary of the data is shown in Table 2. The main conclusions obtained

**Table 2** Summary statistics for the detected compounds in the 30 WWTP effluents evaluated, and normative involved<sup>f</sup>

Class	Compound name	Concentration ( $\mu\text{g L}^{-1}$ )					Directive 2008/105/EC (surface water)		Directive 2008/105/EC (drinking water)		
		FD (%)	SD	Average	Median	Min	Max	MAC-EQS <sup>d</sup> ( $\mu\text{g L}^{-1}$ )	AA-EQS <sup>e</sup> ( $\mu\text{g L}^{-1}$ )	MCL <sup>f</sup> ( $\mu\text{g L}^{-1}$ )	
Non-polar pesticides <sup>a</sup>	<b>2-Phenylphenol<sup>f</sup></b>	53	2.02	0.73	0.19	0.08	8.26	Not included	Not included	Not included	
	<b>Chlorfenvinphos</b>	73	0.23	0.14	0.09	0.03	0.96	0.3	0.1	Not included	
	<b>Cyproconazole</b>	23	0.02	0.06	0.06	0.03	0.09	Not included	Not included	Not included	
	Cyprodinil	3	—	0.09	0.09	0.09	0.09	Not included	Not included	Not included	
	<b>Diazinon</b>	60	2.19	0.80	0.10	0.04	8.63	Not included	Not included	Not included	
	Dimethomorph	10	—	0.66	0.66	0.66	0.66	Not included	Not included	Not included	
	Endosulfan lactone	7	—	0.08	0.08	0.08	0.08	Not included	Not included	Not included	
	<b>Ethoprophos</b>	50	0.01	0.03	0.03	0.01	0.07	Not included	Not included	Not included	
	Fludoxonil	13	0.25	0.26	0.34	0.08	0.43	Not included	Not included	Not included	
	Isodrin	17	0.05	0.09	0.09	0.04	0.17	Not applicable	$\Sigma = 0.005$	Not included	
	<b>Penconazole</b>	20	0.10	0.20	0.21	0.11	0.32	Not included	Not included	Not included	
	Permethrin	3	—	0.03	0.03	0.03	0.03	Not included	Not included	Not included	
	Terbutryn	3	—	—	—	<LOQ	<LOQ	Not included	Not included	Not included	
	Atrazine desisopropyl	3	—	0.01	0.01	0.01	0.01	Not included	Not included	Not included	
	Polar pesticides <sup>b</sup>	<b>Diuron</b>	73	0.41	0.32	0.19	0.04	1.67	1.8	0.2	Not included
		Isoproturon	7	—	0.05	0.05	0.05	0.05	1.0	0.3	Not included
		Linuron	3	—	—	—	<LOQ	<LOQ	Not included	Not included	Not included
Metribuzin		3	—	—	—	<LOQ	<LOQ	Not included	Not included	Not included	
Propyzamide		3	—	—	—	<LOQ	<LOQ	Not included	Not included	Not included	
<b>Sebutylazine + terbuthylazine</b>		73	0.07	0.07	0.06	0.01	0.19	Not included	Not included	Not included	
Terbutmeton		13	—	—	—	<LOQ	<LOQ	Not included	Not included	Not included	
<b>Terbuthylazine desethyl</b>		33	0.05	0.08	0.08	0.03	0.16	Not included	Not included	Not included	
Acenaphthene		3	—	—	—	<LOQ	<LOQ	Not included	Not included	Not included	
<b>Benzo[a]anthracene</b>		23	0.01	0.02	0.02	0.01	0.04	Not included	Not included	Not included	
PAHs <sup>c</sup>	Benzo[a]pyrene	3	—	0.10	0.10	0.10	0.10	0.1	0.05	0.2	
	<b>Benzo[b]fluoranthene</b>	33	0.00	0.01	0.01	0.01	0.01	Not applicable	$\Sigma = 0.03$	Not included	
	Benzo[g,h,i]perylene	17	0.01	0.02	0.02	0.01	0.02	Not applicable	$\Sigma = 0.002$	Not included	
	Benzo[j]fluoranthene	13	0.00	0.01	0.01	0.01	0.01	Not included	Not included	Not included	
	Benzo[k]fluoranthene	17	0.02	0.02	0.01	0.01	0.05	Not applicable	$\Sigma = 0.03$	Not included	
	<b>Chrysene</b>	43	0.01	0.01	0.01	0.01	0.04	Not included	Not included	Not included	
	<b>Fluorene</b>	90	0.01	0.02	0.02	0.01	0.06	1.0	0.1	Not included	
	Fluoranthene	100	0.17	0.10	0.05	0.03	0.80	Not included	Not included	Not included	
	Indeno[1,2,3- <i>cd</i> ]pyrene	7	0.00	0.02	0.03	0.02	0.03	Not applicable	$\Sigma = 0.002$	Not included	
	Naphthalene	3	—	1.20	1.20	1.20	1.20	Not applicable	1.2	Not included	
<b>Phenanthrene + anthracene</b>	100	0.07	0.06	0.05	0.02	0.44	0.4 <sup>g</sup>	0.1 <sup>g</sup>	Not included		
Phenolic compounds <sup>b</sup>	<b>Pyrene</b>	100	0.01	0.02	0.02	0.01	0.05	Not included	Not included	Not included	
	<b>2,4,5-Trichlorophenol</b>	27	0.07	0.15	0.13	0.08	0.28	Not included	Not included	Not included	
	<b>2,4,6-Trichlorophenol</b>	33	0.03	0.15	0.14	0.12	0.22	Not included	Not included	Not included	
	<b>4-tert-Octylphenol</b>	100	100.74	37.70	0.17	0.07	443.23	Not applicable	0.01	Not included	

