ADVANCING TOWARDS UNIVERSAL SCREENING FOR ORGANIC POLLUTANTS IN WATERS

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ABSTRACT

Environmental analytical chemists face the challenge of investigating thousands of potential organic pollutants that may be present in the aquatic environment. High resolution mass spectrometry (HRMS) hyphenated to chromatography offers the possibility of detecting a large number of contaminants without pre-selection of analytes due to its accurate-mass full-spectrum acquisition at good sensitivity. Interestingly, large screening can be made even without reference standards, as the valuable information provided by HRMS allows the tentative identification of the compound detected. In this work, hybrid quadrupole time-of-flight (QTOF) MS was combined with both liquid and gas chromatography (using a single instrument) for screening of around 2,000 compounds in waters. This was feasible thanks to the use of atmospheric pressure chemical ionization source in GC. The screening was qualitatively validated for around 300 compounds at three levels (0.02, 0.1, 0.5 μg/L), and screening detection limits were established. Surface, ground water and effluent wastewater samples were analyzed, detecting and identifying a notable number of pesticides and transformation products, pharmaceuticals, personal care products, and illicit drugs, among others. This is one of the most universal approaches in terms of comprehensive measurement for broad screening of organic contaminants within a large range of polarity and volatility in waters.

KEYWORDS: liquid chromatography, gas chromatography, quadrupole time of flight mass spectrometry, universal screening, water samples, organic micropollutants

1. INTRODUCTION

Over the last decades, environmental pollution has become a matter of increasing concern due to the high number of both regulated and unregulated organic pollutants that can be present in environmental waters. The majority of these compounds, such as pesticides, pharmaceuticals, drugs of abuse, surfactants, biocides, personal care products, sweeteners, etc. are originated by human use. They can enter in the surface water (and even groundwater) mainly via treated and untreated wastewater [1-2]. Despite the evident advances in analytical chemistry, the comprehensive determination of organic contaminants in waters is still a challenge at present. The main difficulty arises from the elevated number of compounds (in addition to their metabolites and/or transformation products) that may be present in the samples. This fact, together with the very different physico-chemical properties of analytes, makes the application of a single analytical methodology, appropriate for all potential contaminants, unfeasible.

Most analytical methods developed until now have used chromatographic techniques coupled to mass spectrometry (MS) analyzers, as single quadrupole or ion trap, and in the last decade, triple quadrupole. In these target methods, the list of analytes rarely exceeds 200-300 compounds, and relevant contaminants other than the target analytes that might be present in the samples are commonly ignored. Therefore, there is a need for the development of wide-scope "universal" screening methods able to detect and identify a long list of contaminants, offering in this way more realistic and complete information on undesirable compounds present in environmental samples.

Full spectrum acquisition techniques such as high resolution mass spectrometry (HRMS) offer the possibility for screening a huge number of contaminants in post-targeted approaches

(i.e. the selection of compounds to be searched is made once mass data have been acquired) without the need of pre-selecting the analytes for method development. Besides, the subsequent searching of any other compound at any time, in a retrospective analysis, is also feasible without the need of new sample injections. An additional value of HRMS is that it provides accurate-mass full-spectra data with reasonable sensitivity [3]. Interestingly, search and detection of contaminants can be made even without reference standards, as the valuable information provided by HRMS commonly allows reliable tentative identifications [4].

Time of flight (TOF) and Orbitrap analyzers have been frequently used in LC-HRMS based methods for screening of many different families of contaminants in the aquatic environment. Target analytes include compounds of medium/high polarity compatible with LC analysis (e.g. many pesticides, pharmaceuticals -antibiotics included-, illicit drugs, veterinary drugs, etc.) [5-12].

As a complement to LC-MS methods, GC-MS allows to investigate GC-amenable contaminants, such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs), and certain pesticides, among others. Although single nominal analyzers like single quadrupole, ion trap or triple quadrupole can be used to this aim, HRMS is a superior technique for screening purposes, for the same reasons indicated above. With the exception of analysis of dioxins and related compounds using magnetic sectors [5], GC-HRMS has seldom been explored in environmental pollution monitoring until recently. The first applications of GC-HR TOF MS were reported in 2004[13-15]. Almost all applications have dealt with the determination of persistent and other priority pollutants in environmental [3,16] and biological fields [17-18]. Electron ionization (EI) source is the preferred ionization technique and the most widely applied due to its

robustness, reproducibility and the existence of standardized commercial spectra libraries, which facilitates the identification of compounds. There is a number of databases available (for example, NIST) that have already designed non-target tools (such as AMDIS) that identify fragments and match them against a database of over 200,000 individual compounds obtaining satisfactory results and making this approach a reference in the field [19-20].

However, EI commonly leads to extensive fragmentation. EI mass spectra are characterized by an abundance of fragment ions and in many cases the molecular ion is absent or has low abundance. In the last few years, the atmospheric pressure chemical ionization (APCI) source has been implemented in GC-MS instruments offering attractive features for screening. The soft and universal ionization in this source leads to the presence of abundant molecular ion and/or protonated molecule in the mass spectra, facilitating the sensitive and selective detection of analytes in the samples [21-22]. The availability of this source has allowed the combined use of GC and LC coupled to TOF MS, a combination that appears nowadays as one of the most potent approaches for large screening. The use of a single TOF platform coupled to both GC and LC opens fascinating perspectives in the environmental field. A huge number of compounds, from low polarity and/or high volatility (GC-amenable compounds) to high polarity and/or low volatility (LC-compounds), can be investigated with satisfactory sensitivity and excellent performance in terms of detection and identification/elucidation purposes. Even more useful is hybrid quadrupole time-of-flight (QTOF MS), which offers additional possibilities for identification, such as the acquisition of low (LE) and high collision energy (HE) spectra in one run, or performing additional MS/MS experiments.

The aim of this work is to evaluate the potential of QTOF MS coupled to both LC and GC (using a single instrument) for screening of more than 2,000 compounds in water samples of

different origin and matrix compositions. This strategy has not been explored in the environmental field until now. The method has been qualitatively validated in different water samples (surface water, groundwater and wastewater) for hundreds of selected compounds (141 for LC and 166 for GC, with some compounds having been evaluated by both techniques) at three concentrations (0.02, 0.1 and 0.5 µg/L). The screening procedure has subsequently been applied to water samples, allowing the detection and identification of a high number of organic contaminants. Tentative identifications of compounds detected have been made when the reference standards were unavailable, on the basis of 1) accurate mass (mass errors) of the molecular ion, commonly in the LE spectrum; 2) main fragments observed, typically in the HE spectrum; and 3) isotopic distribution.

2. EXPERIMENTAL

2.1. Reagents and chemicals

Information on reagents and chemicals used in this work is shown in **Supplementary Information.**

2.2. Instrumentation

A hybrid quadrupole-orthogonal acceleration-TOF mass spectrometer (Xevo G2 QTOF, Waters Micromass, Manchester, UK) was interfaced to a Waters Acquity UPLC system (Waters, Milford, MA, USA) or to an Agilent 7890A GC system (Palo Alto, CA, USA), using a single instrument. For details, see **Supplementary Information**.

For MS^E experiments, two acquisition functions with different collision energies were created: the low energy (LE) function, selecting as collision energy 4eV, and the high energy (HE) function, with a collision energy ramp from 10 to 40 eV.

Data were automatically processed by ChromaLynx XS (target mode) software (MassLynx v 4.1, Waters).

2.3. Water samples

Several groundwater (GW) (12 samples), surface water (SW) (12 samples) and effluent wastewater (EWW) (9 samples) were collected from the Spanish Mediterranean area of Valencia during July 2012and analyzed to investigate the presence of organic contaminants. This is an important agricultural area, with predominance of citrus crops; therefore, the presence of pesticides is expected in environmental samples. SW were collected from rivers (2), reservoirs (2) and lakes (8), whereas GW samples were collected from 12 different wells located in the Castellon area. EWW were collected from different WWTPs of the same area. Concretely, they were sampled from Nules, Vall d'Uixó, Castelló de la Plana and Benicàssim. All samples were stored in darkness at <−18 ◦C in polyethylene high-density bottles until analysis. Immediately before analysis, samples were thawed at room temperature.

2.4 Sample treatment

Figure 1 illustrates the screening methodology applied. Samples were analysed by UHPLC-ESI-(Q)TOF MS and GC-APCI-(Q)TOF MS, after a generic solid-phase extraction (SPE) (see **Figure 1a**). Briefly, 250 mL of centrifuged water samples were passed by gravity through Oasis HLB (200 mg, Waters) cartridges, previously conditioned with 5 mL methanol and 5 mL HPLC-grade water. After drying under vacuum, analytes were eluted with 10 mL methanol. The extract was divided into 2 aliquots. The 5 mL-GC aliquot was evaporated under a gentle nitrogen stream at 35ºC down to a volume of 1 mL. Then 1 mL of ethyl acetate was added and evaporated again to 250 µL (final pre-concentration factor x500). The 5 mL-LC aliquot was evaporated to dryness under a gentle nitrogen stream at 35°C and reconstituted with 0.5 mL methanol–water (10:90, v/v) (final pre-concentration factor x250). Finally, 1 and 50 µL of the extracts were injected into the GC-(Q)TOF MS and UHPLC-(Q)TOF MS systems, respectively.

2.5 Data processing

After injection of the sample extracts, full-spectrum acquisition data generated at low and high collision energy (MS^E) were processed, using the specialized application manager ChromaLynx XS (within MassLynx) in combination with a home-made database (see **Figure 1b**). It offers the possibility of applying a "post-target" processing method based on monitoring theoretical exact masses of selected analytes, obtaining the narrow-window eXtracted Ion Chromatograms (nw-XICs), commonly at 10-20 mDa. This permits a rapid and simple reviewing by classifying candidates as a function of the mass error. In addition, this software allows the simultaneous visualization of the complete mass spectra of positive findings at LE and HE. This methodology, commonly applied in LC-MS screening, has

recently become feasible in GC-MS thanks to the availability of the APCI source for GC that allows the soft ionization leading to the formation of the molecular ion and/or the protonated molecule as base peak of the spectrum [23].

In this work, the LC homemade database contained around 1,600 organic contaminants, including pesticides, pharmaceuticals of human consumption, veterinary drugs, drugs of abuse, UV-filter agents, X-ray contrast media, colorants, preservatives, and a notable number of degradation products.

Regarding GC, the database contained 280 compounds, including pesticides, PAHs, PCBs, PBDEs, fragrances, musks, antimicrobials, insect repellents, UV filters and polychloronaphthalenes (PCNs).

When reference standards were available at our laboratory, they were injected onto the LC or GC system, using the same instrumental conditions described in section 2.1 in S.I. Information about retention time (Rt), the main fragment ions observed, and adduct formation was then included in the target list (a *txt* file) in order to facilitate and enhance the reliability in the identification/elucidation process. When standards were unavailable, the only information available was the exact mass of the (de)protonated molecule. In the case of GC-(APCI)QTOF MS analysis, both molecular ion and the protonated molecule were included in the processing screening method for those compounds whose behavior in the APCI source had not been previously evaluated.

The strategy applied consisted on evaluating the presence of the (de)protonated molecule/molecular ion (occasionally adducts), measured at its accurate mass, in the LE function of both GC and LC QTOF mass data. For this purpose, nw-XICs at the *m/z* of all

compounds included in the database were automatically performed in the LE function. Due to the narrow mass window employed, usually only one single chromatographic peak was observed at the expected retention time (Rt). Thus, when reference standards were available, the presence of a chromatographic peak at the expected Rt, together with the evaluation of the fragment ions, all measured at accurate mass (mass accuracy accepted was ± 2 mDa), and characteristic isotopic ions, allowed the unequivocal confirmation of the identity of the compound detected.

When one or more peaks were observed at a given exact mass but the reference standard was not available at our lab (i.e. information on Rt was unavailable), it was necessary to evaluate which peak (if any) corresponded to the candidate. Collision induced dissociation (CID) fragments (in any of the two functions acquired), or characteristic isotopic ions of the same chromatographic peak, were evaluated. UHPLC and GC were valuable tools for choosing perfectly co-eluting fragment ions that in principle correspond to the same "precursor", while at the same time avoiding spectrum interferences that would complicate the identification process. MassFragment software (Waters) was used to propose compatible structures from accurate mass measurements of the observed fragment ions. When available, the tentative identification was supported by MS/MS product ions reported in the literature for the suspect compound (either in exact or nominal mass). After a careful evaluation process, the reference standards (when commercially available) were finally acquired and injected to unequivocally confirm the identity of the compound.

2.6. Qualitative validation

In order to evaluate the applicability of the method, a qualitative validation was performed. For this purpose, a total of nine water samples (3 surface waters, 3 ground waters and 3 effluent wastewaters) were spiked (after centrifugation of the samples) with a standard mixture of around 250 organic contaminants from different chemical families at three concentration levels (0.02, 0.1 and 0.5 µg/L). After solid-phase extraction with Oasis HLB, sample extracts were analyzed by UHPLC-(ESI)QTOF MS and GC-(APCI)QTOF MS and accurate-mass full-spectrum acquisition data processed. The screening detection limit (SDL) was established as the lowest concentration tested for which a compound was detected in all the samples, using the most abundant ion (normally, the (de)protonated molecule or the molecular ion) at the expected retention time (2.5% deviation tolerance in LC and 0.5% in GC) measured at its exact mass with a maximum mass error of 2 mDa.

Selectivity, considered as the ability of the method to discriminate between the analyte and other compounds that might be present in the sample, was tested for every analyte in the presence of the rest of compounds included in the screening. It was based on the presence of characteristic *m/z* ions, measured at accurate mass, for each compound in the LE and HE spectra.

