Multiclass determination of 66 organic micropollutants in environmental water samples by fast gas chromatography-mass spectrometry

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Abstract

A multiresidue method has been developed for quantification and identification of 66 multiclass priority organic pollutants in water by fast gas chromatography (GC) coupled to mass spectrometry (MS). Capabilities and limitations of single quadrupole mass spectrometer as detector in fast GC were studied evaluating the chromatographic responses in terms of sensitivity and chromatographic peak shapes, as they were influenced by scan time. The number of monitored ions in a selected ion monitoring (SIM) group strongly conditioned the scan time and subsequently the number of data points per peak. A compromise between peak shape and scan time was adopted in order to reach the proper conditions for quantitative analysis. An average of 10 to 15 points per peak was attained for most compounds, involving scan times between 0.1 and 0.22 s.

The method was validated for mineral, surface and groundwater. A solid phase extraction (SPE) pre-concentration step using C_{18} cartridges was applied. Four isotopically labeled standards were added to the samples before extraction, and used as surrogates to ensure a reliable quantification. Analyses were performed by GC-MS in electron ionization mode, monitoring the three most abundant and/or specific ions for each compound and using the intensity ratios as a confirmatory parameter. With a chromatographic run of less than 10 minutes, SIM mode provided excellent sensitivity and

identification capability due to the monitoring of three ions and the evaluation of their intensity ratio. Limits of detection below 10 ng/L were reached for most of the 66 compounds in the three matrices studied. Accuracy and precision of the method were evaluated by means of recovery experiments at two fortification levels (10 and 100 ng/L), obtaining recoveries between 70 and 120% in most cases and relative standard deviations below 20%. The possibilities of a simultaneous SIM-scan method have also been explored for non-target qualitative analysis. The developed method has been applied to the analysis of surface water samples collected from the Mediterranean region of Spain.

Key words

Pesticides, organic pollutants, fast gas chromatography, mass spectrometry, water analysis.

1. Introduction

The presence of organic pollutants in environmental water is related to the wide use of many synthetic products mainly in the agricultural and industrial practices, but urban waste water can also be an important source of pollution in the aquatic environment. Although there can be hundreds of potential contaminants, only a few have been defined as priority contaminants in the framework of the Water Directive 2008/105/CE [1], and maximum allowable concentrations have been established for them in order to perform a strict control on their concentration levels. Most concentration levels regulated are over 10 ng/L; therefore, the development of highly sensitive analytical methods that ensure the reliable quantification and confirmation of the compounds in samples at the ng/L level is required.

Gas chromatography coupled to mass spectrometry (GC-MS) has been widely applied for determination of semivolatile and volatile organic pollutants with satisfactory sensitivity and selectivity [2]. Single quadrupole has been commonly used [3-5], although this MS analyzer does not always ensure the sensitivity and selectivity required for most analyte/matrix combinations. This fact has led to an increased use of ion trap detector (ITD) and triple quadrupole (QqQ) analyzers, which allow working in tandem mass spectrometry mode (MS-MS) [6, 7]. The use of tandem MS techniques dramatically minimizes matrix interferences and chemical noise in the chromatograms, notably improving the selectivity and sensitivity [6, 7]. However, gas chromatographic runs are still long in most multiresidue multiclass analysis, even when using capillary GC instruments. Nowadays, the interest in reducing analysis time has increased and methods able to determine as many compounds as possible in a single analysis in a short time are encouraged. The use of fast GC reveals itself as a good approach to reduce analysis time in routine analysis due to the similar or even higher separation efficiency than conventional capillary GC, the higher sensitivity and simultaneous reduction of operating cost of a GC analysis. Nevertheless, despite the benefits, the technique has not been implemented yet as a common routine analysis in analytical laboratories. Some reviews have been published in the last decade [8-11] illustrating the advantages, limitations and practical applications,

looking for the best way to speed up the GC separations. Different routes towards a faster separation have been described in the literature, but the option to be selected greatly depends on the combination of sample and analytes (number and type), on the analysis purposes and on the application under study [12-15].

As a first approach, shortening the column lenght [12, 13], but maintaining the internal diameter, reduces chromatographic times, but also contributes to loss in resolution. This option is only adequate for the determination of a few compounds since coelutions can become an important drawback. In this way, using faster temperature programming is sometimes better than using shorter columns [14]. Moreover, increasing the carrier gas velocity, as well as modifying pressure or flow conditions, is another option to reduce analysis time [13].

Alternatively, the use of narrow-bore columns (I.D. < 0.15 mm) [15] combined with any of the previously indicated approaches restores the resolution to adequate values, allowing the determination of a larger number of compounds, but still maintaining short chromatographic runs. Several authors have also reported another way to reduce analysis time by applying two-dimensional gas chromatography [16]. This is a powerful technique for analysis of complex matrices, but it requires more complex instrumentation.

For an effective application of fast GC, the detector has to contribute adequate characteristics, specially related to scan speed, selectivity and also sensitivity. The use of selective MS detection allows to speed up separations and ensures reliable quantitative and qualitative determinations. An adequate scan speed (high sampling frequency) is required in order to provide sufficient number of data points across the peak. Thus, one of the best choices is time-of-flight (TOF) analyzer [17], which fits well with fast GC since it provides data acquisition rates faster than, for example, ion trap or quadrupole. Quadrupole analyzers that are typically applied in conventional GC have also been coupled to fast GC on narrow-bore capillary columns with satisfactory results. M. Kirchner et al. [18] studied the possibilities and limitations of single quadrupole in fast GC by the measurement of 27 n-

alkanes and pesticides in a run time of less than 10 minutes, evaluating at the same time the limitations of the acquisition in SIM mode related to the quality of the spectra obtained. These authors indicate that only 11 ions could be acquired as a maximum in a SIM group looking for quantitative purposes. Discussion is only related to standard solutions and the application to real samples is missing. L. Mondello et al. [19] applied fast GC-MS with satisfactory results using single quadrupole for the determination of 25 allergens in fragrances in full scan mode. They reported the use of a QP2010 Shimadzu, allowing a scan speed of 1000 amu/s, in scan mode, which is adequate when working with high concentration samples (>100 mg/L). The ultratrace analysis of 25 pesticides in non-fatty food matrices has been also performed combining fast GC-MS with negative chemical ionization, with a total analysis time of 11.45 minutes. The results confirm that quadrupole acquisition rates are fast enough for a proper reconstruction of the chromatographic peaks and are sensitive enough when combined with NCI mode [20].

The main objective of this paper is to study the capabilities of fast GC coupled to MS with single quadrupole analyzer, using narrow-bore capillary column, in the field of environmental (water) analysis. The number of compounds typically included in fast GC has been notably increased, developing and validating a method for the determination of 66 organic pollutants, belonging to different chemical classes, in water samples. During optimization, special effort has been made to find a compromise between efficient chromatographic separation and short run time, still maintaining satisfactory sensitivity.