Table 2 (Contd.)

Class	Compound name	Concentration ( $\mu\text{g L}^{-1}$ )						FD (%)	SD	Directive 2008/105/EC (surface water)			Directive 2008/105/EC (drinking water)	US-EPA (drinking water)
		Average	Median	Min	Max	MAC-EQS <sup>d</sup> ( $\mu\text{g L}^{-1}$ )	AA-EQS <sup>e</sup> ( $\mu\text{g L}^{-1}$ )			MCL <sup>f</sup> ( $\mu\text{g L}^{-1}$ )				
VOCs <sup>g</sup>	<b>Pentachlorophenol</b>						20	0.07	0.06	0.04	0.21	0.4	1.0	1.0
	1,2,3-Trichlorobenzene						10	0.00	0.28	0.28	0.28	Not applicable	0.4	Not included
	1,2,4-Trichlorobenzene						27	—	—	<LOQ	<LOQ	Not applicable	0.4	70
	1,2-Dichloroethane						10	—	—	<LOQ	<LOQ	Not applicable	10.0	5.0
	1,3,5-Trichlorobenzene						3	—	—	<LOQ	<LOQ	Not applicable	0.4	Not included
	<b>Benzene</b>						40	0.05	0.13	0.12	0.30	50.0	8.0	5.0
	<b>Bromodichloromethane</b>						40	20.24	18.85	0.12	44.25	Not included	Not included	Not included
	<b>Bromoform</b>						37	34.35	12.55	0.19	70.79	Not included	Not included	Not included
	<b>Carbon tetrachloride</b>						27	0.02	0.14	0.13	0.17	Not applicable	12.0	5.0
	<b>Dibromochloromethane</b>						60	34.52	18.34	0.14	80.31	Not included	Not included	Not included
<b>Ethylbenzene</b>						30	0.18	0.14	0.11	0.53	Not included	Not included	700	
<b><i>m</i>-Xylene + <i>p</i>-xylene</b>						70	0.29	0.13	0.10	1.21	Not included	Not included	10 000 <sup>h</sup>	
<b><i>o</i>-Xylene</b>						43	0.21	0.14	0.12	0.80	Not included	Not included	10 000 <sup>h</sup>	
<b>Tetrachloroethene</b>						30	0.04	0.14	0.11	0.19	Not included	Not included	10 000 <sup>h</sup>	
<b>Toluene</b>						17	0.30	0.49	0.17	0.81	Not included	Not included	1000	

<sup>a</sup> Total concentration (aqueous phase + suspended particulate matter). <sup>b</sup> Concentration in the aqueous phase. <sup>c</sup> Compounds in bold were included in multivariate analysis. <sup>d</sup> Environmental quality standards (EQS) expressed as a maximum allowable concentration (MAC) established by Directive 2008/105/EC in surface water. <sup>e</sup> Environmental quality standards (EQS) expressed as an annual average (AA) value established by Directive 2008/105/EC in surface water. <sup>f</sup> Maximum contaminant level established by the US-EPA in drinking water. <sup>g</sup> Value established only for anthracene. <sup>h</sup> Value established for the total of xylenes. <sup>i</sup> Other abbreviations: FD: frequency of detection; LOQ: limit of quantification; Min: minimum concentration; Max: maximum concentration; SD: standard deviation; US-EPA: Environmental Protection Agency of the United States.



from these results are described below for each family of contaminants. Considering that there is no legislation establishing maximum concentration levels in WW, the levels reported in this study have been compared with the maximum concentration levels legislated by both the EU in surface water<sup>16</sup> and the EPA in drinking water,<sup>17</sup> which are also shown in Table 2.

