# Development and validation of a rapid and wide-scope qualitative screening method for detection and identification of organic pollutants in natural water and wastewater by gas chromatography time-of-flight mass spectrometry

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## ABSTRACT

In this work, a multiclass screening method for organic contaminants in natural and wastewater has been developed and validated for qualitative purposes, i.e. to ensure the reliable and sensitive identification of compounds detected in samples at a certain level of concentration. The screening is based on the use of GC-TOF MS, and the sample procedure involves solid phase extraction with $C_{18}$ cartridges. Around 150 organic contaminants from different chemical families were investigated, including PAHs, octyl/nonyl phenols, PCBs, PBDEs and a notable number of pesticides, such as insecticides (organochlorines, organophosphorus, carbamates and pyrethroids), herbicides (triazines and chloroacetanilides), fungicides and several relevant metabolites. Surface water, ground water and effluent wastewater were spiked with all target analytes at three concentration levels (0.02, 0.1 and 1 μg/L). Influent wastewater and raw leachate from a municipal solid waste treatment plant were spiked at two levels (0.1 and 1 μg/L). Up to five $m/z$ ions were evaluated for every compound. The identification criterion was the presence of, at least, two $m/z$ ions at the expected retention time, measured at their accurate mass, and the accomplishment of the $Q/q_i$ intensity ratio within specified tolerances. The vast majority of compounds investigated were correctly identified in the samples spiked at 1 μg/L. When analyte concentration was lowered down to 0.1 μg/L the identification was more problematic, especially in complex-matrix samples like influent wastewater. On the contrary, many contaminants could be properly identified at the lowest level 0.02 μg/L in cleaner matrices. The procedure was applied to the screening of water samples of different origin and matrix composition and allowed the detection of several target contaminants. A highly reliable identification could be carried out thanks to the sensitive full-spectrum acquisition at accurate mass, the high selectivity reached with the use of narrow-mass window extracted ion chromatograms, the low mass errors observed in the positive detections and the $Q/q$ ratio accomplishment.

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## 1. Introduction

The number of potentially hazardous chemicals that can reach the environment is continuously increasing and new chemical substances are constantly being synthesized and released. Water pollution is one of the main consequences and one of the most prominent environmental concerns. Modern analytical chemistry has to give an answer to this problem by developing advanced multi-analyte (multi-class) methodologies that can be applied in monitoring programs, providing a broad and realistic knowledge about water pollution in a rapid, sensitive and selective way. Additionally, it is crucial that these methodologies can be easily updated, as "emerging contaminants" are continuously appearing and being a new reason of concern [1,2].

The number of papers related to multi-residue, multi-analyte methodologies in water samples have much increased over recent years [3–8]. Most of these methods are focused on target analysis with quantitative purposes and their scope rarely exceeds several tens of analytes, being quite unusual to find analytical methods for the determination of more than 100 organic pollutants. The most widely applied techniques are gas chromatography (GC) or liquid-chromatography (LC) coupled to mass spectrometry (MS) with different analyzers, mainly single quadrupole in selected ion monitoring (SIM), or triple quadrupole and ion trap working under tandem MS (MS/MS) conditions. The sensitivity and selectivity of these techniques, especially when using tandem MS, are powerful tools, as demonstrated by the large number of applications reported in different fields. Using these configurations, identification and quantification of pre-defined contaminants (those for which MS data have been acquired) can be successfully carried out at low analyte concentrations. However, the number of compounds to be included in the scope of the method is restricted, and other poten-

tially harmful compounds that might be present in the samples would not be detected under these conditions. This is an important drawback of most quantitative methods reported, as the knowledge of aquatic environment pollution requires as much information as possible on the presence of as many pollutants as possible, not only on a group of selected compounds. In addition, from a practical point of view, it would be useful to reconsider whether quantitative results are always necessary. Thus, instead of pursuing the quantification of pollutants as the first goal, it would be better in many occasions to assure if they are present above or below the permitted concentration level in the samples [9]. Qualitative methods, used for screening purposes before quantification with the routine method, allow the selection of positive samples and considerably reduce time and cost of confirmatory/quantification analysis [10]. This strategy is in the line of increasing demands for rapid yes/no binary responses about samples and analytes [11].

In the last decade there has been a notable increase in the use of full spectrum acquisition techniques, such as time-of-flight mass spectrometry (TOF MS), which allows acquiring huge amount of chemical information on the sample in a single analysis. This facilitates widening the number of analytes that can be searched in a single experiment, with the additional advantage that data can be re-examined at any time to search for other compounds not included in the first screening, without the need of additional analysis. TOF MS and hybrid quadrupole-TOF MS have been successfully applied for screening purposes in combination with GC or LC in different applied fields, like environmental analysis, food safety or toxicology [12–22]. This analyzer provides the selectivity and sensitivity required for wide-scope screening, as it combines high full-spectral sensitivity with high mass resolution. Accurate mass data obtained can be processed in both "post-target" and/or non-target way, which gives high versatility to the instrument which allows the user to tackle an analytical problem in different ways, depending on the aim of the analysis [12–14,22,23].

The aim of a qualitative screening applied to environmental samples is to detect and identify a large number of analytes; therefore, the sample treatment applied should be as universal as possible in order to include the maximum number of compounds, even if they have quite different physicochemical characteristics. In principle, analyte recovery should not be the key point, as quantification would not be the main objective of the screening. However, it would be necessary to test the analytical methodology applied is robust, reproducible and adequately detects the target contaminants included in the screening. The analytical requirements must be defined and the values of the performance parameters assessed before they are used as routine methods in the laboratory, i.e., qualitative methods validated similar to quantitative methods [9]. The wide majority of validation processes described in the literature are addressed to quantitative methods and it is easy to find well-established protocols and international guidelines [24]. By contrast, the issue of qualitative methods has received less attention. Although there are some guidelines and documents available at present, there is no general, widely accepted, guideline to be applied, for example, in the field of environmental analysis [9,10,25–28]. In the validation of qualitative methods, selectivity/specificity and limit of detection (LOD) are the most important parameters [29].

The objective of this work is to develop and qualitatively validate a wide-scope screening for around 150 organic contaminants in natural water and wastewater based on the use of gas chromatography coupled to high-resolution time-of-flight mass spectrometry (GC-TOF MS). Critical parameters affecting the identification and confirmation process of the compounds detected are discussed. Once validated, the screening method has been applied to the analysis of different water matrices, including ground, surface water and wastewater, in order to test its applicability. Also, a brief dis-

cussion about the state-of-the-art in qualitative methods validation is made.

## 2. Experimental

### 2.1. Reagents

Reference standards of pesticides, octyl/nonyl phenols, polychlorinated biphenyls (PCBs) (Mix 3, 100 μg/mL in cyclohexane; Mix 41, 10 μg/mL in cyclohexane) and polyaromatic hydrocarbons (PAHs) (Mix 9, 100 μg/mL) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Polybrominated diphenyl ethers (PBDEs) standard mixture "Lake Michigan Study", containing BDE 28, 47, 66, 85, 99, 100, 138, 153 and 154 (50 μg/mL in isooctane) and two individual standards of BDE 71 and 183 (50 μg/mL in isooctane) were purchased from Chiron (Trondheim, Norway). Stock solutions (around 500 μg/mL) were prepared by dissolving solid reference standards in acetone and stored in a freezer at −20 °C. Working solutions were prepared by diluting stock solutions in acetone for sample fortification and diluting in hexane for injection in the chromatographic system.

Acetone (residue analysis), ethyl acetate, dichloromethane (DCM) and hexane (ultra-trace quality) were purchased from Scharlab (Barcelona, Spain). HPLC-grade water was obtained by purifying demineralised water in a Milli-Q Gradient A10 (Millipore, Bedford, MA, USA). 500 mg Bond Elut cartridges $C_{18}$ (Varian, Harbor City, CA, USA) were used for solid-phase extraction.

### 2.2. Samples

Water samples of different types and origin were collected from different sites of the Castellón province (Spain). Concretely, two surface water (SW) (Villarreal and Burriana), two ground water (GW) (Almassora and Castellón), and two effluent water samples (EWW) from a wastewater treatment plant (WWTP) of Castellón were collected for method validation in less-complex sample matrices. Additionally, three influent water samples (IWW) from the WWTP (Castellón) and three raw leachate water samples (RLW) from a municipal solid waste treatment plant sited at Onda were selected for validation in highly complex sample matrices.

In addition to the samples used for validation purposes, the developed procedure was applied to some other water samples. Six SW samples were collected at different sites from the Comunidad Valenciana and from Ebro River surroundings (Tarragona). Five GW samples were also collected from wells in the Comunidad Valenciana. GW sampling points corresponded to high vulnerability aquifers within areas with intensive agriculture practices. All samples were collected in high-density polyethylene bottles and stored in the dark at a temperature below −18 °C until analysis.

### 2.3. Instrumentation

GC instrumentation consisted of an Agilent 6890N GC system (Paloalto, CA, USA), equipped with an Agilent 7683 autosampler, coupled to a time-of-flight mass spectrometer, GCT (Waters Corporation, Manchester, UK), operating in electron ionization (EI) mode. The GC separation was performed using a fused silica HP-5MS capillary column of 30 m × 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: 90 °C (1 min); 5 °C/min to 300 °C (2 min). Splitless injections of 1 μL sample were carried out. Helium was used as carrier gas at 1 mL/min.

The interface and source temperatures were both set to 250 °C and a solvent delay of 3 min was selected. TOF MS was operated at 1 spectrum/s acquiring the mass range $m/z$ 50–650 and using a multi-channel plate voltage of 2800 V. TOF-MS resolution was

about 8500 (FWHM) at $m/z$ 614. Heptacosa, used for the daily mass calibration as well as lock mass, was injected via syringe in the reference reservoir at 30 °C. The $m/z$ ion monitored was 218.9856. The application manager TargetLynx, a module of MassLynx software, was used to process data obtained from standards and samples for target compounds. The application manager ChromaLynx, also a module of MassLynx software, was used to investigate the presence of non-target compounds in samples. Library searching was performed using the commercial NIST library.

### 2.4. Analytical procedure

The procedure applied was based on our previous work for determination of priority organic pollutants in water [7] with a few modifications. RLW samples were diluted 2.5 times with HPLC-grade water before SPE treatment due to their high organic matter content and density. Those water samples where particulate matter was observed were centrifuged before SPE. 250 mL of water sample (RLW were previously diluted 2.5 times) were passed through a 500 mg $C_{18}$ SPE cartridge previously conditioned by passing 6 mL methanol, 6 mL ethyl acetate:DCM (50:50), 6 mL methanol and 6 mL water avoiding dryness. After loading the sample, cartridges were washed with 3 mL water. The cartridge was air-dried, using vacuum for at least 15 min, and then eluted with 5 mL ethyl acetate:DCM (50:50). The extract collected was evaporated under a gentle nitrogen stream at 40 °C and redissolved in 0.5 mL hexane. The final extract obtained was injected into the GC-TOF MS.

### 2.5. Qualitative validation protocol

Validation of the screening method was mainly based on Eurachem guidelines for qualitative validation [25]. Two SW, two GW and two EWW samples were spiked at three concentration levels each (0.02, 0.1 and 1 μg/L) and analyzed together with their respective blanks for qualitative validation in less-complex sample matrices. In addition, six wastewater samples (three IWW and three RLW) were spiked at two levels each (0.1 and 1 μg/L) and analyzed together with their respective blanks for qualitative validation in highly complex samples. The limit of identification (LOI) was established as the lowest concentration for which a compound was satisfactorily identified in all spiked samples tested. The identification criterion was the presence of, at least, two $m/z$ ions at the expected retention time, measured at their accurate mass (which means that, at least, two peaks had to be observed in the respective narrow-window eXtracted Ion Chromatograms, nw-XIC) and the attainment of their $Q/q_i$ intensity ratio within specified tolerances ($Q/q$: 1–2, max. deviation ±10%; 2–5, ±15%; 5–10, ±20%; >10, ±50%) [26]. $Q/q_i$ was the ratio between the most abundant ion ($Q$) and every one of the other measured ions ($q_i$).

Selectivity, considered as the ability of the method to discriminate between the analyte and each of the other compounds [30], was tested by determining every analyte in the presence of the rest of compounds included in the screening. It was based on the presence of characteristics $m/z$ ions, measured at accurate mass, for each compound in the EI spectrum. The elevated mass resolution of the TOF instrument allowed us using narrow mass windows (0.02 Da) to perform the XICs, which highly improved the selectivity required for this application. In addition, the use of a narrow mass window also led to a notable improvement of sensitivity due to the decrease in the background noise in the chromatogram and the improvement of the signal-to-noise ratio. Specificity, considered as the ability of the detector (supported by the selectivity of the extraction, clean-up, derivatization or separation, if necessary) to provide signals that effectively identify the analyte [30], was checked by analyzing six "blank" natural water samples and six

"blank" wastewater samples. Specificity could not be demonstrated for a few compounds that were present in the "blank" samples.