Specificity, considered as the ability of the detector (supported by the selectivity of the extraction, clean-up, derivatization or separation, if applicable) to provide signals that effectively identify the analyte, was checked by analyzing nine "blank" water samples (3 SW, 3 GW and 3 EWW) and also a deionized water sample (blank of procedure). Some of these non-spiked samples contained several of the organic pollutants under study; therefore, it was unfeasible to evaluate specificity in these particular cases.

3. RESULTS AND DISCUSSION

In this paper, a simple and quite generic approach, based on solid phase extraction (SPE) using Oasis HLB polymeric cartridges was selected. This sorbent has been frequently used in multi-residue methods and is able to retain a great variety of contaminants, from non-polar to rather polar ones. Obviously, in a "universal" method an extensive sample treatment able to extract all potential contaminants present in the sample would be required; this is, from ionic to nonpolar analytes, also avoiding potential losses of volatile compounds that might occur in evaporation steps. However, the approach selected in this work was directed towards a "universal" sample analysis, trying to detect and identify all compounds that passed the sample treatment, more than towards a tedious and long sample manipulation. Therefore, a rather "universal" although simple sample treatment was selected, such as SPE with Oasis HLB, and the analytical effort was focused on the measurement of the organic pollutants in the sample.

With the objective of having available analytical methodology for screening of water samples, able to detect as many contaminants as possible independently on their polarity and volatility, the approach selected in this work was tested for different water types and qualitatively validated for a notable number of model compounds in both LC-QTOF MS and GC-QTOF MS modes. The availability of the APCI source in GC-QTOF MS was relevant for this purpose, as it allowed to use a common strategy based on searching for the molecular ion/(de)protonated molecule. The use of this ion, highly abundant in APCI and ESI spectra, gives more sensitivity and specificity to the screening methodology.

3.1. Validation results

Several aqueous matrices were tested in method validation: surface water, groundwater and effluent wastewater. Three samples of each water type were spiked at 0.02, 0.1 and 0.5 µg/L for a notable number of selected compounds, and analyzed together with the non-spiked blank samples. The difficulties encountered when trying to find realistic samples free of all target analytes must be highlighted. Under these circumstances, those waters previously analyzed and proven to have less positive findings were selected as "sample blanks" to facilitate the validation process. **Tables S1-S2** of **Supplementary Information** show the results obtained by UHPLC-QTOF MS and GC-QTOF MS, respectively.

Figure 2 summarizes the SDL (the lowest SDL obtained either by UHPLC-QTOF MS or by GC-QTOF MS is shown) for each analyte. As it can be seen, the vast majority of compounds (around 80%) could be detected at the 0.1 µg/L level, while the percentage of detection decreased down to 60% at 0.02 µg/L. At the highest level tested, i.e. 0.5 µg/L, more than 90% of the contaminants could be satisfactorily detected in all matrices tested.

Surely, SDLs for several of the more hydrophobic compounds, such as high molecular weight PCBs, PAHs and pyrethroid pesticides, could be improved if a specific method was applied for them, e.g. avoiding the use of methanol as SPE eluent (some of these compounds might not completely elute with this solvent), or using another SPE sorbent as C_{18}. Additionally, the evaporation step and the subsequent change of the solvent from methanol to ethyl acetate might lead to losses for volatile compounds. Thus, the sample treatment was selected as a compromise between efficiency and simplicity trying to avoid an extensive sample handling, and taking into account that less favorable recoveries might be compensated by a selective and sensitive measurements of the sample extracts by QTOF MS.

The consequence of using real-world samples for validation was that several of the "blank" samples contained some of the contaminants under study. In these particular cases, the SDL was only established when a minimum of 5 samples were available as a true blank. Thus, the SDL could not be established when the compound was present in more than 50% of the samples (see **Table 1** and **Tables S.1, S.2**).

3.2. Application to routine samples

A total of 33 water samples (12 GW, 12 SW, 9 EWW) collected in different sites of the Mediterranean Spanish region were analysed following the developed procedure. The applied screening allowed the detection and identification of a notable number of compounds in a highly reliable way. In total, 78 pesticides and metabolites/transformation products, 24 pharmaceuticals and metabolites, 4 drugs of abuse and metabolites, 4 preservatives, 2 sweeteners, 2 X-ray agents, 3 PAHs, 2 musks, 5 UV-filters, 1 antimicrobial and 2 insect repellents were found (see **Table S3** in **S.I.**). The presence of at least two accurate-mass measured ions (typically the (de)protonated molecule and one fragment ion) was used for reliable identification.

Triazine herbicides (particularly, terbuthylazine and terbutryn), the insecticides diazinon and chlorpyrifos-ethyl, and the fungicides thiabendazol, carbendazim and propiconazole, were the most frequently identified pesticides. Among pharmaceuticals, the antibiotic ofloxacin, the anti-inflammatory/analgesic drug diclofenac, the angiotensin II receptor antagonists valsartan and irbesartan, the antidepressant venlafaxine and the anti-epileptic carbamazepine were the most frequently found. Regarding drugs of abuse, benzoylecgonine (the main

302 metabolite of cocaine) was the most detected. Tonalide and octocrylene were the musk and
303 the UV filter most frequently found in the water samples, respectively.

304 For most of the compounds detected, reference standards were available and therefore the
305 identification was straightforward. As an example, **Figure S.1** in **Supplementary**
306 **Information** illustrates the detection and identification of the organophosphate insecticide
307 chlorpyrifos in effluent wastewater by GC-QTOF MS. The protonated molecule was detected
308 in the LE function, with a mass error of 1.4 mDa, at the expected retention time (21.24 min).
309 Moreover, the combined spectrum of this chromatographic peak showed a typical three-
310 chlorine atoms isotopic pattern, being therefore in accordance with the chemical structure of
311 chlorpyrifos ($C_9H_{11}Cl_3NO_3PS$). Its identity was unequivocally confirmed by the presence of
312 four *m/z* ions at the expected retention time in the HE function, with negligible mass errors.

313 In a few positive samples, the reference standards were not available in our laboratory.
314 Despite this fact, a tentative identification was possible based on the ions observed
315 ((de)protonated molecule/molecular ion and fragment ions), their compatibility with the
316 chemical structure of the candidate, and by comparison with the ions reported in the
317 literature. This was the case of the pesticides tebuconazole, penconazole and myclobutanil,
318 the veterinary pharmaceutical levamisole (also used as adulterant in cocaine), the X-ray
319 contrast media iopromide and iomeprol, the main metabolite of methadone (ethylidene-1,5-
320 dimethyl-3,3-diphenyl-pyrrolidine or EDDP), the sweeteners acesulfame and sucralose, the
321 insect repellent Bayrepel and the UV filters isoamylmethoxycinnamate and ethyl hexyl
322 dimethyl PABA.

Figure 3 illustrates the detection and tentative identification of the methadone metabolite (EDDP) in effluent wastewater by UHPLC-QTOF MS. The protonated molecule of EDDP was detected in the LE function, with a mass error of -0.6 mDa (**Figure 3a**, bottom). As the reference standard was not available, chemical structures for the most abundant fragment ions were suggested based on their accurate masses, using the MassFragment software (Waters). This software applies a bond-disconnecting methodology to obtain possible structures for the fragment ions from a given molecule. In order to avoid spectrum interferences that would complicate the identification process, recognizing which ions are fragments and which are not, becomes mandatory. For this purpose, UHPLC turned valuable for choosing perfectly co-eluting ions (see chromatographic peaks at 8.40 min versus the ones at 8.42, in **Figure 3b**). In the HE function (**Figure 3a**, top), up to 4 fragments (*m/z* 249.1512, 234.1279, 186.1278 and 98.0967) were observed with chromatographic peaks at the same retention time, and mass errors lower than 1 mDa in relation to the theoretical predicted exact masses. All structures proposed for the fragments were compatible with the chemical structure of EDDP, making the identification even more reliable. Moreover, the tentative identification of EDDP was supported by the MS/MS product ions reported in the literature. Two fragments (*m/z* 234.1278 and 186.1277) observed in the HE spectrum had been previously reported for this compound by using an LTQ-Orbitrap with a resolving power of 30,000 [24]. After this careful evaluation process, the reference standard was finally acquired and injected, allowing the ultimate confirmation of this compound in the sample.

After tentative identification, reference standards were acquired for almost all contaminants indicated above (except for isoamyl methoxycinnamate, ethyl hexyl dimethyl PABA and

346 Bayrepel, which are still pending), being unequivocally confirmed in all cases. After injecting
347 the standards, the information obtained on fragmentation was subsequently included to
348 improve the target list for future screenings.

349 A summary of the positive findings found in the samples analyzed is shown in **Figure 4.**
350 Among the detected compounds in **surface water** samples, around 70% corresponded to
351 pesticides, being herbicides and fungicides the most commonly identified. The wide presence
352 of triazine herbicides (atrazine, simazine, terbumeton, terbuthylazine and terbutryn) is
353 noteworthy as well as their transformation products (terbumeton-desethyl, atrazine-desethyl,
354 atrazine-desisopropyl, atrazine-2-hydroxy, terbuthylazine-desethyl and terbuthylazine-2-
355 hydroxy), which were detected in around 90% of the surface water samples (see **Figure S.2**).
356 The herbicide diflufenican, the insecticide diazinon, and fungicides such as thiabendazol,
357 fenarimol, carbendazim, propiconazole and imazalil, were also frequently found.

358 The high number of pharmaceuticals detected in one of the surface waters is striking (**Table**
359 **S.3**). This sample was collected in the estuary of the Mijares River, located a few kilometers
360 downstream from the discharge point of an urban wastewater treatment plant. Valsartan and
361 irbesartan, used for the treatment of hypertension, the antibiotics clindamicyn, lincomycin
362 and ofloxacin, 4-aminoantipyrine-N-formyland 4-aminoantipyrine-N-acetyl (two
363 metabolites of the analgesic metamizol, also known under the commercial trademark
364 Nolotil®), as well as the anti-depressant venlafaxine or the anti-epileptic and mood-
365 stabilizing drug carbamazepine were found in this sample.

366 Some personal care products (PCPs) were also found in surface water, mainly the musk
367 tonalide and the UV filter octocrylene, which were both detected in 11 out of 12 samples

368 analysed. The PAHs anthracene, fluoranthene and pyrene were detected in two of the
369 samples.

370 Regarding **ground waters**, the presence of contaminants was in general much lower than in
371 surface waters, with 76% of detections corresponding to pesticides (**Figure 4**). The presence
372 of terbuthylazine and its transformation product desethyl-terbuthylazine in 11 out of 12
373 samples analysed (**Table S.3**) is remarkable. Other herbicides such as atrazine, simazine,
374 diflufenican, the transformation products atrazine-desisopropyl and terbumeton-desethyl, the
375 insecticide chlorpyriphos-ethyl and the fungicides fenarimol and propiconazole were also
376 detected in a large number of samples (9-10 out of 12).Concerning pharmaceuticals, it is
377 interesting to point out the presence of several compounds in one of the samples, which
378 contained carbamazepine, irbesartan, venlafaxine, sulfamethoxazole and phenazone. In
379 addition, two sweeteners (acesulfame and sucralose), two X-ray agents (iomeprol and
380 iopromide) and several preservatives were also found in this groundwater sample, which was
381 collected near an urban wastewater treatment plant, suggesting possible influence of this
382 plant in the groundwater of the surrounding area. Different personal care products, such as
383 UV-filters (octocrylene, benzophenone-3 and ethylhexylmethoxycinnamate), the fragrances
384 tonalide and galaxolide, and the insect repellent DEET were also detected in groundwater
385 samples.

386

387 In relation to **effluent wastewaters**, the contaminants most frequently found were pesticides
388 (51% of total detections) followed by pharmaceuticals (30%) and drugs of abuse (3%).
389 Similarly to the rest of water samples analysed, PCPs such as musks and UV filters, were

390 also detected accounting for 6-8% of the identified compounds. The insecticide chlorpyrifos-
391 ethyl and the herbicide diuron were the most detected compounds together with the
392 fungicides thiabendazol, carbendazim and imazalil, and the triazine herbicides terbuthylazine
393 and terbutryn.

394 The presence of several pharmaceuticals in the same sample was rather common in effluent
395 wastewater, with emphasis on antibiotics (ofloxacin, ciprofloxacin, azithromycin,
396 sulfamethoxazole, sulfathiazole, trimethoprim and clarithromycin), anti-
397 inflammatory/analgesics drugs (ketoprofen, naproxen, phenazone and diclofenac) and
398 angiotensin receptor blockers (valsartan and irbesartan). Benzodiazepines (diazepam and
399 oxazepam), anti-depressant venlafaxine, anti-epileptic carbamazepine and veterinary
400 pharmaceutical levamisole (also used as an adulterant in cocaine) were detected in effluent
401 wastewater. Metabolites such as fenofibric acid (metabolite of the lipid regulator fenofibrate)
402 and 4-aminoantipyrine, 4-aminoantipyrine-N-formyl and 4-aminoantipyrine-N-acetyl
403 (metabolites of the analgesic metamizole/dypirone) were also found. Thus, antibiotics,
404 NSAIDs, angiotensin II receptor antagonists and antidepressants were detected (at least one
405 member of each family) in almost 90% of the effluent wastewater samples analysed (**Figure**
406 **S.2**).

407 Regarding drugs of abuse, benzoylecgonine (cocaine metabolite) was the most frequently
408 detected. EDDP (metabolite of methadone) and cocaine were detected in two effluent
409 wastewater samples. Other emerging contaminants, such as musks, UV-filters,
410 antimicrobials and insect repellents were detected too.

411 It is worth mentioning that some of the detected compounds, such as atrazine, endosulfan,
412 chlorpyriphos, chlorfenvinphos, diuron, simazine, trifluralin, terbutryn and the PAHs
413 anthracene and fluoranthene, are included in the list of priority contaminants of the European
414 Union [25]. Environmental quality standards (EQS), expressed as maximum allowable
415 concentration, have been established for these compounds in inland surface water, mostly
416 ranging from 0.1 to 4 µg/L (with the exception of endosulfan; EQS 0.01µg/L). All these
417 priority compounds have been included in method validation, and SDLs have been shown to
418 be 0.02 µg/L for all of them (0.1 µg/L for anthracene and fluoranthene). According to the
419 data shown in this paper, the proposed screening methodology is applicable for a huge
420 number of organic contaminants in water, including priority substances listed in the current
421 European legislation.