### Pesticides

A wide range of pesticides has been evaluated. As it can be seen in Table S-1,† compounds considered as priority pollutants by the EU<sup>13</sup> and the EPA,<sup>15</sup> as well as compounds considered as persistent organic pollutants (POPs) by the United Nations (UN),<sup>22</sup> have been included in this study.

**Non-polar pesticides.** Bearing in mind the high number of non-polar pesticides analyzed in this study (131 compounds), only 13 compounds were detected, and only 4 of them had a FD equal or higher than 50% (Table 2), showing the obtained results for the different WWTPs in Table S-3.† The most frequently detected compound was chlorfenvinphos (FD = 73%) followed by diazinon (FD = 60%). The presence of these pesticides can be explained because they are insecticides widely used in several crops, such as fruit trees, citrus fruit, vines, olives, vegetables, rice and cotton,<sup>23</sup> cultivated in the studied area. In other studies, the presence of chlorfenvinphos in the water phase of constructed wetlands has been demonstrated, exceeding limit values established in drinking water.<sup>24</sup>

In general, non-polar pesticides were detected at concentrations below  $1 \mu\text{g L}^{-1}$ , although there are some exceptions such as 2-phenylphenol, which was detected in one of the effluents from CENTA (WWTP21f: horizontal subsurface-flow constructed wetland with *Phragmites australis*) at  $8.26 \mu\text{g L}^{-1}$ , and diazinon, which was detected at  $8.63 \mu\text{g L}^{-1}$  in WWTP8 (activated sludge + material filters + UV). However, it is necessary to consider that this was a punctual detection due to these compounds were detected in the other WW effluents at lower levels (below  $1 \mu\text{g L}^{-1}$ ), as it was observed for the rest of detected non-polar pesticides in this survey. Regarding 2-phenylphenol, it is necessary to highlight that it was only detected in the particulate matter. Thus, if this phase of the WW had been discarded during the analysis, and only the aqueous phase had been analyzed, an underestimation of the concentration of this compound in the effluents evaluated would have been reported.

In general, non-polar pesticides were detected at concentrations below the limits established by both the EU<sup>16</sup> (surface water) and the EPA<sup>17</sup> (drinking water), which were taken as a reference (see Table 2). Only chlorfenvinphos was detected in WWTP19 at a concentration above the maximum concentration set by the EU in surface water ( $0.96 \mu\text{g L}^{-1} > 0.3 \mu\text{g L}^{-1}$ ). However, it cannot be taken as a non-compliant result since there is no specific legislation for WWs.

Non-polar pesticides are commonly found in WWs, as it has been reported worldwide,<sup>6,7,12,24</sup> so the results obtained in this study are in accordance with those obtained in the literature.

**Polar pesticides.** Atrazine desisopropyl, diuron, isoproturon, linuron, metribuzin, propyzamide, sebuthylazine, terbuthylazine, terbumeton and terbuthylazine desethyl were the polar

pesticides detected in this study (Table 2). Among them, the most frequently detected compounds were herbicides as diuron (FD = 73%), the mixture of sebuthylazine and terbuthylazine (FD = 73%), and terbuthylazine desethyl (FD = 33%), a transformation product of terbuthylazine. In general, polar pesticides were detected at concentrations below  $0.2 \mu\text{g L}^{-1}$ , except diuron, which was detected at higher concentrations ( $1.0$  and  $1.6 \mu\text{g L}^{-1}$ ) in three of the effluents evaluated (Table S-4†). The results obtained for diuron were in agreement with those obtained in other studies,<sup>7,12,18</sup> highlighting the common presence of this pesticide in WWTP effluents. The occurrence of this compound in WW can be explained considering that it can be used as an antifouling paint biocide<sup>25</sup> and it is strongly associated with both urban and agricultural land use,<sup>26</sup> and therefore, it can be considered as a source of pollution in the aquatic environment. Furthermore, diuron is an herbicide used in many crops, including vines and olives,<sup>23</sup> which are typical Andalusian crops from both the center and the western areas. This compound was detected with an average concentration slightly above the annual average established by the EU in surface water<sup>16</sup> ( $0.32 \mu\text{g L}^{-1} > 0.20 \mu\text{g L}^{-1}$ ). This result is in agreement with that obtained by Muñoz *et al.*,<sup>27</sup> who evaluated the effluents of two WWTPs from the north and south of Spain and diuron was detected at average concentrations lower than  $0.45 \mu\text{g L}^{-1}$ .