2. Experimental

2.1. Reagents

Organic pollutants investigated in this work, which included several chemical classes, are listed in Table 1. All pesticide standards (organochlorine (OC) and organophosphorus (OP) insecticides and herbicides) and octyl/nonyl phenols were purchased from Dr. Ehrenstorfer (Augsburg, Germany). PCB Mix 3 from Dr. Ehrenstorfer (100 μg/mL in cyclohexane) was used for single quantification of PCB congeners 28, 52, 101, 118, 138, 153 and 180. PAH Mix 9 from Dr. Ehrenstorfer (10 μg/mL in cyclohexane) provided sixteen polycyclic aromatic hydrocarbons regulated by US Environmental Protection Agency (EPA). Standards of brominated diphenyl ethers (BDEs) were purchased from Chiron (Stiklestadveien, Trondheim, Norway).

Stock standard solutions (nominal concentration of 500 μg/mL) were prepared by dissolving reference standards in acetone and stored in a freezer at -20 ºC. Working standard mixtures were prepared by volume dilution of stock solutions in acetone, for sample fortification, and in hexane, for GC injection.

Acetone (pesticide residue analysis), ethyl acetate, dichloromethane (DCM) and hexane (ultra-trace quality) were purchased from Scharlab (Barcelona, Spain).

Four isotopically labeled internal standards (ILIS) were used: p,p'-DDE-D_8, benzo(a)anthracene-D_{12} and terbutylazine-D_5 (Dr. Ehrenstorfer), and hexachlorobenzene (HCB)-$^{13}C_6$ (Cambridge Isotope Labs Inc., Andover, MA, USA). A working mixed solution of labeled standards was prepared by volume dilution of individual stock solutions with hexane, for calibration preparation, and with acetone, for sample fortification, and stored at 4 ºC.

Bond Elut solid phase extraction (SPE) cartridges (500 mg C_{18}) (Varian, Harbor City, CA, USA) were used for solid-phase extraction (SPE).

2.2. Sample matrices

Three different water samples were used during the validation study: mineral, surface and groundwater. Mineral water was purchased directly from a local market in Castellón (Spain); surface water samples were collected from Mijares River (Vila-Real, Castellón) and groundwater samples were collected from an irrigation well (Serra d'Irta, Castellón).

Additionally, ten surface water samples from the Spanish Mediterranean area (Tarragona) were analyzed to investigate the presence of selected organic contaminants and to test the applicability of the method.

2.3. GC instrumentation

Measurements were performed on a Shimadzu QP2010 Plus GC system equipped with an autosampler (Shimadzu AOC-5000) and coupled to a single quadrupole mass spectrometer (Shimadzu GCMS-QP2010 Plus). Compounds were separated on a SAPIENS-5MS capillary column (length 20 m x I.D. 0.10 mm x film 0.10 μm) purchased from Teknokroma. Injector was operated in splitless mode, injecting 1 μL at 320 ºC; splitless time was 1 min. The oven was programmed as follows: 80 ºC (1.2 min); 90 ºC/min to 225 ºC; 15 ºC/min to 270 ºC; 150 ºC/min to 330 ºC (3.4 min), resulting in a total chromatographic time of 9.6 min. Helium was used as carrier gas. A pressure pulsed injection was carried out using an initial pressure of 850 kPa (1.25 mL/min) maintained during 1.2 min and then changed to a constant flow of 0.75 mL/min (this corresponds to a linear velocity of 39 cm/s).

Mass spectrometer was operated in the electron ionization (EI) mode (70 eV). The source and the interface temperatures were adjusted to 225 ºC and 300 ºC, respectively. The scan time in scan mode was set initially at 0.1 s; when SIM mode was applied, scan time ranged from 0.1 to 0.22 s. A solvent delay of 1.5 min was used to prevent damage to the filament in the ion source.

Shimadzu software GCMSsolution was used through all the work to process the data automatically.

2.4. Analytical procedure

Samples were prepared by adding 1mL of surrogate standard mixture in acetone (containing the four ILIS) to 250 mL of water. SPE cartridges were conditioned by passing 6 mL methanol, 6 mL ethyl acetate:DCM (50:50), 6 mL methanol and 6 mL deionized water, avoiding dryness. The water sample was loaded and passed through the cartridge using vacuum. Then the cartridge was washed with 3 mL deionized water and dried by passing air, using vacuum for at least 30 min to ensure no residual water would be eluted with the final extract. The retained analytes were eluted with 5 mL ethyl acetate:DCM (50:50). The collected extract was evaporated to dryness under a gentle nitrogen stream at 40 ºC, redissolved in 0.5 mL of hexane and injected into the GC system under the experimental conditions indicated before.

Quantification of analytes in samples was carried out from calibration curves prepared with standards in solvent also containing ILIS, using relative responses of each compound to the corresponding internal standard. The selection of the ILIS to be used for each analyte was based on their chromatographic behavior and similarity in chemical structure, and it is shown in Table 2.

2.5. Validation study

The developed method was validated in mineral, surface and groundwater. The analytical parameters evaluated were: linearity, accuracy, precision, limits of detection and quantification and confirmation capability of the method for positive samples.

Linearity was studied by means of calibration curves obtained with standard solutions (n=3), at eight concentration levels: 0.5, 1, 5, 10, 50, 100, 200 and 250 μg/L. Linearity was considered satisfactory when regression coefficient was higher than 0.99 and the residuals lower than 30%, and without any clear tendency in their distribution (aleatory distribution of positives and negatives).

Accuracy was estimated from recovery experiments, analyzing six replicates of the water spiked at two levels (10 and 100 ng/L). Precision was expressed as repeatability in terms of relative standard deviation (R.S.D., %) (n=6) calculated for each fortification level.

Limit of quantification (LOQ), as the analyte concentration that produced a peak signal of ten times the background noise, was estimated from the chromatogram at the lowest fortification level tested with satisfactory recovery (70-120%) and precision (R.S.D.< 20%). Limit of detection (LOD) was estimated in the same way but using a signal to noise ratio of three.

In order to confirm peak identity in samples, the ratio between the quantification ion (target, Q) and the reference ions (q_i) was evaluated and compared with the theoretical value obtained for reference standards. The confirmation criterion is based on the European Commission Decision 2002/657/EC [21], which also established the maximum tolerances as a function of relative intensities. Although this Decision applies to the determination of contaminants and residues in food of animal origin, it is also widely applied in environmental pollution measurements due to the lack of guidelines in this field. Coincidence between the retention time in a sample and the corresponding standard was also required to confirm a positive finding (maximum allowed deviation ± 0.5 %).

3. Results and discussion

3.1. GC-MS optimization

Preliminary experiments for optimization of chromatographic conditions were performed using hexane standard solutions, with the GC-MS operating in full scan mode using a 10 m x 0.1 mm I.D. GC column. Due to its short length, the chromatographic run was shorter than 6 minutes and showed a great number of coelutions that could not be avoided even by modifying temperature programming or by adjusting MS parameters. Problems with coelutions became even more important when the SIM mode was developed for the 66 selected compounds (and 4 ILIS), making an adequate quantification impossible. Therefore, a 20 m column with the same internal diameter (0.10 mm) and film thickness (0.10 μm) was considered instead, since increasing the column length should also increase the number of theoretical plates and resolution, although at the cost of higher chromatographic times.