## 3. Results and discussion

### 3.1. General aspects of qualitative validation protocols

The output of a qualitative analysis is the yes/no binary response depending on the presence of a given analyte in the sample [31]. The extent of the validation depends on the aim of the analytical method, and the first step is to decide which performance parameters must be studied and then design the validation procedure accordingly [29]. Some papers have been reported on qualitative validation of screening methods in the field of pesticide residue analysis [32] or anti-doping analysis [33]. Several organizations have published guidances or proposals about the validation of qualitative analytical methods. One of the recommendations is the participation in collaborative studies as AOAC suggests [9,28]. In "The Fitness for Purpose of Analytical Methods" document [25], Eurachem specifies that the qualitative performance parameters that should be evaluated are: confirmation of identity, sensitivity, selectivity/specificity and precision. In addition to the limit of detection and selectivity/specificity, the European Union (EU) proposes the evaluation of other parameters like stability, applicability and robustness [26]. The European Cooperation for Accreditation (EAL) in the guide entitled "Validation of Test Methods" states that the uncertainty associated with the method is the most important quality parameter [27]. Although performance parameters are normally well defined, it is still necessary to establish the methodology for their evaluation. Moreover, the nomenclature related to qualitative analysis as well as the classification of qualitative methods is still confusing for the users [9]. Recently, European Union has proposed some performance criteria for qualitative validation of screening methods in food and feed pesticide residue analysis. For these methods, validation is focused on detectability at the lowest spiking level for which has been demonstrated that a certain analyte can be detected in at least 95% of the samples; so a false-negative rate of 5% is accepted [30].

In this work, the screening method validation was performed based on Eurachem guidelines for qualitative validation [25]. The qualitative validation protocol has been described above (see Section 2). Because the main purpose of the qualitative screening is to distinguish between negative and positive samples at a determined level, the method proposed in this work was considered as satisfactorily validated at certain concentration level only when the target analyte was detected and correctly identified in all different-matrix spiked samples tested, independently on their recovery and precision [33].

### 3.2. GC-TOF MS screening measurement

The final extracts obtained after application of the analytical procedure were injected in the GC-TOF MS system. Then, full-spectrum acquisition data were treated using an automated processing method, which consisted of obtaining between 2 and 5 nw-XICs (mass window 0.02 Da), at pre-selected characteristic $m/z$ ions at their exact masses for every compound. The screening method was validated for a total number of 150 organic pollutants. Table 1 shows the exact masses for the three main $m/z$ ions of each compound. For some analytes, it was feasible to use up to 5 ions giving extra reliability to the identification process. Analyte identification was performed by comparing the experimental $Q/q_i$ intensity ratios in samples with the theoretical ones, which were calculated from injection of standards in solvent. The presence of at least two ions at the expected retention time, measured at

**Table 1**
m/z ions selected for the identification of target compounds.[a]

| Compound | $R_t$ (min) | Molecular mass | Molecular formula | m/z 1 | Ion 1 (Q) | m/z 2 | Ion 2 ($q_1$) | m/z 3 | Ion 3 ($q_2$) |
|---|---|---|---|---|---|---|---|---|---|
| Naphthalene | 6.50 | 128.0626 | $C_{10}H_8$ | 128.0626 | $C_{10}H_8$ | 127.0548 | $C_{10}H_7$ | 126.0470 | $C_{10}H_6$ |
| Methamidophos | 7.35 | 141.0013 | $C_2H_8NO_2PS$ | 94.0058 | $CH_5NO_2P$ | 95.0136 | $CH_6NO_2P$ | 141.0013 | $C_2H_8NO_2PS$ |
| Dichlorvos | 7.85 | 219.9459 | $C_4H_7Cl_2O_4P$ | 109.0055 | $C_2H_6O_3P$ | 184.9770 | $C_4H_7ClO_4P$ | 186.9743 | $C_4H_7{}^{37}ClO_4P$ |
| Mevinphos | 12.08 | 224.0450 | $C_7H_{13}O_6P$ | 127.0160 | $C_2H_8O_4P$ | 164.0238 | $C_5H_9O_4P$ | 192.0188 | $C_6H_9O_5P$ |
| Acenaphthylene | 12.43 | 152.0626 | $C_{12}H_8$ | 152.0626 | $C_{12}H_8$ | 151.0548 | $C_{12}H_7$ | 150.0470 | $C_{12}H_6$ |
| Acenaphthene | 13.25 | 154.0783 | $C_{12}H_{10}$ | 153.0704 | $C_{12}H_9$ | 154.0783 | $C_{12}H_{10}$ | 152.0626 | $C_{12}H_8$ |
| Methacrifos | 13.80 | 240.0221 | $C_7H_{13}O_5PS$ | 124.9826 | $C_2H_6O_2PS$ | 93.0099 | $C_2H_6O_2P$ | 207.9959 | $C_6H_9O_4PS$ |
| Pentachlorobenzene | 14.09 | 247.8521 | $C_6HCl_5$ | 249.8492 | $C_6H{}^{35}Cl_4{}^{37}Cl$ | 247.8521 | $C_6HCl_5$ | 251.8462 | $C_6H{}^{35}Cl_3{}^{37}Cl_2$ |
| Molinate | 15.38 | 187.1031 | $C_9H_{17}NOS$ | 126.0919 | $C_7H_{12}NO$ | 187.1031 | $C_9H_{17}NOS$ | 98.0970 | $C_6H_{12}N$ |
| Heptenophos | 15.45 | 250.0162 | $C_9H_{12}ClO_4P$ | 124.0080 | $C_7H_5Cl$ | 126.0051 | $C_7H_5{}^{37}Cl$ | 109.0055 | $C_2H_6O_3P$ |
| Fluorene | 15.47 | 166.0783 | $C_{13}H_{10}$ | 165.0704 | $C_{13}H_9$ | 166.0783 | $C_{13}H_{10}$ | 164.0626 | $C_{13}H_8$ |
| Omethoate | 15.72 | 213.0225 | $C_5H_{12}NO_4PS$ | 110.0133 | $C_2H_7O_3P$ | 109.0055 | $C_2H_6O_3P$ | 156.0010 | $C_3H_9O_3PS$ |
| Tecnazene | 15.95 | 258.8761 | $C_6HCl_4NO_2$ | 200.8832 | $C_5HCl_4$ | 212.8832 | $C_6HCl_4$ | 258.8761 | $C_6HCl_4NO_2$ |
| 4-t-Octylphenol | 15.99 | 206.1671 | $C_{14}H_{22}O$ | 135.0810 | $C_9H_{11}O$ | 107.0497 | $C_7H_7O$ | 95.0497 | $C_6H_7O$ |
| Diphenylamine | 16.33 | 169.0891 | $C_{12}H_{11}N$ | 169.0891 | $C_{12}H_{11}N$ | 168.0813 | $C_{12}H_{10}N$ | 167.0735 | $C_{12}H_9N$ |
| Atrazine desisopropyl | 16.98 | 173.0468 | $C_5H_8ClN_5$ | 158.0233 | $C_4H_5ClN_5$ | 173.0468 | $C_5H_8ClN_5$ | 145.0155 | $C_3H_4N_5Cl$ |
| Chlorpropham | 17.08 | 213.0557 | $C_{10}H_{12}ClNO_2$ | 127.0189 | $C_6H_6ClN$ | 152.9981 | $C_7H_4NClO$ | 213.0557 | $C_{10}H_{12}ClNO_2$ |
| Terbumeton desethyl | 17.18 | 197.1277 | $C_8H_{15}N_5O$ | 182.1042 | $C_7H_{12}N_5O$ | 141.0651 | $C_4H_7N_5O$ | 197.1277 | $C_8H_{15}N_5O$ |
| Atrazine desethyl | 17.28 | 187.0625 | $C_6H_{10}ClN_5$ | 172.0390 | $C_5H_7ClN_5$ | 174.0361 | $C_5H_7{}^{37}ClN_5$ | 187.0625 | $C_6H_{10}ClN_5$ |
| Terbuthylazine desethyl | 17.68 | 201.0781 | $C_7H_{12}ClN_5$ | 186.0546 | $C_6H_9ClN_5$ | 188.0518 | $C_6H_9{}^{37}ClN_5$ | 201.0781 | $C_7H_{12}ClN_5$ |
| Trifluraline | 17.79 | 335.1093 | $C_{13}H_{16}F_3N_3O_4$ | 306.0702 | $C_{11}H_{11}F_3N_3O_4$ | 290.0753 | $C_{11}H_{11}F_3N_3O_3$ | 248.0283 | $C_8H_5F_3N_3O_3$ |
| Phorate | 17.97 | 260.0128 | $C_7H_{17}O_2PS_3$ | 121.0418 | $C_4H_{10}O_2P$ | 230.9737 | $C_5H_{15}O_2PS_3$ | 260.0128 | $C_7H_{17}O_2PS_3$ |
| Hexachlorobenzene | 18.30 | 281.8131 | $C_6Cl_6$ | 283.8102 | $C_6{}^{35}Cl_5{}^{37}Cl$ | 281.8131 | $C_6Cl_6$ | 248.8413 | $C_6{}^{35}Cl_4{}^{37}Cl$ |
| Dimethoate | 18.68 | 228.9996 | $C_5H_{12}NO_3PS_2$ | 87.0143 | $C_3H_5NS$ | 93.0105 | $C_2H_6O_2P$ | 124.9826 | $C_2H_6O_2PS$ |
| Simazine | 18.95 | 201.0781 | $C_7H_{12}ClN_5$ | 201.0781 | $C_7H_{12}ClN_5$ | 186.0546 | $C_6H_9N_5Cl$ | 173.0468 | $C_5H_8ClN_5$ |
| Atrazine | 19.20 | 215.0938 | $C_8H_{14}ClN_5$ | 200.0703 | $C_7H_{11}ClN_5$ | 202.0674 | $C_7H_{11}{}^{37}ClN_5$ | 215.0938 | $C_8H_{14}ClN_5$ |
