

# Comprehensive monitoring of organic micro-pollutants in surface and groundwater in the surrounding of a solid-waste treatment plant of Castellón, Spain

Elena Pitarch<sup>1</sup>, María Inés Cervera<sup>1</sup>, Tania Portolés<sup>1</sup>, María Ibáñez<sup>1</sup>, Mercedes Barreda<sup>1</sup>, Arianna Renau-Pruñonosa<sup>1</sup>, Ignacio Morell<sup>1</sup>, Francisco López<sup>1</sup>, Fernando Albarrán<sup>2</sup>, Félix Hernández<sup>1\*</sup>

<sup>1</sup>*Research Institute for Pesticides and Water, University Jaume I, Avda. Sos Baynat, E-12071 Castellón, Spain. Tel. +34 964387366. Fax +34 964387368*

<sup>2</sup>*RECIPLASA, Reciclados de Residuos La Plana, S.A., E-12200 Onda, Castellón, Spain*

\*Corresponding author: [felix.hernandez@uji.es](mailto:felix.hernandez@uji.es)

## Highlights

Evaluation of the impact of a solid waste treatment plant on the surrounding water  
Screening of around 1,500 organic contaminants in surface and groundwater  
Complementary use of LC-QTOF MS and GC-(Q)TOF MS  
Quantitation of target contaminants by LC-MS/MS QqQ

## **ABSTRACT**

The solid-waste treatment plant of RECIPLASA is located in the municipality of Onda (Castellón province), which is an important agricultural area of Spain, with predominance of citrus crops. In this plant, all urban solid wastes from the town of Castellón (around 200.000 inhabitants) and other smaller towns as Almassora, Benicàssim, Betxí, Borriana, L'Alcora, Onda and Vila-Real are treated. In order to evaluate the potential impact of this plant on the surrounding water, both surface and groundwater, a comprehensive monitoring of organic pollutants has been carried out along 2011, 2012 and 2013. To this aim, an advanced analytical strategy was applied for wide-scope screening, consisting on the complementary use of liquid chromatography (LC) and gas chromatography (GC) coupled to mass spectrometry (MS) with quadrupole (Q)-time of flight analyser (TOF). A generic solid-phase extraction with Oasis HLB cartridges was applied prior to the chromatographic analysis. The screening included more than 1,500 organic pollutants as target compounds, such as pesticides, pharmaceuticals, veterinary drugs, drugs of abuse, UV-filters, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), among others. Pesticides, mainly herbicides, were the compounds more frequently detected. Other compounds as antioxidants, cosmetics, drugs of abuse, PAHs, pharmaceuticals and UV filters, were also identified in the screening though at much lower frequency.

Once the screening was made, quantitative analysis focused on the compounds more frequently detected was subsequently applied using LC coupled to tandem MS with triple quadrupole analyzer. In this way, up to 24 pesticides and transformation products (TPs), 7 pharmaceuticals, one drug of abuse and its metabolite could be quantified at sub-ppb concentrations. Along the three years of study, ten compounds were found at

concentrations higher than 0.1 µg/L. Most of them were pesticides and TPs, a fact that illustrates that the main source of pollution seems to be the agricultural activities in this area.

**Key words**

Organic pollutants, screening of ground and surface water, solid-waste treatment plant, QTOF MS, LC-MS/MS, pesticides

## 1. INTRODUCTION

Nowadays, a large number of organic micro-contaminants of very different chemical families and diverse physico-chemical characteristics can be found in the environment. Some of them are “classical” organic pollutants, as pesticides, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), while others can be classified into the wide group named emerging contaminants as, for example, personal care products, pharmaceuticals, veterinary drugs, drugs of abuse, UV-filters, contrast agents for X-Ray, or polybrominated diphenyl ethers (PBDEs), as well as a huge number of transformation products (TP), which in many cases are still unknown (Moschet et al., 2014; Postigo and Barceló, 2015; Thomaidi et al., 2015). They can enter into the surface and groundwater from different pollution sources. Waste-water treatment plants (WWTPs) and solid-waste treatment plants (SWTPs) are between the potential sources of pollution as they treat large amount of wastes that commonly contain many organic pollutants (Bijlsma et al., 2012; Bijlsma et al., 2014; Du et al., 2014; García et al., 2013; Huerta et al., 2015; Ibáñez et al., 2013). There is a need to perform reliable research on the large variety of organic compounds that can be present on treated water (e.g. in WWTPs) and on the surrounding water of SWTPs in order to protect water quality and avoid consumption or usage of contaminated water that can cause health problems (Directive 2013/39/EU). In addition, emerging contaminants can be a potential risk to the environment and for human health safety, but they are not currently covered by water-quality regulations (Bletsou et al., 2015).

Monitoring organic compounds that may be present in environmental water (commonly at very low concentrations, i.e. sub- $\mu\text{g/L}$  levels) relies on the use of advanced analytical methodology, able to detect, identify and quantify these compounds (Richardson, 2012; Richardson, 2014). To this aim, the hybridation of chromatography (both liquid chromatography (LC) and gas chromatography (GC)) to mass spectrometry (MS) is

needed. Thus, LC coupled to tandem mass spectrometry (MS/MS) is commonly used for determination of polar, non-volatile, analytes in aquatic environments (Gilart et al., 2012; Gracia-Lor et al., 2010; Gros et al., 2006; López-Serna et al., 2010; Marín et al., 2009), while GC-MS/MS is highly appropriate for determination of non-polar and volatile contaminants (Hernández et al., 2013; Martínez-Moral and Tena, 2014; Pitarch et al., 2007; Zhang et al., 2015). However, using target quantitative methods in environmental analysis is not sufficient as only a limited number of analytes are included. The analyte-specific information acquired in LC-MS/MS methods implies that other compounds present in the sample are ignored, without the possibility of investigating other contaminants within the same injection. To have a more realistic overview of the water pollution it is necessary to apply wide-scope screening methods based on high resolution mass spectrometry (HRMS) able to detect and identify a large list of contaminants (Agüera and Martínez-Bueno, 2013; Hernández et al., 2015a; Leendert et al., 2015). The main advantage of HRMS comes from the acquisition of accurate-mass full-spectra data with reasonable sensitivity, which makes possible to investigate an unlimited number of compounds with the possibility to perform a retrospective analysis of data acquired at any time without additional sample analysis (Agüera and Martínez-Bueno, 2013; Hernández et al., 2007; Ibáñez et al., 2008). Time-of-flight (TOF) and Orbitrap analyzers have been used for LC-HRMS screening of compounds such as drugs of abuse, pharmaceuticals, pesticides and their TPs (Leendert et al., 2015; Ibáñez et al., 2008) in waters. Multiclass screening methods based on GC-TOF MS have been also applied for the investigation of persistent organic pollutants (POPs) (Plaza-Bolaños et al., 2013; van Leeuwen and de Boer, 2008) and other non-polar organic contaminants including several pesticides, PAHs, and octyl/nonyl phenols (Portolés et al., 2011; Portolés et al., 2014). The combined use of LC and GC, both coupled to HRMS, is nowadays the most powerful strategy to investigate large number

of contaminants with different polarities and volatilities. This approach has been presented as the closest to the “universal” screening pursued in environmental analytical chemistry (Hernández et al., 2015a; Pitarch et al., 2010).

In order to have an appropriate evaluation of the water quality in relation to the presence of organic contaminants, not only a qualitative screening (i.e. detection and identification) is required, but also to determine the concentration levels of the most relevant compounds, i.e. a quantitative analysis. To this aim, strategies that combine HRMS-based screening and LC-MS/(MS) (Pitarch et al., 2010; Chen et al., 2014) or GC-MS/(MS) quantitative analysis (Guibal et al., 2015; Masiá et al., 2014; Pitarch et al., 2010; Vergeynst et al., 2014) are the most suited.

The objective of this work was to perform a comprehensive research on the presence of a large number of organic micro-pollutants in surface and groundwater samples in order to evaluate the potential impact of a SWTP on the surrounding areas. Several water samples were collected from sampling points close to the SWTP along 3 years (in total, 5 monitoring campaigns). An analytical strategy based on the complementary use of LC-QTOF MS and GC-(Q)TOF MS was applied for wide-scope screening (around 1,500 compounds). Additionally, all samples were also analyzed by LC-MS/MS with triple quadrupole for quantitative determination of selected pesticides and TPs, drugs of abuse and pharmaceuticals.

## 2. EXPERIMENTAL

### 2.1 Reagents

See **Supplementary Information**

### 2.2 Hydrogeological description of the sampling area

In this work, water samples were collected in five campaigns between 2011 and 2013, along different periods: January 2011 (1<sup>st</sup> campaign), April 2012 (2<sup>nd</sup> campaign), December 2012 (3<sup>rd</sup> campaign), May 2013 (4<sup>th</sup> campaign) and December 2013 (5<sup>th</sup> campaign). 10 surface and 23 groundwater samples were in total collected from different locations in the environment of RECIPLASA, a SWTP sited in Onda (Castellón province, Spain). **Figure S1 (Supplementary Information)** shows an aerial map with the 9 sampling points, selected upstream and downstream of the flow direction of the Castellón aquifer.

The landfill site is located on low permeability material (clay and sandstone, Weald Facies-lower Cretaceous) and next to a large outcrop of cretaceous and jurassic limestone with high permeability due to karstic process. These materials form a part of the groundwater body called Onda-Espadán, which is recharging from the Castellón aquifer. The Castellón is another groundwater body of detrital nature (Plio-Quaternary aquifer) and great hydrogeological interest.

The sampling points corresponded to water from different origins. Samples collected from points 5 and 6 were surface water of the Mijares River, located around 1,600 m north-eastern of the SWTP. Upstream piezometer (point 1) and Reciplasa well (point 8) are located on low permeability material (Weald Facies) sited inside of the SWTP, located to 40 and 350 m, respectively, from the dumping/landfill body. Sabater I (point 3) and Sabater II (point 4) are pumping wells that pull out groundwater from the

cretaceous limestone about 1,000 m southern of the SWTP. Ntra. Sra Desamparados (point 2), San Martin de Porres (point 7) and El Salvador (point 9) are pumping wells, which pull out water from gravel aquifer and quaternary conglomerates of Castellón (Plio-Quaternary aquifer), over 2,000 m away from hypothetical polluting source.

The existence of hydraulic connection between the limestones (Cretaceous) and conglomerates (Plio-quaternary), as well as the preferred direction of groundwater flow (NNW-SSE), with an estimated hydraulic gradient of 1.25 ‰, gives a high degree of vulnerability to the aquifers studied.

## **2.3 GC-MS instrumentation**

### ***2.3.1 GC-(EI)TOF MS***

An Agilent 6890N GC system (Palo Alto, CA, USA) equipped with an Agilent 7683 autosampler coupled to a time-of-flight mass spectrometer, GCT (Waters Corp., Milford, MA, USA), operating in EI mode, was used for GC-(EI)TOF MS screening. For more details, see **Supplementary Information**.

### ***2.3.2 GC-(APCI)QTOF MS***

An Agilent 7890A GC system, equipped with an Agilent 7693 autosampler, coupled to a quadrupole time of flight MS, Xevo G2 QTOF (Waters Corp.) operating with APCI source was used for GC-(APCI)QTOF MS screening. For more details, see **Supplementary Information**.

## **2.4 LC-MS instrumentation**

### ***2.4.1 UHPLC-(ESI)QTOF MS***

Two systems were used for LC-QTOF MS screening of water samples:



- An ultra-performance Acquity liquid chromatography (UPLC<sup>TM</sup>) (Waters Corp.) interfaced to a QTOF Premier mass spectrometer (Waters Corp.), using an orthogonal Z-spray electrospray (ESI) interface.
- A Waters Acquity UPLC<sup>TM</sup> interfaced to a hybrid quadrupole-orthogonal acceleration-TOF mass spectrometer Xevo G2 QTOF (Waters Corp.), using an orthogonal Z-spray- electrospray (ESI) interface.