GC parameters that could affect to peak resolution and analysis time, such as initial and final temperature, linear velocity of the carrier gas and oven temperature program, were evaluated and optimized. Early eluting compounds determined the choice of the best value for initial temperature, which was studied between 60 and 100 °C (the lower value selected was 60 °C since hexane was used as injection solvent). Final temperature was selected according to the behavior of the last eluting compounds, which required temperatures between 300 and 350 °C. The optimum results responded to a compromise between resolution, sensitivity and peak shape. Linear velocity of the carrier gas was also optimized in order to obtain satisfactory results, testing values between 30 and 50 cm/s. Although linear velocity changes did not produce an important impact on the results, a good compromise between sensitivity and resolution was achieved at 39 cm/s, and this value was used for further experiments.

The oven temperature program was the most complex parameter to be optimized since it notably influenced analysis time and resolution. Programs with a single temperature ramp (50, 100 and 120 °C/ min) were tested, but they resulted in too many chromatographic coelutions that could not be

overcome by adjusting MS parameters. The main goal was to achieve a rapid separation with adequate resolution. In this way, different temperature ramp rates were tested: slower rates were selected for chromatographic zones where many compounds eluted at nearly the same time and higher rates were applied to speed up the analysis time. After several experiments, the best conditions corresponded to 80 ºC (1.2 min); then a high speed ramp rate of 90 ºC/min was applied up to 225 ºC to accelerate the elution of the most volatile compounds and facilitate the elution of the rest. Later, due to the large number of compounds that eluted in the next minutes, a low rate of 15 ºC/min was used up to 270 ºC, allowing good resolution without increasing significantly the analysis time (lower rates did not imply significant chromatographic changes, but time did increase considerably). Finally, a rate of 150 ºC/ min up to 330 ºC was selected to speed up the elution of the less volatile compounds, which did not show coelution problems.

The last GC parameter studied was the use of pressure pulsed injection, which was found to improve the sensitivity for most compounds, as a result of a faster transfer from the injector to the column, thus allowing a very narrow initial chromatographic band. Figure 1 shows the total ion chromatogram for a standard mixture in hexane obtained in scan mode under the optimum conditions. This chromatogram illustrates that all compounds (except BDE 209) elute in less than 10 minutes, with good sensitivity for most of them.

MS parameters for scan mode were also optimized in order to obtain good peak shapes but still maintaining satisfactory sensitivity for each compound. The ion source temperature was modified between 175 and 225 ºC, and the interface temperature between 225 and 300 ºC to obtain the best performance. The scan time, that notably affects the peak shape, was tested between 0.1 and 0.3 seconds. As expected, a scan time of 0.1 s led to the best peak shapes with 10 to 15 points per peak, corresponding to a scan speed of 3333 amu/s, without a decrease in sensitivity.

Once the GC-MS conditions for scan mode were optimized, the selection of target and reference ions for each compound was carried out. Generally, the most abundant and/or characteristic ions were selected for identification and quantification of the analytes. In cases where coelutions were

unavoidable, a careful selection of *m/z* values was necessary in order to use those ions that did not interfere in the quantitative determination of the coeluting analytes. Thus, in spite of the large number of compounds to be determined in a very short chromatographic time, selected analytes could be determinated using the mass spectrometer capabilities. Table 1 shows the quantitative (target) and the reference (confirmative) ions selected for each compound.

The developed scan mode method allowed the determination of all compounds, except BDE 209, in a short time (9.6 min). In order to improve method sensitivity, a SIM method was created automatically from the scan injection selecting appropriate target and reference ions (as indicated before, with three ions per compound), with some manual corrections.

Compounds had to be sorted into groups (time window) of at least 0.2 minutes (because this is a system restriction limiting the minimum SIM group width). Another aspect to take into account is that 64 is the maximum number of ions that system is capable of acquiring in a SIM group, so this limits the number of compounds to be included. Furthermore, in this acquisition mode, scan time depends on the number of ions included in each group, in such a way that scan time increases when the number of ions acquired increases [22, 23].

The minimum number of data points required to have satisfactory chromatographic peaks for quantitative purposes has been widely discussed in the literature [24-26]. A number of 8-10 data points per peak (including the baseline points) is commonly accepted for a satisfactory peak reconstruction and quantification [18, 27]. The convenience of "collecting as many points across the peak as possible to meet quantitative and qualitative needs of the application" has also been reported [28].

Considering that the method proposed in this work strongly emphasizes the mass spectrometer aspect, including the large number of compounds that can be determined in a very short analysis time, it is necessary to study the maximum number of ions that can be included in a SIM group without degrading peak shape more than it is acceptable. In this way, several chromatographic methods were

prepared including a SIM group with a variable number of ions monitored, from 9 to 52. In order to determine peak quality, a model compound (mevinphos) was selected and its extracted ion chromatogram (m/z 127) obtained after each injection (Figure 2). As can be seen, when 9 ions were monitored in the SIM group (a total of 3 compounds) it was possible to select a scan time of 0.1 s (giving a total of 15 points per peak). When the number of ions increased, the scan time also increased resulting in fewer data points for mevinphos peak. From the results obtained (as depicted in Figure 2) it is concluded that, with our mass spectrometer system, a maximum of 20 ions should be included in a SIM group (corresponding to a scan time of 0.2s) to obtain satisfactory peak shape.

The number of compounds to be detected in a given (short) time and the resolution between peaks determines the number of SIM groups. If the number of compounds in a SIM group exceeds the maximum number of ions recommended before, two approaches in method design can be considered. In the first approach, monitoring only one or two ions per compound should maintain the number of compounds per SIM group without loosing satisfactory peak shape. This approach has not been considered in the present work, as adequate confirmatory capabilities of the method have to be achieved, being necessary to record at least three ions per compound as indicated in the Directive 96/23/CE [21]. The second approach relies in reducing the SIM group width (time), increasing the total number of SIM groups with less compounds in each one. This is not an easy task, as in many cases there are not gaps between compounds to establish the cut of the SIM group, making it necessary to sacrifice one or more compounds that elute in the group change zone.

These limitations forced a compromise to be reached between peak shape, number of compounds and analysis time. In the present work, most SIM groups (of a total of 22 groups) contained less than 15 ions, enabling the attainment of 10 to 15 points per peak. Only one SIM group included 20 ions (see Table 1, time window 3.95-4.24 min), resulting in 7-10 data points per peak depending on the analyte peak width, which is in the limit of acceptability for satisfactory peak shape. Even in this unfavorable case, the quantification of these compounds was likewise satisfactory, as supported by the validation data.