| Lindane | 19.39 | 287.8601 | $C_6H_6Cl_6$ | 180.9374 | $C_6H_4Cl_3$ | 182.9349 | $C_6H_4{}^{35}Cl_2{}^{37}Cl$ | 216.9145 | $C_6H_5Cl_4$ |
| 4-n-Octylphenol | 19.44 | 206.1671 | $C_{14}H_{22}O$ | 107.0497 | $C_7H_7O$ | 206.1671 | $C_{14}H_{22}O$ | 91.0548 | $C_7H_7$ |
| Terbumeton | 19.47 | 225.1590 | $C_{10}H_{19}N_5O$ | 210.1355 | $C_9H_{16}N_5O$ | 169.0964 | $C_5H_{11}N_5O$ | 154.0729 | $C_5H_8N_5O$ |
| Phenanthrene | 19.72 | 178.0783 | $C_{14}H_{10}$ | 178.0783 | $C_{14}H_{10}$ | 176.0626 | $C_{14}H_8$ | 152.0626 | $C_{12}H_8$ |
| Terbuthylazine | 19.77 | 229.1094 | $C_9H_{16}ClN_5$ | 214.0859 | $C_8H_{13}ClN_5$ | 216.0831 | $C_8H_{13}{}^{37}ClN_5$ | 229.1094 | $C_9H_{16}ClN_5$ |
| Fonofos | 19.80 | 246.0302 | $C_{10}H_{15}OPS_2$ | 108.9877 | $C_2H_6OPS$ | 137.0190 | $C_4H_{10}OPS$ | 246.0302 | $C_{10}H_{15}OPS_2$ |
| Propyzamide | 19.92 | 255.0218 | $C_{12}H_{11}Cl_2NO$ | 172.9561 | $C_7H_3OCl_2$ | 174.9532 | $C_7H_3O{}^{35}Cl{}^{37}Cl$ | 144.9612 | $C_6H_3Cl_2$ |
| Anthracene | 19.92 | 178.0783 | $C_{14}H_{10}$ | 178.0783 | $C_{14}H_{10}$ | 176.0626 | $C_{14}H_8$ | 152.0626 | $C_{12}H_8$ |
| Diazinon | 20.37 | 304.1010 | $C_{12}H_{21}N_2O_3PS$ | 137.0715 | $C_7H_9N_2O$ | 152.0950 | $C_8H_{12}N_2O$ | 179.1184 | $C_{10}H_{15}N_2O$ |
| Terbacil | 20.54 | 216.0666 | $C_9H_{13}ClN_2O_2$ | 161.0118 | $C_5H_6ClN_2O_2$ | 160.0040 | $C_5H_5ClN_2O_2$ | 116.9981 | $C_4H_4ClNO$ |
| Etrimfos | 20.92 | 292.0647 | $C_{10}H_{17}N_2O_4PS$ | 181.0977 | $C_9H_{13}N_2O_2$ | 292.0647 | $C_{10}H_{17}N_2O_4PS$ | 277.0412 | $C_9H_{14}N_2O_4PS$ |
| Endosulfan ether | 21.04 | 339.8550 | $C_9H_6Cl_6O$ | 276.8727 | $C_8H_4{}^{35}Cl_4{}^{37}Cl$ | 169.9690 | $C_8H_4Cl_2$ | 236.8413 | $C_5{}^{35}Cl_4{}^{37}Cl$ |
| Pirimicarb | 21.35 | 238.1430 | $C_{11}H_{18}N_4O_2$ | 166.0980 | $C_8H_{12}N_3O$ | 72.0449 | $C_3H_6NO$ | 238.1430 | $C_{11}H_{18}N_4O_2$ |
| 4-n-Nonylphenol | 21.57 | 220.1827 | $C_{15}H_{24}O$ | 107.0497 | $C_7H_7O$ | 220.1827 | $C_{15}H_{24}O$ | 91.0548 | $C_7H_7$ |
| PCB 28 | 21.69 | 255.9613 | $C_{12}H_7Cl_3$ | 255.9613 | $C_{12}H_7Cl_3$ | 257.9585 | $C_{12}H_7{}^{35}Cl_2{}^{37}Cl$ | 259.9557 | $C_{12}H_7{}^{35}Cl{}^{37}Cl_2$ |
| Fosfamidon | 21.78 | 299.0689 | $C_{10}H_{19}ClNO_5P$ | 127.0160 | $C_2H_8O_4P$ | 138.0918 | $C_8H_{12}NO$ | 264.1001 | $C_{10}H_{19}NO_5P$ |
| Chlorpyrifos methyl | 21.95 | 320.8950 | $C_7H_7Cl_3NO_3PS$ | 285.9261 | $C_7H_7Cl_2NO_3PS$ | 124.9826 | $C_2H_6O_2PS$ | 287.9232 | $C_7H_7{}^{35}Cl{}^{37}ClNO_3PS$ |
| Parathion methyl | 22.05 | 263.0017 | $C_8H_{10}NO_5PS$ | 124.9826 | $C_2H_6O_2PS$ | 109.0055 | $C_2H_6O_3P$ | 263.0017 | $C_8H_{10}NO_5PS$ |
| Chlozolinate | 22.08 | 331.0014 | $C_{13}H_{11}Cl_2NO_5$ | 186.9803 | $C_4H_7NO_3Cl_2$ | 188.9774 | $C_4H_7NO_3{}^{35}Cl{}^{37}Cl$ | 258.9803 | $C_{10}H_7NO_3Cl_2$ |
| Heptachlor | 22.20 | 369.8211 | $C_{10}H_5Cl_7$ | 271.8102 | $C_5{}^{35}Cl_5{}^{37}Cl$ | 236.8413 | $C_5{}^{35}Cl_4{}^{37}Cl$ | 229.9457 | $C_{10}H_5Cl_3$ |
| Carbaryl | 22.22 | 201.0790 | $C_{12}H_{11}NO_2$ | 144.0575 | $C_{10}H_8O$ | 115.0548 | $C_9H_7$ | 116.0626 | $C_9H_8$ |
| Alachlor | 22.39 | 269.1183 | $C_{14}H_{20}ClNO$ | 146.0970 | $C_{10}H_{12}N$ | 160.1126 | $C_{11}H_{14}N$ | 118.0657 | $C_8H_8N$ |
| Fenchlorphos | 22.62 | 319.8997 | $C_8H_8Cl_3O_3PS$ | 284.9309 | $C_8H_8Cl_2O_3PS$ | 286.9280 | $C_8H_8{}^{35}Cl{}^{37}ClO_3PS$ | – | – |
| Metalaxyl | 22.63 | 279.1471 | $C_{15}H_{21}NO_4$ | 206.1181 | $C_{12}H_{16}NO_2$ | 220.1388 | $C_{12}H_{18}NO_2$ | 234.113 | $C_{13}H_{16}NO_3$ |
| Methiocarb sulfone | 22.92 | 257.0722 | $C_{11}H_{15}NO_4S$ | 121.0653 | $C_8H_9O$ | 200.0507 | $C_9H_{12}O_3S$ | 185.0272 | $C_8H_9O_3S$ |
| PCB 52 | 23.05 | 289.9224 | $C_{12}H_6Cl_4$ | 291.9195 | $C_{12}H_6{}^{35}Cl_3{}^{37}Cl$ | 289.9224 | $C_{12}H_6Cl_4$ | 254.9535 | $C_{12}H_6Cl_3$ |
| Terbutryn | 23.09 | 241.1361 | $C_{10}H_{19}N_5S$ | 185.0735 | $C_6H_{11}N_5S$ | 226.1126 | $C_9H_{16}N_5S$ | 170.0500 | $C_5H_8N_5S$ |
| Methiocarb | 23.14 | 225.0824 | $C_{11}H_{15}NO_2S$ | 168.0609 | $C_9H_{12}OS$ | 153.0374 | $C_8H_9OS$ | 109.0653 | $C_7H_9O$ |
| Fenitrothion | 23.17 | 277.0174 | $C_9H_{12}NO_5PS$ | 124.9826 | $C_2H_6O_2PS$ | 109.0055 | $C_2H_6O_3P$ | 277.0174 | $C_9H_{12}NO_5PS$ |
| Pirimiphos methyl | 23.32 | 305.0963 | $C_{11}H_{20}N_3O_3PS$ | 290.0728 | $C_{10}H_{17}N_3O_3PS$ | 276.0572 | $C_9H_{15}N_3O_3PS$ | 305.0963 | $C_{11}H_{20}N_3O_3PS$ |
| Aldrin | 23.52 | 361.8757 | $C_{12}H_8Cl_6$ | 262.8570 | $C_7H_2{}^{35}Cl_4{}^{37}Cl$ | 260.8599 | $C_7H_2Cl_5$ | 292.9273 | $C_{12}H_7{}^{35}Cl_3{}^{37}Cl$ |
| Dichlofluanide | 23.42 | 331.9623 | $C_9H_{11}Cl_2FN_2O_2S_2$ | 123.0143 | $C_6H_5NS$ | 223.9504 | $C_7H_5Cl_2FNS$ | 225.9474 | $C_7H_5{}^{35}Cl{}^{37}ClFNS$ |
| Malathion | 23.67 | 330.0361 | $C_{10}H_{19}O_6PS_2$ | 127.0395 | $C_6H_7O_3$ | 124.9826 | $C_2H_6O_2PS$ | 173.0814 | $C_8H_{13}O_4$ |
| Metolachlor | 23.79 | 283.1339 | $C_{15}H_{22}ClNO$ | 162.1283 | $C_{11}H_{16}N$ | 238.0999 | $C_{13}H_{17}ClNO$ | 240.0973 | $C_{13}H_{17}{}^{37}ClNO$ |
| Fenthion | 23.92 | 278.0200 | $C_{10}H_{15}O_3PS_2$ | 278.0200 | $C_{10}H_{15}O_3PS_2$ | 169.0146 | $C_8H_9S_2$ | 109.0055 | $C_2H_6O_3P$ |
| Chlorpyrifos | 24.00 | 348.9263 | $C_9H_{11}Cl_3NO_3PS$ | 196.9202 | $C_5H_2Cl_3NO$ | 198.9173 | $C_5H_2{}^{35}Cl_2{}^{37}ClNO$ | 257.8948 | $C_5H_3Cl_2NO_3PS$ |
| Parathion ethyl | 24.02 | 291.0330 | $C_{10}H_{14}NO_5PS$ | 109.0055 | $C_2H_6O_3P$ | 291.0330 | $C_{10}H_{14}NO_5PS$ | 96.9513 | $H_2O_2PS$ |
| Isodrin | 24.62 | 361.8757 | $C_{12}H_8Cl_6$ | 192.9379 | $C_7H_4Cl_3$ | 194.9349 | $C_7H_4{}^{35}Cl_2{}^{37}Cl$ | 262.8570 | $C_7H_2{}^{35}Cl_4{}^{37}Cl$ |
| Pirimiphos ethyl | 24.90 | 333.1276 | $C_{13}H_{24}N_3O_3PS$ | 318.1041 | $C_{12}H_{21}N_3O_3PS$ | 333.1276 | $C_{13}H_{24}N_3O_3PS$ | 304.0890 | $C_{11}H_{19}N_3O_3PS$ |
| Cyprodinil | 24.95 | 225.1266 | $C_{14}H_{15}N_3$ | 224.1188 | $C_{14}H_{14}N_3$ | 225.1266 | $C_{14}H_{15}N_3$ | 210.1031 | $C_{13}H_{12}N_3$ |
| Heptachlor epoxide B | 25.09 | 385.8160 | $C_{10}H_5Cl_7O$ | 352.8442 | $C_{10}H_5{}^{35}Cl_5{}^{37}ClO$ | 350.8472 | $C_{10}H_5Cl_6O$ | 354.8413 | $C_{10}H_5{}^{35}Cl_4{}^{37}Cl_2O$ |
| Fluoranthene | 25.20 | 202.0783 | $C_{16}H_{10}$ | 202.0783 | $C_{16}H_{10}$ | 201.0704 | $C_{16}H_9$ | 200.0626 | $C_{16}H_8$ |
| Penconazole | 25.25 | 283.0643 | $C_{13}H_{15}Cl_2N_3$ | 158.9768 | $C_7H_5Cl_2$ | 160.9739 | $C_7H_5{}^{35}Cl{}^{37}Cl$ | 248.0955 | $C_{13}H_{15}ClN_3$ |
| Heptachlor epoxide A | 25.25 | 385.8160 | $C_{10}H_5Cl_7O$ | 216.9379 | $C_9H_4Cl_3$ | 250.8989 | $C_9H_3Cl_4$ | 236.8423 | $C_5{}^{35}Cl_4{}^{37}Cl$ |
| Thiabendazole | 25.30 | 201.0361 | $C_{10}H_7N_3S$ | 201.0361 | $C_{10}H_7N_3S$ | 174.0252 | $C_9H_6N_2S$ | – | – |
| Chlorfenvinphos | 25.57 | 357.9695 | $C_{12}H_{14}Cl_3O_4P$ | 266.9381 | $C_8H_6Cl_2O_4P$ | 268.9353 | $C_8H_6{}^{35}Cl{}^{37}ClO_4P$ | 323.0007 | $C_{12}H_{14}Cl_2O_4P$ |
| Isofenphos | 25.60 | 345.1164 | $C_{15}H_{24}NO_4PS$ | 213.0317 | $C_9H_{10}O_4P$ | 121.0293 | $C_7H_5O_2$ | 255.0786 | $C_{12}H_{16}O_4P$ |
| Quinalphos | 25.65 | 298.0541 | $C_{12}H_{15}N_2O_3PS$ | 146.0480 | $C_8H_6N_2O$ | 157.0760 | $C_{10}H_9N_2$ | 156.0682 | $C_{10}H_8N_2$ |
| Procymidone | 25.85 | 283.0167 | $C_{13}H_{11}Cl_2NO_2$ | 96.0575 | $C_6H_8O$ | 283.0167 | $C_{13}H_{11}Cl_2NO_2$ | 285.0139 | $C_{13}H_{11}{}^{35}Cl{}^{37}ClNO_2$ |
| Hexythiazox | 26.04 | 352.1012 | $C_{17}H_{21}ClN_2O_2S$ | 155.9800 | $C_7H_5ClS$ | 184.0113 | $C_9H_9ClS$ | 227.0172 | $C_{10}H_{10}ClNOS$ |