For additional details, see **Supplementary Information**.

#### **2.4.2 UHPLC-(ESI)QqQ MS/MS**

Two different triple quadrupole instruments (QqQ) operated in MS/MS mode were used:

- Waters Acquity UPLC<sup>TM</sup> (Waters Corp.), equipped with a quaternary pump system, interfaced to triple quadrupole mass spectrometer TQD<sup>TM</sup> with orthogonal (ESI) Z-spray (Waters Corp.).
- Waters Acquity UPLC<sup>TM</sup> (Waters Corp.), equipped with a binary pump system, interfaced to triple quadrupole mass spectrometer Xevo TQ-S<sup>TM</sup> (Waters Corp.) equipped with TWave devices and an orthogonal ESI source.

For further details, see **Supplementary Information**.

#### **2.5 Sample treatment**

Water samples collected were stored in darkness at <-18°C in polyethylene high-density bottles until analysis. All samples corresponding to the same campaign were analysed at the same time within a period of 60 days as maximum. Immediately before analysis, samples were thawed at room temperature.

Sample extraction and pre-concentration was made by solid-phase extraction (SPE). For TOF MS screening, 250 mL of centrifuged water samples were passed by gravity

through Oasis HLB (200 mg, Waters) cartridges, previously conditioned with 5 mL of methanol and 5 mL of HPLC-grade water. After drying under vacuum, the analytes were eluted with 10 mL of methanol. The extract was divided into 2 aliquots (5 mL each). The 5 mL aliquot for GC screening was evaporated under a gentle nitrogen stream at 35°C down to a volume of ca.1 mL. Then, 1 mL of ethyl acetate was added and evaporated again down to 250 µL (final volume). The pre-concentration factor along the sample procedure was 500. The 5 mL aliquot for LC-screening was evaporated to dryness under a gentle nitrogen stream at 35°C and reconstituted with 0.5 mL of methanol:water (10:90, v/v). The pre-concentration factor was in this case 250. Finally, 1 and 50 µL of the extracts were injected in GC-(Q)TOF MS and UHPLC-QTOF MS, respectively.

A similar procedure was applied for LC-MS/MS QqQ quantitative analysis. Due to the higher sensitivity provided by QqQ instruments, only 100 mL of centrifuged water samples were passed through Oasis HLB (60 mg) cartridges, which were previously conditioned with 3 mL of acetone, 3 mL of methanol and 3 mL of HPLC-grade water. The analytes were eluted with 5 mL of methanol; the extract evaporated to dryness under a gentle nitrogen stream at 35°C and reconstituted with 0.5 mL of a mixture of methanol:water (10:90, v/v), and finally 1 µL of the extract was injected into the UHPLC-MS/MS QqQ.

## **2.6 Screening by (Q)TOF MS**

The presence of organic pollutants in the selected water samples was investigated by complementary screening using both GC-(Q)TOF MS and UHPLC-QTOF MS. The methodology by using QTOF MS with both LC and GC (Xevo G2, Waters) was previously validated in different types of water samples using model compounds with satisfactory results (Hernández et al., 2015a).

Different instruments were used along the three years of this study depending on their availability and/or time of acquisition. Samples from the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>th</sup> campaigns were analysed by combined use of GC-(EI)TOF MS (GCT, Waters) and UHPLC-QTOF MS (Premier, Waters). The latest samples, corresponding to 4<sup>th</sup> and 5<sup>th</sup> campaigns, were analysed by a newer generation instrumentation, GC-(APCI) QTOF MS and UHPLC-QTOF MS (both Xevo G2, Waters). The main difference between this instrumentation and the previous one was the better sensitivity associated to the Xevo G2 analyser, and the use of APCI source in GC-QTOF MS instead of the GC-(EI)TOF MS used in previous campaigns. The better sensitivity of the later instruments might have some influence in the results, although we did not observe a relevant change in the trends in the last campaigns, revealing that the change in the instrumentation did not have significant influence on the objective of the study.

The full-spectrum acquisition data generated at low and high collision energy (MS<sup>E</sup> mode) in the QTOF instrument were processed by ChromaLynx XS software (target way) in combination with a customised home-made compound database. It applies a “post-target” processing method by monitoring theoretical exact masses of the selected analytes and obtaining the corresponding narrow-window eXtracted Ion Chromatogram (nw-XICs), commonly with 150 ppm. This allowed searching for the presence of a large number of contaminants (presence of a chromatographic peak in the XIC generated). Full-spectrum acquisition data generated by GC-(EI)TOF were processed by TargetLynx software. A non-target research was also made in this case by using ChromaLynx XS software (non-target way) in combination with NIST commercial library.

As can be seen in **Table S1 of Supplementary Information**, in the LC-QTOF screening a candidate list of 1,597 organic pollutants including pesticides and TPs,

pharmaceuticals and veterinary drugs, drugs of abuse and UV-filters was used. Regarding GC-QTOF, the target list contained 525 compounds including some GC-amenable pesticides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), perfluorinated compounds (PFCs), musks, antimicrobials and insect repellents. **Table S1** also shows the number of compounds whose reference standards were available at the laboratory.

Different approaches were applied in the screening as a function of the availability of reference standard of the compounds searched (Hernández et al., 2015a; Hernández et al., 2015b). Briefly, information about elemental composition, retention time (Rt), main fragment ions and adduct formation was included in the target list when the standard was available in order to facilitate and enhance the reliability in the identification/elucidation process. On the contrary, the only information available was the elemental composition of the parent compound (occasionally adducts) when the standard was unavailable. The protonated molecule and fragment ions were evaluated in both LE and HE functions, and also the characteristic isotope pattern when Cl or Br were present. With the accurate-mass full-spectrum data obtained, the compatibility of fragment ions with the chemical structure of the suspect compound was tested, and a tentative identification was feasible. The tentative identification was supported by MS/MS product ions reported in the literature for the suspect compound (either in exact or nominal mass). The final acquisition of the reference standard allowed to confirm the compounds tentatively identified, and then all information gathered on the new confirmed compound was included to update the database.

In the case of GC-(APCI)QTOF MS analysis, both the molecular ion and the protonated molecule were included in the processing screening method. In GC-(EI)TOF MS analyses, a non-target screening was also performed using ChromaLynx (in non-target

way) to automatically process data. When a peak was found to satisfy user defined parameters the software displayed its deconvoluted mass spectrum, submitted it to an automatic library search routine (library match >70%) and performed an accurate mass confirmation for the up to five most intense ions to confirm/reject the finding (Portolés et al., 2014).

## **2.7 Target quantitative analysis by LC-MS/MS QqQ**

Quantitative analysis was performed by UHPLC-MS/MS QqQ (Xevo TQD™ for samples from 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> campaigns; TQ-S™ for the 4<sup>th</sup> and 5<sup>th</sup> campaigns). In total, the compounds investigated along the three years were 42 pesticides, 49 pharmaceuticals and 11 drugs of abuse. The experimental conditions selected are shown in **Table S2 of Supplementary Information**, only for those compounds that were found in the samples analysed. A total of 33 organic compounds were quantified, including 24 pesticides and TPs, 7 pharmaceuticals and one drug of abuse (cocaine) and its major metabolite, benzoylecgonine. In order to allow the simultaneous quantification and reliable identification of the positive findings, two SRM transitions were acquired for every compound, with the exception of ibuprofen where only one transition was monitored due to its poor fragmentation. The better sensitivity of the TQS instrument allowed to reach limits of quantification (LOQ) notably lower than with the TQD instrument.

### 3. RESULTS AND DISCUSSION

In this work the presence of organic contaminants in ground and surface water samples was investigated in order to evaluate the potential impact of the Reciplasa SWTP in the contamination of the surrounding area. This SWTP treats all the urban solid wastes and hospital wastes (groups I and II) from the town of Castellón and from other seven smaller towns of the province. The 100% of wastes (dangerous waste is not treated in the plant) are treated, and organic wastes are subjected to composting. The solid wastes treated by this plant correspond to a population of around 300.000 inhabitants.

The focus of the research was on the detection and identification of the main contaminants (i.e. qualitative analysis) by using an efficient and wide-scope screening based on the combined use of two complementary techniques, GC-(Q)TOF MS and LC-QTOF MS. Using both techniques, a high number of organic contaminants could be included in the screening, with very different polarities and volatilities (Hernández et al., 2015a). In addition, based on data obtained in the screening and on our previous experience (Pitarch et al., 2010), a quantitative UHPLC- MS/MS QqQ method was applied, for the determination of selected organic contaminants, mainly pesticides and TPs.

The study was carried out from January 2011 to December 2013, collecting a total of 33 water samples (10 surface and 23 groundwater samples). The above approach (initial screening by (Q)TOF MS followed by quantitative analysis by LC-MS/MS) was applied to the analysis of all samples investigated. All compounds detected and reported as positive findings were confirmed by the presence of the quantification ion/transition (*Q*, the most abundant ion/transition) and the confirmation ion/transition (*q*, qualifier ion/transition) together with the accomplishment of  $R_t$  within  $\pm 0.2$  min deviation. Specifically, in case of QTOF data, the presence of the *Q* ion, at low energy (LE)

function, and of the  $q$  ion, at high energy (HE) function, were required, both with mass errors lower than 2 mDa.

### 3.1 Screening analysis (GC-(Q)TOF MS and UHPLC-QTOF MS)

**Table 1** shows the frequency of detection for organic contaminants after the application of the screening in the water samples collected, using different (Q)TOF instruments depending on sampling period. Pesticides were by far the most commonly detected compounds, especially herbicides (belonging to the chloroacetanilide, phenoxyacetic, phenylurea, triazine and uracil families), fungicides (anilide, anilinopyrimidine, benzimidazole, conazole and thiazole) and insecticides (dimethylcarbamate, organophosphorus (OP) and pyridylmethylamine). All pesticides were confirmed in the samples using the corresponding reference standard.

The highest number of findings corresponded to herbicides, especially triazines and their TPs. Up to 14 compounds from this group were identified, the most frequently being terbuthylazine (76% of the samples analysed) and two of its TPs, 2- hydroxy and desethyl terbuthylazine (64 and 56%, respectively). Simazine was also present in 51% of the samples analysed. Moreover, around 30 % of the samples contained other herbicides, such as atrazine and its TPs (DIA and DEA), bromacil, terbumeton and its TP terbumeton-desethyl. Among fungicides, seven compounds were identified, the most detected being carbendazim (27%) and metalaxyl and thiabendazol (18%). Regarding insecticides, five OPs were found but only in one sample.

The frequent detection of pesticides can be explained by the fact that this is an important agricultural area of orange production, where the application of pesticides is quite common. The compounds detected in waters, mainly herbicides from the triazine group and their TPs, are commonly reported as contaminants of ground and surface waters in the literature (Carabias-Martínez et al., 2003; Hernández et al., 2008;

Hernández et al., 2013; Marín et al., 2009; Masiá et al., 2013). It should be noted that nine pesticides detected in the present study, bromacil, pyridaphenthion, terbacil, terbumeton and terbutryn (2002/2076/EC), simazine (2004/247/EC), atrazine (2004/248/EC), carbaril (2007/355/EC) and carbofuran (2007/416/EC) were banned in Spain at the time of sampling campaigns.

