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

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HIGHLIGHTS

- Evaluation of the impact of a solid waste treatment plant on the surrounding water
- Screening of around 1500 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

GRAPHICAL ABSTRACT
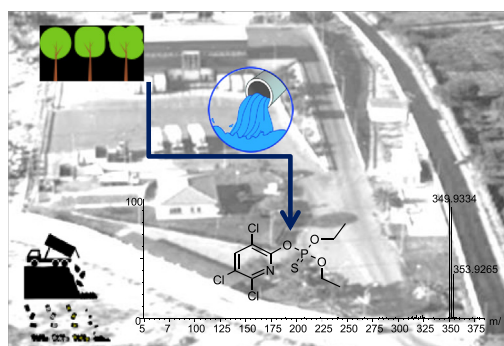
ABSTRACT

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 1500 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 analyser. In this way, up to 24 pesticides and transformation products (TPs), 7 pharmaceuticals, one drug of abuse and its metabolite could be

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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.

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-μg/L levels) relies on the use of advanced analytical methodology, able to detect, identify and quantify these compounds (Richardson, 2012; Richardson and Ternes, 2014). To this aim, the hybridization 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 analysers 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 1500 compounds). Additionally, all samples were also analysed 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 (1st campaign), April 2012 (2nd campaign), December 2012 (3rd campaign), May 2013 (4th campaign) and December 2013 (5th 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). Fig. 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 1600 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 1000 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 2000 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™) (Waters Corp.) interfaced to a QTOF Premier mass spectrometer (Waters Corp.), using an orthogonal Z-spray electrospray (ESI) interface.
- A Waters Acquity UPLC™ 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™ (Waters Corp.), equipped with a quaternary pump system, interfaced to triple quadrupole mass spectrometer TQD™ with orthogonal (ESI) Z-spray (Waters Corp.).
- Waters Acquity UPLC™ (Waters Corp.), equipped with a binary pump system, interfaced to triple quadrupole mass spectrometer Xevo TQ-S™ (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.

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.

Family	Compound	Positive samples (%)
FUNG unclassified	2-Phenylphenol[b,d]	12
HERB triazine	Atrazine[a,b,d]	33
HERB triazine	Atrazine 2-hydroxy[a]	15
HERB triazine	Atrazine deisopropyl (DIA)[a,b,d]	30
HERB triazine	Atrazine desethyl (DEA)[a,b]	24
HERB uracil	Bromacil[a]	27
FUNG benzimidazole bebebenzimidazdimethylcarbamate	Carbendazim[a]	27
INS dimethylcarbamate	Carbofuran[a,d]	3
INS OP	Chlorpyriphos ethyl[a,b,d]	3
INS OP	Chlorpyriphos methyl[a,b,d]	3
INS OP	Coumaphos[a,b,d]	3
INS OP	Diazinon[a,b,d]	3
INS OP	Dimethoate[a,b,d]	3
HERB phenylurea	Diuron[a]	21
FUNG conazole	Imazalil[a,b,d]	6
INS pyridylmethylamine	Imidacloprid[a]	9
FUNG anilide	Metalaxyl[a,b,d]	18
INS dimethylcarbamate	Pirimicarb[a,b,d]	3
INS OP	Pirimiphos methyl[a,b,d]	3
FUNG anilinopyrimidine	Pyrimethanil[a,d]	8
HERB triazine	Simazine[a,b,d]	51
HERB triazine	Simazine 2-hydroxy[a]	12
FUNG conazole	Tebuconazole[a,b,d]	3
HERB uracil	Terbacil[a,b,d]	9
HERB triazine	Terbumeton[a,b,d]	33
HERB triazine	Terbumeton desethyl[a,b,d]	33
HERB triazine	Terbuthylazine[a,b,d]	76
HERB triazine	Terbuthylazine 2-hydroxy[a]	64
HERB triazine	Terbuthylazine desethyl[a,b,d]	56
HERB triazine	Terbuthylazine desethyl 2-hydroxy[a]	6
HERB triazine	Terbutryn[a,b,d]	15
HERB triazine	Terbutryn desethyl[a]	3
FUNG thiazole	Thiabendazol[a,b,d]	18
Antioxidant	BHT[c]	57
Antioxidant	BHT-CHO[c]	29
Cosmetic	Myristate isopropyl[c]	71
Cosmetic	Myristate n-butyl[c]	43
Drugs of abuse	Benzoylecgonine[a]	3
Drugs of abuse	Caffeine[c]	43
Insect repellent	N,N-diethyl-meta-toluamide (DEET)[e]	8
Musk	Tonalide[e]	50
PAH	Naphtalene[b,d]	18
PAH	Napthalene 2-methyl[c]	100
Pharmaceutical	Ibuprofen[a]	3
Plant growth regulators	Naphthalene 2,6-diisopropyl (2,6-DIPN)[c]	57
Plasticizer	N-butyl benzene sulphonamide (N-BBSA)[c]	86
Preservative	Buthylparaben[a]	15
Preservative	Ethylparaben[a]	12
Preservative	Propylparaben[a]	21
Preservative	Methylparaben[a]	21
UV filter	Benzophenone[c]	71
UV filter	Ethylhexyl methoxycinnamate (EHC)[e]	17
UV filter	Octocrylene[e]	42