422
423 **4. CONCLUSIONS**
424

425 Nowadays, thanks to recent improvements in analytical instrumentation, it is possible to
426 advance towards the desired "universal" screening. With the complementary use of GC-
427 QTOF MS and UHPLC-QTOF MS it is possible to increase the number of investigated
428 contaminants up to figures which were unthinkable until now. This combination allows the
429 investigation of thousands of compounds, including pesticides, pharmaceuticals, drugs of
430 abuse, chlorinated persistent compounds, polycyclic aromatic hydrocarbons, among others,
431 in different types of aqueous matrices, such as ground water, surface water and effluent
432 wastewater. The strategy applied in this work can be seen as one of the most "universal"
433 screening approaches proposed until now, as a huge number of contaminants with very

434 distinct polarity and volatility, can be detected and identified at reasonably low
435 concentrations.

436 Another advantage of the screening method applied is that TOF MS always works under
437 accurate-mass full-spectrum acquisition mode, which implies that MS data remain available
438 to be reprocessed at any time. This fact allows investigating the presence of other compounds
439 that might be of interest in the future, once data have been obtained and without the need of
440 additional sample analysis, as well as the processing of data in a non-target way [26-27]
441 searching for unknowns.

442 From the point of view of the authors, the most attractive approach when investigating
443 environmental pollution is the application of wide-scope screening methodologies, like the
444 one proposed in this work, able to detect and identify as many organic pollutants as possible,
445 in order to have wide and realistic information on the sample quality. In a subsequent step,
446 those pollutants detected and considered as relevant should be included in monitoring
447 programs that would normally apply target quantitative methods, e.g. using MS/MS with
448 triple quadrupole analyzer. Obviously, some difficult compounds that need specific
449 methodologies due to their high polarity, like glyphosate, glufosinate, paraquat, ethefon or
450 fosetil-Al, should be investigated separately and, at the moment, cannot be included in any
451 "universal" screening. Similarly, highly volatile compounds might be lost in the evaporation
452 step included in the sample procedure, and would benefit from sample treatments directed
453 specifically towards them. The approach proposed in this work uses an easy and rapid sample
454 procedure as a compromise between efficiency and simplicity, trying to avoid extensive

455 sample handling, while the “universal” character come from the analytical measurement, able
456 to detect the wide majority of compounds that might be present in samples.

457

458

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465

466

FIGURE CAPTIONS

Figure 1. Overall scheme of the screening method applied: (left) Sample treatment; (right) (Q)TOF MS data processing.

Figure 2. Screening Detection Limit (SDL) for studied compounds

Figure 3. Detection and identification of EDDP, main metabolite of methadone, by UHPLC-QTOF MS in a wastewater sample (the reference standard was not available at our laboratory in the time of the detection): (a) LE (bottom) and HE (top) spectra of the compound eluting at 8.4 min. Proposed structures for fragment ions; (b) Extracted-ion chromatograms (0.02 Da mass width) for protonated molecule in LE function and different fragment ions in HE function. (×) indicates that this ion is not related with EDDP.

Figure 4. Percentage of positive findings for different families of organic pollutants in ground water, surface water and effluent wastewater samples by combined screening using GC(APCI)-QTOF MS and UHPLC(ESI)-QTOF MS.

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TABLES

Table 1. Screening Detection Limit (SDL) for all studied compounds. The lowest SDL obtained by UHPLC-QTOF MS or GC-QTOF MS is given

Compound	*SDL (µg/L)*	*Compound*	*SDL (µg/L)*	*Compound*	*SDL (µg/L)*	*Compound*	*SDL (µg/L)*
PESTICIDES							
Alachlor	0.1	Chlorfenvinphos	0.02	Diuron	0.02	β-HCH	0.02
Aldrin	0.5	Chlorothalonil	-	α-Endosulphan	0.1	δ-HCH	0.02
Atrazine	0.02	Chlorpropham	0.02	β-Endosulfan	0.02	γ-HCH	0.02
Atrazine-desethyl (DEA)	0.02	Chlorpyrifos-ethyl	0.02	Endosulfan-ether	0.02	Heptachlor epoxide A	0.5
Atrazine-desisopropyl (DIA)	0.02	Chlorpyrifos-methyl	0.1	Endosulfan-sulfate	0.1	Heptachlor epoxide B	0.5
Atrazine-2-hydroxy	0.02	Coumaphos	0.02	Endrin	0.02	Hexachlorobutadiene	0.1
Azinphos-methyl	-	Cyanazine	0.02	EPN	0.02	Hexythiazox	0.5
Azoxystrobin	0.02	Cyanophos	0.02	Ethalfluralin	0.02	Imazalil	0.02
Bifenthrin	0.02	Cyfluthrin	0.1	Ethion	0.02	Imidacloprid	0.02
Boscalid	0.02	λ-Cyhalothrin	0.02	Ethoxyquin	0.5	Iprodione	0.5
Bromacil	0.1	Cypermethrin	0.1	Etofenprox	0.1	Isodrin	0.5
Bromophos	0.02	Cyprodinil	0.02	Famphur	0.02	Leptophos	0.02
Bromophos-ethyl	0.02	p,p'-DDD	0.02	Fenamiphos	0.02	Linuron	0.02
Buprofezin	0.02	p,p'-DDE	0.02	Fenarimol	0.02	Malathion	0.02
Cadusafos	0.02	p,p-DDT	0.02	Fenhexamid	0.02	MCPA	0.02
Captafol	-	Deltamethrin	0.5	Fenitrothion	0.02	Metalaxyl	0.02
Captan	-	Diazinon	0.02	Fenoxycarb	0.02	Methidathion	0.02
Carbaryl	0.1	Dichlofenthion	0.02	Fenthion	0.02	Methiocarb	0.1
Carbendazim	0.02	Dichloran	0.5	Fenvalerate	0.1	Methoxychlor	0.02
Carbofuran	0.02	4,4'-Dichlorobenzophenone	0.02	Fipronil	0.02	Metolachlor	0.02
Carbophenothion	0.02	Dichlorvos	0.5	Flucythrinate	0.1	Metribuzin	0.02
Carfentrazone-ethyl	0.02	Dieldrin	0.1	Fludioxonyl	0.02	Mirex	0.1
Chinomethionat	-	Diflufenican	(a)	Fluroxypyr	-	Molinate	0.02
Trans-Chlordane	0.5	Dimethoate	0.02	τ-Fluvalinate	0.5	Monocrotophos	0.02
Chlorfenapyr	0.02	Dioxathion	0.02	HCB	0.02	Omethoate	0.1
Chlorfenson	0.02	Diphenylamine	0.02	α-HCH	0.02	Oxadixyl	0.02

Compound	*SDL (µg/L)*	*Compound*	*SDL (µg/L)*	*Compound*	*SDL (µg/L)*	*Compound*	*SDL (µg/L)*
PESTICIDES				**PCBs**		**PAHs**	
Oxychlordane	0.5	Tefluthrin	0.1	PCB 28	0.1	Acenaphthene	0.1
Oxyfluorfen	0.02	Terbacil	0.1	PCB 52	0.02	Acenaphthylene	0.1
Parathion-ethyl	0.02	Terbufos	0.5	PCB 77	0.5	Anthracene	0.1
Parathion-methyl	0.1	Terbumeton	0.02	PCB 81	0.5	Benzo(a)anthracene	-
Pendimethalin	0.02	Terbumeton-desethyl	0.02	PCB 101	0.02	Benzo(b)fluoranthene	0.5
Pentachlorobenzene	0.02	Terbuthylazine	(a)	PCB 105	0.02	Benzo(k)fluoranthene	0.5
Permethrin	0.1	Terbuthylazine-desethyl	(a)	PCB 114	0.02	Benzo(g,h,i)perylene	-
2-Phenylphenol	0.02	Terbuthylazine-2-hydroxy	(a)	PCB 118	0.02	Benzo(a)pyrene	0.5
Phorate	0.1	Terbutryn	0.02	PCB 123	0.02	Chrysene	-
Phosmet	-	Tetraconazole	0.02	PCB 126	0.5	Dibenzo(a,h)anthracene	-
Phosphamidon	-	Tetradifon	0.02	PCB 138	0.02	Fluoranthene	0.1
Pirimicarb	0.02	Thiabendazole	0.02	PCB 153	0.02	Fluorene	0.1
Pirimiphos methyl	0.02	Thiacloprid	0.02	PCB 156	0.5	Indeno(1,2,3,cd)pyrene	-
Procymidone	0.02	Thiobencarb	0.02	PCB 157	0.1	Naphthalene	0.1
Promecarb	-	Tolclofos methyl	0.1	PCB 167	0.1	Phenanthrene	0.1
Propachlor	0.02	Tolyfluanid	0.1	PCB 169	0.5	Pyrene	0.1
Propanil	0.02	Triadimefon	0.02	PCB 180	0.02		
Propetamphos	0.1	Triflumizole	0.02	PCB 189	0.5		
Propham	0.1	Trifluralin	0.02				
Propiconazole	0.02	Vinclozolin	0.1				
Propoxur	0.02						
Propyzamide	0.1						
Pyridaphenthion	0.02						
Pyriproxyfen	0.02						
Quinalphos	0.02						
Resmethrin	0.1						
Simazine	0.02						

Compound	*SDL (µg/L)*	*Compound*	*SDL (µg/L)*	*Compound*	*SDL (µg/L)*	*Compound*	*SDL (µg/L)*
PHARMACEUTICALS				**DRUGS OF ABUSE**		**UV FILTERS**	
4-Aminoantipyrine	0.02	Naproxen	0.1	Amphetamine	-	Benzophenone-2 (BP-2)	0.1
Alprazolam	0.02	Norfloxacin	-	Benzoylecgonine	0.02	Benzophenone-3 (BP-3)	0.5
Atorvastatin	0.5	Ofloxacin	0.02	Cocaethylene	0.02	Benzophenone-4 (BP-4)	0.02
Azithromycin	0.1	Olanzapine	0.5	Cocaine	0.02		
Bezafibrate	0.02	Omeprazole	0.02	Heroin	0.02		
Carbamazepine	0.02	Oxolinic acid	0.02	Ketamine	0.02		
Chloramphenicol	0.02	Pantoprazol	0.02	MDEA	0.02		
Ciprofloxacin	0.1	Paracetamol/Acetaminophen	-	MDMA	0.02	**PRESERVATIVES**	
Clarythromycin	0.1	Paroxetine	0.5	Methamphetamine	0.02	Methylparaben	0.02
Clindamycin	0.02	Pefloxacin	0.02	Methcathinone	-	Ethylparaben	0.02
Cloxacillin	0.5	Penicillin G	-	Norbenzoylecgonine	0.02	Propylparaben	0.02
Codeine	0.1	Pipedimic acid	-	Norcocaine	0.02	Butylparaben	0.02
Diclofenac	0.02	Pravastatin	0.02			Triclosan/Irgasan	0.5
Dicloxacillin	0.5	Risperidone	0.02				
Enalapril	0.5	Roxythromycin	0.5				
Enrofloxacin	-	Sarafloxacin	0.5				
Erythromycin A	-	Sulfadiazine	0.02				
Flumequine	0.02	Sulfamethazine	0.02				
Furazolidone	0.02	Sulfamethoxazole	0.02				
Furosemide	0.02	Sulfathiazole	0.02				
Gemfibrozil	0.02	Trimethoprim	0.02				
Ibuprofen	0.02	Tylosin A	0.5				
Irbesartan	0.02	Valsartan	0.02				
Ketoprofen	0.02	Venlafaxine	0.02				
Lincomycin	0.02						
Moxifloxacin	0.02						
Nalidixic acid	0.02						

(-) means that this compound could not be validated at any of the three levels studied

(a) the SDL could not be established as the compound was present in more than 50% of the “blank samples” used in validation.