Table 1 (*Continued*)

| Compound | $R_t$ (min) | Molecular mass | Molecular formula | m/z 1 | Ion 1 (Q) | m/z 2 | Ion 2 ($q_1$) | m/z 3 | Ion 3 ($q_2$) |
|---|---|---|---|---|---|---|---|---|---|
| Methidathion | 26.12 | 301.9619 | $C_6H_{11}N_2O_4PS_3$ | 145.0072 | $C_4H_5N_2O_2S$ | 85.0402 | $C_3H_5N_2O$ | 124.9826 | $C_2H_6O_2PS$ |
| Pyrene | 26.15 | 202.0783 | $C_{16}H_{10}$ | 202.0783 | $C_{16}H_{10}$ | 201.0704 | $C_{16}H_9$ | 200.0626 | $C_{16}H_8$ |
| PCB 101 | 26.35 | 323.8834 | $C_{12}H_5Cl_5$ | 325.8805 | $C_{12}H_5{}^{35}Cl_4{}^{37}Cl$ | 323.8834 | $C_{12}H_5Cl_5$ | 290.9117 | $C_{12}H_5{}^{35}Cl_3{}^{37}Cl$ |
| Fenoxycarb | 26.37 | 301.1334 | $C_{17}H_{19}NO_4$ | 255.0895 | $C_{15}H_{13}NO_3$ | 186.0681 | $C_{12}H_{10}O_2$ | 185.0603 | $C_{12}H_9O_2$ |
| α-Endosulfan | 26.42 | 403.8169 | $C_9H_6Cl_6O_3S$ | 169.9690 | $C_8H_4Cl_2$ | 306.8832 | $C_9H_6{}^{35}Cl_4{}^{37}ClO$ | 336.8760 | $C_9H_6Cl_5O_3$ |
| Imazalil | 27.20 | 296.0483 | $C_{14}H_{14}Cl_2N_2O$ | 172.9561 | $C_7H_3ClO$ | 215.003 | $C_{10}H_5Cl_2O$ | 174.9532 | $C_7H_3{}^{35}Cl^{37}ClO$ |
| PCB 77 | 27.32 | 289.9224 | $C_{12}H_6Cl_4$ | 291.9195 | $C_{12}H_6{}^{35}Cl_3{}^{37}Cl$ | 289.9224 | $C_{12}H_6Cl_4$ | 254.9535 | $C_{12}H_6Cl_3$ |
| Profenofos | 27.35 | 371.9351 | $C_{11}H_{15}BrClO_3PS$ | 138.9983 | $C_3H_8O_2PS$ | 205.9134 | $C_6H_4BrClO$ | 336.9663 | $C_{11}H_{15}BrO_3PS$ |
| Dieldrin | 27.39 | 377.8706 | $C_{12}H_8Cl_6O$ | 262.8570 | $C_7H_2{}^{35}Cl_4{}^{37}Cl$ | 260.8599 | $C_7H_2Cl_5$ | 274.8755 | $C_8H_4Cl_5$ |
| p,p'-DDE | 27.45 | 315.9380 | $C_{14}H_8Cl_4$ | 246.0003 | $C_{14}H_8Cl_2$ | 247.9975 | $C_{14}H_8{}^{35}Cl^{37}Cl$ | 317.9352 | $C_{14}H_8{}^{35}Cl_3{}^{37}Cl$ |
| PCB 81 | 27.69 | 289.9224 | $C_{12}H_6Cl_4$ | 291.9195 | $C_{12}H_6{}^{35}Cl_3{}^{37}Cl$ | 289.9224 | $C_{12}H_6Cl_4$ | 254.9535 | $C_{12}H_6Cl_3$ |
| Buprofezin | 27.87 | 305.1562 | $C_{16}H_{23}N_3OS$ | 105.0578 | $C_7H_7N$ | 104.0500 | $C_7H_6N$ | 172.1034 | $C_8H_{16}N_2S$ |
| Bupimirate | 28.07 | 316.1569 | $C_{13}H_{24}N_4O_3S$ | 273.1021 | $C_{10}H_{17}N_4O_3S$ | 208.1450 | $C_{11}H_{18}N_3O$ | 316.1569 | $C_{13}H_{24}N_4O_3S$ |
| β-Endosulfan | 28.52 | 403.8169 | $C_9H_6Cl_6O_3S$ | 169.9690 | $C_8H_4Cl_2$ | 306.8832 | $C_9H_6{}^{35}Cl_4{}^{37}ClO$ | 336.8760 | $C_9H_6Cl_5O_3$ |
| PCB 105 | 28.55 | 323.8834 | $C_{12}H_5Cl_5$ | 325.8805 | $C_{12}H_5{}^{35}Cl_4{}^{37}Cl$ | 323.8834 | $C_{12}H_5Cl_5$ | 327.8774 | $C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$ |
| PCB 118 | 28.64 | 323.8834 | $C_{12}H_5Cl_5$ | 325.8805 | $C_{12}H_5{}^{35}Cl_4{}^{37}Cl$ | 323.8834 | $C_{12}H_5Cl_5$ | 327.8774 | $C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$ |
| BDE 28 | 28.68 | 403.8047 | $C_{12}H_7OBr_3$ | 405.8027 | $C_{12}H_7O^{79}Br_2{}^{81}Br$ | 407.8007 | $C_{12}H_7O^{79}Br^{81}Br_2$ | 245.9680 | $C_{12}H_7OBr$ |
| p,p'-DDD | 28.97 | 317.9537 | $C_{14}H_{10}Cl_4$ | 235.0081 | $C_{13}H_9Cl_2$ | 237.0053 | $C_{13}H_9{}^{35}Cl^{37}Cl$ | 165.0704 | $C_{13}H_9$ |
| PCB 114 | 29.04 | 323.8834 | $C_{12}H_5Cl_5$ | 325.8805 | $C_{12}H_5{}^{35}Cl_4{}^{37}Cl$ | 323.8834 | $C_{12}H_5Cl_5$ | 327.8774 | $C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$ |
| Oxadixyl | 29.15 | 278.1267 | $C_{14}H_{18}N_2O_4$ | 163.0997 | $C_{10}H_{13}NO$ | 132.0813 | $C_9H_{10}N$ | 105.0704 | $C_8H_9$ |
| Ethion | 29.24 | 383.9876 | $C_9H_{22}O_4P_2S_4$ | 230.9737 | $C_5H_{12}O_2PS_3$ | 153.0139 | $C_4H_{10}O_2PS$ | 124.9826 | $C_2H_6O_2PS$ |
| PCB 153 | 29.47 | 357.8444 | $C_{12}H_4Cl_6$ | 359.8415 | $C_{12}H_4{}^{35}Cl_5{}^{37}Cl$ | 357.8444 | $C_{12}H_4Cl_6$ | 324.8727 | $C_{12}H_4{}^{35}Cl_4{}^{37}Cl$ |
| PCB 123 | 29.59 | 323.8834 | $C_{12}H_5Cl_5$ | 325.8805 | $C_{12}H_5{}^{35}Cl_4{}^{37}Cl$ | 323.8834 | $C_{12}H_5Cl_5$ | 327.8774 | $C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$ |
| Endosulfan sulfate | 30.09 | 419.8118 | $C_9H_6Cl_6O_4S$ | 271.8102 | $C_5{}^{35}Cl_5{}^{37}Cl$ | 269.8131 | $C_5Cl_6$ | 386.8400 | $C_9H_6{}^{35}Cl_4{}^{37}ClO_4S$ |
| p,p'-DDT | 30.30 | 351.9147 | $C_{14}H_9Cl_5$ | 235.0081 | $C_{13}H_9Cl_2$ | 246.0003 | $C_{14}H_8Cl_2$ | 237.0053 | $C_{13}H_9{}^{35}Cl^{37}Cl$ |
| PCB 138 | 30.45 | 357.8444 | $C_{12}H_4Cl_6$ | 359.8415 | $C_{12}H_4{}^{35}Cl_5{}^{37}Cl$ | 357.8444 | $C_{12}H_4Cl_6$ | 324.8727 | $C_{12}H_4{}^{35}Cl_4{}^{37}Cl$ |
| PCB 126 | 30.75 | 323.8834 | $C_{12}H_5Cl_5$ | 325.8805 | $C_{12}H_5{}^{35}Cl_4{}^{37}Cl$ | 323.8834 | $C_{12}H_5Cl_5$ | 327.8774 | $C_{12}H_5{}^{35}Cl_3{}^{37}Cl_2$ |
| Tebuconazole | 30.80 | 307.1451 | $C_{16}H_{22}ClN_3O$ | 125.0158 | $C_7H_6Cl$ | 150.1031 | $C_8H_{12}N_3$ | 250.0747 | $C_{12}H_{13}N_3OCl$ |
| Diflufenican | 31.14 | 394.0741 | $C_{19}H_{11}F_5N_2O_2$ | 266.0429 | $C_{13}H_7F_3NO_2$ | 394.0741 | $C_{19}H_{11}F_5N_2O_2$ | 267.0461 | $^{12}C_{12}{}^{13}CH_7F_3NO_2$ |
| PCB 156 | 31.45 | 357.8444 | $C_{12}H_4Cl_6$ | 359.8415 | $C_{12}H_4{}^{35}Cl_5{}^{37}Cl$ | 357.8444 | $C_{12}H_4Cl_6$ | 324.8727 | $C_{12}H_4{}^{35}Cl_4{}^{37}Cl$ |
| Benzo(a)anthracene | 31.84 | 228.0939 | $C_{18}H_{12}$ | 228.0939 | $C_{18}H_{12}$ | 226.0783 | $C_{18}H_{10}$ | 200.0626 | $C_{16}H_8$ |
| Iprodione | 31.89 | 329.0334 | $C_{13}H_{13}Cl_2N_3O_3$ | 314.0099 | $C_{12}H_{10}N_3O_3Cl_2$ | 316.0072 | $C_{12}H_{10}N_3O_3{}^{35}Cl^{37}Cl$ | 186.9592 | $C_7H_3NOCl_2$ |
| Chrysene | 32.02 | 228.0939 | $C_{18}H_{12}$ | 228.0939 | $C_{18}H_{12}$ | 226.0783 | $C_{18}H_{10}$ | 200.0626 | $C_{16}H_8$ |
| Phosmet | 32.08 | 316.9945 | $C_{11}H_{12}NO_4PS_2$ | 160.0399 | $C_9H_6NO_2$ | 161.0430 | $^{12}C_8{}^{13}CH_6NO_2$ | 316.9945 | $C_{11}H_{12}NO_4PS_2$ |
| PCB 157 | 32.24 | 357.8444 | $C_{12}H_4Cl_6$ | 359.8415 | $C_{12}H_4{}^{35}Cl_5{}^{37}Cl$ | 357.8444 | $C_{12}H_4Cl_6$ | 324.8727 | $C_{12}H_4{}^{35}Cl_4{}^{37}Cl$ |
| Bifenthrin | 32.39 | 422.1260 | $C_{23}H_{22}ClF_3O_2$ | 181.1017 | $C_{14}H_{13}$ | 166.0783 | $C_{13}H_{10}$ | 165.0704 | $C_{13}H_{12}$ |
| BDE 71 | 32.40 | 481.7152 | $C_{12}H_6OBr_4$ | 325.8765 | $C_{12}H_6O^{79}Br^{81}Br$ | 323.8785 | $C_{12}H_6OBr_2$ | 483.7132 | $C_{12}H_6O^{79}Br_3{}^{81}Br$ |
| Metoxychlor | 32.42 | 344.0138 | $C_{16}H_{15}Cl_3O_2$ | 227.1072 | $C_{15}H_{15}O_2$ | 212.0837 | $C_{14}H_{12}O_2$ | 274.0761 | $C_{16}H_{15}ClO_2$ |
| PCB 167 | 32.44 | 357.8444 | $C_{12}H_4Cl_6$ | 359.8415 | $C_{12}H_4{}^{35}Cl_5{}^{37}Cl$ | 357.8444 | $C_{12}H_4Cl_6$ | 324.8727 | $C_{12}H_4{}^{35}Cl_4{}^{37}Cl$ |
| PCB 180 | 32.84 | 391.8055 | $C_{12}H_3Cl_7$ | 393.8025 | $C_{12}H_3{}^{35}Cl_6{}^{37}Cl$ | 395.7996 | $C_{12}H_3{}^{35}Cl_5{}^{37}Cl$ | 391.8055 | $C_{12}H_3Cl_7$ |
| BDE 47 | 32.92 | 481.7152 | $C_{12}H_6OBr_4$ | 325.8765 | $C_{12}H_6O^{79}Br^{81}Br$ | 323.8785 | $C_{12}H_6OBr_2$ | 483.7132 | $C_{12}H_6O^{79}Br_3{}^{81}Br$ |
| Tetradifon | 33.07 | 353.8843 | $C_{12}H_6Cl_4O_2S$ | 158.9665 | $C_6H_4ClOS$ | 226.8892 | $C_6H_2OSCl_3$ | 353.8843 | $C_{12}H_6Cl_4O_2S$ |
| Phosalone | 33.44 | 366.9869 | $C_{12}H_{15}ClNO_4PS_2$ | 182.0009 | $C_8H_5NO_2Cl$ | 183.9981 | $C_8H_5NO_2{}^{37}Cl$ | 366.9869 | $C_{12}H_{15}ClNO_4PS_2$ |
| BDE 66 | 33.47 | 481.7152 | $C_{12}H_6OBr_4$ | 325.8765 | $C_{12}H_6O^{79}Br^{81}Br$ | 323.8785 | $C_{12}H_6OBr_2$ | 483.7132 | $C_{12}H_6O^{79}Br_3{}^{81}Br$ |
| PCB 169 | 33.55 | 357.8444 | $C_{12}H_4Cl_6$ | 359.8415 | $C_{12}H_4{}^{35}Cl_5{}^{37}Cl$ | 357.8444 | $C_{12}H_4Cl_6$ | 324.8727 | $C_{12}H_4{}^{35}Cl_4{}^{37}Cl$ |
| Mirex | 33.62 | 539.6262 | $C_{10}Cl_{12}$ | 271.8102 | $C_5{}^{35}Cl_5{}^{37}Cl$ | 269.8131 | $C_5Cl_6$ | 236.8413 | $C_5{}^{35}Cl_4{}^{37}Cl$ |
| λ-Cyhalothrin | 34.34 | 449.1006 | $C_{23}H_{19}ClF_3NO_3$ | 181.0653 | $C_{13}H_9O$ | 197.0345 | $C_8H_9ClF_3$ | – | – |
| Fenarimol | 34.39 | 330.0327 | $C_{17}H_{12}Cl_2N_2O$ | 138.9951 | $C_7H_4OCl$ | 251.0030 | $C_{13}H_9Cl_2O$ | 313.0299 | $C_{17}H_{11}Cl_2N_2$ |
| Pyrazophos | 34.74 | 373.0861 | $C_{14}H_{20}N_3O_5PS$ | 221.0800 | $C_{10}H_{11}N_3O_3$ | 232.1080 | $C_{12}H_{14}N_3O_2$ | 373.0861 | $C_{14}H_{20}N_3O_5PS$ |
| PCB 189 | 34.82 | 391.8055 | $C_{12}H_3Cl_7$ | 393.8025 | $C_{12}H_3{}^{35}Cl_6{}^{37}Cl$ | 395.7996 | $C_{12}H_3{}^{35}Cl_5{}^{37}Cl_2$ | 391.8055 | $C_{12}H_3Cl_7$ |
| Permethrin I | 35.65 | 390.0790 | $C_{21}H_{20}Cl_2O_3$ | 183.0810 | $C_{13}H_{11}O$ | 163.0081 | $C_9H_9Cl_2$ | 184.0844 | $^{12}C_{12}{}^{13}CH_{11}O$ |
| Permethrin II | 35.90 | 390.0790 | $C_{21}H_{20}Cl_2O_3$ | 183.0810 | $C_{13}H_{11}O$ | 163.0081 | $C_9H_9Cl_2$ | 184.0844 | $^{12}C_{12}{}^{13}CH_{11}O$ |
| BDE 100 | 35.95 | 559.6257 | $C_{12}H_5OBr_5$ | 403.7870 | $C_{12}H_5O^{79}Br_2{}^{81}Br$ | 405.7850 | $C_{12}H_5O^{79}Br^{81}Br_2$ | 563.6216 | $C_{12}H_5O^{79}Br_3{}^{81}Br_2$ |
| Coumaphos | 36.02 | 362.0145 | $C_{14}H_{16}ClO_5PS$ | 362.0145 | $C_{14}H_{16}ClO_5PS$ | 225.9855 | $C_{10}H_7O_2SCl$ | 333.9832 | $C_{12}H_{12}O_5SClP$ |
| Benzo(b)fluoranthene | 36.55 | 252.0939 | $C_{20}H_{12}$ | 252.0939 | $C_{20}H_{12}$ | 250.0783 | $C_{20}H_{10}$ | 248.0626 | $C_{20}H_8$ |
| Benzo(k)fluoranthene | 36.65 | 252.0939 | $C_{20}H_{12}$ | 252.0939 | $C_{20}H_{12}$ | 250.0783 | $C_{20}H_{10}$ | 248.0626 | $C_{20}H_8$ |
| BDE 99 | 36.80 | 559.6257 | $C_{12}H_5OBr_5$ | 403.7870 | $C_{12}H_5O^{79}Br_2{}^{81}Br$ | 405.7850 | $C_{12}H_5O^{79}Br^{81}Br_2$ | 563.6216 | $C_{12}H_5O^{79}Br_3{}^{81}Br_2$ |
| Cypermethrin I | 37.42 | 415.0742 | $C_{22}H_{19}Cl_2NO_3$ | 181.0653 | $C_{13}H_9O$ | 163.0081 | $C_7H_9Cl_2$ | 209.0841 | $C_{14}H_{11}NO$ |
| Cypermethrin II | 37.62 | 415.0742 | $C_{22}H_{19}Cl_2NO_3$ | 181.0653 | $C_{13}H_9O$ | 163.0081 | $C_7H_9Cl_2$ | 209.0841 | $C_{14}H_{11}NO$ |
| Cypermethrin III | 37.79 | 415.0742 | $C_{22}H_{19}Cl_2NO_3$ | 181.0653 | $C_{13}H_9O$ | 163.0081 | $C_7H_9Cl_2$ | 209.0841 | $C_{14}H_{11}NO$ |
| Cypermethrin IV | 37.79 | 415.0742 | $C_{22}H_{19}Cl_2NO_3$ | 181.0653 | $C_{13}H_9O$ | 163.0081 | $C_7H_9Cl_2$ | 209.0841 | $C_{14}H_{11}NO$ |
| Benzo(a)pyrene | 37.81 | 252.0939 | $C_{20}H_{12}$ | 252.0939 | $C_{20}H_{12}$ | 250.0783 | $C_{20}H_{10}$ | 248.0626 | $C_{20}H_8$ |
| BDE 85 | 38.35 | 559.6257 | $C_{12}H_5OBr_5$ | 403.7870 | $C_{12}H_5O^{79}Br_2{}^{81}Br$ | 405.7850 | $C_{12}H_5O^{79}Br^{81}Br_2$ | 563.6216 | $C_{12}H_5O^{79}Br_3{}^{81}Br_2$ |
| Fenvalerate I | 39.15 | 419.1288 | $C_{25}H_{22}ClNO_3$ | 125.0158 | $C_7H_6Cl$ | 181.0653 | $C_{13}H_9O$ | 167.0628 | $C_{10}H_{12}Cl$ |
| BDE 154 | 39.17 | 637.5362 | $C_{12}H_4OBr_6$ | 483.6955 | $C_{12}H_4O^{79}Br_2{}^{81}Br_2$ | 481.6975 | $C_{12}H_4O^{79}Br_3{}^{81}Br$ | 485.6935 | $C_{12}H_4O^{79}Br^{81}Br_3$ |
| Fenvalerate II | 39.55 | 419.1288 | $C_{25}H_{22}ClNO_3$ | 125.0158 | $C_7H_6Cl$ | 181.0653 | $C_{13}H_9O$ | 167.0628 | $C_{10}H_{12}Cl$ |
| τ-Fluvalinate I | 39.57 | 502.1271 | $C_{26}H_{22}ClF_3N_2O_3$ | 250.0610 | $C_{11}H_{12}ClF_3N$ | 252.0583 | $C_{11}H_{12}{}^{37}ClF_3N$ | 181.0653 | $C_{13}H_9O$ |
| τ-Fluvalinate II | 39.70 | 502.1271 | $C_{26}H_{22}ClF_3N_2O_3$ | 250.0610 | $C_{11}H_{12}ClF_3N$ | 252.0583 | $C_{11}H_{12}{}^{37}ClF_3N$ | 181.0653 | $C_{13}H_9O$ |
| BDE 153 | 40.30 | 637.5362 | $C_{12}H_4OBr_6$ | 483.6955 | $C_{12}H_4O^{79}Br_2{}^{81}Br_2$ | 481.6975 | $C_{12}H_4O^{79}Br_3{}^{81}Br$ | 485.6935 | $C_{12}H_4O^{79}Br^{81}Br_3$ |
| Deltamethrin | 40.55 | 502.9732 | $C_{22}H_{19}Br_2NO_3$ | 181.0653 | $C_{13}H_9O$ | 252.9051 | $C_7H_9{}^{81}Br$ | 250.9071 | $C_7H_9Br$ |
| BDE 138 | 41.85 | 637.5362 | $C_{12}H_4OBr_6$ | 483.6955 | $C_{12}H_4O^{79}Br_2{}^{81}Br_2$ | 481.6975 | $C_{12}H_4O^{79}Br_3{}^{81}Br$ | 485.6935 | $C_{12}H_4O^{79}Br^{81}Br_3$ |
| Indeno(1,2,3,cd)pyrene | 41.89 | 276.0939 | $C_{22}H_{12}$ | 276.0939 | $C_{22}H_{12}$ | 274.0783 | $C_{22}H_{10}$ | 272.0626 | $C_{22}H_8$ |
| Dibenzo(a,h)anthracene | 42.07 | 278.1096 | $C_{22}H_{14}$ | 278.1096 | $C_{22}H_{14}$ | 276.0939 | $C_{22}H_{12}$ | 274.0783 | $C_{22}H_{11}$ |
| Benzo(g,h,I)perylene | 42.69 | 276.0939 | $C_{22}H_{12}$ | 276.0939 | $C_{22}H_{12}$ | 274.0783 | $C_{22}H_{10}$ | 272.0626 | $C_{22}H_8$ |
| BDE 183 | 43.65 | 715.4467 | $C_{12}H_3OBr_7$ | 561.6060 | $C_{12}H_3O^{79}Br_3{}^{81}Br_2$ | 563.6040 | $C_{12}H_3O^{79}Br_2{}^{81}Br_3$ | 559.6080 | $C_{12}H_3O^{79}Br_4{}^{81}Br$ |