Once an adequate SIM mode quantitative method was developed for the 66 studied compounds, the possibility of simultaneous scan and SIM mode was tested in order to fully exploit the capabilities of our GC-MS instrument. This option, available in this equipment, seems useful for screening purposes. Working under this mode, selected analytes can be quantified (target analysis in SIM mode) while simultaneous full scan acquisition allows the identification of unknown analytes (non-target analysis in scan mode).

Thus, three SIM-scan methods were prepared, monitoring different number of target analytes (SIM) in each method, in all cases including a simultaneous scan event in the 70-500 *m/z* range. For this purpose, five surface water samples, fortified at 0.1 μg/L with all the 66 target analytes, were analyzed using the three SIM-scan methods. The first conclusion is that when performing a scan event simultaneously to SIM detection, a decrease in the number of points per peak occurs; thus, the number of compounds included in the SIM group was decreased from the initially selected 66 down to 33 (all priority pollutants considered in the Directive 2008/105/CE [1]) or to 10.

When only 10 compounds (30 ions distributed in 8 SIM groups) were included in the SIM acquisition, the chromatographic peak shapes were satisfactory, achieving 8-10 points per peak. However, even under these conditions, two analytes could not be satisfactorily quantified (recoveries around 50%), as they were in the limit of acceptability for satisfactory peak shape. As it seems reasonable to develop a method for the determination of the regulated contaminants, the 33 priority contaminants studied in this work (shown in italic, Table 1) were included in a second SIM-scan method. As expected, a notable reduction in the number of points per peak was observed, and around 20 compounds could not be properly quantified (recoveries around or below 50%) since they presented 4-5 points per peak.

On the other hand, scan spectra obtained by the three SIM-scan methods were compared, without observing notable differences among them. Although scan acquisition was also affected by the increment of the scan time in the simultaneous mode, a non-target screening in the SIM-scan method can be performed in parallel to the quantification of the target analytes for which the method was

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satisfactory. In this way, when performing an automatic search of the scan data, some of the spiked compounds could be identified (by library match) even at the relatively low concentration 0.1 μg/L (50 pg injected). This means that non-target scan (in a SIM-scan method) can be easily applied for those compounds chromatographically separated and at relatively high concentrations (above 0.5 μg/L, 250 pg injected).

As satisfactory quantification of target analytes under SIM mode strongly depends on the number of data points per peak, it is concluded that the best results were obtained from single scan and SIM injections, rendering the acquisition under simultaneous SIM-scan mode futile.

3.2. SPE procedure

The SPE step applied in this work is based on previous work performed at our laboratory for the determination of organic micropollutants in water [29]. Using SPE with the well known C_{18} cartridges is widely accepted and commonly applied for organic contaminants that are GC-amenable [29-32]. This step was used under the experimental conditions applied at our laboratory [29] without further optimization.

Ethyl acetate:DCM (50:50) was chosen as the elution solvent (5 mL). 250 mL of water sample was pre-concentrated to a final extract volume of 0.5 mL. The 500-fold concentration factor allowed reaching the required sensitivity for determination of the selected analytes at the sub-ppb levels.

3.3. Analytical parameters

Validation of the method was carried out in terms of accuracy, precision, LODs and LOQs, as well as confirmation criteria for compound identity. These parameters were evaluated in three different types of water. All the samples were fortified at two levels, using four ILIS added before the SPE procedure (surrogate standards), to correct possible losses along the overall procedure and/or instrumental deviations. The selection of the internal standards was based on our previous experience on their extraction and chromatographic behavior [29]. HCB-$^{13}C_6$ was used as internal standard for

pentachlorobenzene and HCB; terbutylazine-D_5 for herbicides and OP insecticides; DDE-D_8 for octyl/nonyl phenols, BDEs, PCBs and OC pesticides; and benzo(a)anthracene-D_{12} for PAHs. The internal standard applied for each individual compound is shown in Table 2.

Linearity was evaluated with pure solvent standard solutions also containing the internal standards, so relative responses were used; each concentration level was injected in triplicate. For the most sensitive compounds, like PCBs, trifluraline, metolachlor or chlorpyriphos, the concentration range studied was 0.5-250 μg/L. For chlorfenvinphos, endosulfan I and II, endrin, endosulfan sulfate, dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene it was 10-250 μg/L, and for BDE 183, 50-250 μg/L. The regression coefficients were higher than 0.99 for all compounds (ranging from 0.9913 for endrin to 0.9999 for aldrin) over the whole range tested and the residuals lower than 30%. BDE 209 could not be measured with adequate sensitivity, so this analyte could not be validated at realistic environmental levels since the selected chromatographic conditions were not appropriate for this compound. As discussed in the literature [33], shorter columns and higher final temperatures would be recommended for the determination of this PBDE.

Precision and accuracy were evaluated by means of recovery experiments (n=6) of samples fortified at 10 and 100 ng/L. Table 2 shows the results obtained for the three types of water tested. Most compounds presented recoveries between 70 and 120% at both spiking levels in all matrices. Some compounds presented recoveries over 120% at the lowest level in the three matrices (as BDE 28, 71, 47 and 66), but recoveries were in all cases satisfactory at the highest level. Furthermore some other compounds could not be quantified at the lowest level in none of the matrices due to their low sensitivity. The two more volatile PAHs, naphthalene and acenaphthylene, and also PAHs like dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene were poorly recovered in groundwater and surface water, which is in compliance with the literature [32], so the method was not fully satisfactory for these compounds. Other remarkable cases were aldrin and isodrin, whose recoveries at the highest level were lower than 60%, probably due to an inappropriate correction from the ILIS used.

R.S.D. lower than 20% were obtained for most compounds and only in some specific cases, like chlorfenvinphos in mineral water or 4-t-octylphenol in surface water, slightly higher values were obtained, although still with satisfactory recoveries. Several problematic analytes, whose recoveries were unsatisfactory, also presented poor precision with high R.S.D., sometimes nearly 50%, indicating that the method did not properly work for these few compounds.

LOQs were typically in the range 0.2-20 ng/L, with exceptions like chlorpropham (in surface and groundwater) and endosulfan sulfate, beta-HCH, metribuzin, chlorpyrifos, endrin, endosulfan II and *p,p'*-DDT (in groundwater) that presented values ≥40 ng/L. Low LOD values, between 0.1 and 10 ng/L, were reached for the majority of the compounds. In general, the values obtained for both LODs and LOQs were rather similar in the three types of water tested, although, as expected, in some particular cases they were slightly higher in surface and groundwater due to the higher complexity of the matrix (e.g. chlorpropham, beta-HCH, metribuzin, endrin or endosulfan II). These LOQ and LOD values are in the same order than those reported in the literature for most of the compounds studied under similar conditions [20], and even for analytes determined by conventional GC in tandem mass spectrometry [34], so this data show the extensive quantitative capabilities of single quadrupole in fast GC.