Fig 1

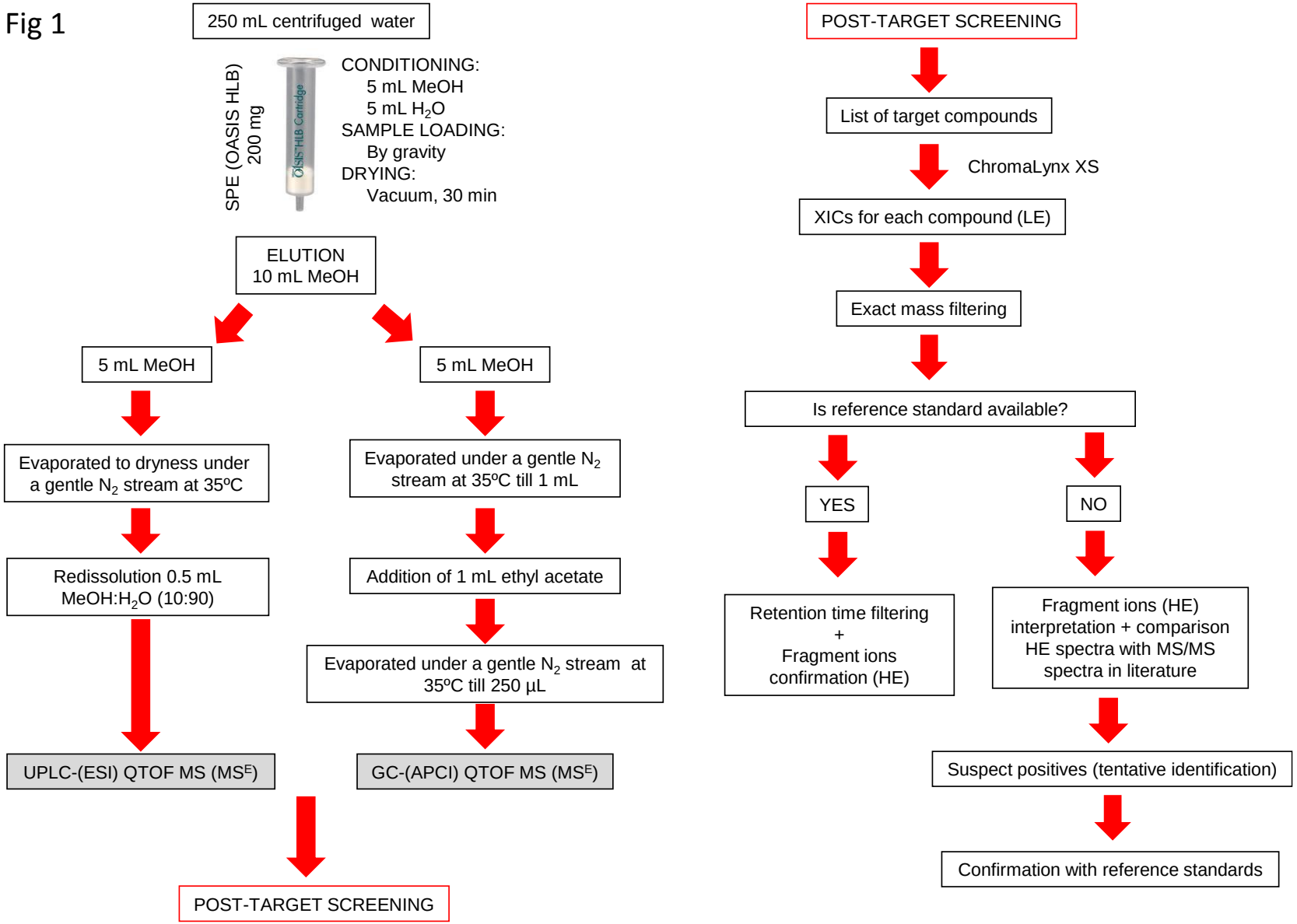

250 mL centrifuged water
SPE (OASIS HLB) 200 mg
CONDITIONING:
5 mL MeOH
5 mL H2O
SAMPLE LOADING:
By gravity
DRYING:
Vacuum, 30 min
ELUTION
10 mL MeOH
5 mL MeOH
5 mL MeOH
Evaporated to dryness under a gentle N2 stream at 35ºC
Evaporated under a gentle N2 stream at 35ºC till 1 mL
Redissolution 0.5 mL MeOH:H2O (10:90)
Addition of 1 mL ethyl acetate
Evaporated under a gentle N2 stream at 35ºC till 250 µL
UPLC-(ESI) QTOF MS (MSE)
GC-(APCI) QTOF MS (MSE)
POST-TARGET SCREENING
POST-TARGET SCREENING
List of target compounds
ChromaLynx XS
XICs for each compound (LE)
Exact mass filtering
Is reference standard available?
YES
NO
Retention time filtering + Fragment ions confirmation (HE)
Fragment ions (HE) interpretation + comparison HE spectra with MS/MS spectra in literature
Suspect positives (tentative identification)
Confirmation with reference standards

Fig 2

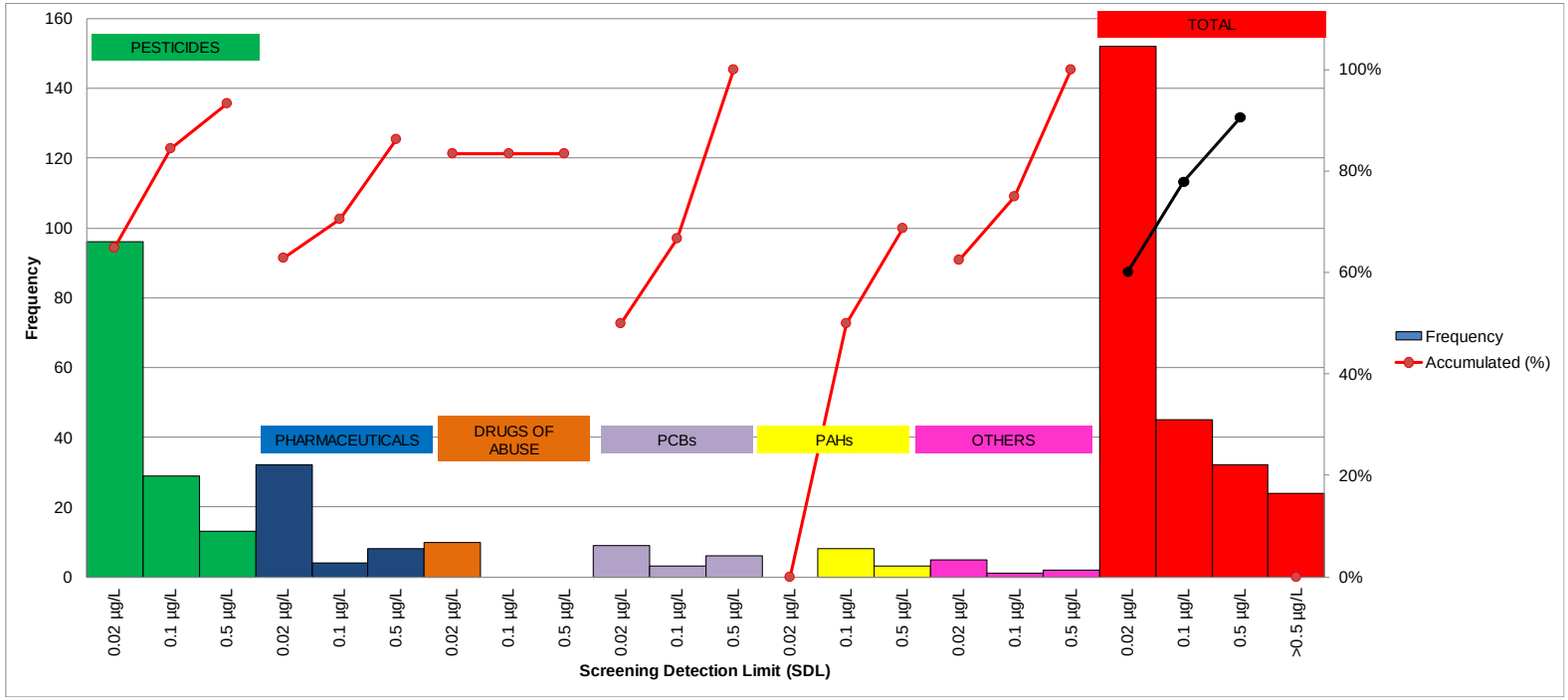
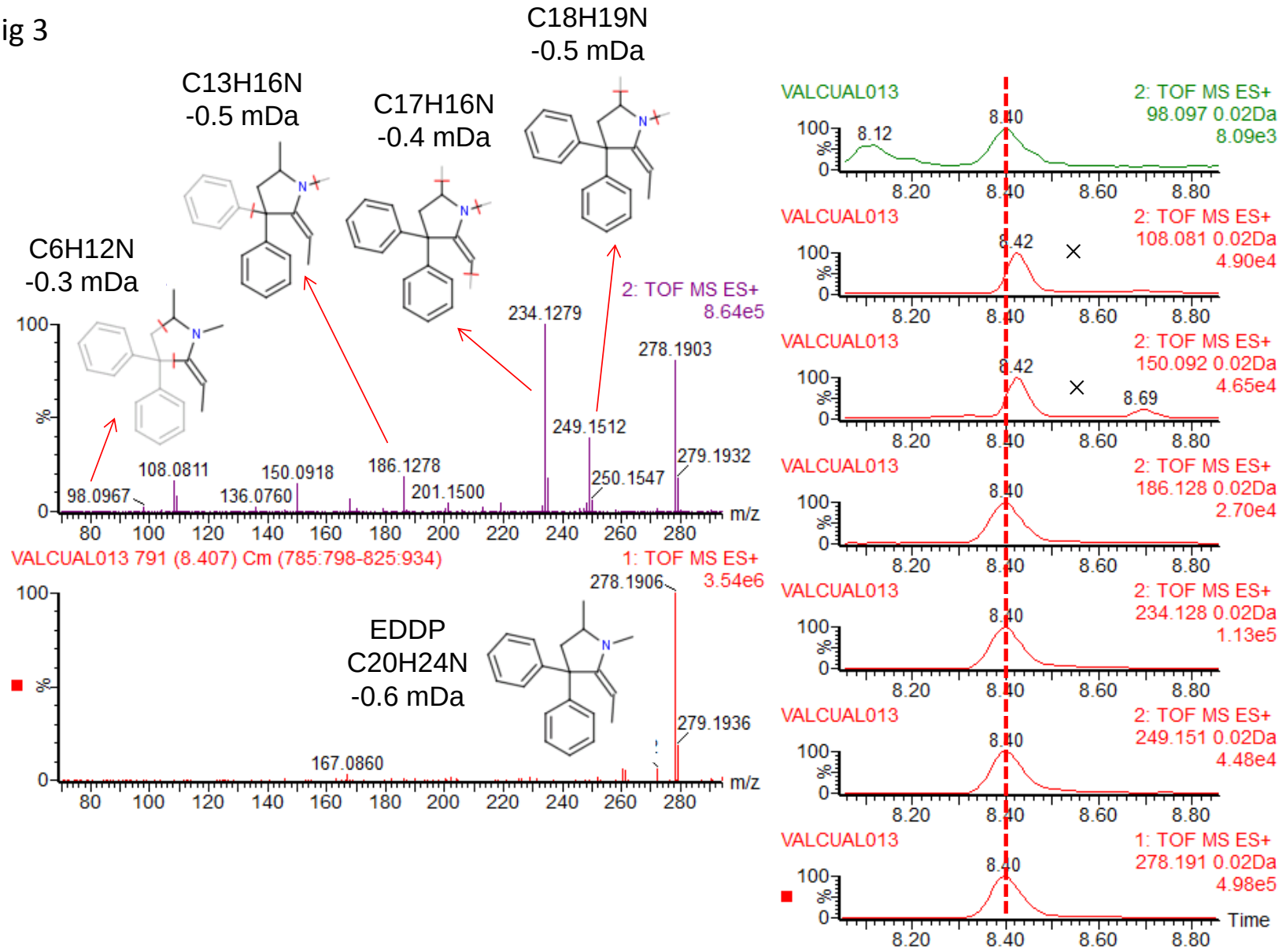

PESTICIDES
PHARMACEUTICALS
DRUGS OF ABUSE
PCBs
PAHs
OTHERS
TOTAL
Frequency
Accumulated (%)
Screening Detection Limit (SDL)
0.02 µg/L
0.1 µg/L
0.5 µg/L
>0.5 µg/L

Fig 3


C18H19N
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C13H16N
-0.5 mDa
C17H16N
-0.4 mDa
C6H12N
-0.3 mDa
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8.64e5
234.1279
278.1903
249.1512
279.1932
250.1547
108.0811
150.0918
186.1278
98.0967
136.0760
201.1500
m/z
VALCUAL013 791 (8.407) Cm (785:798-825:934)
1: TOF MS ES+
3.54e6
278.1906
EDDP
C20H24N
-0.6 mDa
279.1936
167.0860
VALCUAL013
2: TOF MS ES+
98.097 0.02Da
8.09e3
8.12
8.40
2: TOF MS ES+
108.081 0.02Da
4.90e4
8.42
2: TOF MS ES+
150.092 0.02Da
4.65e4
8.69
2: TOF MS ES+
186.128 0.02Da
2.70e4
2: TOF MS ES+
234.128 0.02Da
1.13e5
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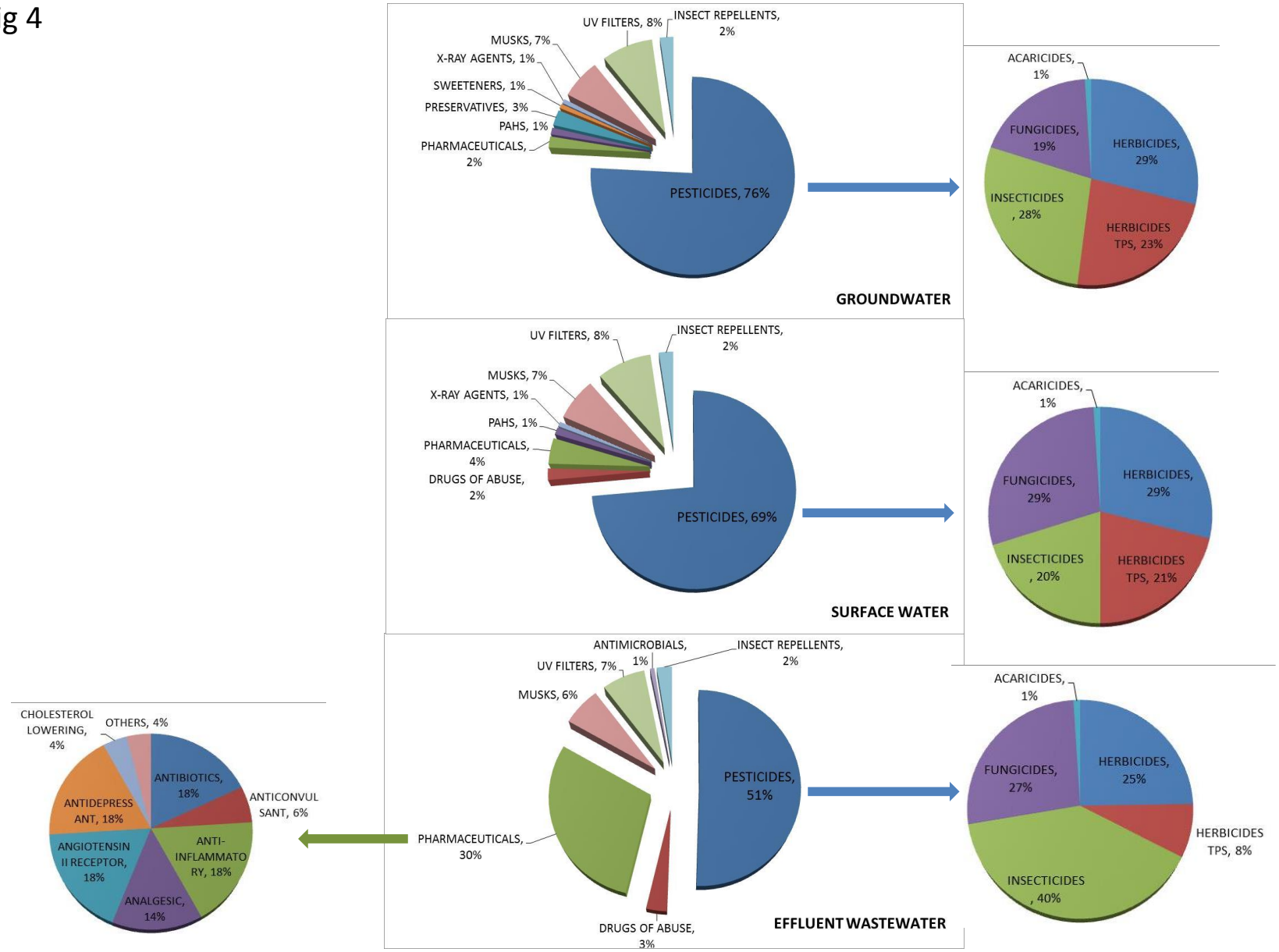
4.98e5
Time