FUNG: fungicide; HERB: herbicide; INS: insecticide; OP: organophosphorus; PAH: polycyclic aromatic hydrocarbon; UV: ultraviolet.
[a] Compounds analysed by UHPLC–QTOF MS (n = 33).
[b] Compounds analysed by GC–TOF MS (n = 21).
[c] Compounds analysed by GC–TOF MS (non-target) (n = 7).
[d] Compounds analysed by GC–QTOF MS (n = 12).
[e] Compounds analysed by GC–QTOF MS (suspect, reference standard not available) (n = 12).

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 1st, 2nd and 3rd campaigns were analysed by combined use of GC–(EI)TOF MS (GCT, Waters) and UHPLC–QTOF MS (Premier, Waters). The latest samples, corresponding to 4th and 5th 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^E 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 1597 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
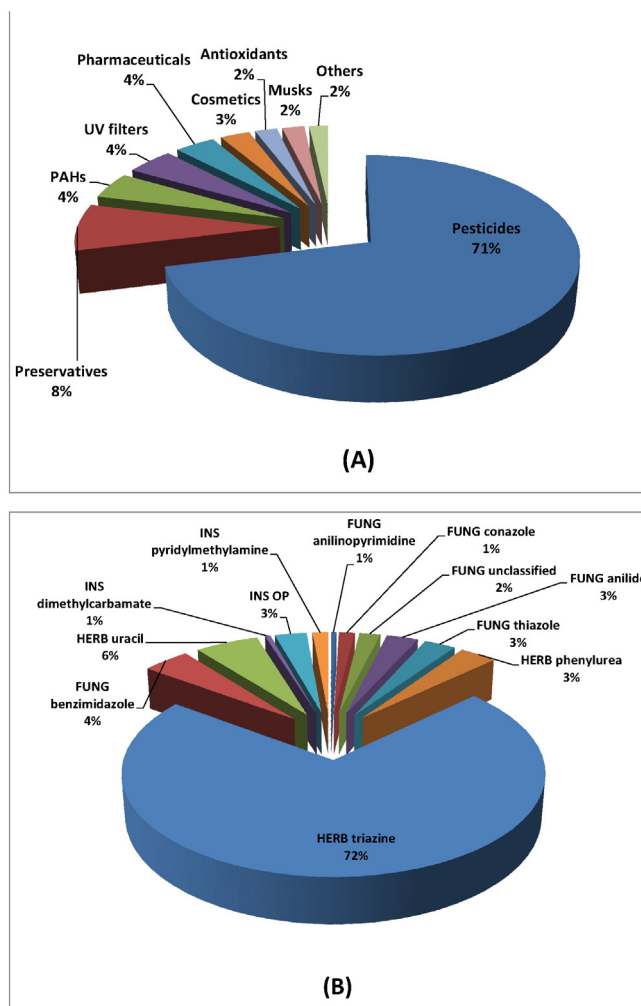