Concerning the rest of detected polar pesticides, atrazine desisopropyl was only found in one effluent at  $0.01 \mu\text{g L}^{-1}$  whereas isoproturon, linuron, metribuzin, propyzamide and terbumeton were always detected at trace levels (below the LOQ).

### PAHs

Table S-1† shows the 24 PAHs analyzed in this study, including the 16 EPA PAHs<sup>15</sup> as well as PAHs legislated by the EU.<sup>13</sup> A summary of the obtained results is shown in Table 2. As it can be observed, these compounds were detected at low concentrations (below  $0.1 \mu\text{g L}^{-1}$ ) except fluorene, which was detected in two effluents at  $0.80$  and  $0.62 \mu\text{g L}^{-1}$  (WWTP21e and WWTP3, respectively) and naphthalene, which was detected only in WWTP3 at  $1.20 \mu\text{g L}^{-1}$  (Table S-5†). All the compounds were detected below the maximum concentration level set by the EU and EPA in surface water<sup>16</sup> and drinking water,<sup>17</sup> respectively (see Table 2). Only the average concentration for benzo[*a*]pyrene ( $0.1 \mu\text{g L}^{-1}$ ) and the mixture of benzo[*g,h,i*]perylene and indeno[1,2,3-*cd*]pyrene ( $\Sigma = 0.04 \mu\text{g L}^{-1}$ ) exceeded the annual average set by EU legislation for surface waters ( $0.05 \mu\text{g L}^{-1}$  and  $\Sigma = 0.002 \mu\text{g L}^{-1}$ , respectively).

Although the concentrations for the majority of the detected compounds were almost negligible, fluorene, the mixture of phenanthrene + anthracene and pyrene were detected in all the effluents evaluated, and fluoranthene was detected with a FD of 90%, indicating the ubiquity of these contaminants. In general, regarding the occurrence of PAHs in WWTP effluents, the presence of these compounds is very common as it has been demonstrated by different studies.<sup>10,12,19</sup>

## Phenolic compounds

Phenolic compounds belonging to different families such as chlorophenols, alkylphenols, nitrophenols and cresols (Table S-1†) were evaluated and the results are shown in Table 2. Only 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol and 4-*tert*-octylphenol were detected in the analyzed samples, although 2,4,5-trichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol were always detected at concentrations below  $0.2 \mu\text{g L}^{-1}$  with a FD lower than 30%. However, in this study it is necessary to highlight the results obtained for 4-*tert*-octylphenol, which was detected in all the evaluated effluents at higher concentration levels than the other phenolic compounds. Particularly, it was detected at extremely high concentrations (between  $73.45$  and  $443.23 \mu\text{g L}^{-1}$ ) in five of the evaluated effluents, as it is shown in Table S-6.† This compound is widely detected in WW effluents either at lower concentrations ( $0.27 \mu\text{g L}^{-1}$ ,<sup>8</sup>  $0.62 \mu\text{g L}^{-1}$ ,<sup>10</sup>  $0.16 \mu\text{g L}^{-1}$  (ref. 20)) or at higher concentrations than those reported in this survey ( $2.4 \text{ mg L}^{-1}$  (ref. 12)). Concerning the presence of this compound, it can be attributed to alkylphenol ethoxylates, which are anionic surfactants used in detergents, industrial cleaners, and emulsifiers. Moreover alkylphenols can also be used in some pesticides formulations.<sup>28</sup>