Other compounds different than pesticides were also identified in the screening, as it can be seen in **Table 1**. These belonged to very different families, as antioxidants, cosmetics, drugs of abuse, insect repellents, musks, PAHs, pharmaceuticals, plasticizers, preservatives or UV filters. Most of these compounds were detected using a post-target approach on the basis of the home-made accurate-mass data base employed, but nine of them were found by a non-target approach by GC-(EI)-TOF MS in analyses of the 7 samples collected in the 1<sup>st</sup> campaign (January 2011). Among them, BHT, myristate isopropyl and n-butyl, caffeine, naphthalene 2-methyl, 2,6-DIPN, N-BBSA and benzophenone, were detected in 3 or more out of the 7 samples analysed in that campaign (>43%). Four compounds were just tentatively identified on the basis of the information obtained, as their corresponding reference standards were not available in our laboratory (one insect repellent (DEET), one musk (tonalide) and two UV filters (EHC and octocrylene)). These suspect compounds were investigated in 12 samples (4<sup>th</sup> and 5<sup>th</sup> campaigns, 2013), being tonalide and octocrylene the most frequently detected (50 and 42%, respectively). On the contrary, the great majority of compounds were detected by using a target screening approach, and their identity was confirmed with reference standards. The presence of the pharmaceutical ibuprofen and two drugs of abuse, benzoylegonine and caffeine, could be examples of consumption of these compounds by the population and the fact that they can reach surface and ground waters not only from urban waste waters but also (although with minor extension) from



SWTPs. The detection of parabens was rather frequent as they are commonly used in cosmetic (personal care products) and pharmaceutical industries, as well as preservatives in chemical prescriptions.

**Figure 1** shows a summary of the different families of compounds found in water samples by using QTOF MS screening. As can be seen, (**Figure 1A**), pesticides represented 71% of the positive findings, being the rest of the families below 10%. Within the group of pesticides (**Figure 1B**), triazine herbicides were far the most frequent (72%). The rest of pesticide families raised percentages below 6%.

As an example, **Figure 2** illustrates the detection and identification of the uracil herbicide bromacil in San Martin de Porres groundwater (point 7, 5<sup>th</sup> campaign) by UHPLC-QTOF MS. The protonated molecule as well as its sodium adduct were observed in the LE function, with mass errors lower than 2 ppm, at the expected retention time (7.5 min). Moreover, the combined spectrum of this chromatographic peak showed a typical one-bromine atom isotopic pattern, being therefore in accordance with the chemical structure of bromacil ( $C_9H_{14}N_2O_2Br$ ). Its identity was supported by the presence of three  $m/z$  ions at the expected retention time in the HE function, with negligible mass errors.

As regards GC-(APCI)-QTOF MS screening, **Figure 3** shows a positive of chlorpyrifos ethyl in Sabater I groundwater (point 3, 5<sup>th</sup> campaign). The protonated molecule was observed in the LE function, with a mass error of 2.0 ppm, at the expected retention time (22.37 min). Moreover, the combined spectrum showed a typical three-chlorine atoms isotopic pattern in accordance with the chemical structure of chlorpyrifos ( $C_9H_{11}Cl_3NO_3PS$ ). Finally, for the presence of 4 fragment ions (in HE function) led to the confirmation of the compound identity.

**Figure S2** (in **Supplementary Information**) shows a summary of the analytes detected in every sample analyzed. The major number of detections corresponded to the 1<sup>st</sup> and 2<sup>nd</sup> campaigns (January 2011 and April 2012, respectively), meanwhile the last sampling (December 2013) presented the lowest number of findings. As expected, one of the less polluted water samples corresponded to upstream piezometer (point 1). Also the Reciplasa well (point 8) sited inside the Solid-Waste Treatment Plant showed very little contamination. This might be explained by the low permeability (sandstones and clays of Weald Facies-lower Cretaceous), which reduced the probability of contaminants coming from leaching of landfill body to reach groundwater. Surface waters from Mijares river (points 5 and 6) also presented low contamination. The only exception was the sample collected at the Gauging-station (point 6) in the first campaign (January 2011) which contained the highest number of contaminants (19 compounds), a fact that was not expected and might be explained by the heavy rains around the sampling period. The waters collected from Sabater I (point 3) and Sabater II (point 4) presented a notable number of contaminants especially during the first monitoring campaign. The strong karstic character of the carbonated materials (Cretaceous) from both points, could have facilitate the infiltration of those contaminants and then their discharged into Mijares river.

Screening data illustrated that groundwater samples containing the highest number of pollutants ( $\geq 16$  compounds) corresponded to Ntra. Sra. Desamparados, located into the Plio-Quaternary aquifer (sampling point 2, April 2012 and May 2013), and Sabater I, sited into Cretaceous aquifer (sampling point 3, December 2013).

### **3.2 Quantitative analysis by UHPLC-QqQ MS/MS**

Surface and groundwater samples were also analysed by UHPLC-MS/MS QqQ (see experimental conditions in **Table S2, Supplementary Information**). The compounds

included in the quantitative method were mostly pesticides and TPs. Some pharmaceuticals and drugs of abuse were also considered, on the basis of our own data obtained in other studies performed in influent and effluent wastewaters and surface water samples. The acquisition of two MS/MS transitions per compound (Q for quantification, and q for confirmation) enabled the simultaneous quantification and reliable identification of the compounds detected. The quantification was carried out by using external standard calibration (between 0.1 and 100 ng/mL) with 10 isotope labelled internal standards.

**Table 2** shows the frequency of detection (% positive samples) for the contaminants found by application of the quantitative method. As regards pesticides, the results were mostly in agreement with the screening data, with triazine herbicides being the most frequent compounds. Terbutylazine and its TPs, as well as the terbutometon desethyl TP presented high percentages of detection (around 90%). Atrazine (48%) and its TP DEA (42%) and simazine (45%) were also frequently found. Above a frequency of 50% were found the herbicide diuron (61%) and the fungicide metalaxyl (58%). With respect pharmaceuticals, carbamazepine and irbesartan were the most detected (42%). Cocaine and its major metabolite benzoylecgonine were in 43% and 32% of the samples analyzed, respectively.

Only eight pesticides (from a total of 24 monitored) exceeded in some occasion 0.1 µg/L, the maximum allowable concentration for pesticide in water for human consumption (Directive 2013/39/UE). These pesticides corresponded to four herbicides and two TPs (diuron, MCPA, simazine, terbutylazine and its two TPs) and two insecticides (carbofuran and imidacloprid), most of them of widespread use in Castellón province. Among them, diuron and simazine are the only compounds included in the list of 45 priority substances (Directive 2013/39/UE) with maximum allowable

concentration of 1.8 and 4  $\mu\text{g/L}$ , respectively, in surface waters. The two terbuthylazine TPs (desethyl and 2-hydroxy) were the most frequently detected at concentrations above 0.1  $\mu\text{g/L}$  (33 and 25% of water samples analysed, respectively). Only in one case, the level of 0.5  $\mu\text{g/L}$  was surpassed, and it occurred for terbuthylazine, with a maximum concentration of 0.65  $\mu\text{g/L}$  (sample point 4, Sabater II, December 2013).

**Figures S3 and S4** (in **Supplementary information**) show the concentrations found for triazine herbicides and other pesticides in the water samples along the five sampling campaigns.

Within the group of drugs of abuse and pharmaceuticals, only two compounds (benzoylecgonine and ibuprofen) exceeded 0.1  $\mu\text{g/L}$  in one sample, but always at concentrations below 0.25  $\mu\text{g/L}$ .

It can be concluded that application of the screening analysis led to the detection of a notable number of organic contaminants; however, the subsequent quantitative analysis showed that only in a few cases the concentration level of 0.1  $\mu\text{g/L}$  was surpassed.

An example of the quantitative analysis is shown in **Figure 4**. UHPLC-QqQ MS/MS chromatograms for some positives in the groundwater sample (Sabater II) collected in December 2013 are depicted. As can be seen, five triazine herbicides and three of its TPs, as well as a phenylurea herbicide, two insecticides and one fungicide were identified and quantified, at concentrations between 0.007 and 0.65  $\mu\text{g/L}$  in sample Sabater II. This water sample was one of the most polluted, and up to 5 compounds (terbuthylazine and its two TPs, carbofuran and diuron) exceeded the 0.1  $\mu\text{g/L}$  level.

#### 4. CONCLUSIONS

In this work, a powerful analytical approach based on the combined use of LC-QTOF MS and GC-(Q)TOF MS has been applied for the screening of around 1,500 organic contaminants in surface and groundwater. The samples were collected from the surrounding of a Solid-Waste Treatment Plant in order to evaluate its potential impact on the water quality. Subsequently, all samples were analysed by LC-MS/MS QqQ to quantify target analytes previously detected in the screening.

The screening results for 33 water samples analysed demonstrated that pesticides were the most commonly detected compounds (71% of the compounds identified). Among them, triazine herbicides were the most detected. Organic contaminants, such as pharmaceuticals, drugs of abuse, antioxidants or UV filters were also found illustrating the potential of the TOF MS-based approach for screening purposes of water samples and its capacity to detect and identify a large variety of contaminants of very different physico-chemical characteristics.

The subsequent LC-MS/MS QqQ quantitative analyses confirmed the presence of compounds found in (Q)TOF screenings and allowed to determine their concentrations in the water samples. Terbutylazine and its TPs (2-hydroxy and desethyl), as well as terbumeton desethyl were detected in nearly all samples analysed (around 90%). Only ten compounds (from 33 monitored) were found at concentrations occasionally above 0.1 µg/L. These were eight pesticides and TPs (carbofuran, diuron, imidacloprid, MCPA, simazine, terbutylazine, terbutylazine 2-hydroxy and terbutylazine desethyl) and also the cocaine metabolite (benzoylecgonine) and one pharmaceutical (ibuprofen). Terbutylazine was the only compound that exceeded 0.5 µg/L, with a maximum concentration of 0.65 µg/L in a groundwater sample.

Data from this work show that pesticides were the main contaminants in ground and surface waters from the surrounding of the SWTP, both in terms of frequency of detection and concentration levels. This suggests that the use of phytosanitary products in this important citric-crops agricultural area is the main source of pollution of the aquatic environment, with triazines and their TPs being the most prominent contaminants reaching groundwater. Other contaminants, mainly pharmaceuticals, might have their origin in the SWTP, but the small number of detections and the low concentrations commonly found in the samples suggest that the potential impact of this plant in the aquatic environment is not much relevant at present. In any case, it is recommend to continue this type of monitoring in the near future to ensure the water quality of the area.