Confirmation of the identity of compounds in the sample was based on acquisition of specific ions under SIM mode. The general criterion was the acquisition of three ions (target (Q) and two reference ions (q_i)) leading to the presence of the three corresponding chromatographic peaks, together with the retention time of the reference standard. Ideally, the comparison of Q/q ratios measured in samples with those measured from reference standard shall lie within the maximum permitted tolerances [21]. Acquiring three ions means that two Q/q ratios are available. Our experience was that the achievement of the two Q/q ratios was rather exceptional, even when performing experiments with a "clean" matrix, like mineral water. It was especially difficult at the low concentration level tested, where the lower abundance of the ions can alter the expected Q/q ratios. According to the literature

[24] and to our own data, a low number of data points per peak also makes more difficult to get ion ratios within the permitted tolerances. Therefore, a more realistic criterion was applied for confirmation: three ions monitored were observed in the sample, and at least one ion ratio was fulfilled (including retention time agreement).

Matrix effects were also checked comparing responses of standards prepared in hexane and in sample extracts at different concentration levels. Since no severe matrix effects were observed, quantification of samples was carried out using calibration curves prepared in solvent for all water samples analyzed. Figure 3 shows illustrative chromatograms for metolachlor, taken as an example.

It is noteworthy the interest of determining 66 compounds in a chromatographic run time as short as 10 minutes. Most reported methods dealing with fast GC limit the scope to a reduced number of compounds, determining around 30 or less analytes in 10 minutes [3, 18, 20, 35]. In this way, our method has shown that it is possible to determine a higher number of compounds in the same analysis time using a single quadrupole. Taking into account the limitations of this analyzer, mentioned above, it is possible to increase the number of analytes in a fast single run if they are selected to be separated within the appropriate gaps for changing SIM groups.

3.4. Application to the analysis of water samples

Ten surface waters collected in the Spanish Mediterranean area (Tarragona province) were analyzed in order to test the applicability of the developed method.

The herbicides terbutylazine, propyzamide and metolachlor and the PAHs phenanthrene and pyrene were detected in all the ten samples at levels higher than their respective LOQs. Terbutylazine was found at concentration levels between 30 and 70 ng/L, higher than those for propizamide or metolachlor, which generally were around 10 ng/L, except in one sample that contained 340 ng/L of metolachlor. These herbicides are used on rice crops, which are predominant in the area under study. Phenanthrene and pyrene presented lower levels (in the range 0.5-3 ng/L), close to the LOQs.

Fluoranthene was occasionally detected but at low levels, sometimes below the LOQ. The persistent organic pollutant 4-*n*-nonylphenol (between 5 and 15 ng/L) was also frequently detected. A few samples gave positive findings for the herbicide atrazine (two samples, 10 ng/L) and the OP insecticide chlorpyriphos (one sample, 24 ng/L). Naphthalene and indeno(1,2,3-*cd*)pyrene were found in most samples but they could not be quantified since this method could not be validated for these analytes in surface water. None of the compounds detected exceeded the maximum allowable concentration established for surface waters [1].

Confirmation of a positive finding requires reproducible retention times, the presence of the three monitored ions and the at least one Q/q ratio within the allowed tolerance. As an example of worse-case situations, Figure 4 (a) shows the ion chromatograms for metolachlor and phenanthrene, where retention time is an important factor for confirmation, as only two of the three ions are clearly detected and only one of the Q/q ratios is accomplished. Another analytes, shown in Figure 4 (b), were satisfactorily identified, as the sensitivity for all *m/z* ions was good enough due to the higher concentrations found in the samples. The main drawback derives from the fact that, in some particular cases, the selected reference ions showed low sensitivity. This led to the non-compliance of the Q/q ratios, or even to the absence of some of the reference ions. This problem could be surely avoided with more sensitive detectors or applying sample preparation procedures with a higher preconcentration factor.

4. Conclusions

Capabilities and limitations of fast GC-MS for the determination of organic micropollutants in water have been studied in this paper. A multiresidue method has been developed for the rapid determination of around 60 compounds in water samples with a chromatographic run of less than 10 minutes, based on a compromise between analysis time and resolution. The operating SIM mode provided good sensitivity, making the quantification feasible at levels as low as 0.01 µg/L, which was the lowest concentration level validated. The presence of the three ions monitored for each compound and the compliance of, at least, one intensity ratio was used as confirmatory parameter. The variability of ion intensities observed in replicate injections of standards was obviously higher in sample extracts, especially at low analyte concentrations, making difficult the compliance the two intensity ratios available in spiked samples. Agreement of retention time between standard and sample was also required for confirmation.

The scan time was the parameter that mostly limited the SIM mode, so it was thoroughly studied. Scan time, which depends on the number of ions in a SIM group, affects the chromatographic analyte peak shape. A value of 0.2 s was established as the maximum scan time that allowed the acquisition of sufficient number of data points per peak to perform the quantitative analysis of the 66 compounds selected.

A simultaneous scan and SIM mode was also optimized in order to test the capabilities of the mass spectrometer, but a loss of sensitivity in comparison with the SIM mode was noticed. Moreover, the extension of the mass range acquired in this mode increased the scan time and, consequently, the number of data points per peak was reduced. In this way, the SIM-scan mode would be efficiently applied only for a low number of target analytes, still maintaining short chromatographic run times, but requiring higher analyte concentrations than in SIM mode. The main advantage is the possibility of performing a non-target analysis at high concentration levels simultaneously with target analysis in SIM mode of a limited number of compounds.

Analysis of surface water samples showed the presence of several target pollutants in the samples and the most frequently found were terbutylazine, propyzamide, metolachlor, phenantrene and pyrene.

Acknowledgments

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Figure captions

Fig. 1. Full scan chromatogram of a 100 ng/mL standard mixture in hexane obtained by fast GC-MS in full scan mode.

Fig. 2. Effect of scan time over peak shape in SIM mode. Peak shape of the pesticide mevinphos when included in a SIM group where 9, 17, 21, 29, 40 or 52 ions were monitored.

Fig. 3. Matrix effect. Comparison of metolachlor responses in **(a)** standard solution in hexane at 50 µg/L and **(b)** surface water matrix-matched standard at 50 µg/L); **(c)** standard solution in hexane at 5 µg/L and **(d)** surface water matrix-matched standard at 5 µg/L.