## VOCs

A list of the target compounds analyzed in this study as well as the normative involved is shown in Table S-1.† Due to their ubiquitous character, the presence of these compounds in WW effluents was expected (Tables 2 and S-7†). The most frequently detected VOCs were dibromochloromethane and the sum of *m*-xylene and *p*-xylene, which showed a FD of 60% and 70%, respectively, although the xylenes were detected at relatively low concentrations (between  $0.10$  and  $1.21 \mu\text{g L}^{-1}$ ). These levels were similar to those previously reported in other studies.<sup>12,29</sup> The presence of isomeric xylenes is very common due to their presence in numerous products including paints, solvents, fuels, and in agricultural chemicals production and chemical intermediates.<sup>30</sup> It is important to notice the results obtained for bromodichloromethane, bromoform and dibromochloromethane, which were found at higher concentrations (up to  $80.3 \mu\text{g L}^{-1}$ ) than the rest of detected VOCs in effluents from tertiary treatments such as extended oxidation + sand filters + ozone + chloration (WWTP1) and extended aeration + physico-chemical + decantation + sand filters + UV (WWTP11).

In spite of the results obtained, there was not any compound showing concentrations above those established by the EU in surface water<sup>16</sup> and the EPA in drinking water<sup>17</sup> (see Table 2).

## Occurrence of the evaluated compounds in the experimental WWTP (CENTA)

As it was aforementioned, one of the WWTPs evaluated (WWTP21) was the experimental plant belonging to the Foundation CENTA. This WWTP consists of a line with different treatments applied to the same influent so it allowed us to make a comparison between the removal efficiency of the different

technologies evaluated, considering that all of them must have the same initial concentration of the studied compounds. The obtained results are shown in Tables S-3–S-7.† In this sense, it was observed that non-polar pesticides were detected at similar concentrations in all the treatments evaluated, except for intensive green filter (effluent 21h), where these compounds were not detected. Furthermore, 2-phenylphenol was only detected in the particulate matter. The same trend was observed for polar pesticides, which were not detected or detected at very low concentrations (Table S-4†).

Concerning PAHs, it was observed that fluoranthene, fluorene, phenanthrene and pyrene were detected in almost all the effluents (ubiquitous compounds), detecting fluorene at higher concentrations (up to  $0.80 \mu\text{g L}^{-1}$ ). However, it is necessary to highlight that in two of the evaluated treatments, intensive green filter and maturation pond (effluents 21h and 21i respectively), the FD of these contaminants and the concentrations obtained were slightly lower than those observed for the other evaluated treatments (Table S-5†).

For phenolic compounds, the results observed were different. Thus, the treatments based on constructed wetlands (effluents 21a to 21f) as well as extended aeration + sand filters + UV (effluent 21g), which was the unique tertiary treatment, showed similar results, with low concentrations for the four detected compounds (Table S-6†). However, in intensive green filter and maturation pond (effluents 21h and 21i), only 4-*tert*-octylphenol was detected but at high concentrations (up to  $83.71 \mu\text{g L}^{-1}$ ), suggesting that intensive green filter and maturation pond presented poor removal efficiencies for 4-*tert*-octylphenol. Finally, the comparison of VOC concentrations showed similar results for the 9 effluents evaluated from the experimental plant. Nevertheless, a lower number of compounds were detected in the effluent from the maturation pond treatment, whereas for the isomeric xylenes, the higher concentrations were detected in the effluent from intensive green filter (Table S-7†).

Thus, in general, it can be concluded that intensive green filter is quite effective for the removal of the monitored contaminants, except for 4-*tert*-octylphenol. These results are a first approach and a more extensive study would be necessary bearing in mind that only a punctual sample could be analyzed, and thus it was not possible to carry out a prolonged study in time, which would provide more complete information.

## Correlation and multivariate analysis

In order to achieve a complete view of the obtained results, a correlation study and multivariate analysis (including cluster analysis and PCA) were carried out. For that purpose, 29 compounds (those detected in more than 20% of the samples with concentrations above the LOQ) were included in this statistical evaluation (Table 2).

First, the Spearman correlation coefficients were determined to check the relation between the compounds selected in this assay (Table S-8†). The highest coefficients (most strongly correlated pairs of variables) were found for PAHs such as pyrene, fluoranthene, chrysene, benzo[*b*]phenanthrene and

benz[*a*]anthracene. Furthermore, the pair sebuthylazine-terbutylazine (which are detected simultaneously in the analytical method) is correlated with terbutylazine desethyl, which is a transformation product of terbutylazine. High correlation can also be noted for some VOCs such as bromodichloromethane and dibromochloromethane with bromoform, as well as ethylbenzene with *o*-xylene. Finally, a strong correlation between compounds belonging to several families was also observed. These results can be explained considering that for instance, PAHs are ubiquitous compounds, and different compounds belonging to this family can be detected in the analyzed WWs. The same reason could be adduced for the correlation between some VOCs, whereas the correlation between cyproconazole and tetrachloroethene is not straightforward.