Fig. 1. Percentages of positive findings for (A) the different families of compounds, and (B) the different families of pesticides, detected in water samples by screenings using GC–(Q)TOF MS and UHPLC–QTOF MS.
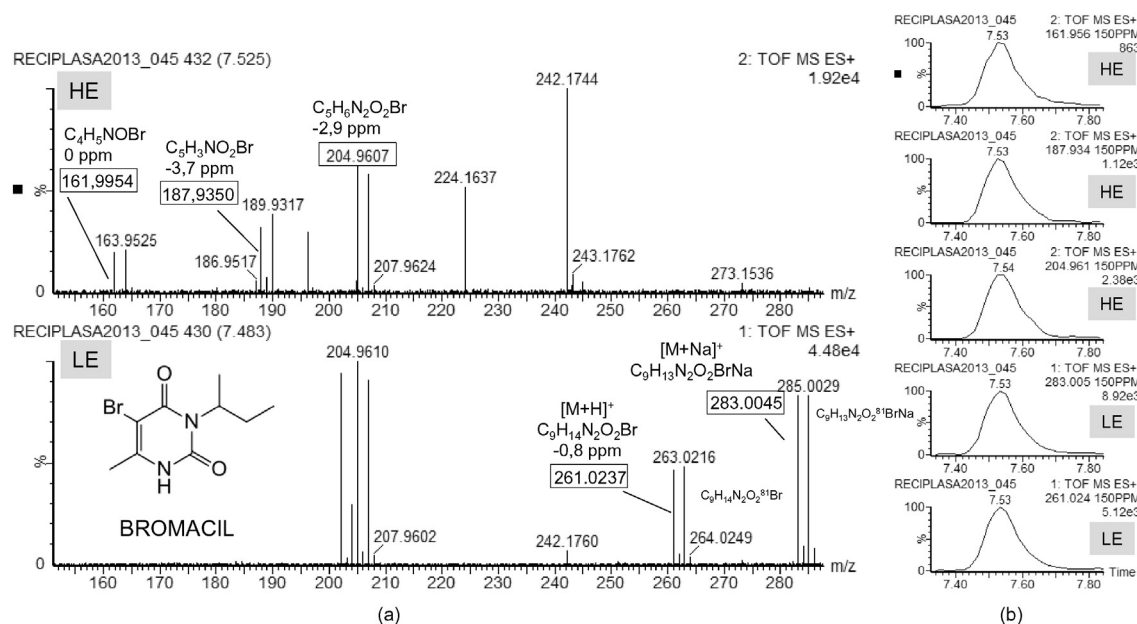
Fig. 2. Positive finding of bromacil after UHPLC–QTOF MS screening to groundwater sample San Martin de Porres (December 2013). (a) LE (low energy) and HE (high energy) TOF mass spectra for the chromatographic peak at 7.53 min (see the bromine pattern). Elemental composition and mass errors in mDa are 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.

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 1st, 2nd and 3rd campaigns; TQ-S™ for the 4th and 5th 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
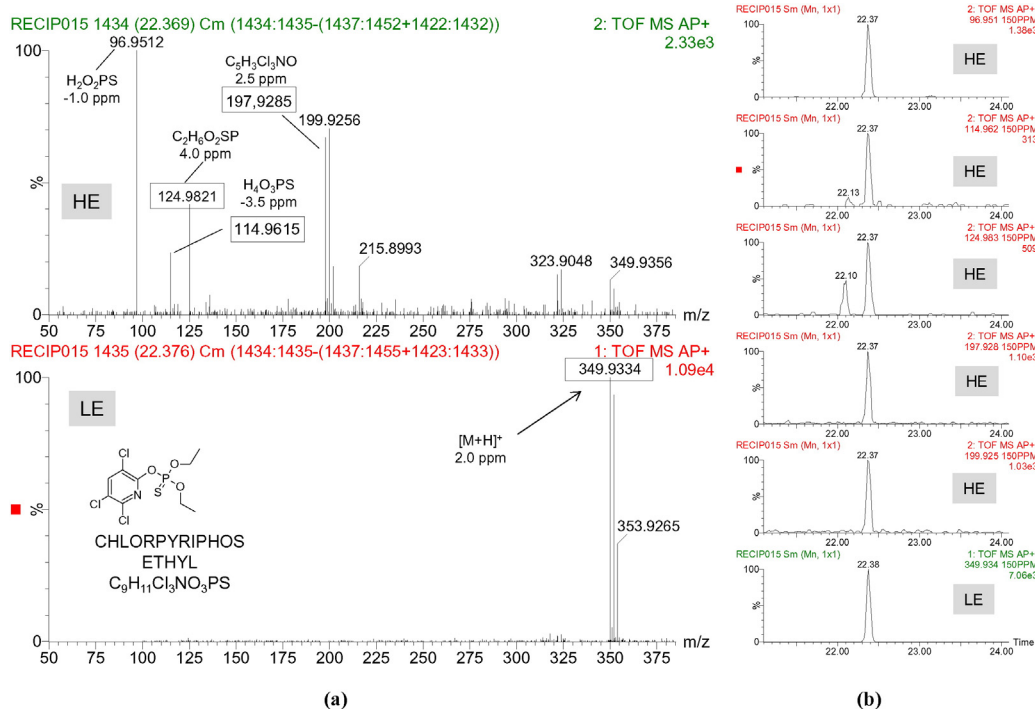