### **Acknowledgments**

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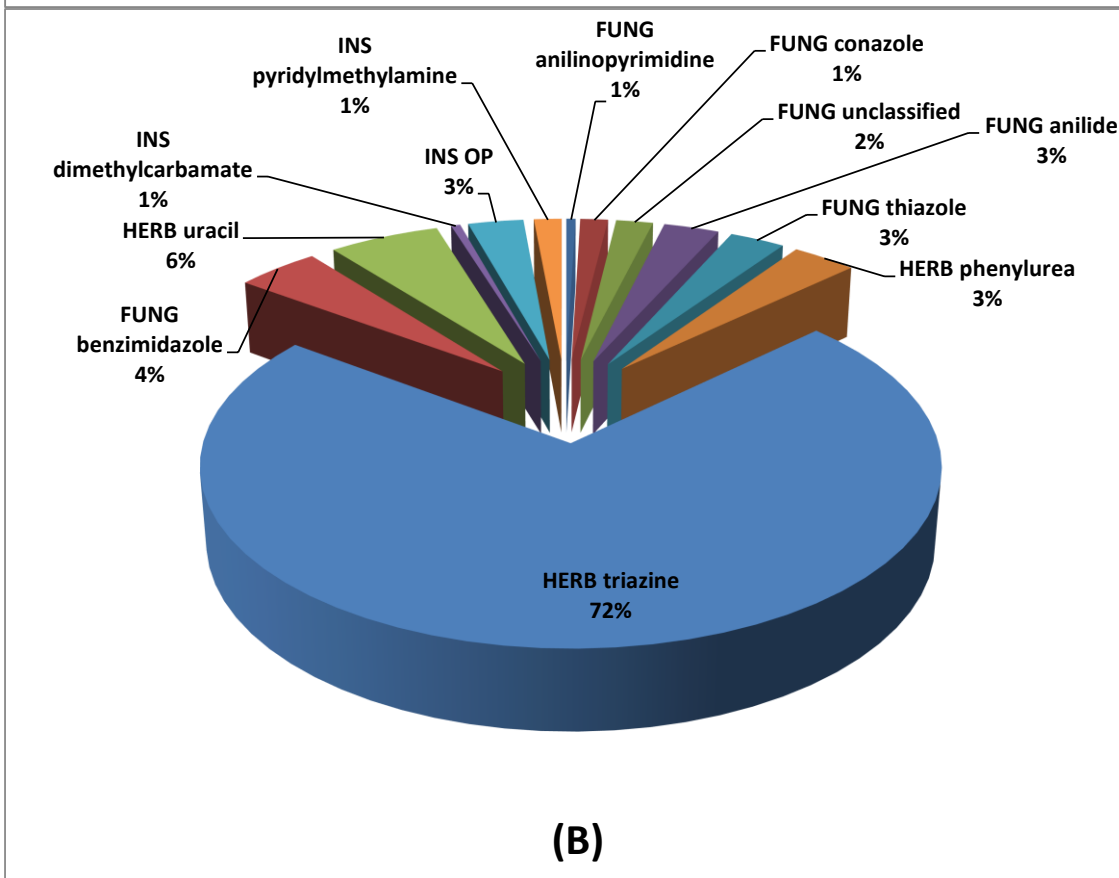
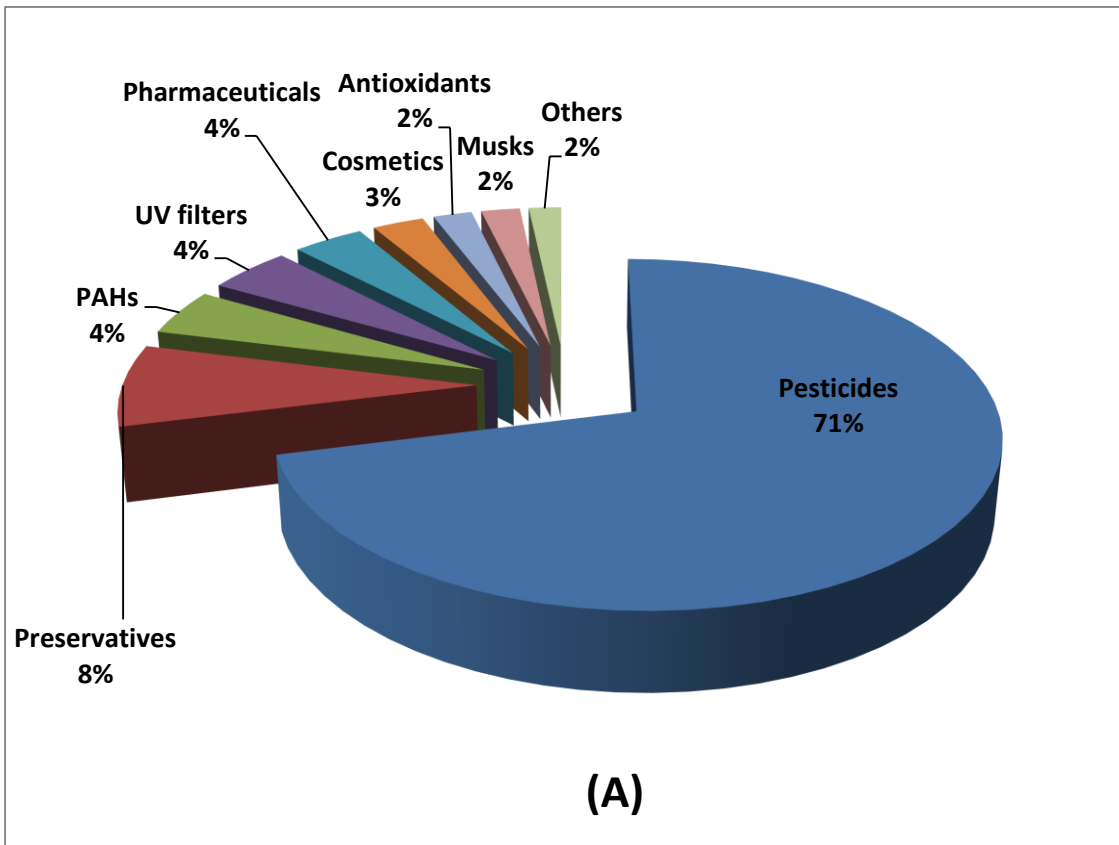
## FIGURE CAPTIONS

**Figure 1.** Percentages of positive findings for (A) the different families of compounds, and (B) the different families of pesticides, detected in water samples by screenings using GC-(Q)TOF MS and UHPLC-QTOF MS.

**Figure 2.** Positive finding of bromacil after UHPLC-QTOF MS screening to groundwater sample San Martin de Porres (December 2013). a) LE (low energy) and HE (high energy) TOF mass spectra for the chromatographic peak at 7.53 min (see the bromine pattern). Elemental composition and mass errors in mDa are also shown. (b) Extracted Ion Chromatograms (XICs) at 150 ppm mass window for  $[M+H]^+$  and  $[M+Na]^+$  in LE function and its main fragment in HE function.

**Figure 3.** Positive finding of chlorpyrifos ethyl after GC-QTOF MS screening to groundwater sample Sabater I (December 2013). a) LE (low energy) and HE (high energy) TOF mass spectra for the chromatographic peak at 22.39 min (see the chlorine pattern). Elemental composition and mass errors in mDa are shown. (b) Extracted Ion Chromatograms (XICs) at 150 ppm mass window for  $[M+H]^+$  in LE function and the main fragments in HE function.

**Figure 4.** UHPLC-QqQ MS/MS chromatograms that illustrate several compounds found in Sabater II groundwater sample (point 4, December 2013). Only the quantification transition (Q) is shown for every analyte.



**Figure 1**

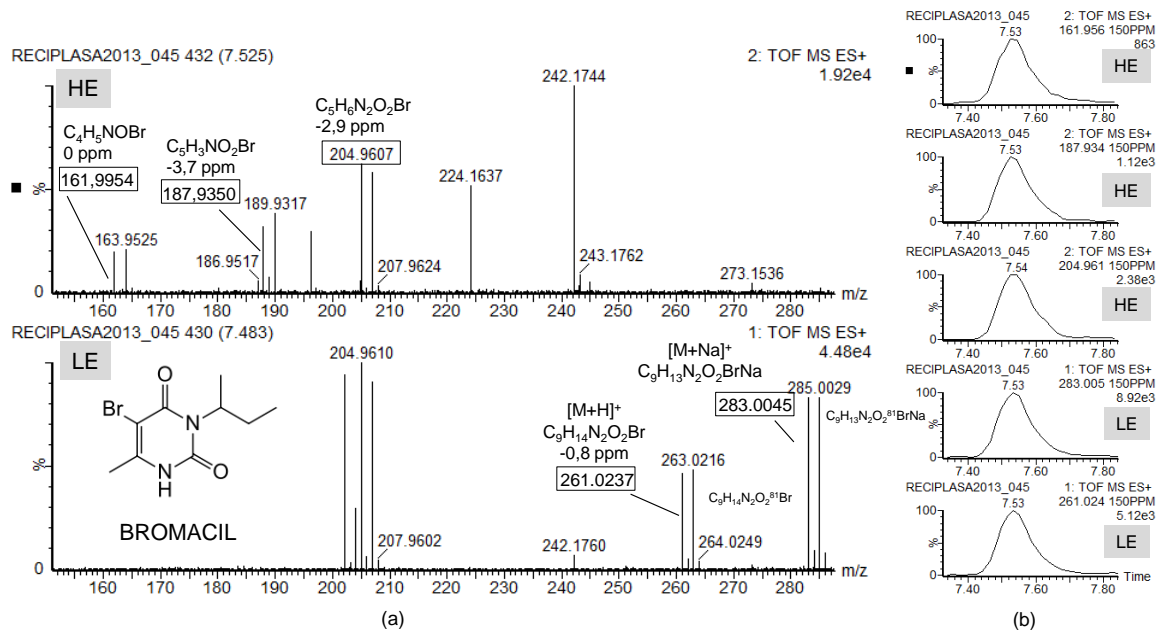


Figure 2

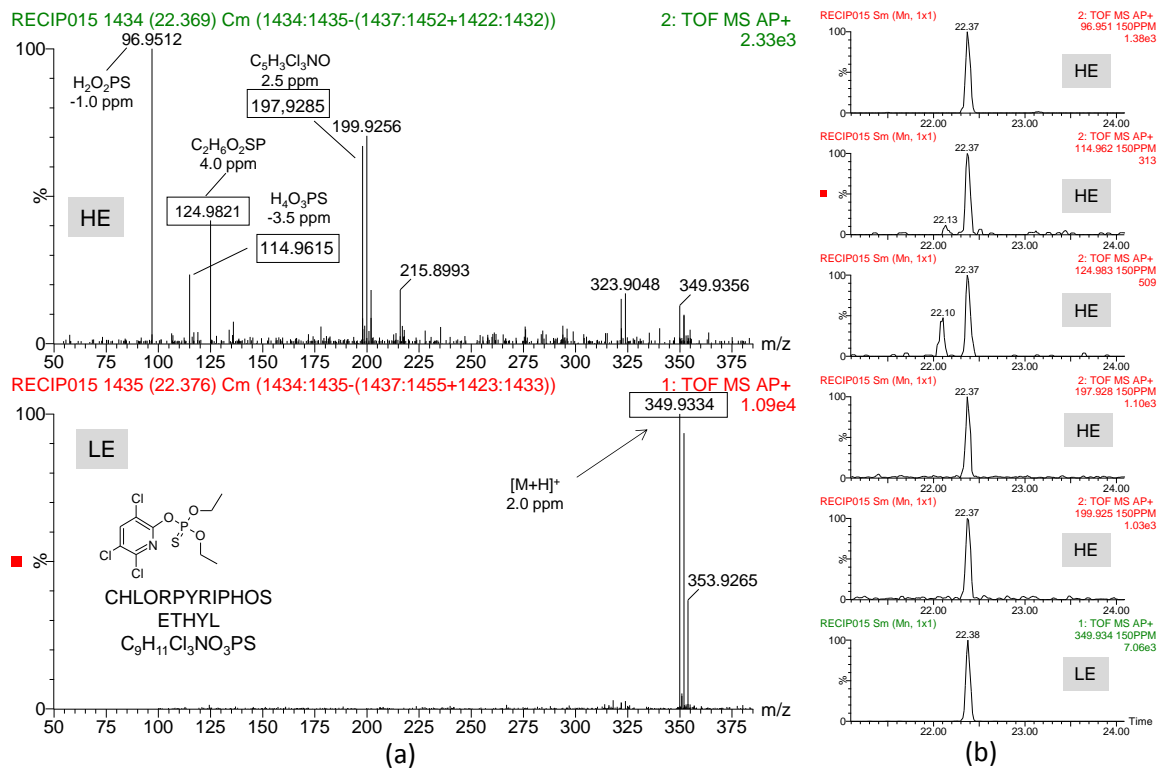
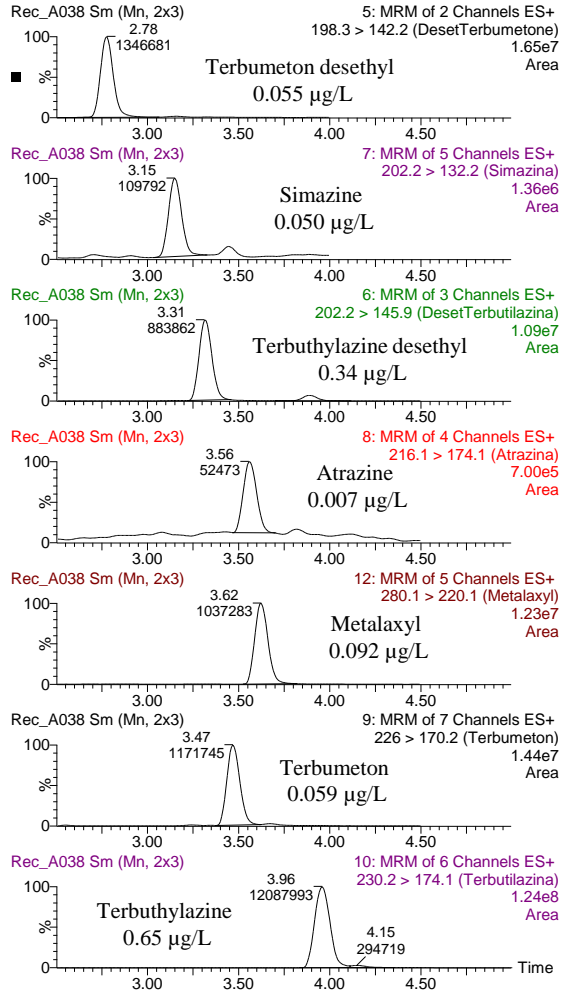