Fig 4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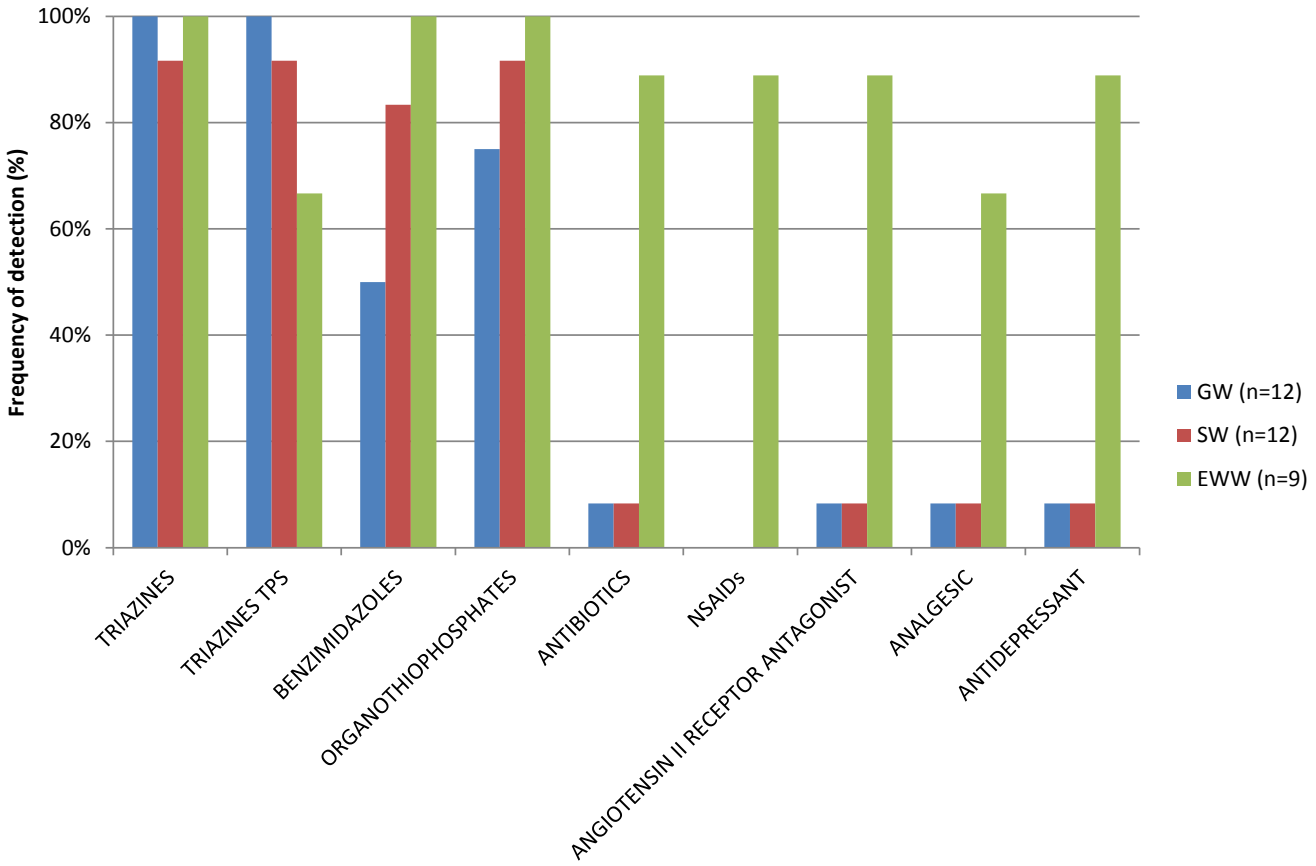
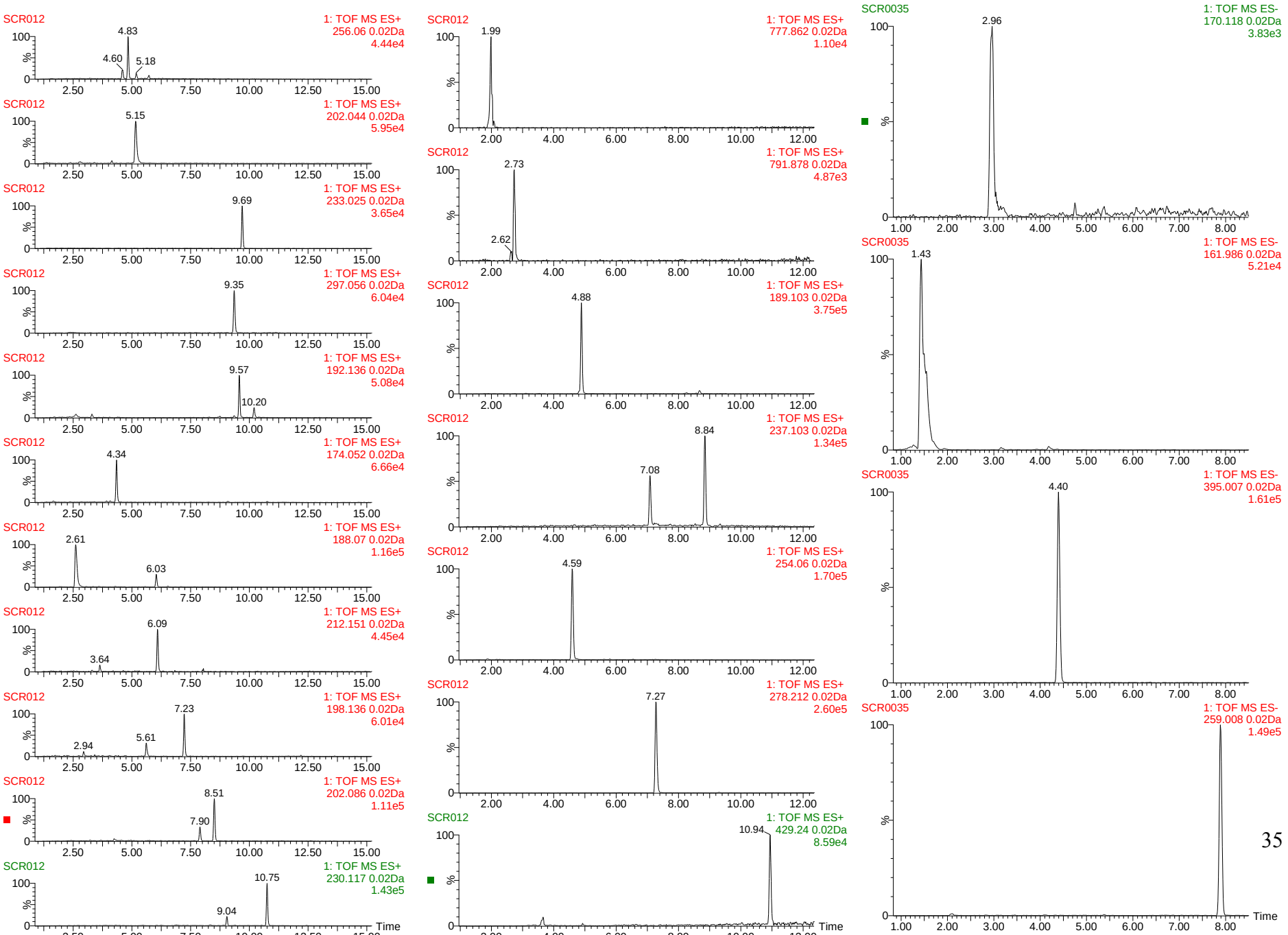
INSECT REPELLENTS, 2%
MUSKS, 7%
X-RAY AGENTS, 1%
SWEETENERS, 1%
PRESERVATIVES, 3%
PAHS, 1%
PHARMACEUTICALS, 2%
PESTICIDES, 76%
GROUNDWATER
ACARICIDES, 1%
FUNGICIDES, 19%
HERBICIDES, 29%
INSECTICIDES, 28%
HERBICIDES TPS, 23%
UV FILTERS, 8%
INSECT REPELLENTS, 2%
MUSKS, 7%
X-RAY AGENTS, 1%
PAHS, 1%
PHARMACEUTICALS, 4%
DRUGS OF ABUSE, 2%
PESTICIDES, 69%
SURFACE WATER
ACARICIDES, 1%
FUNGICIDES, 29%
HERBICIDES, 29%
INSECTICIDES, 20%
HERBICIDES TPS, 21%
ANTIMICROBIALS, 1%
INSECT REPELLENTS, 2%
UV FILTERS, 7%
MUSKS, 6%
PESTICIDES, 51%
PHARMACEUTICALS, 30%
DRUGS OF ABUSE, 3%
EFFLUENT WASTEWATER
ACARICIDES, 1%
FUNGICIDES, 27%
HERBICIDES, 25%
HERBICIDES TPS, 8%
INSECTICIDES, 40%
CHOLESTEROL LOWERING, 4%
OTHERS, 4%
ANTIBIOTICS, 18%
ANTICONVULSANT, 6%
ANTIDEPRESSANT, 18%
ANTI-INFLAMMATORY, 18%
ANGIOTENSIN II RECEPTOR, 18%
ANALGESIC, 14%

Fig 5


100%
80%
60%
40%
20%
0%
Frequency of detection (%)
TRIAZINES
TRIAZINES TPS
BENZIMIDAZOLES
ORGANOTHIOPHOSPHATES
ANTIBIOTICS
NSAIDs
ANGIOTENSIN II RECEPTOR ANTAGONIST
ANALGESIC
ANTIDEPRESSANT
GW (n=12)
SW (n=12)
EWW (n=9)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7.08
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1.70e5
4.59
SCR012
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2.60e5
7.27
SCR012
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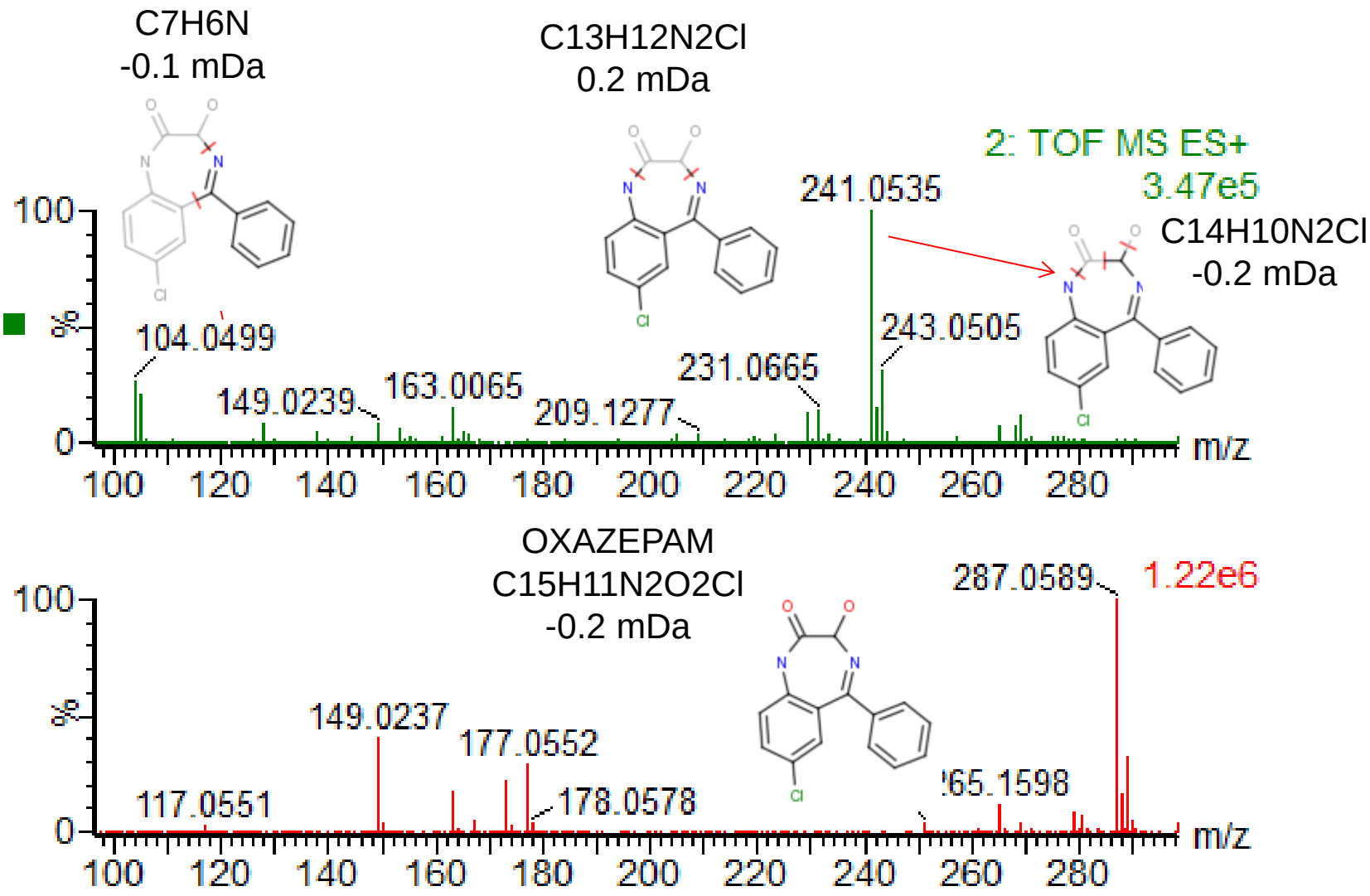
429.24 0.02Da
8.59e4
10.94
SCR0035
1: TOF MS ES-
170.118 0.02Da
3.83e3
2.96
SCR0035
1: TOF MS ES-
161.986 0.02Da
5.21e4
1.43
SCR0035
1: TOF MS ES-
395.007 0.02Da
1.61e5
4.40
SCR0035
1: TOF MS ES-
259.008 0.02Da
1.49e5
Time