Fig. 4. Typical chromatograms obtained after SPE and fast GC-MS applied to surface water samples quantified at: **(a)** low concentrations levels and **(b)** higher concentration levels. Signal-to-noise ratio (S/N) has been calculated for target (bold letter) and reference ions.
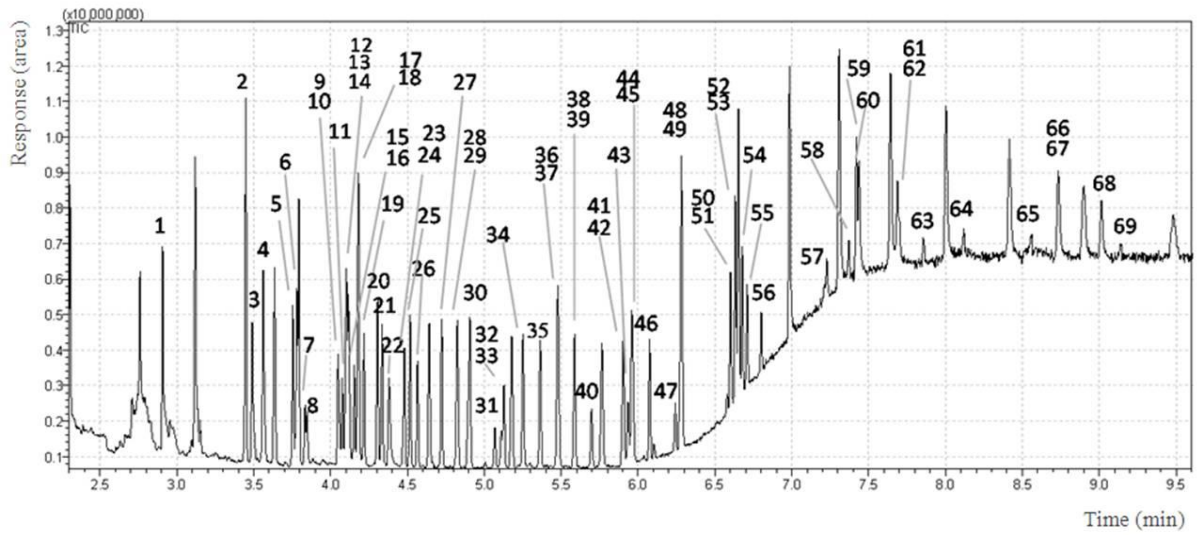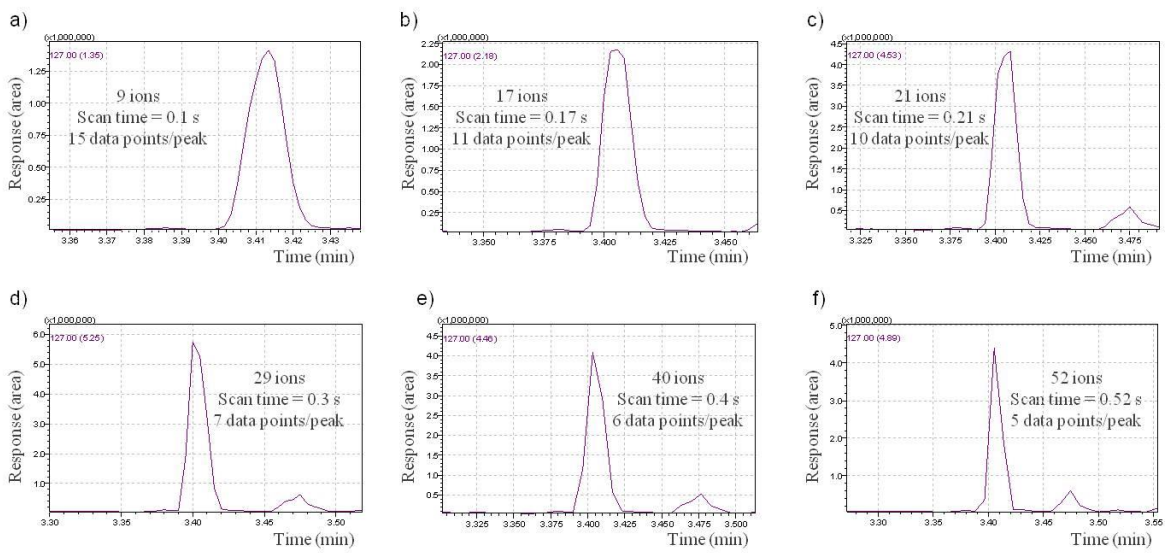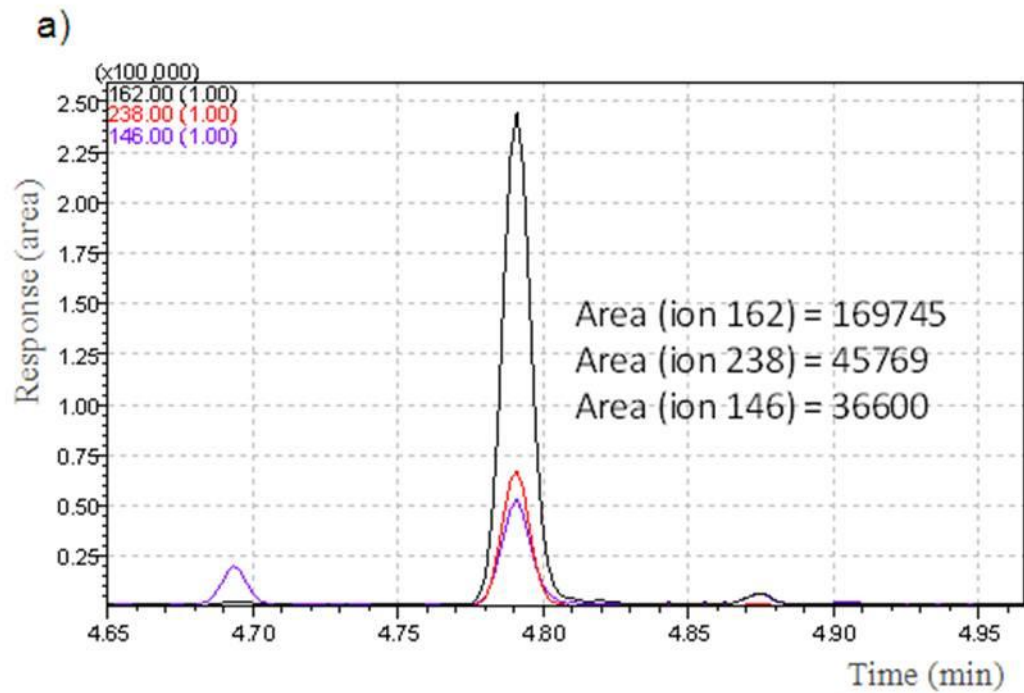
Fig. 1

Fig. 2

a)