Figure 3



**Sabater II 131213-2**



**Sabater II 131213-2**

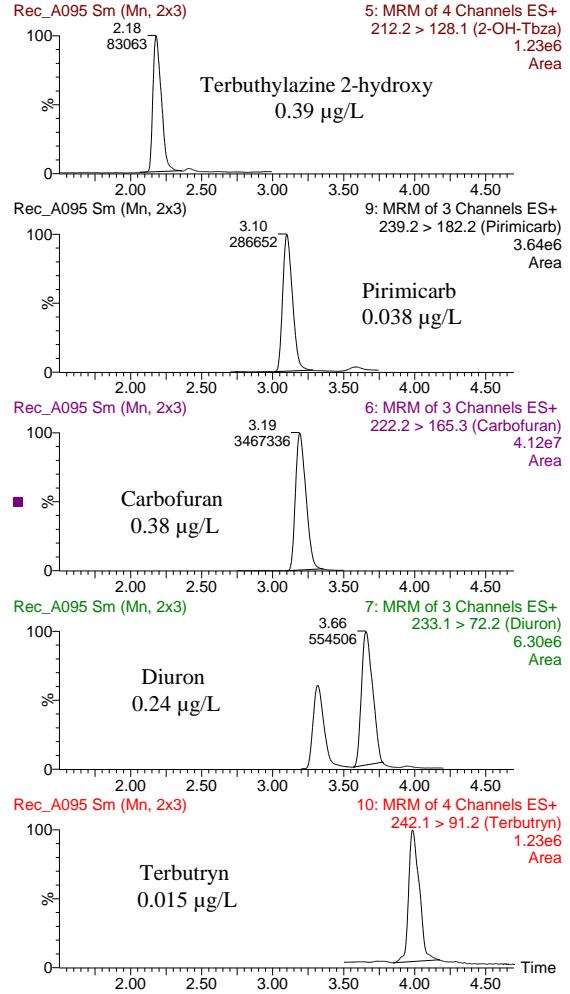


Figure 4

**Table 1.** Positive samples obtained after the application of (Q)TOF screening to water samples collected from the surrounding of a SWTP between January 2011 and December 2013.

FUNG: Fungicide; HERB: Herbicide; INS: Insecticide; OP: Organophosphorus; PAH: Polycyclic aromatic hydrocarbon; UV: Ultraviolet

Family	Compound	Positive samples (%)
FUNG unclassified	2-Phenylphenol <sup>b,d</sup>	12
HERB triazine	Atrazine <sup>a,b,d</sup>	33
HERB triazine	Atrazine 2-hydroxy <sup>a</sup>	15
HERB triazine	Atrazine deisopropyl (DIA) <sup>a,b,d</sup>	30
HERB triazine	Atrazine desethyl (DEA) <sup>a,b</sup>	24
HERB uracil	Bromacil <sup>a</sup>	27
FUNG benzimidazole	Carbendazim <sup>a</sup>	27
INS dimethylcarbamate	Carbofuran <sup>a,d</sup>	3
INS OP	Chlorpyrifos ethyl <sup>a,b,d</sup>	3
INS OP	Chlorpyrifos methyl <sup>a,b,d</sup>	3
INS OP	Coumaphos <sup>a,b,d</sup>	3
INS OP	Diazinon <sup>a,b,d</sup>	3
INS OP	Dimethoate <sup>a,b,d</sup>	3
HERB phenylurea	Diuron <sup>a</sup>	21
FUNG conazole	Imazalil <sup>a,b,d</sup>	6
INS pyridylmethylamine	Imidacloprid <sup>a</sup>	9
FUNG anilide	Metalaxyl <sup>a,b,d</sup>	18
INS dimethylcarbamate	Pirimicarb <sup>a,b,d</sup>	3
INS OP	Pirimiphos methyl <sup>a,b,d</sup>	3
FUNG anilinopyrimidine	Pyrimethanil <sup>a,d</sup>	8
HERB triazine	Simazine <sup>a,b,d</sup>	51
HERB triazine	Simazine 2-hydroxy <sup>a</sup>	12
FUNG conazole	Tebuconazole <sup>a,b,d</sup>	3
HERB uracil	Terbacil <sup>a,b,d</sup>	9
HERB triazine	Terbumeton <sup>a,b,d</sup>	33
HERB triazine	Terbumeton desethyl <sup>a,b,d</sup>	33
HERB triazine	Terbuthylazine <sup>a,b,d</sup>	76
HERB triazine	Terbuthylazine 2-hydroxy <sup>a</sup>	64
HERB triazine	Terbuthylazine desethyl <sup>a,b,d</sup>	56
HERB triazine	Terbuthylazine desethyl 2-hydroxy <sup>a</sup>	6
HERB triazine	Terbutryn <sup>a,b,d</sup>	15
HERB triazine	Terbutryn desethyl <sup>a</sup>	3
FUNG thiazole	Thiabendazol <sup>a,b,d</sup>	18
Antioxidant	BHT <sup>c</sup>	57
Antioxidant	BHT-CHO <sup>c</sup>	29
Cosmetic	Myristate isopropyl <sup>c</sup>	71
Cosmetic	Myristate n-butyl <sup>c</sup>	43
Drugs of abuse	Benzoyllecgonine <sup>a</sup>	3
Drugs of abuse	Caffeine <sup>c</sup>	43
Insect repellent	N,N-Diethyl-meta-toluamide (DEET) <sup>d*</sup>	8

Musk	Tonalide <sup>d*</sup>	50
PAH	Naphthalene <sup>b,d</sup>	18
PAH	Naphthalene 2-methyl <sup>c</sup>	100
Pharmaceutical	Ibuprofen <sup>a</sup>	3
Plant growth regulators	Naphthalene 2,6-diisopropyl (2,6-DIPN) <sup>c</sup>	57
Plasticizer	N-Butyl benzene sulphonamide (N-BBSA) <sup>c</sup>	86
Preservative	Buthylparaben <sup>a</sup>	15
Preservative	Ethylparaben <sup>a</sup>	12
Preservative	Propylparaben <sup>a</sup>	21
Preservative	Methylparaben <sup>a</sup>	21
UV filter	Benzophenone <sup>c</sup>	71
UV filter	Ethylhexyl methoxycinnamate (EHC) <sup>d*</sup>	17
UV filter	Octocrylene <sup>d*</sup>	42

<sup>a</sup> Compounds analyzed by UHPLC-QTOF MS (n=33)

<sup>a\*</sup> Compounds analyzed by UHPLC-QTOF MS (suspect, reference standard not available) (n=33)

<sup>b</sup> Compounds analyzed by GC-TOF MS (n=21)

<sup>c</sup> Compounds analyzed by GC-TOF MS (non-target) (n=7)

<sup>d</sup> Compounds analyzed by GC-QTOF MS (n=12)

<sup>d\*</sup> Compounds analyzed by GC-QTOF MS (suspect, reference standard not available) (n=12)

**Table 2.** Results obtained for compounds quantified from analysis by UHPLC-MS/MS QqQ of ground and surface water samples collected from the surrounding of a SWTP between January 2011 and December 2013 (total number of samples 33)

Family	Compound	Positive samples (%)	Positive samples > 0.1 µg/L (%)	Maximum level found (µg/L)
HERB triazine	Atrazine	48	0	0.019
HERB triazine	Atrazine deisopropyl (DIA) <sup>a</sup>	8	0	0.031
HERB triazine	Atrazine desethyl (DEA) <sup>a</sup>	42	0	0.092
HERB uracil	Bromacil <sup>b</sup>	14	0	<0.025
INS carbamate	Carbaril	15	0	<0.025
INS dimethylcarbamate	Carbendazim <sup>b</sup>	33	0	0.04
INS dimethylcarbamate	Carbofuran	36	6	0.38
HERB phenylurea	Diuron	61	3	0.24
FUNG conazole	Imazalil	0	0	–
INS pyridylmethylamine	Imidacloprid	24	3	0.4
HERB phenylurea	Isoproturon	39	0	0.001
HERB phenoxyacetic	MCPA <sup>b</sup>	14	10	0.11
FUNG anilide	Metalaxyl	58	0	0.092
HERB chloroacetanilide	Metolachlor	6	0	<0.025
INS dimethylcarbamate	Pirimicarb	30	0	0.038
INS OP	Pyridaphenthion	3	0	<0.025
HERB triazine	Simazine	45	3	0.11
HERB uracil	Terbacil	29	0	<0.025
HERB triazine	Terbumeton	36	0	0.059
HERB triazine	Terbumeton desethyl	92	0	0.086
HERB triazine	Terbuthylazine	91	6	0.65
HERB triazine	Terbuthylazine 2-hydroxy <sup>a</sup>	92	25	0.39
HERB triazine	Terbuthylazine desethyl <sup>a</sup>	92	33	0.34
HERB triazine	Terbutryn	21	0	0.03
FUNG thiazole	Thiabendazol	15	0	<0.025
Drugs of abuse	Benzoyllecgonine <sup>c</sup>	32	5	0.17
Drugs of abuse	Cocaine <sup>d</sup>	43	0	<0.025
Pharmaceutical	Carbamazepine <sup>a</sup>	42	0	0.001
Pharmaceutical	Clarithromycin <sup>d</sup>	29	0	<0.025
Pharmaceutical	Erithromycin <sup>d</sup>	14	0	<0.025
Pharmaceutical	Ibuprofen <sup>d</sup>	14	14	0.23
Pharmaceutical	Irbesartan <sup>a</sup>	42	0	<0.0004
Pharmaceutical	Valsartan <sup>a</sup>	33	0	<0.006
Pharmaceutical	Acetaminophen <sup>d</sup>	29	0	0.054

<sup>a</sup> n= 12 samples

<sup>b</sup> n= 21 samples

<sup>c</sup> n= 19 samples

<sup>d</sup> n= 7 samples

## SUPPLEMENTARY INFORMATION

### **Comprehensive monitoring of organic micro-pollutants in surface and groundwater in the surrounding of a solid-waste treatment plant of Castellón, Spain**

Elena Pitarch<sup>1</sup>, María Inés Cervera<sup>1</sup>, Tania Portolés<sup>1</sup>, María Ibáñez<sup>1</sup>, Mercedes Barreda<sup>1</sup>, Arianna Renau-Pruñonosa<sup>1</sup>, Ignacio Morell<sup>1</sup>, Francisco López<sup>1</sup>, Fernando Albarrán<sup>2</sup>, Félix Hernández<sup>1\*</sup>

<sup>1</sup>*Research Institute for Pesticides and Water, University Jaume I, Avda. Sos Baynat, E-12071 Castellón, Spain. Tel. +34 964387366. Fax +34 964387368*

<sup>2</sup>*RECIPLASA, Reciclados de Residuos La Plana, S.A., E-12200 Onda, Castellón, Spain*

\*Corresponding author: [felix.hernandez@uji.es](mailto:felix.hernandez@uji.es)

## **2. EXPERIMENTAL**

### **2.1 Reagents**

Reference standards of organic contaminants were purchased from Dr. Ehrenstorfer (Augsburg, Germany), Wellington Laboratories (Guelph, Ontario, Canada), Fluka (Buchs, Switzerland), Riedel de Hën (Seelze, Germany) or Sigma (St Louis, MO, USA). All reference standards presented purity higher than 93%.