C7H6N
-0.1 mDa
C13H12N2Cl
0.2 mDa
2: TOF MS ES+
3.47e5
241.0535
C14H10N2Cl
-0.2 mDa
243.0505
104.0499
149.0239
163.0065
209.1277
231.0665
100
%
0
m/z
100 120 140 160 180 200 220 240 260 280
OXAZEPAM
C15H11N2O2Cl
-0.2 mDa
287.0589
1.22e6
149.0237
177.0552
178.0578
117.0551
265.1598

SUPPLEMENTARY INFORMATION

ADVANCING TOWARDS UNIVERSAL SCREENING FOR ORGANIC POLLUTANTS IN WATERS

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2. EXPERIMENTAL

2.1 Reagents and chemicals

Reference standards of organic contaminants were purchased from Dr. Ehrenstorfer (Augsburg, Germany), Wellington Laboratories (Guelph, Ontario, Canada), Fluka (Buchs, Switzerland), Riedel de Haën (Seelze, Germany), Sigma–Aldrich (St Louis, MO, USA), LGC Promochem (London, UK), Toronto Research Chemicals Inc. (Ontario, Canada), Across Organics (Geel, Belgium), Bayer Hispania (Barcelona, Spain), Fort Dodge Veterinaria (Gerona, Spain),

Vetoquinol Industrial (Madrid Spain) and Aventis Pharma (Madrid, Spain). All reference standards presented purity higher than 93%.

HPLC-grade water was obtained by purifying demineralised water in a Milli-Q plus system from Millipore (Bedford, MA, USA). Acetone (residue analysis), ethyl acetate, dichloromethane, hexane (all ultra-trace quality), HPLC-grade acetonitrile, HPLC-grade methanol (MeOH), sodium hydroxide >99% (NaOH), ammonia solution (25%), and formic acid (98–100%) were acquired from Scharlau (Barcelona, Spain). Leucine enkephalin, used as lock mass, was purchased from Sigma-Aldrich.

2.2 Instrumentation

2.2.1 UHPLC-(ESI)QTOF MS

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 positive and negative ion modes. The UHPLC separation was performed using an Acquity UPLC BEH C_{18} 1.7 µm particle size analytical column 100 × 2.1 mm (Waters) at a flow rate of 300 µL/min. The mobile phases used were A=H_2O with 0.01% HCOOH and B =MeOH 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%. 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 3.0 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 650ºC and the source temperature to 130ºC. The column temperature was set to 40ºC. TOF MS resolution was approximately 20,000 at full width half maximum (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 lockmass a solution of leucine enkephalin (2 µg/mL) in acetonitrile:water (50:50) at 0.1% HCOOH pumped at 20 µL/min through the lock-spray needle. 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-).

2.2.2. GC-(APCI)QTOF MS

For the GC instrumentation, an Agilent 7890A GC system (Palo Alto, CA, USA) equipped with an Agilent 7683 autosampler was coupled to the Xevo G2 QTOF, operating in APCI mode. The GC separation was performed using a fused silica DB-5MS capillary column with a length of 30 m x 0.25 mm i.d. and a film thickness of 0.25 µm (J&W Scientific, Folson, CA, USA). The oven temperature was programmed as follows: 90ºC (1 min); 5ºC/min to 300ºC (2 min). Pulsed splitless (50 psi) injections of 1 µL of sample extracts were carried out with an injector temperature of 280 ºC 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. The interface and source temperatures were set to 310ºC

and 150 ºC, respectively. The desolvation gas (N_2) was set at 300 L/h flow and the cone gas at 16 L/h. The voltage of the sampling cone was set at 20 V, the voltage of the extraction cone was 4 V, and the APCI corona pin was fixed at a current 1.7 µA. The ionization process occurred within an enclosed ion volume, which enabled control over the protonation/charge transfer processes. TOF MS resolution was approximately 20,000 (FWHM) at *m/z* 614. A scan time of 0.4 s was selected. MS data were acquired over an *m/z* range of 50-650. 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 ($[M-H]^+$ 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.

Table S.1. Positive findings score after analysis of nine different spiked samples (3 groundwater, 3 surface and 3 effluent wastewaters) at different concentration levels. Screening Detection Limit (SDL) for compounds monitored by UHPLC-QTOF MS

	Blank samples				*0.02 µg/L*			*0.1 µg/L*			*0.5 µg/L*			**SDL (µg/L)**
Compounds	*GW*	*SW*	*EWW*		*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	
PESTICIDES														
Alachlor	0/3	0/3	0/3		3/3	3/3	1/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Atrazine	1/3	1/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Atrazine-desethyl (DEA)	1/3	1/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Atrazine-desisopropyl (DIA)	2/3	1/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Atrazine-2-hydroxy	2/3	1/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Azoxystrobin	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Boscalid	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Bromacil	0/3	0/3	1/3		3/3	1/3	1/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Bromacil[a]	0/3	0/3	1/3		3/3	3/3	1/3	3/3	3/3	1/3	3/3	3/3	3/3	**0.5**
Buprofezin	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Carbaryl	0/3	0/3	0/3		2/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Carbendazim	0/3	2/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Carbofuran	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Chlorfenvinphos	0/3	0/3	2/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Chlorpyrifos-ethyl	0/3	0/3	1/3		0/3	0/3	0/3	0/3	0/3	0/3	3/3	3/3	3/3	**0.5**
Chlorpyrifos-methyl	0/3	0/3	0/3		2/3	2/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Coumaphos	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Cyanazine	0/3	0/3	0/3		3/3	1/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Cyprodinil	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Dimethoate	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Diphenylamine	0/3	0/3	0/3		2/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Diuron	0/3	1/3	3/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Fenarimol	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**

	Blank samples				*0.02 µg/L*			*0.1 µg/L*			*0.5 µg/L*			**SDL (µg/L)**
Compounds	*GW*	*SW*	*EWW*		*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	
Fenhexamid	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Fenitrothion	0/3	0/3	0/3		1/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Fenoxycarb	0/3	0/3	0/3		2/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Fenthion	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Fludioxonil	0/3	0/3	0/3		1/3	0/3	0/3	3/3	3/3	1/3	3/3	3/3	1/3	**-**
Fludioxonil[a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Fluoroxypyr	0/3	0/3	0/3		1/3	0/3	0/3	3/3	3/3	1/3	3/3	3/3	1/3	**-**
Fluoroxypyr[a]	0/3	0/3	0/3		3/3	3/3	1/3	3/3	3/3	1/3	3/3	3/3	1/3	**-**
Hexythiazox	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	3/3	3/3	3/3	**0.5**
Imazalil	0/3	2/3	2/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Imidacloprid	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Linuron	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Malathion	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
MCPA[a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Metalaxyl	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Methidathion	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Methiocarb	0/3	0/3	0/3		2/3	2/3	2/3	3/3	3/3	2/3	3/3	3/3	2/3	**-**
Metolachlor	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Metribuzin	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Molinate	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Monocrotophos	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Omethoate	0/3	0/3	0/3		2/3	2/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Parathion-ethyl	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Parathion-methyl	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Pirimicarb	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Pirimiphos-methyl	0/3	0/3	0/3		3/3	2/3	2/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Promecarb	0/3	0/3	0/3		3/3	2/3	2/3	3/3	2/3	2/3	3/3	2/3	2/3	**-**

	Blank samples				*0.02 µg/L*			*0.1 µg/L*			*0.5 µg/L*			**SDL (µg/L)**
Compounds	*GW*	*SW*	*EWW*		*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	
Propachlor	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Propanil	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Propanil[a]	1/3	1/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Propiconazole	0/3	0/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Propoxur	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Propyzamide	0/3	0/3	0/3		3/3	1/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Pyridaphenthion	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Pyriproxyfen	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	3/3	3/3	3/3	**0.5**
Quinalphos	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Simazine	3/3	0/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Terbacil[a]	0/3	0/3	1/3		3/3	3/3	1/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Terbumeton	2/3	0/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Terbumeton-desethyl	2/3	2/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Terbuthylazine	2/3	3/3	2/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**-[b]**
Terbuthylazine-desethyl	3/3	2/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**-[b]**
Terbuthylazine-2-hydroxy	3/3	3/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**-[b]**
Terbutryn	0/3	2/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Tetraconazole	0/3	2/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Thiabendazole	0/3	2/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Thiacloprid	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Thiobencarb	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Tolclofos-methyl	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	3/3	3/3	3/3	**0.5**
Triadimefon	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
PHARMACEUTICALS														
4-Aminoantipyrine	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Alprazolam	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Atorvastatin	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	3/3	3/3	3/3	**0.5**

	Blank samples				*0.02 µg/L*			*0.1 µg/L*			*0.5 µg/L*			**SDL (µg/L)**
Compounds	*GW*	*SW*	*EWW*		*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	
Atorvastatin[a]	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	**-**
Azithromycin	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Bezafibrate	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Carbamazepine	0/3	0/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Chloramphenicol	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Ciprofloxacin	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Clarythromycin	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Clindamycin	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Cloxacillin	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	3/3	3/3	3/3	**0.5**
Codeine	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Diclofenac	0/3	0/3	2/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Diclofenac[a]	0/3	0/3	2/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Dicloxacillin	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	3/3	3/3	3/3	**0.5**
Enalapril	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	1/3	3/3	3/3	3/3	**0.5**
Enrofloxacin	0/3	0/3	0/3		0/3	0/3	0/3	3/3	2/3	1/3	3/3	2/3	1/3	**-**
Erythromycin A	0/3	0/3	0/3		0/3	0/3	0/3	1/3	3/3	1/3	1/3	3/3	1/3	**-**
Flumequine	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Furazolidone	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Furosemide[a]	0/3	0/3	2/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Gemfibrozil	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Gemfibrozil[a]	0/3	0/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Ibuprofen[a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Irbesartan	0/3	0/3	2/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Irbesartan[a]	0/3	0/3	2/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Ketoprofen	0/3	0/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Lincomycin	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Moxifloxacin	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**

	Blank samples				*0.02 µg/L*			*0.1 µg/L*			*0.5 µg/L*			**SDL (µg/L)**
Compounds	*GW*	*SW*	*EWW*		*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	
Nalidixic acid	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Naproxen	0/3	0/3	1/3		0/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Norfloxacin	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	1/3	3/3	3/3	1/3	**-**
Ofloxacin	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Olanzapine	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	3/3	3/3	3/3	**0.5**
Omeprazole	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Oxolinic acid	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Pantoprazol	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Paracetamol/Acetaminophen	0/3	0/3	0/3		0/3	0/3	0/3	3/3	1/3	1/3	3/3	1/3	1/3	**-**
Paroxetine	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	1/3	3/3	3/3	3/3	**0.5**
Pefloxacin	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Penicillin G	0/3	0/3	0/3		0/3	0/3	0/3	3/3	2/3	1/3	3/3	2/3	1/3	**-**
Pipedimic acid	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	1/3	3/3	3/3	1/3	**-**
Pravastatin	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	1/3	3/3	3/3	3/3	**0.5**
Pravastatin[a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Risperidone	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Roxythromycin	0/3	0/3	0/3		3/3	3/3	1/3	3/3	3/3	1/3	3/3	3/3	3/3	**0.5**
Sarafloxacin	0/3	0/3	0/3		3/3	3/3	1/3	3/3	3/3	1/3	3/3	3/3	3/3	**0.5**
Sulfadiazine	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Sulfamethazine	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Sulfamethoxazole	0/3	0/3	2/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Sulfathiazole	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Trimethoprim	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Tylosin A	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	3/3	3/3	3/3	**0.5**
Valsartan	0/3	0/3	2/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Valsartan	0/3	0/3	2/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Venlafaxine	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**

	Blank samples				*0.02 µg/L*			*0.1 µg/L*			*0.5 µg/L*			**SDL (µg/L)**
Compounds	*GW*	*SW*	*EWW*		*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	
DRUGS OF ABUSE														
Amphetamine	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	**-**
Benzoylecgonine	0/3	0/3	2/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Cocaethylene	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Cocaine	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Heroin	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Ketamine	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
MDEA	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
MDMA	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Methamphetamine (METH)	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Methcathinone	0/3	0/3	0/3		0/3	0/3	0/3	2/3	2/3	2/3	2/3	2/3	2/3	**-**
Norbenzoylecgonine	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Norcocaine	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
UV FILTERS														
Benzophenone-2 (BP-2) [a]	0/3	0/3	0/3		3/3	3/3	1/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Benzophenone-3 (BP-3) [a]	0/3	0/3	2/3		0/3	0/3	0/3	0/3	0/3	0/3	3/3	3/3	3/3	**0.5**
Benzophenone-4 (BP-4) [a]	0/3	0/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
PRESERVATIVES														
Methylparaben[a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Ethylparaben[a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Propylparaben[a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Butylparaben[a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Triclosan/Irgasan[a]	0/3	0/3	0/3		0/3	0/3	0/3	0/3	3/3	1/3	3/3	3/3	3/3	**0.5**

[a]Investigated in negative ESI mode.