Q: most abundant ion; $q_i$: other m/z ions.

[a] Data for some of these compounds were taken from our previous work [13].

**Table 2**
Positive findings score after analysis of six different spiked samples at different concentration levels.

| Compound | Family | Surface, ground and effluent water | | | | | Wastewater | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $n^a$ | 0.02 µg/L | 0.1 µg/L | 1 µg/L | LOI (µg/L) | $n^a$ | 0.1 µg/L | 1 µg/L | LOI (µg/L) |
| Bupimirate | FG | | 0/6 | 6/6 | 6/6 | 0.1 | | 1/6 | 6/6 | 1 |
| Chlozolinate | FG | | 0/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| Cyprodinil | FG | | 4/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| Dichlofluanid | FG | | 0/6 | 6/6 | 6/6 | 0.1 | | 0/6 | 1/6 | – |
| Diphenylamine | FG | 3/6 | 6/6 | 6/6 | 6/6 | 0.02 | 2/6 | 6/6 | 6/6 | 0.1 |
| Fenarimol | FG | | 0/6 | 6/6 | 6/6 | 0.1 | | 0/6 | 6/6 | 1 |
| Imazalil | FG | | 0/6 | 4/6 | 6/6 | 1 | | 6/6 | 6/6 | 0.1 |
| Iprodione | FG | | 0/6 | 6/6 | 6/6 | 0.1 | | 0/6 | 6/6 | 1 |
| Metalaxyl | FG | | 0/6 | 4/6 | 6/6 | 1 | | 4/6 | 6/6 | 1 |
| Oxadixyl | FG | | 0/6 | 0/6 | 6/6 | 1 | | 0/6 | 6/6 | 1 |
| Penconazole | FG | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Procymidone | FG | | 0/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| Pyrazophos | FG | | 0/6 | 6/6 | 6/6 | 0.1 | | 0/6 | 6/6 | 1 |
| Tebuconazole | FG | | 0/6 | 6/6 | 6/6 | 0.1 | | 0/6 | 6/6 | 1 |
| Tecnazene | FG | | 0/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| Thiabendazole | FG | | 0/6 | 6/6 | 6/6 | 0.1 | 2/6 | 5/6 | 6/6 | 1 |
| Pentachlorobenzene | FG | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Hexachlorobenzene | FG | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Chlorpropham | HB | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Diflufenican | HB | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Molinate | HB | | 1/6 | 6/6 | 6/6 | 0.1 | | 0/6 | 6/6 | 1 |
| Propizamide | HB | | 0/6 | 6/6 | 6/6 | 0.1 | | 3/6 | 6/6 | 1 |
| Terbacil | HB | | 0/6 | 6/6 | 6/6 | 0.1 | 3/6 | 3/6 | 6/6 | 1 |
| Trifluraline | HB | | 2/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| Alachlor | HB CA | | 5/6 | 6/6 | 6/6 | 0.1 | | 3/6 | 6/6 | 1 |
| Metolachlor | HB CA | | 3/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| Atrazine | HB TZ | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Atrazine desethyl | HB TZ | | 2/6 | 0/6 | 6/6 | 1 | | 6/6 | 6/6 | 0.1 |
| Atrazine desisopropyl | HB TZ | | 0/6 | 0/6 | 6/6 | 1 | | 0/6 | 6/6 | 1 |
| Simazine | HB TZ | | 6/6 | 6/6 | 6/6 | 0.02 | 3/6 | 3/6 | 6/6 | 1 |
| Terbumeton | HB TZ | | 2/6 | 6/6 | 6/6 | 0.1 | | 0/6 | 6/6 | 1 |
| Terbumeton desethyl | HB TZ | | 0/6 | 6/6 | 6/6 | 0.1 | | 0/6 | 6/6 | 1 |
| Terbuthylazine | HB TZ | | 6/6 | 6/6 | 6/6 | 0.02 | 3/6 | 6/6 | 6/6 | 0.1 |
| Terbuthylazine desethyl | HB TZ | | 6/6 | 6/6 | 6/6 | 0.02 | 1/6 | 6/6 | 6/6 | 0.1 |
| Terbutryn | HB TZ | | 1/6 | 6/6 | 6/6 | 0.1 | | 4/6 | 6/6 | 1 |
| Buprofezin | INS | | 0/6 | 6/6 | 6/6 | 0.1 | | 0/6 | 6/6 | 1 |
| Fenoxycarb | INS | | 0/6 | 6/6 | 6/6 | 0.1 | | 0/6 | 1/6 | – |
| Hexythiazox | INS | | 0/6 | 0/6 | 6/6 | 1 | | 6/6 | 6/6 | 0.1 |
| Carbaryl | INS CAR | | 0/6 | 0/6 | 6/6 | 1 | | 0/6 | 3/6 | – |
| Pirimicarb | INS CAR | | 0/6 | 6/6 | 6/6 | 0.1 | | 0/6 | 6/6 | 1 |
| Methiocarb | INS CAR | | 0/6 | 4/6 | 6/6 | 1 | | 1/6 | 6/6 | 1 |
| Methiocarb sulfone | INS CAR | | 0/6 | 0/6 | 6/6 | 1 | | 0/6 | 6/6 | 1 |
| Aldrin | INS OC | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| α-Endosulfan | INS OC | | 3/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| β-Endosulfan | INS OC | | 1/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| Dieldrin | INS OC | | 3/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| Endosulfan ether | INS OC | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Endosulfan sulfate | INS OC | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Heptachlor | INS OC | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Heptachlor epoxide B | INS OC | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Heptachlor epoxide A | INS OC | | 3/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| Isodrin | INS OC | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Lindane | INS OC | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Mirex | INS OC | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Metoxychlor | INS OC | | 6/6 | 6/6 | 6/6 | 0.02 | | 3/6 | 6/6 | 1 |
| p,p′-DDE | INS OC | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| p,p′-DDD | INS OC | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| p,p′-DDT | INS OC | | 0/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| Chlorfenvinphos | INS OP | | 2/6 | 6/6 | 6/6 | 0.1 | 3/6 | 6/6 | 6/6 | 0.1 |
| Chlorpyrifos | INS OP | 3/6 | 6/6 | 6/6 | 6/6 | 0.02 | 6/6 | 6/6 | 6/6 | 0.1 |
| Chlropyrifos methyl | INS OP | | 6/6 | 6/6 | 6/6 | 0.02 | | 5/6 | 6/6 | 1 |
| Coumaphos | INS OP | | 0/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| Diazinon | INS OP | 2/6 | 3/6 | 6/6 | 6/6 | 0.1 | 1/6 | 0/6 | 6/6 | 1 |
| Dichlorvos | INS OP | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Dimethoate | INS OP | | 0/6 | 6/6 | 6/6 | 0.1 | 5/6 | 3/6 | 6/6 | 1 |
| Ethion | INS OP | | 0/6 | 6/6 | 6/6 | 0.1 | | 0/6 | 6/6 | 1 |
| Etrimfos | INS OP | | 0/6 | 6/6 | 6/6 | 0.1 | | 0/6 | 6/6 | 1 |
| Fenchlorphos | INS OP | | 0/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| Fenitrothion | INS OP | | 0/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| Fenthion | INS OP | | 0/6 | 0/6 | 6/6 | 1 | | 3/6 | 6/6 | 1 |
| Fonofos | INS OP | | 0/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| Heptenophos | INS OP | | 0/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |

Table 2 (*Continued*)

| Compound | Family | Surface, ground and effluent water | | | | | Wastewater | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $n^a$ | 0.02 µg/L | 0.1 µg/L | 1 µg/L | LOI (µg/L) | $n^a$ | 0.1 µg/L | 1 µg/L | LOI (µg/L) |
| Isofenphos | INS OP | | 0/6 | 6/6 | 6/6 | 0.1 | | 3/6 | 6/6 | 1 |
| Malathion | INS OP | | 0/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| Metacrifos | INS OP | | 0/6 | 0/6 | 6/6 | 1 | | 0/6 | 6/6 | 1 |
| Metamidophos | INS OP | | 0/6 | 0/6 | 0/6 | – | | 0/6 | 0/6 | – |
| Methidathion | INS OP | | 0/6 | 6/6 | 6/6 | 0.1 | | 0/6 | 6/6 | 1 |
| Mevinphos | INS OP | | 0/6 | 6/6 | 6/6 | 0.1 | | 0/6 | 6/6 | 1 |
| Omethoate | INS OP | | 0/6 | 0/6 | 0/6 | – | | 0/6 | 0/6 | – |
| Parathion-ethyl | INS OP | | 0/6 | 0/6 | 6/6 | 1 | | 0/6 | 6/6 | 1 |
| Parathion-methyl | INS OP | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Phorate | INS OP | | 0/6 | 0/6 | 6/6 | 1 | | 0/6 | 6/6 | 1 |
| Phosalone | INS OP | | 0/6 | 4/6 | 6/6 | 1 | | 6/6 | 6/6 | 0.1 |
| Pirimiphos ethyl | INS OP | | 0/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| Profenofos | INS OP | | 0/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| Pirimiphos methyl | INS OP | | 3/6 | 6/6 | 6/6 | 0.1 | | 0/6 | 6/6 | 1 |
| Phosmet | INS OP | | 0/6 | 0/6 | 6/6 | 1 | | 1/6 | 6/6 | 1 |
| Quinalphos | INS OP | | 0/6 | 4/6 | 6/6 | 1 | | 0/6 | 6/6 | 1 |
| Bifenthrin | INS PY | | 1/6 | 6/6 | 6/6 | 0.1 | | 3/6 | 6/6 | 1 |
| Cypermethrin I | INS PY | | 0/6 | 0/6 | 0/6 | – | | 0/6 | 0/6 | – |
| Cypermethrin II | INS PY | | 0/6 | 0/6 | 0/6 | – | | 0/6 | 0/6 | – |
| Cypermethrin III | INS PY | | 0/6 | 0/6 | 0/6 | – | | 0/6 | 0/6 | – |
| Cypermethrin IV | INS PY | | 0/6 | 0/6 | 0/6 | – | | 0/6 | 0/6 | – |
| λ-Cyhalothrin | INS PY | | 0/6 | 0/6 | 6/6 | 1 | | 0/6 | 6/6 | 1 |
| Deltamethrin | INS PY | | 0/6 | 0/6 | 6/6 | 1 | | 0/6 | 0/6 | – |
| Fenvalerate I | INS PY | | 0/6 | 0/6 | 6/6 | 1 | | 0/6 | 1/6 | – |
| Fenvalerate II | INS PY | | 0/6 | 0/6 | 6/6 | 1 | | 0/6 | 0/6 | – |
| Permethrin I | INS PY | | 0/6 | 0/6 | 6/6 | 1 | | 0/6 | 6/6 | 1 |
| Permethrin II | INS PY | | 0/6 | 0/6 | 6/6 | 1 | | 0/6 | 6/6 | 1 |
| τ-Fluvalinate I | INS PY | | 0/6 | 0/6 | 6/6 | 1 | | 0/6 | 0/6 | – |
| τ-Fluvalinate II | INS PY | | 0/6 | 0/6 | 6/6 | 1 | | 0/6 | 0/6 | – |
| 4-t-Octylphenol | ONP | | 2/6 | 6/6 | 6/6 | 0.1 | | 0/6 | 6/6 | 0.1 |
| 4-n-Octylphenol | ONP | | 6/6 | 6/6 | 6/6 | 0.02 | | 4/6 | 6/6 | 1 |
| 4-n-Nonylphenol | ONP | | 5/6 | 6/6 | 6/6 | 0.1 | | 3/6 | 6/6 | 1 |
| Acenaphthene | PAH | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Acenaphthylene | PAH | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Anthracene | PAH | 2/6 | 5/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| Benzo(a)anthracene | PAH | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Benzo(b)fluoranthene | PAH | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Benzo(k)fluoranthene | PAH | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Benzo(a)pyrene | PAH | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Benzo(g,h,l)perylene | PAH | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Chrysene | PAH | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Dibenzo(a,h)anthracene | PAH | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Fluoranthene | PAH | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Fluorene | PAH | 1/6 | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Indeno(1,2,3,cd)pyrene | PAH | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Naphthalene | PAH | 3/6 | 6/6 | 6/6 | 6/6 | 0.02 | 5/6 | 6/6 | 6/6 | 0.1 |
| Phenanthrene | PAH | | 5/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| Pyrene | PAH | 2/6 | 3/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| BDE 28 | PBDE | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| BDE 47 | PBDE | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| BDE 66 | PBDE | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| BDE 71 | PBDE | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| BDE 85 | PBDE | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| BDE 99 | PBDE | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| BDE 100 | PBDE | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| BDE 138 | PBDE | | 4/6 | 6/6 | 6/6 | 0.1 | | 6/6 | 6/6 | 0.1 |
| BDE 153 | PBDE | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| BDE 154 | PBDE | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| BDE 183 | PBDE | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| PCB 28 | PCB | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| PCB 52 | PCB | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| PCB 77 | PCB | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| PCB 81 | PCB | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| PCB 101 | PCB | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| PCB 105 | PCB | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| PCB 118 | PCB | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| PCB 114 | PCB | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| PCB 123 | PCB | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| PCB 126 | PCB | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| PCB 138 | PCB | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| PCB 153 | PCB | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| PCB 156 | PCB | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| PCB 157 | PCB | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| PCB 167 | PCB | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| PCB 169 | PCB | | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |

Table 2 (*Continued*)

| Compound | Family | Surface, ground and effluent water | | | | | Wastewater | | | |
|----------|--------|-------|-----------|----------|------------|---|-----------|----------|------------|
| | | $n^a$ | 0.02 μg/L | 0.1 μg/L | 1 μg/L | LOI (μg/L) | $n^a$ | 0.1 μg/L | 1 μg/L | LOI (μg/L) |
| PCB 180 | PCB | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| PCB 189 | PCB | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |
| Fosfamidon | – | 0/6 | 4/6 | 6/6 | 1 | | 0/6 | 6/6 | 1 |
| Tetradifon | AC | 6/6 | 6/6 | 6/6 | 0.02 | | 6/6 | 6/6 | 0.1 |

LOI: limit of identification; FG: fungicide; HB: herbicide; INS: insecticide; ONP: octyl/nonyl phenol; PAH: polyaromatic hydrocarbon; PBDE: polybrominated diphenyl ether; PCB: polychlorinated byphenil; CA: chloroacetanilide; TZ: triazine; CAR: carbamate; OC: organochlorine; OP: organophosphorus; PY: pyrethroid; AC: acaricide.

[a] $n/6$ means that $n$ out of 6 "blank" samples analyzed were positive for the target analyte.

their accurate mass, was required together with the attainment of the $Q/q_i$ ratio within specified tolerances to give the identification of the target analytes as positive. Maximum deviations accepted in $Q/q_i$ ratios were based on the European Commission Decision 2002/657/EC [26], as applied in our previous works [12,13,34].

### 3.3. Validation results

Qualitative validation was carried out considering two different groups of water samples according to their matrix complexity: "clean" and wastewater. Samples with less complex matrix (surface and ground water, and effluent urban wastewater) were considered as "clean" water. Six of these samples were used for validation (2 SW, 2 GW and 2 EWW). Another six samples with higher matrix complexity (3 IWW and 3 RLW) were selected as wastewater. The real world samples used for qualitative validation could not be considered as a blank actually, as several target analytes were present (see Table 2). Taking into account the different complexity of the waters tested, two limit of identification values were proposed for each analyte, one for each type of water matrix ("clean" and waste water). The LOI was estimated for each analyte as the lower concentration tested where a 6/6 positive score was obtained in the spiked samples (Table 2). Consequently, a compound was considered as satisfactorily identified and the screening method qualitatively validated, at a certain concentration level, only when all the six samples spiked at that level were posi-

tive by the accomplishment of the identification criterion defined above.

Qualitative validation in "clean" water was successfully carried out in all different samples, and most of the compounds could be identified in a reliable way at the lowest fortification level tested (0.02 μg/L). For example, PCBs and most PBDEs, PAHs and organochlorine (OC) insecticides achieved the established identification criteria at 0.02 μg/L. As regards organophosphorus (OP) insecticides, most of them showed a LOI of 0.1 μg/L, although four of them (chlorpyrifos, chlorpyrifos methyl, dichlorvos and parathion methyl) could also be satisfactorily validated at 0.02 μg/L. Moreover, seven OP insecticides could be only identified at the highest level studied (1 μg/L) and other two (methamidophos and omethoate) could not be identified at any concentration level probably due to its high polarity which prevents sufficient retention on $C_{18}$ cartridges [35]. LOIs for triazine herbicides were 0.02 or 0.1 μg/L, and for most of alkylphenols, chloroacetanilide herbicides and fungicides was 0.1 μg/L. Carbamate and pyrethroid insecticides could be mostly validated at 1 μg/L. No LOI value could be established for cypermethrin, probably due to the low sensitivity observed for this compound.

Regarding validation in wastewater samples, LOIs for most compounds were normally higher than those for "clean" water samples. This was in part due to that 0.02 μg/L spiking level was not assayed in wastewater (so it could not be set-up as LOI), and also because the higher complexity of the matrix made more complicated the
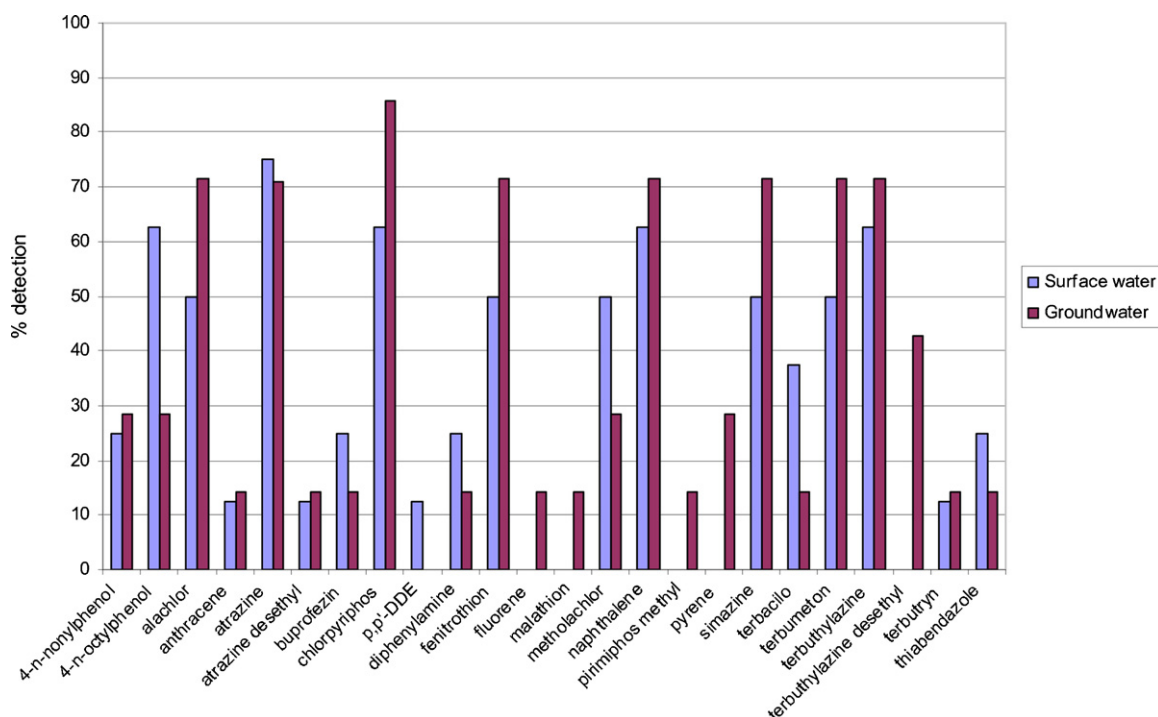