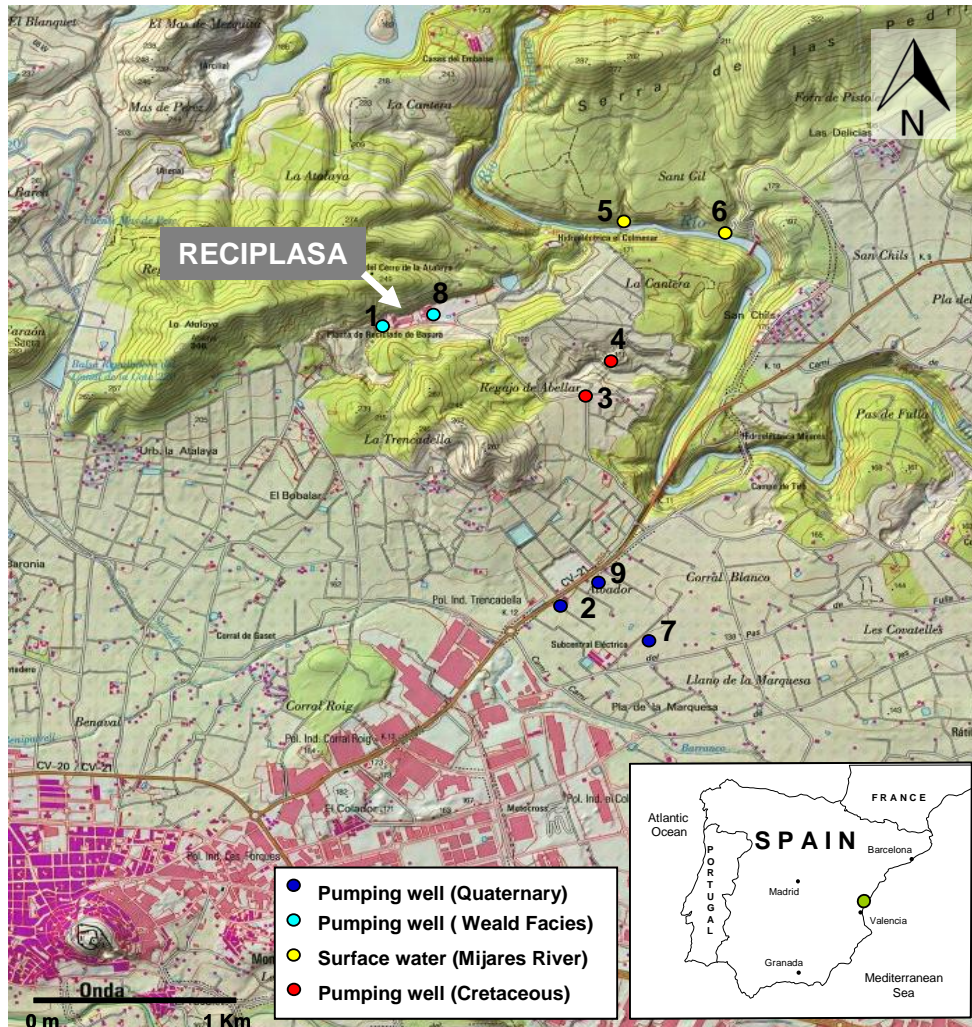
Stock working standards solutions were prepared in acetone. Working mixtures were prepared in hexane for GC analysis and in acetonitrile, methanol or water (depending on the concentration) for LC analysis.

Acetone (pesticide residue analysis quality), hexane and ethyl acetate (ultra-trace quality), acetonitrile and methanol (HPLC-grade), sodium hydroxide (NaOH, >99%), ammonium acetate (>98%) and formic acid (98–100%) were purchased from Scharlab (Barcelona, Spain). HPLC-grade water was obtained by purifying demineralised water in a Milli-Q plus system from Millipore (Bedford, MA, USA).

Leucine enkephalin and heptacose used as lock mass for LC and GC, respectively were purchased from Sigma-Aldrich.

Cartridges used for solid phase extraction were Oasis HLB, 200 mg or 60 mg (Waters, Milford, MA, USA).

## 2.2 Hydrogeological description of the sampling area



Sample number	Name	Water type	Sampling campaigns
1	Upstream piezometer	GW	1 <sup>st</sup> , 2 <sup>nd</sup> , 3 <sup>rd</sup> , 4 <sup>th</sup> , 5 <sup>th</sup>
2	Ntra. Sra Desamparados well	GW	2 <sup>nd</sup> , 3 <sup>rd</sup> , 4 <sup>th</sup>
3	Sabater I well	GW	1 <sup>st</sup> , 2 <sup>nd</sup> , 3 <sup>rd</sup> , 5 <sup>th</sup>
4	Sabater II well	GW	1 <sup>st</sup> , 2 <sup>nd</sup> , 3 <sup>rd</sup> , 4 <sup>th</sup> , 5 <sup>th</sup>
5	Mijares river, Power-plant	SW	1 <sup>st</sup> , 2 <sup>nd</sup> , 3 <sup>rd</sup> , 4 <sup>th</sup> , 5 <sup>th</sup>
6	Mijares river, Gauging-station	SW	1 <sup>st</sup> , 2 <sup>nd</sup> , 3 <sup>rd</sup> , 4 <sup>th</sup> , 5 <sup>th</sup>
7	San Martin de Porres well	GW	2 <sup>nd</sup> , 3 <sup>rd</sup> , 4 <sup>th</sup> , 5 <sup>th</sup>
8	Reciplasa well	GW	1 <sup>st</sup>
9	El Salvador well	GW	1 <sup>st</sup>

SW, surface water; GW, groundwater

**Figure S1.** Aerial map with the selected sampling points, located upstream and downstream of the flow direction of the aquifer.

## **2.3 GC-MS instrumentation**

### **2.3.1 GC-(EI)TOF MS**

An Agilent 6890N GC system (Paloalto, CA, USA) equipped with an Agilent 7683 autosampler was coupled to a time-of-flight mass spectrometer, GCT (Waters), operating in EI mode. The GC separation was performed using the same characteristics as in the above GC-MS/MS system. The interface and source temperatures were both set to 250°C and a solvent delay of 3 minutes was selected. TOF MS was operated at 1 spectrum/s acquiring the mass range  $m/z$  50-650 and using a multi-channel plate voltage of 2850V. TOF MS resolution was about 8500 (FWHM) at  $m/z$  612 and heptacosane was used for the daily mass calibration as well as lock mass ( $m/z$  ion monitored was 218.9856). The application manager TargetLynx, a module of MassLynx software, was used to process the qualitative and quantitative data obtained from standards and samples for target compounds. The application manager ChromaLynx, also a module of MassLynx software, was used to investigate the presence of non-target compounds in samples. Library searching was performed using the commercial NIST library

### **2.3.2 GC-(APCI)QTOF MS**

The chromatographic determinations were performed using an Agilent 7890A GC system (Palo Alto, CA, USA), equipped with an Agilent 7693 autosampler, coupled to a quadrupole time of flight mass spectrometer Xevo G2 QTOF (Waters Corporation, Manchester, UK), operating with APCI source. The GC separation was performed using a fused silica DB-5MS column (30 m; 0.25 mm i.d., 0.25  $\mu$ m f.t.) J&W Scientific (Folsom, CA, USA). The oven temperature was programmed as follows: 90 °C (1 min); 5 °C/min to 275 °C; 40°C/min to 320°C (2 min). Total run: 40 min. Pulsed splitless (50 psi) injections of 1  $\mu$ L of sample extracts were carried out with an injector temperature



of 280 °C and with a splitless time of 1 min. Helium 99.999 % (Praxair, Valencia, Spain) was used as carrier gas at a constant flow of 2 mL/min.

In order to promote the protonation ionization mechanism in the APCI source an uncapped vial containing HPLC-grade water was placed in the designed holder into the APCI source door. The interface temperature was set to 310 °C and of the source to 150 °C using N<sub>2</sub> as auxiliary gas at 150 L/h flow, a make-up gas at 300 mL/min and the cone gas flow was set at 16 L/h. APCI corona pin was set at 1.6 µA and the cone voltage at 26 V. The Xevo G2 QTOF MS was operated at a scan time of 0.4 s acquiring the mass range  $m/z$  50-650. The TOF MS resolution was approximately 18,000 at full width half maximum (FWHM) at  $m/z$  614.

For MS<sup>E</sup> measurements, two consecutive acquisition functions were used: a low energy function (LE), where a collision energy of 4 eV was selected, and a high energy function (HE), where a collision energy ramp (10-40 eV) was applied.

Heptacose was used for the daily mass calibration. Continuous internal calibration was performed using a background ion coming from the GC-column bleed as lock mass ([M+H]<sup>+</sup> of octamethylcyclotetrasiloxane,  $m/z$  297.0830). Two injections were performed for sample: the first one promoting the formation of the molecular ion, and the second one, promoting the formation of the protonated molecule.

MassLynx software v 4.1 (Waters Corporation) was used to acquire data. ChromaLynx application manager was used in order to investigate the presence of the studied analytes.

## 2.4 LC-MS instrumentation

### 2.4.1 UHPLC-(ESI)QTOF MS

Two systems were used:

- An ultra-performance Acquity liquid chromatography (UPLC™) system (Waters) was interfaced to a QTOF mass spectrometer (QTOF Premier, Waters) using an orthogonal Z-spray electrospray interface. LC separation was performed using an Acquity UPLC HSS T3 column, 1.8  $\mu\text{m}$ , 100 mm x 2.1 mm I.D at a flow rate of 300  $\mu\text{L}/\text{min}$ . The mobile phase consisted of water/methanol gradient (both 0.1 mM  $\text{NH}_4\text{Ac}$ ) where the methanol percentage was changed linearly as follows: 0 min, 5%; 7 min, 90%; 8 min, 90%; 8.1 min, 5%. The injection volume was 20  $\mu\text{L}$ . TOF-MS resolution was  $\sim 10,000$  FWHM (V-mode) at  $m/z$  556. The MCP detector potential was set to 1750 V in positive ionization mode. A cone voltage of 25 V and a capillary voltage of 3 kV were used. The interface temperature was set to 350  $^\circ\text{C}$  and the source temperature to 120  $^\circ\text{C}$ . A scan time of 0.05 s was chosen. The automated attenuated function (dynamic range enhancement, DRE) was selected to correct possible mass peak saturations, making it feasible to achieve quantification and accurate mass measurements over a wide concentration range. Calibration experiments from 50 to 1000  $m/z$  were performed monthly using a mixture of NaOH 0.05 M: HCOOH 10% (50:50). A 2 mg/L standard solution of leucine enkephalin was introduced via the lock spray needle (cone, voltage, 90 V) at a flow rate of 30  $\mu\text{L}/\text{min}$ .
- A Waters Acquity UPLC system (Waters, Milford, MA, USA) was interfaced to a hybrid quadrupole-orthogonal acceleration-TOF mass spectrometer (Xevo G2 QTOF, Waters Micromass, Manchester, UK), using an orthogonal Z-spray-ESI interface operating in both positive and negative ionisation modes. The UHPLC

separation was performed using an Acquity UPLC BEH C<sub>18</sub> (Waters) 1.7  $\mu$ m particle size 100  $\times$  2.1 i.d. mm analytical column at a flow rate of 300  $\mu$ L/min. The mobile phases used were A=H<sub>2</sub>O with 0.01% HCOOH and B=methanol with 0.01% HCOOH. The percentage of organic modifier (B) was changed linearly as follows: 0 min, 10%; 14 min, 90%; 16 min, 90%; 16.01 min, 10%; 18 min, 10%. The injection volume was 50  $\mu$ L.