In a second step, multivariate analysis was performed applying unsupervised methods. Firstly, cluster analysis was used to search for natural grouping among samples, selecting hierarchical agglomerative, the squared Euclidean distance as similarity measurement and Ward's method as the amalgamation rule. The obtained dendrogram is shown in Fig. 2. Despite any clear distinction between the several WWTPs evaluated could be observed attending to the concentration of the analytes monitored or WW treatment, it must be noticed that 6 WWTPs belonging to CENTA form a group, whereas the other three WWTPs are classified in other groups. Furthermore, two WWTPs from the same municipality (WWTP6a and WWTP6b) belong to the same group, indicating that in spite of applying different treatments (activated sludge and physicochemical + biofilters, respectively), the effluents have similar

characteristics. Therefore, some grouping can be carried out attending to the characteristics of the municipalities where the WWTPs were located. Thus, coastal WWTPs are grouped at the top and the bottom of the dendrogram, whereas inland WWTPs are located between these two areas of the dendrogram. Although geographical and/or environmental conditions could also be interesting variables that could affect WWTPs grouping, in this study no relation between the groups and WWTP location was observed. The two groups of coastal WWTPs did not show any geographical similarity. Only the grouping of inland WWs was clear, suggesting a possible discrimination to coastal populations. However, further studies should be carried out in order to confirm this issue.

Secondly, PCA was also used considering that this is a projection method that reduces the dimensionality of the data matrix, retaining the most significant information. Varimax normalized rotation was carried out, and the 29 variables were reduced to 9 new variables (eigen values higher than 1), as it can be observed in Table S-9,† explaining more than 85% of the experimental variance. Fig. S-1† shows the loadings for the six main components, and it can be observed that PC1 explains the variability due to some PAHs (fluorene and the sum of phenanthrene and anthracene) and VOCs (ethylbenzene and xylenes), whereas other PAHs and 4-*tert*-octylphenol contribute to PC2. Then, VOCs mainly contribute to the variability of PC3 and PC4, whereas the most detected herbicides (terbutylazine desethyl and the mixture of sebuthylazine and terbutylazine) explain the variability in PC5, and 2-phenylphenol and cyproconazole (non-polar pesticides) explain the variability of PC6. Thus, PAHs and VOCs are the main sources of contamination in WWTPs, although some herbicides and non-polar pesticides are also relevant as well as 4-*tert*-octylphenol, which was detected at significantly high concentrations.

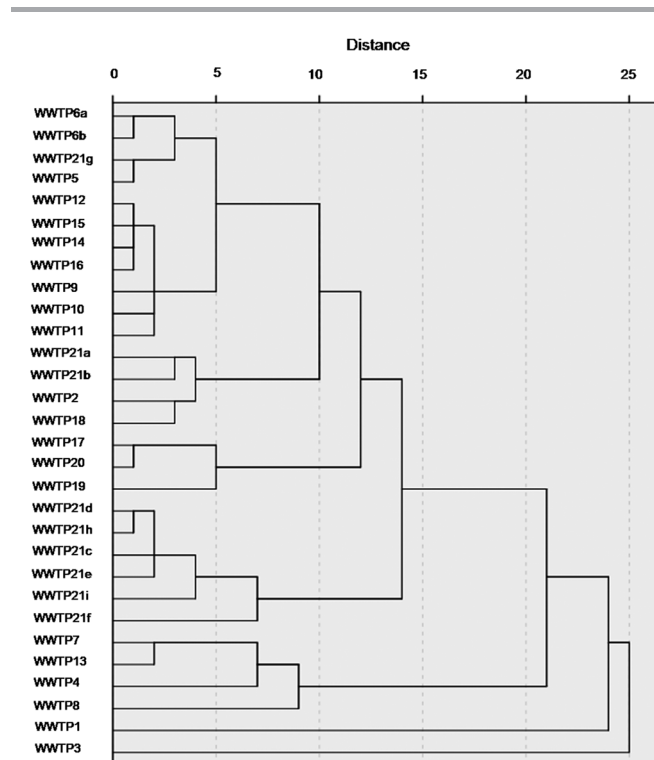


Fig. 2 Dendrogram constructed with Ward's method showing the results of cluster analysis.