Fig. 3. Positive finding of chlorpyriphos ethyl after GC–QTOF MS screening to groundwater sample Sabater I (December 2013). (a) LE (low energy) and HE (high energy) TOF mass spectra for the chromatographic peak at 22.39 min (see the chlorine pattern). Elemental composition and mass errors in mDa are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

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 Rt within ± 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

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)[a]	8	0	0.031
HERB triazine	Atrazine desethyl (DEA)[a]	42	0	0.092
HERB uracil	Bromacil[b]	14	0	<0.025
INS carbamate	Carbaril	15	0	<0.025
INS dimethylcarbamate	Carbendazim[b]	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[b]	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[a]	92	25	0.39
HERB triazine	Terbuthylazine desethyl[a]	92	33	0.34
HERB triazine	Terbutryn	21	0	0.03
FUNG thiazole	Thiabendazol	15	0	<0.025
Drugs of abuse	Benzoylecgonine[c]	32	5	0.17
Drugs of abuse	Cocaine[d]	43	0	<0.025
Pharmaceutical	Carbamazepine[a]	42	0	0.001
Pharmaceutical	Clarithromycin[d]	29	0	<0.025
Pharmaceutical	Erythromycin[d]	14	0	<0.025
Pharmaceutical	Ibuprofen[d]	14	14	0.23
Pharmaceutical	Irbesartan[a]	42	0	<0.0004
Pharmaceutical	Valsartan[a]	33	0	<0.006
Pharmaceutical	Acetaminophen[d]	29	0	0.054

[a] n = 12 samples.
[b] n = 21 samples.
[c] n = 19 samples.
[d] n = 7 samples.