**Fig. 1.** Frequency of detection (%) of organic contaminants in the surface and ground water samples analyzed.
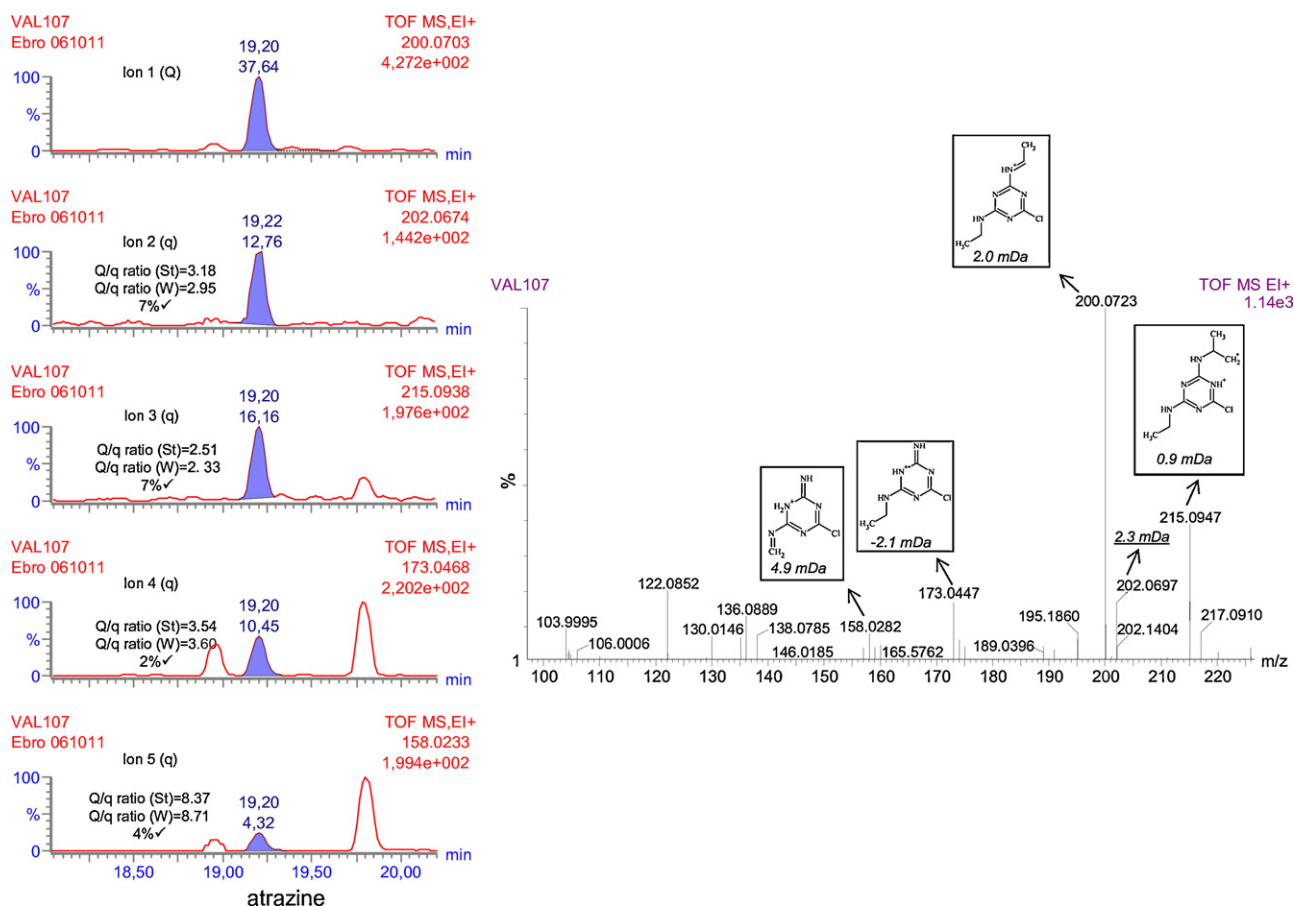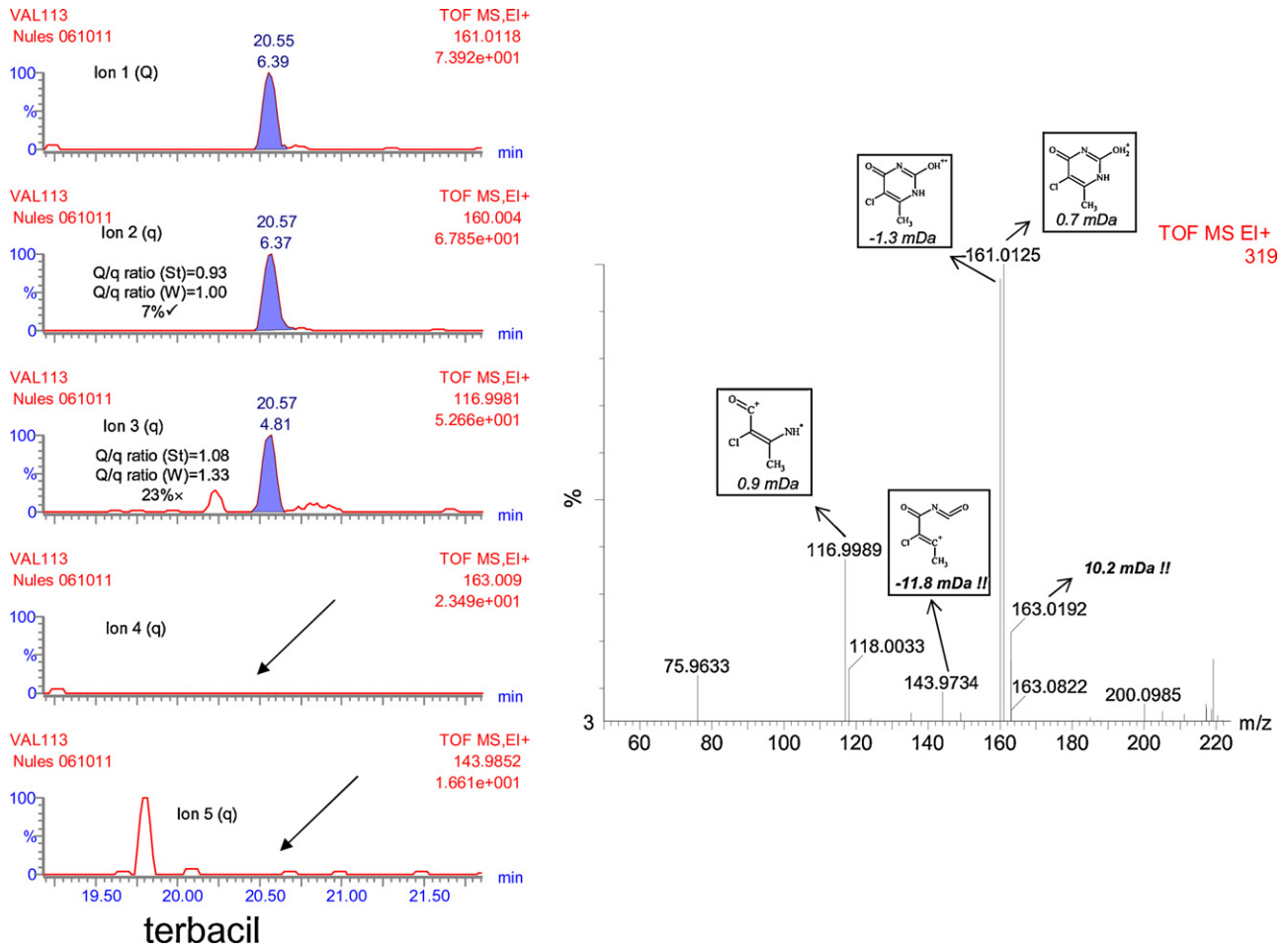
**Fig. 2.** Extracted-ion chromatograms (mass window 0.02 Da) showing a positive finding of atrazine in surface water. Experimental EI accurate mass spectrum. Chemical structures proposed for the most abundant EI fragment ions. $Q$: quantitative ion; $q_i$: confirmative ion; St: reference standard; W: water sample; $\sqrt{}$: $Q/q_i$ ratio within tolerance limits; ×: $Q/q_i$ ratio out of tolerance limits.

identification of the analytes. In spite of this, a large number of PCBs, PBDEs, PAHs and OC insecticides achieved the established identification criteria at the lowest concentration tested (0.1 μg/L). For these compounds, it would have been possible to decrease the LOI as the peak intensity obtained at 0.1 μg/L was rather high. As regards OP insecticides, 13 out of 30 could be validated at 0.1 μg/L, and 15 out of 30 at 1 μg/L. Similarly to "clean" water, methamidophos and omethoate could not be validated at any concentration level. As regards other target insecticides, seven could be validated at 1 μg/L and hexythiazox at 0.1 μg/L. Alkylphenols, herbicides and fungicides, LOIs were set-up at 0.1 or 1 μg/L, with the exception of dichlofluanid, for which the identification criterion was not accomplished even at the higher level tested.

It is worth to mention that 12 compounds with LOI 1 μg/L (methacrifos, thiabendazole, isofenphos, bupirimate, ethion, iprodione, fenarimol, diazinon, pirimicarb, methiocarb, pirimiphos methyl and fenthion) (see Table 2), were satisfactorily detected (i.e. chromatographic peaks were observed for at least two $m/z$ ions in the corresponding nw-XIC) in the six wastewater samples spiked at 0.1 μg/L. However, they could not be reported as satisfactorily validated at this level because the $Q/q_i$ ratio was out of specified tolerances. This fact made us to realize on the strict criteria established regarding $Q/q_i$ ratio deviation tolerances, especially when dealing with highly complex matrices. Although theoretical $Q/q_i$ ratios, calculated from standards in solvent, were updated in every sequence/day by injection of reference standards within the sample sequence, in some cases the variations observed along a sequence/day together with the effect of the matrix made difficult to accomplish the $Q/q_i$ ratio, mainly at low analyte concentration. At

present this interesting topic is under study in our group, as surely higher tolerances could be admitted in some particular problematic cases.

It should be mentioned at this point that in cases of high sensitivity (compounds like OC insecticides, PCBs, PAHs and PBDEs) it was necessary to discard the most abundant ion when validating at the highest level (1 μg/L) due to detector saturation. The selection of other $m/z$ ions from the EI spectrum for these compounds (see Table 1) helped us to solve this problem. This aspect has to be taken into account; otherwise, when saturation occurs the analyte would not be satisfactorily identified at high concentrations because of the non accomplishment of the identification criteria. So, special care should be taken in those samples where the presence of high analyte concentrations might lead to detector saturation (for some $m/z$ ions) with the risk of reporting false negatives.

### 3.4. Application to routine samples

A total of 23 water samples (8SW, 7GW, 2EWW, 3IWW, 3RLW) were analyzed following the developed procedure. Up to 24 pollutants were detected and properly identified in surface and ground water (see Fig. 1). The compounds more frequently detected in surface water were atrazine (6 out of 8 samples), and 4-n-octylphenol, chlorpyrifos, naphthalene and terbuthylazine (5 out of 8 samples). As regards ground water, the most frequently detected were chlorpyrifos (6 out of 7 samples), followed by alachlor, atrazine, fenitrothion, naphthalene, simazine, terbumeton and terbuthylazine (5 out of 7 samples). In the two effluent water samples collected from the WWTP of Castellón, only one positive find-
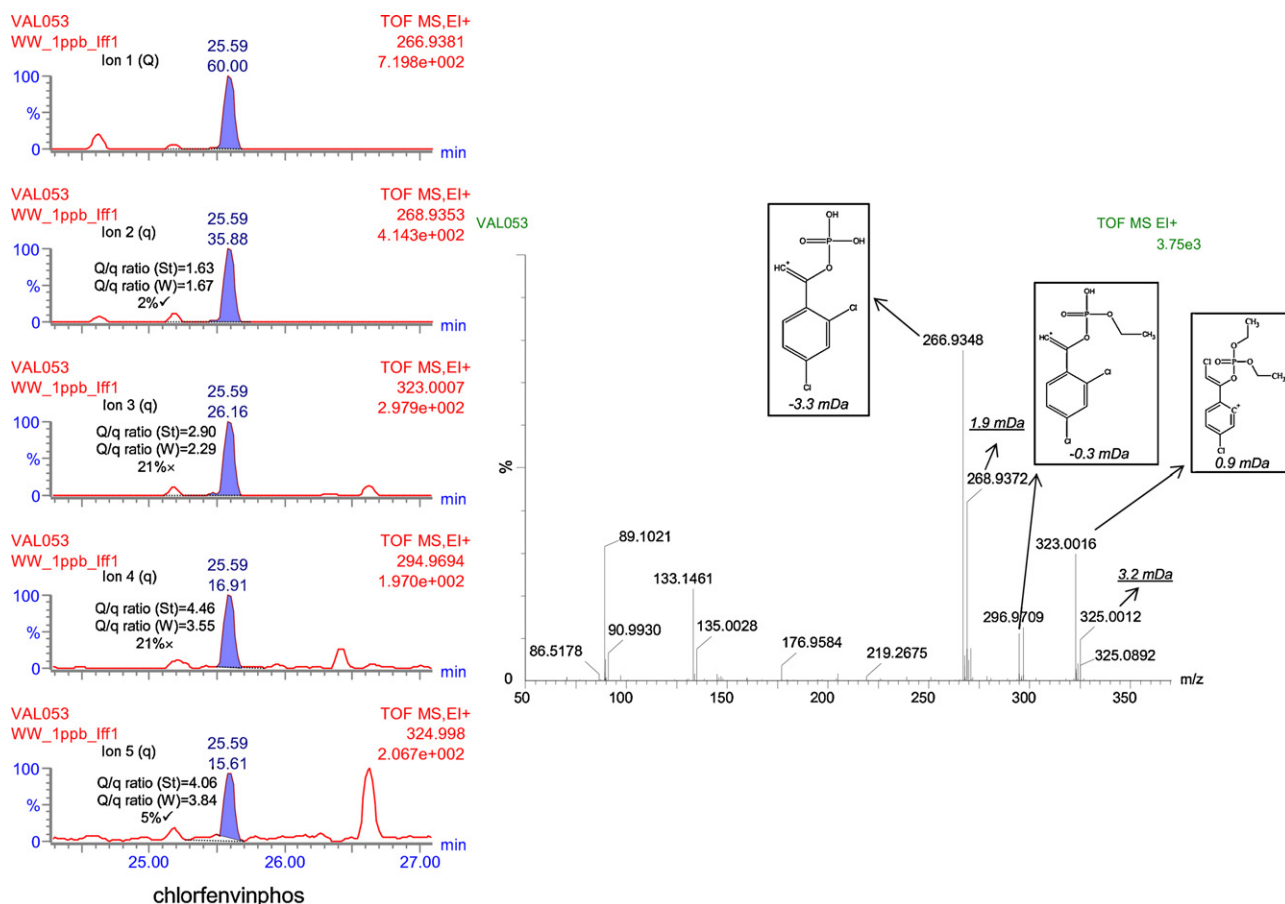
**Fig. 3.** Extracted-ion chromatograms (mass window 0.02 Da) showing a positive finding of chlorfenvinphos in influent wastewater sample. Experimental EI accurate mass spectrum. Chemical structures proposed for the most abundant EI fragment ions. Q: quantitative ion; $q_i$: confirmative ion; St: reference standard; W: water sample; $\checkmark$: $Q/q_i$ ratio within tolerance limits; $\times$: $Q/q_i$ ratio out of tolerance limits.