### Risk assessment approach

The potential risks associated with the detected compounds in WWTP effluents were assessed by the estimation of the risk quotient (RQ), which was calculated following the strategy described by Carsten von der Ohe *et al.*<sup>31</sup> Thus, a comparison between maximum environmental concentrations (MEC) and predicted no-observed-effect concentration (PNEC) was performed. Median and maximum detected concentrations were used as MECs for the general case ( $RQ_m$ )<sup>32</sup> and the worst case ( $RQ_{ex}$ ), respectively. The following considerations were taken into account to estimate the potential risk of the detected compounds: (i) when  $RQ > 1$ , a high ecological risk is suspected, (ii) when  $0.1 < RQ < 1$ , medium risk can be considered and (iii) when  $RQ < 0.1$  it can be considered that there is no potential risk. It is necessary to highlight that this evaluation was only possible for those compounds with a reported PNEC. As it can be observed in Table 3, in the general case ( $RQ_m$ ), values higher than 1 were obtained for diazinon, isodrin, sebutylazine, benz[*a*]anthracene, benzo[*a*]pyrene, pyrene and 4-*tert*-octylphenol, indicating high risk of environmental threat. It can be noticed that when the worst case is considered (the maximum concentration detected was taking into account ( $RQ_{ex}$ )), together



**Table 3** Predicted no-effect concentrations (PNECs) and median and extreme risk quotients (RQ<sub>m</sub> and RQ<sub>ex</sub>) for the detected compounds<sup>d</sup>

Class	Compound name	PNEC ( $\mu\text{g L}^{-1}$ )	RQ <sub>m</sub>	RQ <sub>ex</sub>	
Non-polar pesticides	2-Phenylphenol	2.58 <sup>a</sup>	0.074	3.202	
	Chlorfenvinphos	0.1 <sup>b</sup>	0.900	9.600	
	Cyproconazole	NR			
	Cyprodinil	1.2 <sup>b</sup>	0.075	0.075	
	Diazinon	0.017 <sup>b</sup>	5.882	507.647	
	Dimethomorph	NR			
	Endosulfan lactone	NR			
	Ethoprophos	0.05 <sup>a</sup>	0.600	1.400	
	Fludioxonil	NR			
	Isodrin	0.01 <sup>a</sup>	9.000	17.000	
	Penconazole	NR			
	Permethrin	NR			
	Terbutryn	0.013 <sup>b</sup>	NE	NE	
	Polar pesticides	Atrazine desisopropyl	NR		
		Diuron	0.20 <sup>b</sup>	0.950	8.350
Isoproturon		0.30 <sup>b</sup>	0.167	0.167	
Linuron		1.0 <sup>b</sup>	NE	NE	
Metribuzin		0.0079 <sup>a</sup>	NE	NE	
Propyzamide		8.2 <sup>b</sup>	NE	NE	
Sebuthylazine		0.03 <sup>a</sup>	2.000	6.333	
Terbuthylazine		NR			
Terbumeton		NR			
Terbuthylazine desethyl		NR			
PAHs		Acenaphthene	3.8 <sup>b</sup>	NE	NE
		Benz[ <i>a</i> ]anthracene	0.012 <sup>b</sup>	1.667	3.333
		Benzo[ <i>a</i> ]pyrene	0.050 <sup>b</sup>	2.000	2.000
	Benzo[ <i>b</i> ]fluoranthene	0.030 <sup>b</sup>	0.333	0.333	
	Benzo[ <i>g,h,i</i> ]perylene	NR			
	Benzo[ <i>j</i> ]fluoranthene	NR			
	Benzo[ <i>k</i> ]fluoranthene	0.030 <sup>b</sup>	0.333	1.667	
	Chrysene	0.070 <sup>c</sup>	0.143	0.571	
	Fluoranthene	0.1 <sup>b</sup>	0.200	0.600	
	Fluorene	2.5 <sup>a</sup>	0.020	0.320	
	Indeno[1,2,3- <i>cd</i> ]pyrene	NR			
	Naphthalene	2.4 <sup>b</sup>	0.500	0.500	
	Phenanthrene	1.3 <sup>b</sup>	0.038	0.338	
	Anthracene	0.1 <sup>b</sup>	0.500	4.400	
Pyrene	0.0046 <sup>c</sup>	4.348	10.870		
Phenolic compounds	2,4,5-Trichlorophenol	0.60 <sup>c</sup>	0.217	0.467	
	2,4,6-Trichlorophenol	NR			
	4- <i>tert</i> -Octylphenol	0.1 <sup>b</sup>	1.700	4432.300	
	Pentachlorophenol	0.4 <sup>b</sup>	0.150	0.525	
VOCs	1,2,3-Trichlorobenzene	4.0 <sup>b</sup>	0.070	0.070	
	1,2,4-Trichlorobenzene	4.0 <sup>b</sup>	NE	NE	
	1,2-Dichloroethane	10 <sup>b</sup>	NE	NE	
	1,3,5-Trichlorobenzene	4.0 <sup>b</sup>	NE	NE	
	Benzene	10 <sup>a</sup>	0.013	0.030	
	Bromodichloromethane	58 <sup>a</sup>	0.325	0.763	
	Bromoform	47 <sup>a</sup>	0.267	1.506	
	Carbon tetrachloride	12 <sup>b</sup>	0.012	0.014	
	Dibromochloromethane	NR			
	Ethylbenzene	100 <sup>b</sup>	0.001	0.005	
	<i>m</i> -Xylene + <i>p</i> -xylene	1.0 <sup>c</sup>	0.130	1.210	
<i>o</i> -Xylene	1.0 <sup>c</sup>	0.140	0.800		
Tetrachloroethene	10 <sup>b</sup>	0.014	0.019		
Toluene	74 <sup>b</sup>	0.007	0.011		