Nitrogen (from a nitrogen generator) was used as the drying gas and nebulizing gas. The desolvation gas flow was set at 1,000 L/h and the cone gas at 80 L/h. Capillary voltages of 0.7 and 2.5 kV were used in positive and negative ionisation modes, respectively. A cone voltage of 20 V was selected for both ionisation modes. Collision gas was argon 99.995% (Praxair, Valencia, Spain). The interface temperature was set to 650°C and the source temperature to 130°C. The column temperature was set to 40°C. TOF MS resolution was approximately 20,000 at FWHM at  $m/z$  556. MS data were acquired over an  $m/z$  range of 50–1,000. A scan time of 0.4 s was selected.

Calibration of mass axis was conducted from  $m/z$  50 to 1,000 with a 1:1 mixture of 0.05 M NaOH:5% HCOOH diluted (1:25) with acetonitrile:water (80:20). For automated accurate mass measurement, the lock-spray probe was used, using as lock mass a solution of leucine enkephalin (10  $\mu$ g/mL) in acetonitrile:water (50:50) at 0.1% HCOOH pumped at 20  $\mu$ L/min through the lock-spray needle.

For MS<sup>E</sup> measurements, two consecutive acquisition functions were used: a low energy function (LE), where collision energy of 4 eV was selected, and a high energy function (HE), where a collision energy ramp (15-40 eV) was applied.

For recalibrating the mass axis and ensuring a robust accurate mass measurement along time, the (de)protonated molecule of leucine enkephalin was used ( $m/z$  556.2771 in ESI+,  $m/z$  554.2615 in ESI-).

MassLynx software v 4.1 (Waters Corporation) was used to acquire data. ChromaLynx application manager was used in order to investigate the presence of the studied analytes.

#### **2.4.2 UHPLC-(ESI)QqQ MS/MS**

Two different systems were used:

- **UHPLC-(ESI)QqQ MS/MS (TQD)**

A triple quadrupole mass spectrometer was interfaced to a Waters ACQUITY UPLC™ system (Waters Corp., Milford, MA, USA), equipped with a quaternary pump system. Chromatographic separation was carried out using an ACQUITY UPLC BEH C<sub>18</sub> column (50 x 2.1 mm i.d., particle size 1.7 μm) (Waters). An optimized gradient was used at a constant flow rate of 0.3 mL/min using methanol (solvent A) and 5 mM ammonium acetate 0.1% formic acid (solvent B). The gradient elution was: 0 min, 10% A; 0-3 min linear from 10 to 90% A; 3-3.5 min, 90% A; 3.5-3.6 min linear from 90 to 10 % A, return to initial conditions; 3.6–6 min 10% A, equilibration of the column. The injection volume was 1 μL.

A TQD™ (quadrupole-hexapole-quadrupole) mass spectrometer with an orthogonal electrospray ionization source (ESI) Z-spray (Waters Corp., Milford, MA, USA) was used. Dry cone gas as well as desolvation gas was nitrogen generated from pressurized air in a N<sub>2</sub> LC-MS (Claind, Teknokroma, Barcelona, Spain) nitrogen generator. The cone gas and the desolvation gas flows were optimized at approximately 60 L/h and 1100 L/h, respectively. For operation in the MS/MS mode, collision gas was Argon 99.995% (Carbueros Metálicos, Valencia, Spain) with a pressure of  $2 \times 10^{-3}$  mbar in the T-wave cell. Other parameters optimized were: capillary voltage, 3.5 kV in positive and 3 kV in negative

ionisation mode; lens voltage 0.3 V; source temperature, 120 °C and desolvation temperature, 500 °C. Dwell times of 0.01 s/scan were selected.

MassLynx software v 4.1 (Waters Corporation) was used to acquire data. TargetLynx application manager was used to quantify the concentration levels of the target analytes.

- ***UHPLC-(ESI)QqQ MS/MS (TQS)***

A triple quadrupole mass spectrometer was interfaced to a Waters ACQUITY UPLC™ system (Waters Corp., Milford, MA, USA), equipped with a binary pump system. Chromatographic separation was carried out using an ACQUITY UPLC BEH C<sub>18</sub> column (100 x 2.1 mm i.d., particle size 1.7 μm) (Waters). An optimized gradient was used at a constant flow rate of 0.3 mL/min using water/methanol (both 0.01% NH<sub>3</sub>). A binary gradient elution was applied, changing linearly the methanol percentage as follows: 0 min, 40%; 1 min, 40%; 5 min, 95%; 6 min, 95%; 6.1 min, 40%. The chromatographic run time was 10 min. The injection volume was 1 μL.

A Xevo TQ-S™ triple quadrupole mass spectrometer (Waters Micromass, Manchester, UK), equipped with ESI source was used. Determination of analytes was performed using ESI source in both positive and negative ion modes. Drying gas as well as nebulising gas was nitrogen (Praxair, Valencia, Spain). The cone gas flow rate was optimized at 150 L/h and the desolvation gas flow was set to 1200 L/h. The desolvation temperature was 650 °C. For operation in MS/MS mode, collision gas was Argon 99.995% (Praxair, Valencia, Spain) with a pressure of approximately  $4 \times 10^{-3}$  mbar in the collision cell. Electrospray needle capillary voltage was fixed at 3.5 kV in positive ionisation mode. The source temperature was set to 150 °C. The column temperature was maintained at 45 °C.

MassLynx software v 4.1 (Waters Corporation) was used to acquire data. TargetLynx application manager was used to quantify the concentration levels of the target analytes.

## 2.6 Screening by (Q)TOF MS

**Table S1.** Organics compounds included in the screening methodology based on GC-QTOF MS and LC-QTOF MS.

<b>Family</b>	<b>Total number of compounds</b>	<b>Number of compounds with reference standard available</b>
<b>LC-QTOF MS</b>		
Pesticides*	543	281
Pharmaceuticals and vet drugs	892	226
Drugs of abuse	140	29
UV filters	22	3
<b>GC-QTOF MS</b>		
Pesticides*	425	160
PAHs	24	24
PCBs	18	18
PBDEs	11	11
PFCs	24	8
Musks	15	13
Antimicrobials	6	6
Insect repellents	2	1

\*Several pesticides were screened by both GC and LC-QTOF MS. The total number of different pesticides investigated by both techniques was 698

## 2.7 Target quantitative analysis by LC-MS/MS QqQ

**Table S2.** UHPLC-QqQ MS/MS conditions for analyte quantification. Quantification (Q) and confirmation (q) transitions. Other compounds different than pesticides are in italic.

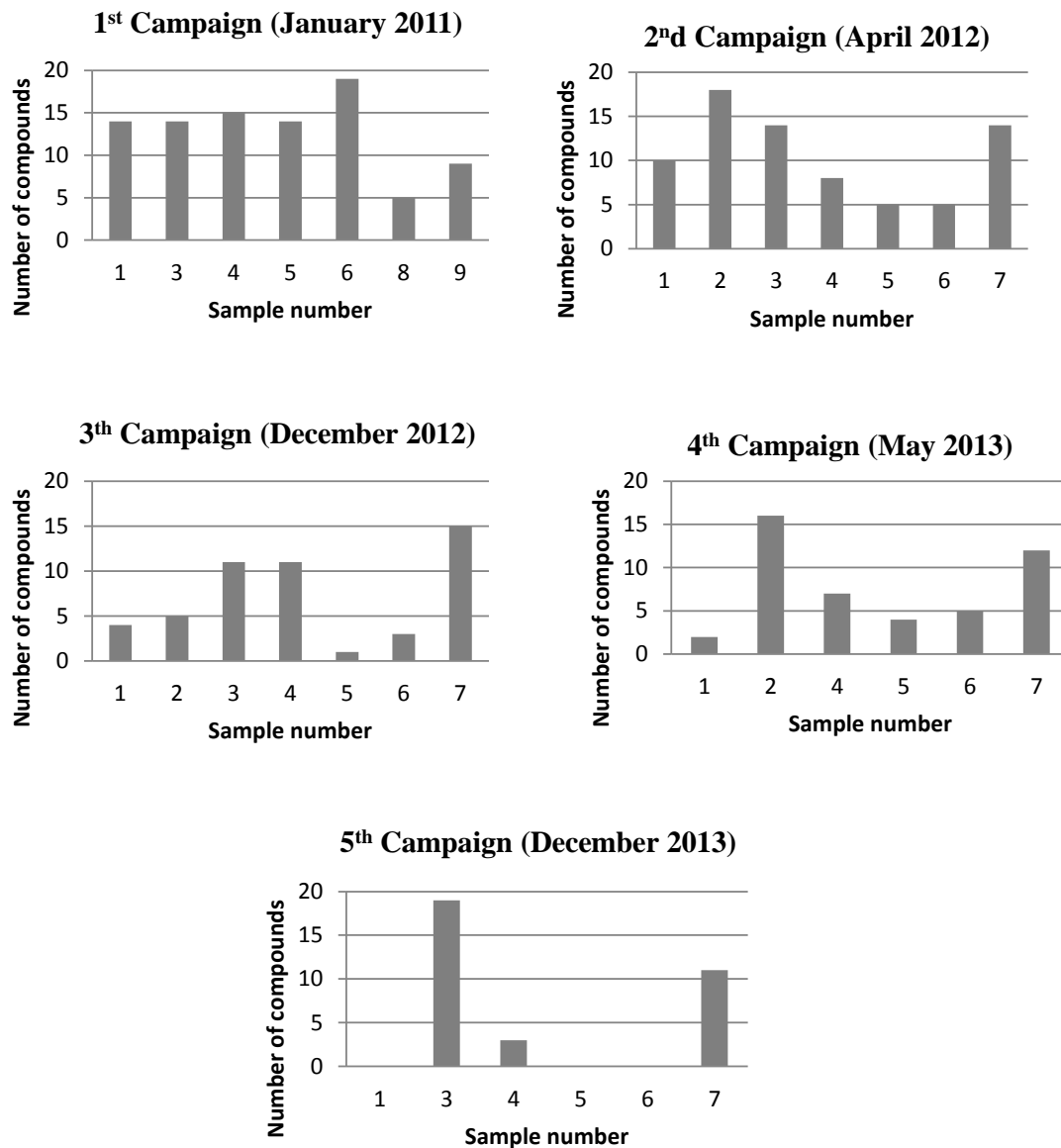
Compounds	Polarity	Cone voltage (V)	Q transition	Collision energy (eV)	q transition	Collision energy (eV)	LOQ (ng/L)
Atrazine	ES+	50	216.1 > 174.1	20	216.1 > 96.2	25	0.4
Atrazine, deisopropyl (DIA)	ES+	50	174.0 > 68.0	20	174.0 > 96.0	15	2
Atrazine, desethyl (DEA)	ES+	50	188.0 > 146.0	15	188.0 > 104.0	15	2
Bromacil <sup>a</sup>	ES-	45	259.0 > 203.0	20	261.0 > 205.0	20	25
Carbaryl	ES+	30	202.0 > 145.1	20	202.0 > 127.2	30	5
Carbendazim <sup>a</sup>	ES+	40	192.0 > 160.0	20	192.0 > 132.0	30	25
Carbofuran	ES+	30	222.2 > 165.3	15	222.2 > 123.2	20	2
Diuron	ES+	30	233.1 > 72.2	20	233.1 > 160.1	20	9
Imidacloprid	ES+	20	256.1 > 209.2	10	256.1 > 175.1	10	9
Isoproturon	ES+	20	207.2 > 72.2	20	207.2 > 134.2	20	0.2
MCPA <sup>a</sup>	ES-	40	199.0 > 141.0	10	201.0 > 143.0	10	25
Metalaxyl	ES+	35	280.1 > 220.1	15	280.1 > 160.1	25	1
Metolachlor	ES+	50	284.2 > 252.0	15	284.2 > 176.1	25	2
Pirimicarb	ES+	20	239.2 > 182.2	20	239.2 > 109.2	20	0.2
Pyridaphention	ES+	20	340.9 > 189.2	20	340.9 > 205.2	20	2
Simazine	ES+	20	202.2 > 132.2	20	202.2 > 124.0	20	3
Terbacil <sup>a</sup>	ES-	40	215.2 > 159.1	15	217.2 > 161.1	15	25
Terbutometone	ES+	50	226.0 > 170.2	20	226.0 > 75.0	30	0.5
Terbutometone, desethyl	ES+	50	198.3 > 142.2	15	198.3 > 86.1	20	0.3
Terbutylazine	ES+	20	230.2 > 174.1	15	230.2 > 96.0	20	0.3
Terbutylazine, 2-hydroxy	ES+	30	212.2 > 156.1	15	212.2 > 86.1	20	0.3
Terbutylazine, desethyl	ES+	20	202.2 > 145.9	25	202.2 > 79.0	25	1
Terbutryn	ES+	30	242.1 > 91.2	30	242.1 > 186.2	30	2
Thiabendazole	ES+	20	202.1 > 131.2	40	202.1 > 175.1	40	1
<i>Acetaminophen<sup>a</sup></i>	ES+	30	152.1 > 110.1	15	152.1 > 93.0	25	25
<i>Carbamazepine</i>	ES+	50	237.1 > 194.2	20	237.1 > 179.0	35	0.2
<i>Clarithromycin<sup>a</sup></i>	ES+	55	590.3 > 158.1	25	748.3 > 158.1	30	25
<i>Erithromycin<sup>a</sup></i>	ES+	35	734.4 > 158.1	30	734.4 > 576.3	25	25
<i>Ibuprofen<sup>a</sup></i>	ES-	30	205.1 > 161.1	10	-	-	25
<i>Irbesartan</i>	ES+	20	429.3 > 207.1	30	429.3 > 195.2	25	0.4
<i>Valsartan</i>	ES+	20	436.3 > 207.0	25	436.5 > 291.1	20	6
<i>Benzoylcegonine</i>	ES+	50	290.3 > 168.2	20	290.3 > 105.0	30	0.3
<i>Cocaine<sup>a</sup></i>	ES+	30	304.1 > 182.2	20	304.1 > 82.0	30	25