Area (ion 162) = 169745
Area (ion 238) = 45769
Area (ion 146) = 36600
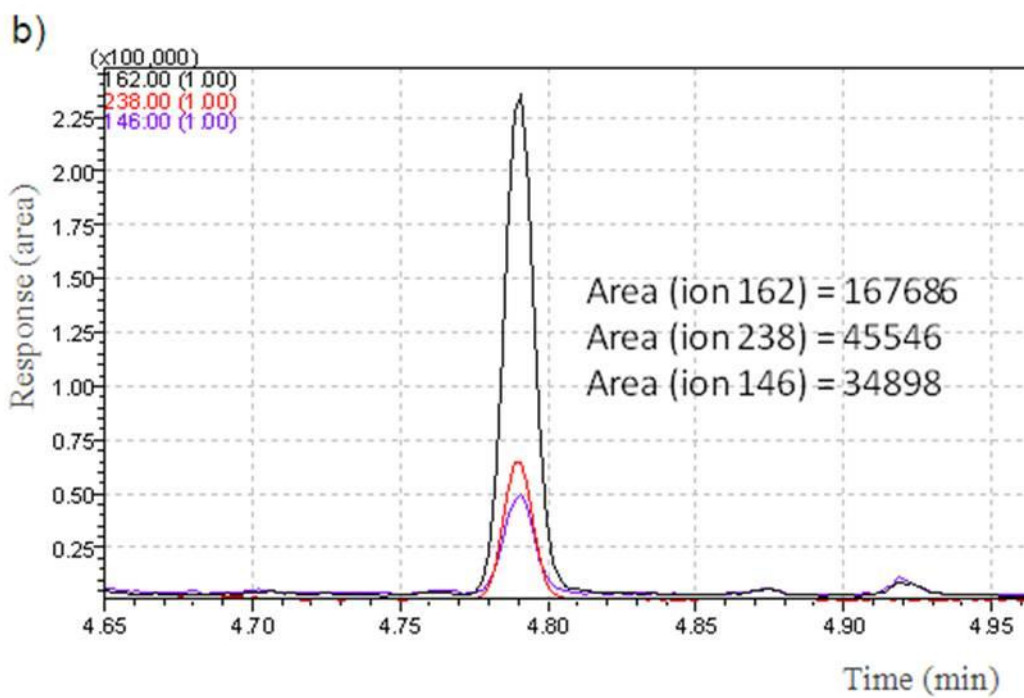
Fig 3 a

b)

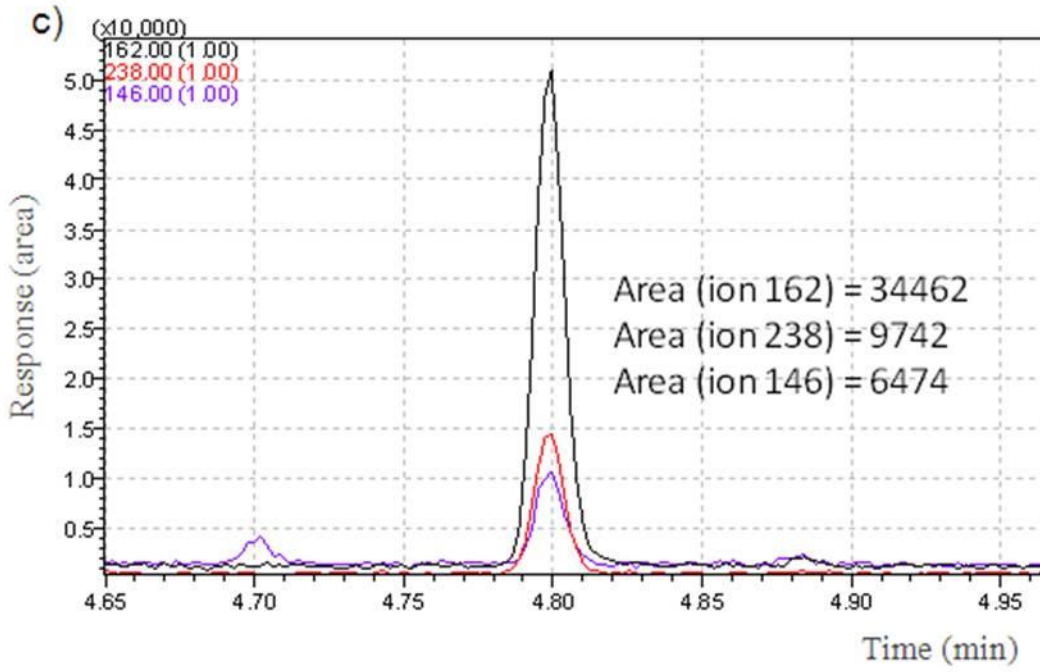Area (ion 162) = 167686
Area (ion 238) = 45546
Area (ion 146) = 34898

Fig. 3 b

Fig. 3 c

Fig. 3 d

a)

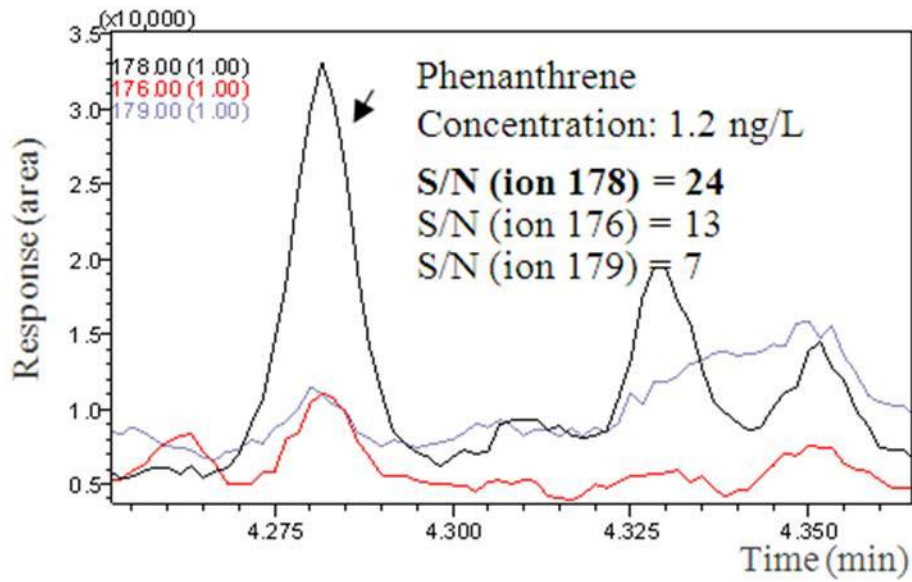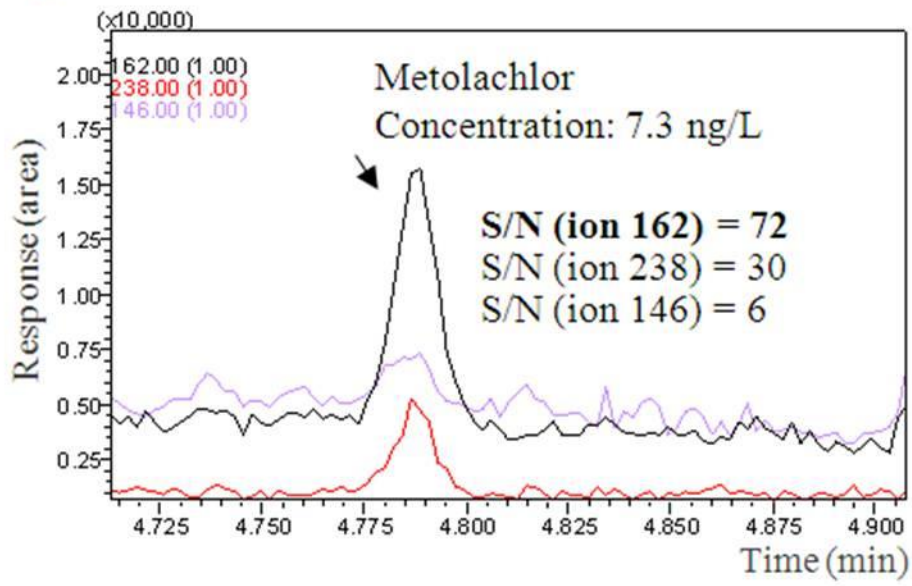Fig. 4 a

b)

Fig. 4 b

Table 1. List of compounds studied and GC-MS parameters used (compounds regulated by the Directive 2008/105/CE are shown in italic).