[b]The SDL could not be established as the compound investigated was present in more than 50% of the "blank" samples analysed.

Table S.2. Positive findings score after analysis of nine different spiked samples (3 groundwater, 3 surface and 3 effluent wastewaters) at different concentration levels. Screening Detection Limit (SDL) for compounds monitored by GC-QTOF MS

	Blank samples				*0.02 µg/L*			*0.1 µg/L*			*0.5 µg/L*			**SDL**
Compounds	*GW*	*SW*	*EWW*		*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	**(µg/L)**
PESTICIDES														
Alachlor	0/3	0/3	0/3		2/3	3/3	2/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Aldrin	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	3/3	3/3	3/3	**0.5**
Atrazine	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Atrazine-desethyl (DEA)	0/3	1/3	0/3		1/3	1/3	2/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Atrazine-desisopropyl (DIA)	0/3	0/3	0/3		1/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Azinphos-methyl	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	**-**
Azoxystrobin	0/3	0/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Bifenthrin	1/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Bromophos	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Bromophos-ethyl	1/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Buprofezin	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Cadusafos	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Captafol	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	**-**
Captan	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	**-**
Carbaryl	0/3	0/3	0/3		1/3	0/3	1/3	1/3	1/3	1/3	3/3	3/3	3/3	**0.5**
Carbofuran	0/3	0/3	0/3		3/3	2/3	2/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Carbophenothion	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Carfentrazone-ethyl	3/3	1/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Chinomethionat	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	1/3	1/3	2/3	**-**
trans-Chlordane[a]	0/3	0/3	0/3		0/3	0/3	0/3	1/3	2/3	2/3	3/3	3/3	3/3	**0.5**
Chlorfenapyr	1/3	1/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Chlorfenson	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Chlorfenvinphos	0/3	0/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**

	Blank samples				*0.02 µg/L*			*0.1 µg/L*			*0.5 µg/L*			**SDL (µg/L)**
Compounds	*GW*	*SW*	*EWW*		*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	
Chlorothalonil	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	**-**
Chlorpropham	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Chlorpyrifos-ethyl	0/3	2/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Chlorpyrifos-methyl	0/3	0/3	0/3		2/3	3/3	2/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Coumaphos	2/3	1/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Cyanazine	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Cyanophos	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Cyfluthrin	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
λ-Cyhalothrin	2/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Cypermethrin	0/3	0/3	0/3		0/3	1/3	1/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Cyprodinil	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
p,p'-DDD[a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
p,p'-DDE[a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
p,p-DDT[a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Deltamethrin	0/3	0/3	0/3		0/3	0/3	0/3	2/3	2/3	2/3	3/3	3/3	3/3	**0.5**
Diazinon	1/3	1/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Dichlofenthion	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Dichloran	0/3	0/3	0/3		1/3	2/3	2/3	1/3	2/3	2/3	3/3	3/3	3/3	**0.5**
4,4'-Dichlorobenzophenone	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Dichlorvos	0/3	0/3	0/3		1/3	3/3	3/3	3/3	3/3	2/3	3/3	3/3	3/3	**0.5**
Dieldrin	0/3	0/3	0/3		3/3	2/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Diflufenican	1/3	3/3	2/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**-[b]**
Dimethoate	0/3	0/3	0/3		1/3	0/3	0/3	1/3	2/3	0/3	3/3	3/3	3/3	**0.5**
Dioxathion	1/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Diphenylamine	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
α-Endosulphan	0/3	0/3	0/3		1/3	1/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**

	Blank samples				*0.02 µg/L*			*0.1 µg/L*			*0.5 µg/L*			**SDL (µg/L)**
Compounds	*GW*	*SW*	*EWW*		*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	
β-Endosulfan	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Endosulfan-ether	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Endosulfan-sulfate	0/3	0/3	0/3		0/3	1/3	1/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Endrin	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
EPN	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Ethalfluralin	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Ethion	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Ethoxyquin	0/3	0/3	0/3		0/3	0/3	0/3	1/3	2/3	1/3	3/3	3/3	3/3	**0.5**
Etofenprox	0/3	0/3	0/3		0/3	0/3	1/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Famphur	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Fenamiphos	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Fenarimol	0/3	2/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Fenhexamid	0/3	0/3	0/3		0/3	0/3	1/3	1/3	0/3	1/3	3/3	3/3	3/3	**0.5**
Fenitrothion	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Fenoxycarb	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Fenthion	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Fenvalerate	0/3	0/3	0/3		0/3	1/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Fipronil	2/3	0/3	2/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Flucythrinate	0/3	0/3	0/3		1/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
τ-Fluvalinate	0/3	0/3	0/3		0/3	0/3	0/3	2/3	0/3	0/3	3/3	3/3	3/3	**0.5**
HCB[a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
α-HCH[a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
β-HCH[a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
δ-HCH[a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
γ-HCH[a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Heptachlor epoxide A	0/3	0/3	0/3		0/3	0/3	0/3	1/3	1/3	2/3	3/3	3/3	3/3	**0.5**
Heptachlor epoxide B	0/3	0/3	0/3		1/3	2/3	1/3	3/3	3/3	2/3	3/3	3/3	3/3	**0.5**

	Blank samples				*0.02 µg/L*			*0.1 µg/L*			*0.5 µg/L*			**SDL (µg/L)**
Compounds	*GW*	*SW*	*EWW*		*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	
Hexachlorobutadiene[a]	0/3	0/3	0/3		0/3	1/3	1/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Imazalil	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	3/3	3/3	3/3	**0.5**
Iprodione	0/3	0/3	1/3		0/3	0/3	2/3	0/3	1/3	2/3	3/3	3/3	3/3	**0.5**
Isodrin	0/3	0/3	0/3		0/3	0/3	0/3	0/3	2/3	2/3	3/3	3/3	3/3	**0.5**
Leptophos	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Malathion	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Metalaxyl	0/3	0/3	0/3		2/3	3/3	2/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Methidathion	0/3	0/3	0/3		1/3	1/3	0/3	1/3	2/3	2/3	3/3	3/3	3/3	**0.5**
Methiocarb	0/3	0/3	0/3		0/3	1/3	1/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Methoxychlor	1/3	1/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Metolachlor	0/3	1/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Metribuzin	0/3	0/3	0/3		1/3	1/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Mirex[a]	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Molinate	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Omethoate	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	**-**
Oxadixyl	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Oxychlordane	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	3/3	3/3	3/3	**0.5**
Oxyfluorfen	0/3	1/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Parathion ethyl	0/3	0/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Parathion methyl	0/3	0/3	0/3		2/3	3/3	2/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Pendimethalin	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Pentachlorobenzene[a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Permethrin	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
2-Phenylphenol	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Phorate	0/3	0/3	0/3		1/3	2/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Phosmet	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	**-**
Phosphamidon	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	**-**

	Blank samples				*0.02 µg/L*			*0.1 µg/L*			*0.5 µg/L*			**SDL (µg/L)**
Compounds	*GW*	*SW*	*EWW*		*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	
Pirimicarb	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Pirimiphos-methyl	1/3	2/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Procymidone	1/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Propetamphos	0/3	0/3	0/3		1/3	2/3	1/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Propham	0/3	0/3	0/3		2/3	2/3	2/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Propiconazole	1/3	1/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Propoxur	0/3	0/3	0/3		1/3	1/3	1/3	2/3	3/3	2/3	3/3	3/3	3/3	**0.5**
Propyzamide	0/3	0/3	0/3		2/3	1/3	1/3	1/3	3/3	1/3	3/3	3/3	3/3	**0.5**
Pyriproxyfen	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Quinalphos	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Resmethrin	0/3	0/3	0/3		2/3	0/3	1/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Simazine	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Tefluthrin	0/3	0/3	0/3		2/3	2/3	2/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Terbacil	0/3	0/3	0/3		1/3	2/3	0/3	1/3	2/3	2/3	3/3	3/3	3/3	**0.5**
Terbufos	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	3/3	3/3	3/3	**0.5**
Terbumeton	2/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Terbumeton-desethyl	2/3	1/3	0/3		2/3	3/3	1/3	2/3	2/3	2/3	3/3	3/3	3/3	**0.5**
Terbuthylazine	3/3	3/3	2/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**-[b]**
Terbuthylazine-desethyl	3/3	2/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**-[b]**
Terbutryn	0/3	2/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Tetradifon	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Thiabendazole	0/3	0/3	1/3		0/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Tolclofos-methyl	0/3	0/3	0/3		2/3	3/3	2/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Tolyfluanid	0/3	0/3	0/3		0/3	1/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Triadimefon	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Triflumizole	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
Trifluralin	0/3	1/3	1/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**

	Blank samples				*0.02 µg/L*			*0.1 µg/L*			*0.5 µg/L*			**SDL (µg/L)**
Compounds	*GW*	*SW*	*EWW*		*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	
Vinclozolin	0/3	0/3	0/3		2/3	3/3	2/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
PCBs														
PCB 28[a]	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
PCB 52 [a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
PCB 77 [a]	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	3/3	3/3	3/3	**0.5**
PCB 81 [a]	0/3	0/3	0/3		0/3	0/3	0/3	0/3	1/3	1/3	3/3	3/3	3/3	**0.5**
PCB 101 [a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
PCB 105 [a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
PCB 114 [a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
PCB 118 [a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
PCB 123 [a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
PCB 126 [a]	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	3/3	3/3	3/3	**0.5**
PCB 138 [a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
PCB 153 [a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
PCB 156 [a]	0/3	0/3	0/3		0/3	0/3	0/3	0/3	1/3	1/3	3/3	3/3	3/3	**0.5**
PCB 157 [a]	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
PCB 167 [a]	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
PCB 169 [a]	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	3/3	3/3	3/3	**0.5**
PCB 180 [a]	0/3	0/3	0/3		3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.02**
PCB 189 [a]	0/3	0/3	0/3		0/3	0/3	0/3	0/3	1/3	1/3	3/3	3/3	3/3	**0.5**
PAHs														
Acenaphthene	0/3	0/3	0/3		1/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Acenaphthylene	0/3	0/3	0/3		0/3	1/3	1/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Anthracene	0/3	0/3	0/3		0/3	1/3	1/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Benzo(a)anthracene	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	**-**
Benzo(b)fluoranthene	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	3/3	3/3	3/3	**0.5**
Benzo(k)fluoranthene	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	3/3	3/3	3/3	**0.5**

	Blank samples				*0.02 µg/L*			*0.1 µg/L*			*0.5 µg/L*			**SDL (µg/L)**
Compounds	*GW*	*SW*	*EWW*		*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	*GW*	*SW*	*EWW*	
Benzo(g,h,i)perylene	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	**-**
Benzo(a)pyrene	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	3/3	3/3	3/3	**0.5**
Chrysene	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	**-**
Dibenzo(a,h)anthracene	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	**-**
Fluoranthene	0/3	0/3	0/3		1/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Fluorene	0/3	0/3	0/3		0/3	0/3	1/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Indeno(1,2,3,cd)pyrene	0/3	0/3	0/3		0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	0/3	**-**
Naphthalene	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Phenanthrene	0/3	0/3	0/3		0/3	0/3	0/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**
Pyrene	0/3	0/3	0/3		0/3	0/3	1/3	3/3	3/3	3/3	3/3	3/3	3/3	**0.1**

[a]Investigated under charge transfer conditions, this is, without adding water as modifier in the source and therefore favouring the formation of $M^{+\cdot}$.

[b]The SDL could not be established as the compound investigated was present in more than 50% of the "blank" samples analysed.