ing of naphthalene, two of chlorpyrifos and two of diazinon were found.

In wastewater samples, the compound most frequently detected was chlorpyrifos (6 out of 6 samples), widely used as insecticide in citric crops in our area, followed by naphthalene and dimethoate (5 out of 6 samples) and chlorfenvinphos (4 out of 6). Also, positive findings of simazine and terbacil (3 out of 6), terbuthylazine, thiabendazole and diphenylamine (2 out of 6) were found.

In every sequence of analysis, two quality control samples (QCs), i.e. a "blank" water sample (previously analyzed) fortified at LOI, were also analyzed. The correct identification of target analytes peaks in the QC samples was tested for quality control analysis in every batch of samples analyzed.

As an illustrative example, Fig. 2 shows a positive finding of the herbicide atrazine in surface water from Ebro river. In this case, we observed 5 characteristic ions at the expected retention time in the nw-XICs. The attainment of all 4 $Q/q_i$ ratios within accepted tolerances led to the unequivocal confirmation of this compound. The accurate mass spectrum of the sample peak is shown together with mass errors for the five ions, which were below 2.3 mDa (except for $m/z$ 158, with 4.9 mDa). Also, chemical structures for the most abundant EI fragment ions were suggested based on the elemental compositions proposed for those ions accordingly to the accurate mass measurements given by the instrument in the target methodology applied (see Table 1). All structures proposed for the fragments were compatible with the chemical structure of atrazine, making the identification still more reliable.

Fig. 3 shows another example, the detection and identification of the OP insecticide chlorfenvinphos in influent wastewater. The

detection was confirmed by the presence of 5 $m/z$ ion at expected retention time in the nw-XICs. However, only 2 out of 4 $Q/q_i$ ratios fulfilled the specified tolerances, possibly due to the low analyte concentration and to the complexity of the influent water matrix. The two $Q/q$ ratios that were out of tolerances showed deviations of 21% with respect to the reference standard (see Fig. 3), while the maximum tolerance for $Q/q$ ratios between 2 and 5 is 15% [26]. The results of our work on wastewater samples suggest that tolerances established in the EU Decision are surely too restrictive for this kind of complex matrices. Examples like that shown in Fig. 3 and many others observed in our work indicate that several ions measured at their accurate mass, corresponding to a given contaminant, can be observed in wastewater samples although without the accomplishment of $Q/q$ ratios. In our opinion, higher deviations could be admitted when dealing with organic contaminants measured at accurate mass in highly complex matrix samples.

Accurate mass measurements are, of course, of much relevance in the confirmation process. However, mass errors in a great deal depend on the ion abundance. Therefore, mass errors higher than usual could be expected when measuring low intensity ions. This is illustrated in Fig. 4, which shows the detection and confirmation of the identity of the herbicide terbacil in ground water. The detection was supported by the presence of 3 out of 5 ions monitored at the expected retention time in the nw-XICs, and the identity was confirmed by the accomplishment of one of the $Q/q_i$ ratios. However, the remaining two ions were absent (see ions $q_4$ and $q_5$ in Fig. 4). The reason was the high mass error for these ions, which exceeded 10 mDa, explaining that no peak was present in the corresponding nw-XICs obtained with a mass window of 0.02 Da ($\pm$10 mDa). In

**Fig. 4.** Extracted-ion chromatograms (mass window 0.02 Da) showing a positive finding of terbacil in ground water. Experimental EI accurate mass spectrum. Chemical structures proposed for the most abundant EI fragment ions. Q: quantitative ion; $q_i$: confirmative ion; St: reference standard; W: water sample; √: $Q/q_i$ ratio within tolerance limits; ×: $Q/q_i$ ratio out of tolerance limits.
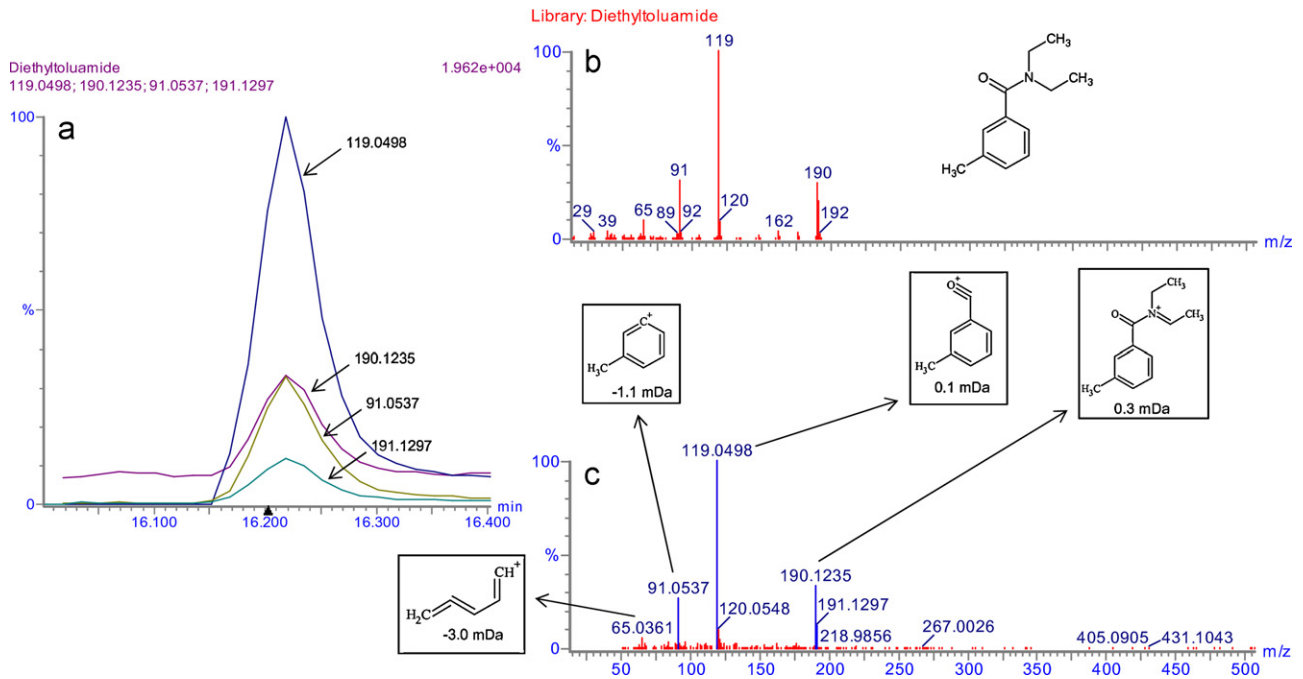


**Fig. 5.** Detection and identification of non-target diethyltoluamide by GC-TOF MS in a raw leachate water sample from a municipal solid waste treatment plant. (a) Extracted-ion chromatograms for four $m/z$ ions. (b) Commercial library mass spectrum of diethyltoluamide at nominal mass. (c) Deconvoluted accurate mass spectrum of diethyltoluamide in the sample (mass errors shown in mDa).

spite of this fact, sufficient evidences existed to give this finding as terbacil.

One of the main advantages of the screening method applied is that TOF MS always works under full-spectrum acquisition mode at accurate mass, which means that all MS data remain available to be reprocessed at any time. This fact makes feasible to investigate the presence of other target compounds that might be of interest after data acquisition without the need of additional analysis, and also the processing of data in a non-target way. As a consequence, interesting perspectives are opened in environmental pollution screening in comparison with those offered by other analytical techniques [36].

When using TOF MS, the number of potential pollutants investigated in a sample can be easily increased after data acquisition, searching for other post-target or even non-target compounds. Obviously, the compounds investigated should meet the requirements associated to sample treatment and analytical measurement. From this point of view, a SPE step using conventional $C_{18}$ cartridges and the use of GC-TOF MS seems to be a good "universal" option. The most reasonable objective in an environmental screening by TOF MS seems to be the detection and identification of as many pollutants as possible in order to have wide and realistic information on the potential pollutants present in a sample. In a subsequent step, the pollutants detected and considered as relevant could be included in the list of target analytes in monitoring programs that would normally apply analytical quantitative methods, e.g. by using GC–MS/MS with triple quadrupole analyzer.

In this paper, the use of GC-TOF MS has allowed us to investigate the presence of other contaminants in the water samples analyzed in a non-target way. This was carried out by applying the ChromaLynx Application Manager, which allowed the automated detection of sample components and their subsequent identification thanks to the useful information acquired in the full accurate mass spectra [12,36]. Using this approach, several contaminants, not included in the target list, were discovered. To illustrate this possibility offered by the TOF MS instrument we will show an example of a contaminant following the non-target approach. Fig. 5 shows a positive finding of diethyltoluamide, an insect repellent, in a raw leachate sample. Accurate mass confirmation automatically performed for four representative ions led to the confirmation of the identity of diethyltoluamide with mass errors around or below 1 mDa for three of them. In addition, the structures proposed for at least four fragment ions observed in the EI spectrum were compatible with the chemical structure of this compound.

## 4. Conclusions

Oppositely to other applied fields, like toxicology or anti-doping analysis, there is a lack of wide-scope screening methods in environment focused on qualitative purposes that are conveniently validated following a widely accepted methodical approach. The objective of these methods is to report a sample as positive or negative to a given contaminant, at a given concentration, relevant from an environmental point of view. Following this objective, in this paper a multiclass wide-scope GC-TOF MS screening of organic contaminants in water has been developed and qualitatively validated. Validation has been made in several types of water matrices at different analyte concentrations. Specificity/selectivity of the screening was supported by accurate mass measurements provided by TOF MS, which allowed using narrow window-XIC ($\pm0.01$ Da) at selected $m/z$ ions. The wide majority of the 150 compounds investigated were detected and correctly identified in all surface, ground and wastewater samples tested spiked at 1 μg/L. A large number of targeted analytes could also be satisfactorily identified at 0.1 μg/L level, although identification was more problematic for

some compounds, especially in complex-matrix samples like influent wastewater or raw leachate from solid waste treatment plant, mainly because of the non-compliance of $Q/q$ ratios. For a notable number of analytes, the method was validated at the lowest concentration level tested (0.02 μg/L) in less-complex matrices, like surface, ground or effluent wastewater.

The screening procedure was applied to around 20 water samples, with the result of detecting and correctly identifying several PAHs (naphthalene and pyrene), triazine herbicides (simazine, terbumeton, terbuthylazine and terbutryn), organophosphorus insecticides (malathion, chlorpyrifos, diazinon), and some herbicides and fungicides like diphenylamine and chlorpropham. Positive findings were correctly identified following the established criterion of monitoring up to 5 $m/z$ ions at accurate mass and the compliance of $Q/q_i$ intensity ratio. The analysis of QCs ("blank" samples spiked at the LOI level, i.e. the lowest concentration tested for which a compound was correctly identified in all spiked samples), included in every sample sequence, was used for quality control purposes and to test the robustness of the screening method. This allowed us to prove that some compounds detected in the samples were present at levels below the empirical LOI, which illustrates the strong potential and excellent sensitivity of the screening approach developed in the present work.

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