<sup>a</sup> Provisional PNEC (P-PNEC). <sup>b</sup> Chronic-based PNEC (PNEC<sub>chronic</sub>). <sup>c</sup> Acute-based PNEC (PNEC<sub>acute</sub>). <sup>d</sup> Other abbreviations: NE: not estimated because the concentrations found were below the limit of quantification; NR: not reported.

with the aforementioned compounds, chlorfenvinphos, ethoprophos, diuron, benzo[*k*]fluoranthene, anthracene, bromoform and the sum of *m*-xylene and *p*-xylene indicate also a high risk. In the case of 4-*tert*-octylphenol and diuron, the high values of RQ are mainly due to a combination of high MEC and low PNEC values.

Finally, it must be mentioned that the environmental risk developed in this work was based on the toxicity of single compounds, without considering synergistic effects.

## Conclusions

The occurrence of organic priority compounds (pesticides, PAHs, phenolic compounds and VOCs) in effluents from WWTPs in Andalusia was studied as well as the effectiveness of different extensive and intensive technologies in WWTPs in relation to the removal of such priority organic pollutants. In general a small number of non-polar pesticides was detected at concentrations below  $1.0 \mu\text{g L}^{-1}$ , except 2-phenylphenol, which was detected in one of the effluents at  $8.26 \mu\text{g L}^{-1}$  and diazinon which was detected at  $8.63 \mu\text{g L}^{-1}$ . Among polar pesticides, herbicides were the most detected (diuron, the mixture of sebuthylazine and terbuthylazine and terbuthylazine desethyl). 13 PAHs were also detected, in general at concentrations below  $0.1 \mu\text{g L}^{-1}$ , and fluorene, phenanthrene, pyrene and fluoranthene were ubiquitous, due to their presence in all the studied effluents. 4-*tert*-Octylphenol was detected at higher concentrations, and it was found in all the effluents at concentrations ranging from 0.07 to  $443.23 \mu\text{g L}^{-1}$ . Finally, VOCs were also detected at relatively low concentrations except bromodichloromethane, bromoform and dibromochloromethane, which were detected at higher levels. The most detected compounds were dibromochloromethane and the sum of *m*-xylene and *p*-xylene.

The results obtained in this study were not significantly different to those reported in the literature, except for 4-*tert*-octylphenol, which was detected at extremely high levels. The occurrence of residues and contaminants suggested that WWTPs could be efficient enough to treat WW, but apparently they are not designed for the specific removal of this kind of compound. Therefore, there is still a release of pollutants of potential high toxicity to the environment, which might cause long-term effects to the ecosystem, although in general, the studied compounds were detected at low concentration levels. Moreover, some pesticides were found only in the SPM, which highlights the need to analyze this WW phase.

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