Table S.3. Positive findings (detected and confirmed) in water samples

COMPOUND/TYPE OF WATER	GW (n=12)	SW (n=12)	EWW (n=9)
PESTICIDES			
Atrazine	10/12	7/12	3/9
Atrazine-desethyl (DEA)	8/12	6/12	1/9
Atrazine-desisopropyl (DIA)	10/12	6/12	1/9
Atrazine-2-hydroxy	3/12	3/12	0/9
2-phenylphenol	3/12	6/12	3/9
4,4'-dichlorobenzophenone	1/12	2/12	0/9
Aldicarb-sulfoxide	1/12	0/12	1/9
Azoxystrobin	3/12	5/12	1/9
Bifenthrin	1/12	0/12	0/9
Bromacil	4/12	0/12	1/9
Bromophos-ethyl	2/12	0/12	1/9
Buprofezin	0/12	0/12	1/9
Carbendazim	6/12	9/12	7/9
Carfentrazone-ethyl	3/12	1/12	0/9
Chlorfenapyr	3/12	2/12	0/9
Chlorfenson	1/12	4/12	0/9
Chlorfenvinphos	2/12	3/12	6/9
Chlorpropham	5/12	4/12	3/9
Chlorpyriphos-ethyl	9/12	11/12	9/9
Chlorpyriphos-methyl	0/12	0/12	1/9
Cianazine	1/12	0/12	0/9
Coumaphos	4/12	4/12	2/9
Cyprodinil	0/12	0/12	1/9
Diazinon	8/12	9/12	6/9
Dichlofenthion	0/12	2/12	1/9
Dieldrin	1/12	0/12	1/9
Diflufenican	9/12	10/12	4/9
Dimethoathe	4/12	3/12	2/9
Dioxathion	1/12	0/12	1/9
Diuron	2/12	0/12	8/9
α-Endosulfan	0/12	0/12	1/9
β-Endosulfan	0/12	0/12	1/9
Endosulfan-ether	0/12	1/12	0/9
Endrin	0/12	0/12	1/9
Etofenprox	0/12	1/12	0/9

COMPOUND/TYPE OF WATER	GW (n=12)	SW (n=12)	EWW (n=9)
Famphur	1/12	1/12	0/9
Fenamiphos	4/12	4/12	0/9
Fenarimol	9/12	9/12	1/9
Fenexhamid	2/12	1/12	0/9
Fenithrotion	0/12	2/12	2/9
Fenthion	0/12	0/12	1/9
Fipronil	4/12	5/12	6/9
Imazalil	6/12	7/12	7/9
Imidacloprid	1/12	0/12	0/9
Iprodione	1/12	1/12	1/9
λ-Cyhalothrin	4/12	0/12	0/9
Leptophos	1/12	0/12	1/9
Metalaxyl	3/12	4/12	3/9
Metolachlor	2/12	2/12	1/9
Metoxychlor	3/12	1/12	2/9
Mycoblutanil	0/12	0/12	2/9
Oxadixyl	0/12	1/12	0/9
Oxyfluorfen	5/12	5/12	2/9
Parathion-ethyl	1/12	0/12	1/9
Penconazole	0/12	0/12	1/9
Pendimethanlin	0/12	0/12	1/9
Permethrin	0/12	0/12	1/9
Pirimiphos-methyl	5/12	4/12	2/9
Procymidone	1/12	0/12	0/9
Propanil	0/12	0/12	1/9
Propiconazole	9/12	8/12	6/9
Propoxur	0/12	0/12	2/9
Pyriproxyfen	3/12	1/12	1/9
Simazine	10/12	8/12	3/9
Tebuconazole	0/12	0/12	4/9
Terbacilo	4/12	3/12	0/9
Terbumeton	5/12	4/12	2/9
Terbumeton-desethyl	10/12	4/12	2/9
Terbuthylazine	11/12	10/12	9/9
Terbuthylazine-desethyl	11/12	10/12	6/9
Terbuthylazine-2-hydroxy	7/12	10/12	1/9
Terbutryn	7/12	10/12	9/9
Tetradifon	1/12	0/12	1/9

COMPOUND/TYPE OF WATER	GW (n=12)	SW (n=12)	EWW (n=9)
Thiabendazol	4/12	8/12	9/9
Triadimefon	4/12	6/12	0/9
Triadimenol	0/12	0/12	1/9
Triflumizole	6/12	7/12	1/9
Trifluralin	0/12	0/12	1/9
DRUGS OF ABUSE			
Caffeine	0/12	2/12	0/9
Cocaine	0/12	0/12	2/9
Benzoylecgonine	0/12	2/12	7/9
EDDP	0/12	0/12	2/9
PHARMACEUTICALS			
4-Aminoantipyrine	0/12	0/12	1/9
4-Aminoantipyrine-N-acetyl	0/12	1/12	5/9
4-Aminoantipyrine-N-formyl	0/12	1/12	5/9
Azithromycin	0/12	0/12	1/9
Carbamazepine	1/12	1/12	8/9
Ciprofloxacin	0/12	0/12	2/9
Clarithromycin	0/12	0/12	1/9
Clindamycin	0/12	1/12	0/9
Diazepam	0/12	0/12	2/9
Diclofenac	0/12	0/12	8/9
Fenofibric acid	0/12	0/12	3/9
Irbesartan	1/12	1/12	8/9
Ketoprofen	0/12	0/12	3/9
Levamisole	0/12	0/12	1/9
Lincomycin	0/12	1/12	0/9
Naproxen	0/12	0/12	4/9
Ofloxacin	0/12	1/12	7/9
Oxazepam	0/12	0/12	3/9
Phenazone	1/12	0/12	1/9
Sulfamethoxazole	1/12	0/12	1/9
Sulfathiazole	0/12	0/12	1/9
Trimethoprim	0/12	0/12	2/9
Valsartan	0/12	1/12	7/9
Venlafaxine	1/12	1/12	7/9
Preservatives			
Butylparaben	2/12	0/12	0/9
Gabapentin	1/12	0/12	0/9

COMPOUND/TYPE OF WATER	GW (n=12)	SW (n=12)	EWW (n=9)
Methylparaben	2/12	0/12	0/9
Propylparaben	2/12	0/12	0/9
Sweeteners			
Acesulfame	1/12	0/12	0/9
Sucralose	1/12	0/12	0/9
X-RAY AGENTS			
Iomeprol	1/12	0/12	0/9
Iopromide	1/12	0/12	0/9
PAHs			
Anthracene	1/12	0/12	0/9
Fluoranthene	1/12	2/12	1/9
Pyrene	1/12	2/12	1/9
MUSKS			
Galaxolide	7/12	6/12	7/9
Tonalide	10/12	11/12	8/9
UV FILTERS			
Benzophenone-3	5/12	2/12	3/9
Ethylhexyl methoxycinnamate (EHMC)	7/12	5/12	3/9
Ethylhexyl dimethyl PABA*	0/12	0/12	7/9
Isoamyl methoxcynnamate*	0/12	2/12	1/9
Octocrylene	10/12	11/12	6/9
ANTIMICROBIALS			
Triclosan	0/12	1/12	2/9
INSECT REPELLENTS			
Bayrepel*	0/12	0/12	1/9
N,N-Diethyl-meta-toluamide (DEET)	6/12	5/12	6/9

*Pending of confirmation as reference standard is not available at our laboratory at this moment.

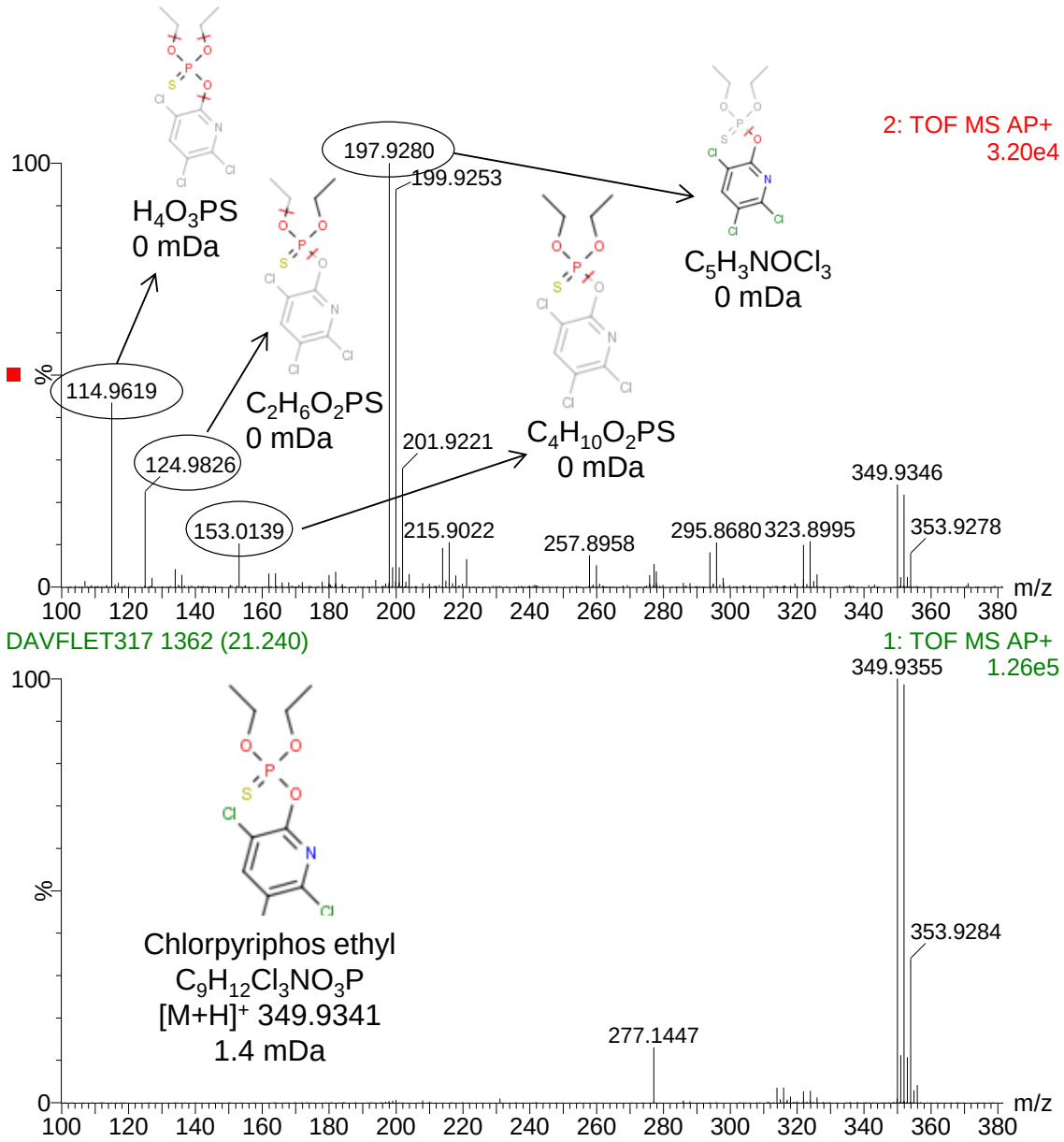

Figure S.1. Detection and identification of the insecticide chlorpyrifos by GC-QTOF MS in a wastewater sample. LE (bottom) and HE (top) spectra, and proposed fragment ions structures.

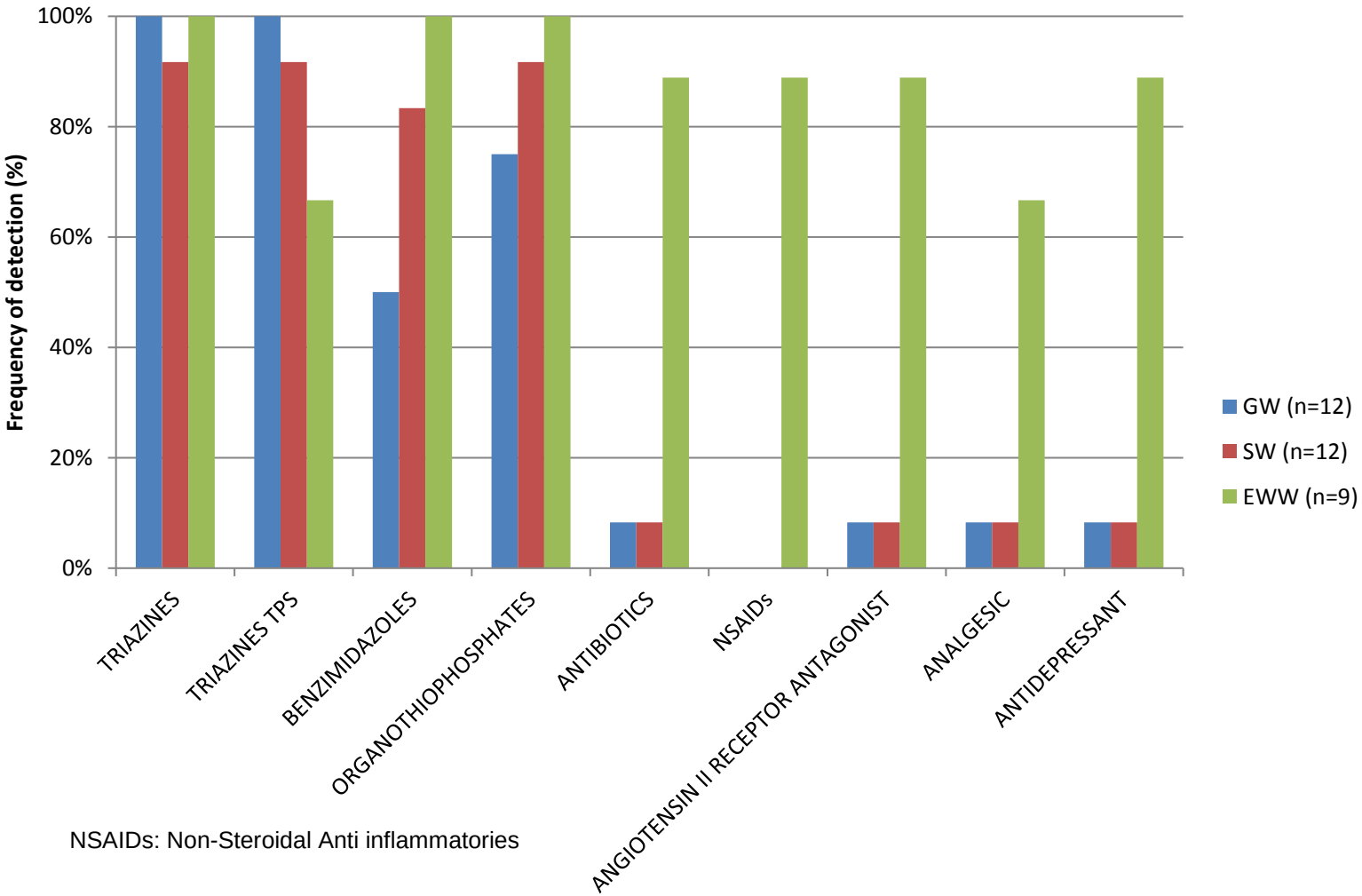

Figure S.2. Compounds most frequently detected (pesticides and pharmaceuticals) in ground water, surface water and effluent wastewater samples analysed