<sup>a</sup>Compounds analyzed only in campaigns 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup>, by using UHPLC-QqQ MS/MS (TQD)



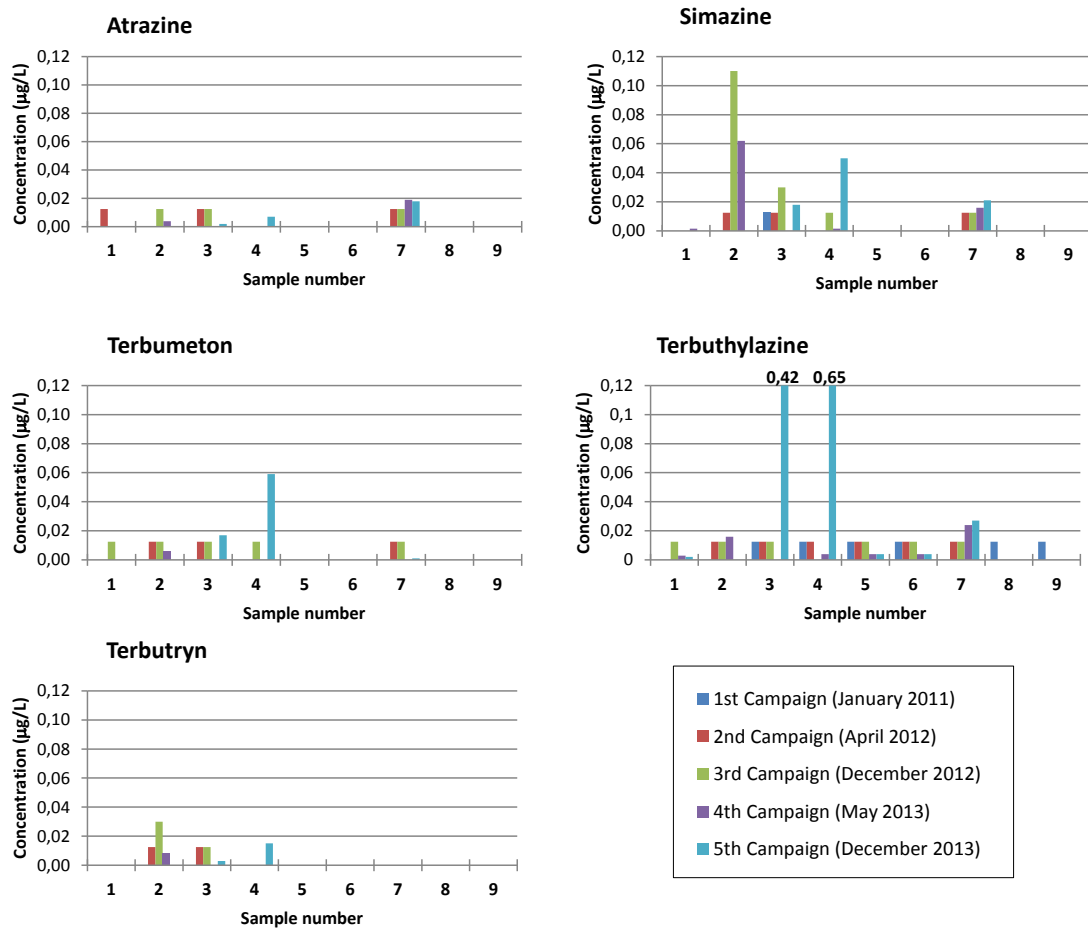
### 3. RESULTS AND DISCUSSION

#### 3.1 Screening analysis (GC-(Q)TOF and UHPLC-QTOF MS)

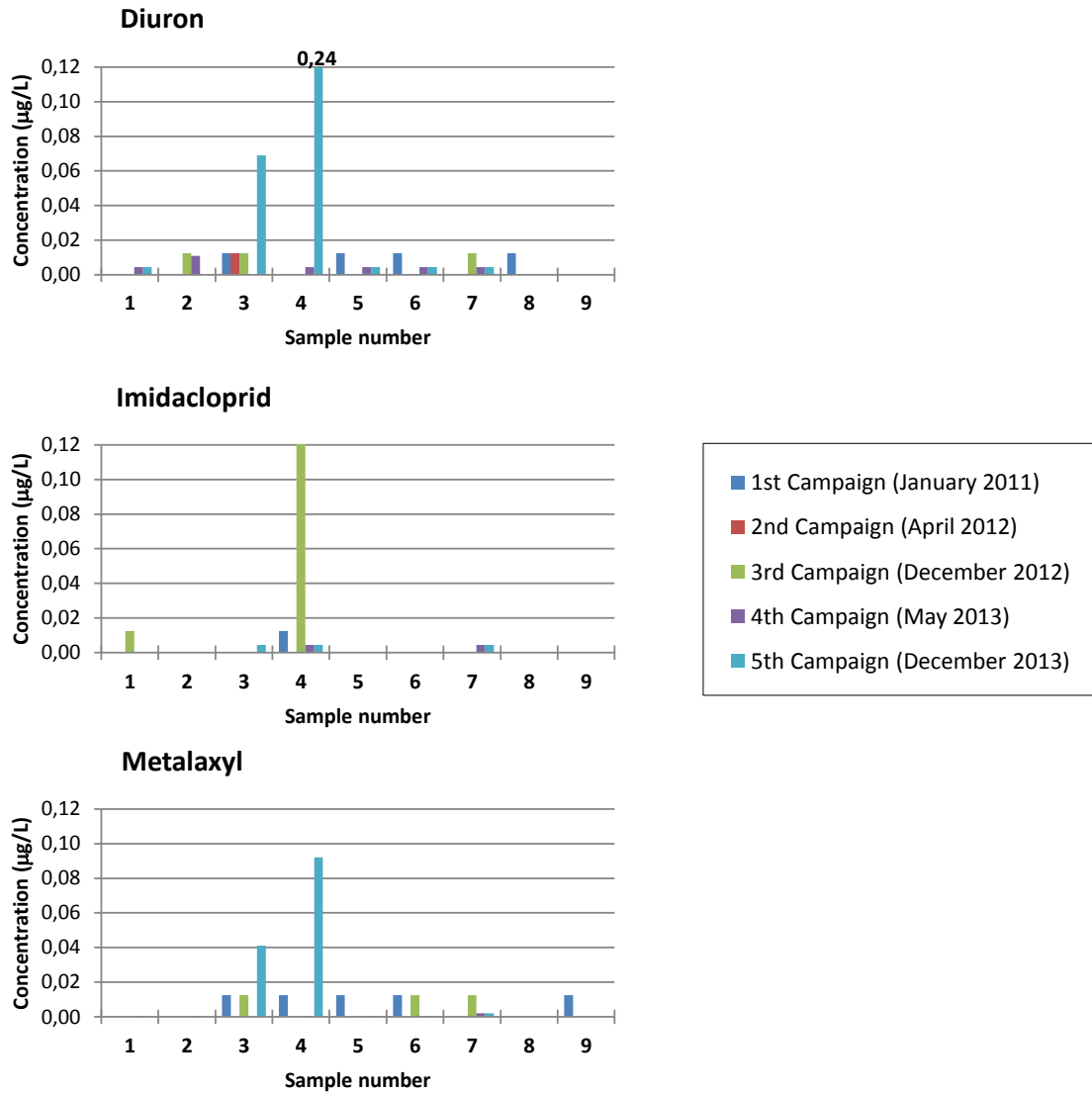


**Figure S2.** Number of compounds detected in every water sample analyzed by GC-(Q)TOF MS and UHPLC-QTOF MS screenings

### 3.2 Quantitative analysis (UHPLC-QqQ MS/MS)



**Figure S3.** Concentrations of positive findings corresponding to five triazine herbicides detected in water samples from the surrounding area. Points 5 and 6 correspond to surface water; the remaining points correspond to groundwater (more information on the sampling sites in Hydrogeological description of the sampling area, and in Figure S1).



**Figure S4.** Concentrations of positive findings corresponding to three pesticides detected in water samples from the surrounding area. Points 5 and 6 correspond to surface water; the remaining points correspond to groundwater (more information on the sampling sites in Hydrogeological description of the sampling area, and in Figure S1).