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 (2007/335/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 1st 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
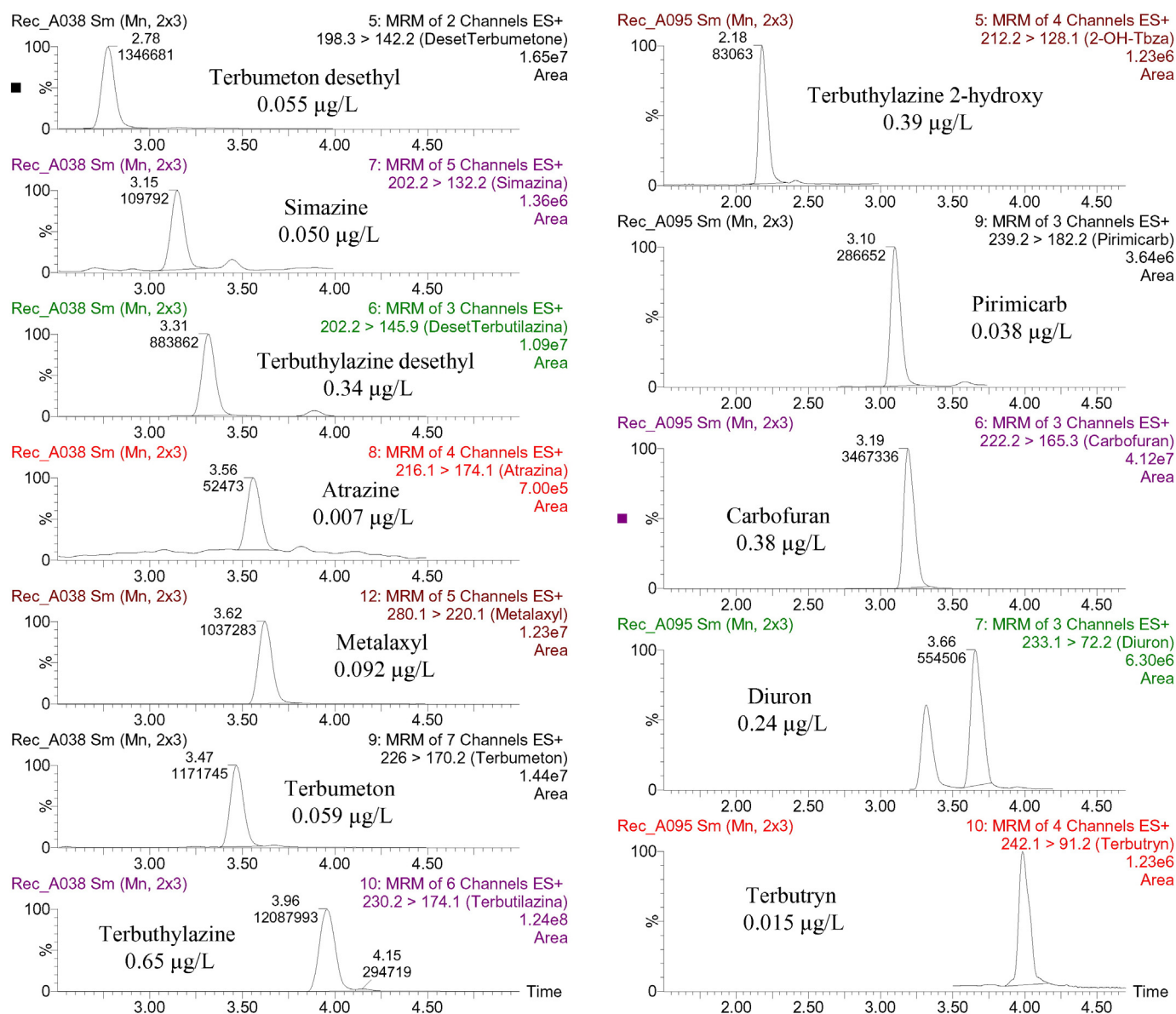

Fig. 4. UHPLC–QqQ MS/MS chromatograms that illustrate several compounds found in Sabater II groundwater sample (point 4, December 2013). Only the quantification transition (Q) is shown for every analyte.

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 (4th and 5th 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.

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

As an example, Fig. 2 illustrates the detection and identification of the uracil herbicide bromacil in San Martin de Porres groundwater (point 7, 5th 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, Fig. 3 shows a positive of chlorpyriphos ethyl in Sabater I groundwater (point 3, 5th 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 chlorpyriphos ($C_9H_{11}Cl_3NO_3PS$). Finally, for the presence of 4 fragment ions (in HE function) led to the confirmation of the compound identity.

Fig. S2 (in Supplementary information) shows a summary of the analytes detected in every sample analysed. The major number of detections corresponded to the 1st and 2nd 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 (≥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. Terbuthylazine and its TPs, as well as the terbumeton 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 analysed, 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, terbuthylazine 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 μg/L, respectively, in surface waters. The two terbuthylazine TPs (desethyl and 2-hydroxy) were the most frequently detected at concentrations above 0.1 μg/L (33 and 25% of water samples analysed, respectively). Only in one case, the level of 0.5 μg/L was surpassed, and it occurred for terbuthylazine, with a maximum concentration of 0.65 μg/L (sample point 4, Sabater II, December 2013).

Figs. 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 μg/L in one sample, but always at concentrations below 0.25 μg/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 μg/L was surpassed.

An example of the quantitative analysis is shown in Fig. 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 μg/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 μg/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 1500 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. Terbuthylazine 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, terbuthylazine, terbuthylazine 2-hydroxy and terbuthylazine desethyl) and also the cocaine metabolite (benzoylecgonine) and one pharmaceutical (ibuprofen). Terbuthylazine 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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.12.166.

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