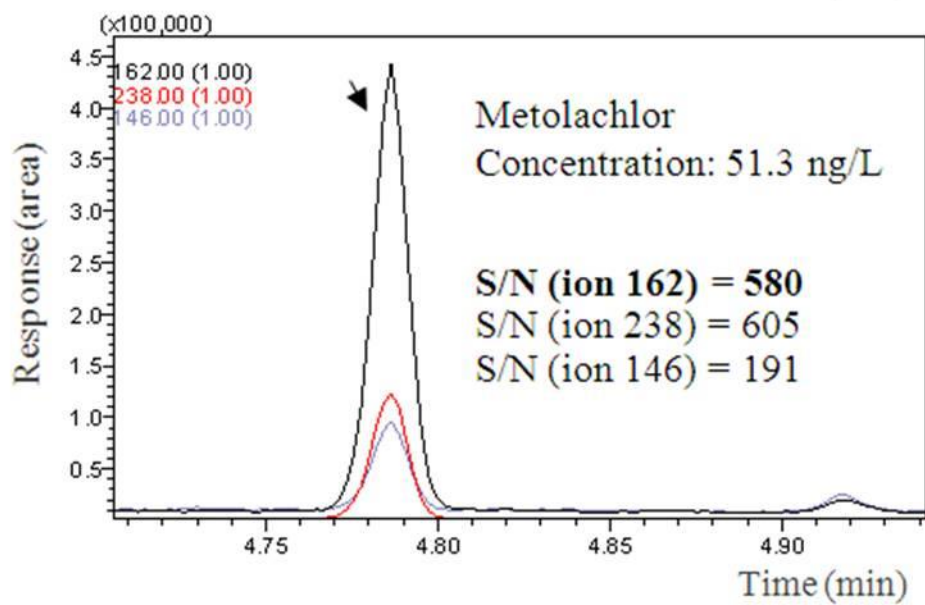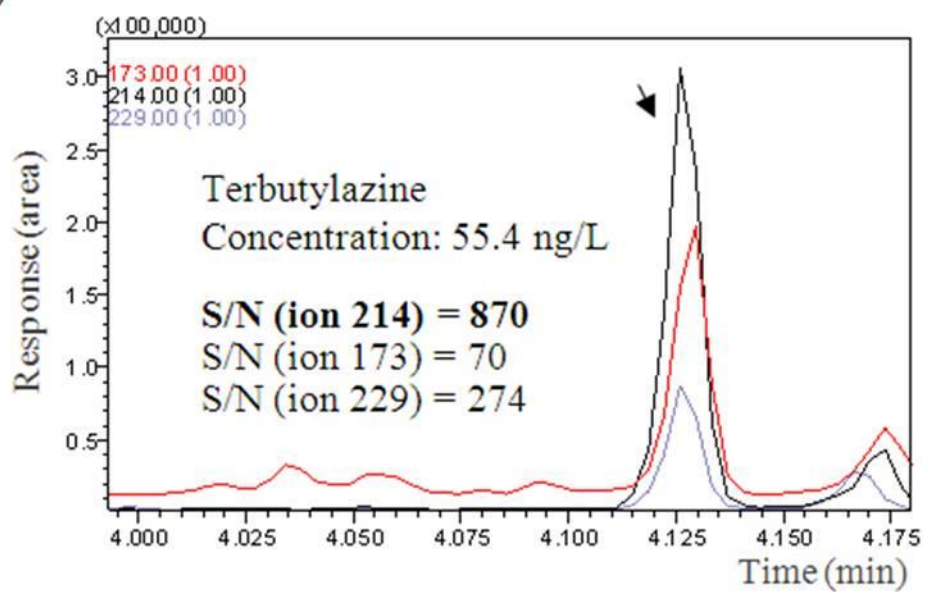| Peak number	t_R (min)	Time window (min) (SIM group)	Compound	Target ion	Reference ions	Scan time (s)
				Monitored ions in SIM		
1	2.900	2.3-3.2	*Naphtalene*	128	102, 127	0.10
2	3.484	3.2-3.7	*Acenaphtylene*	152	151, 153	0.10
3	3.554		*Acenaphthene*	153	152, 154	
4	3.626		*Pentachlorobenzene*	250	248, 252	
5	3.742	3.7-3.95	*4-t-Octylphenol*	107	108, 206	0.12
6	3.770		*Fluorene*	166	165, 167	
7	3.821		Chlorpropham	127	171, 213	
8	3.833		*Trifluralin*	264	290, 306	
9	4.035	3.95-4.24	alfa-HCH	181	183, 219	0.22
10	4.043		*Simazine*	201	173, 186	
11	4.060		*Atrazine*	200	202, 215	
12	4.081		*4-n-Octylphenol*	107	108, 206	
13	4.087		Hexachlorobenzene-$^{13}C_6$ *	292		
14	4.089		*Hexachlorobenzene*	284	282, 286	
15	4.125		Terbuthylazine-D_5 *	219		
16	4.135		Terbuthylazine	214	173, 229	
17	4.155		beta-HCH	181	183, 219	
18	4.161		Propyzamide	173	175, 255	
19	4.202		Lindane	181	183, 219	
20	4.289	4.24-4.44	*Phenantrene*	178	176, 179	0.10
21	4.318		*Anthracene*	178	176, 179	
22	4.362		*4-n-Nonylphenol*	107	108, 220	
23	4.452	4.44-4.65	Metribuzin	198	144, 199	0.12
24	4.463		Endosulfan ether	241	239, 277	
25	4.499		PCB 28	256	186, 258	
26	4.545		*Alachlor*	160	146, 188	
27	4.703	4.65-4.97	PCB 52	220	290, 292	0.13
28	4.800		Metolachlor	162	146, 238	
29	4.805		*Chlorpyrifos*	197	199, 314	
30	4.883		*Aldrin*	263	261, 293	
31	5.043	4.97-5.19	Pendimethalin	252	162, 192	0.10
32	5.085		*Chlorfenvinphos*	267	269, 323	
33	5.103		*Isodrin*	193	195, 263	
34	5.225	5.19-5.42	*Fluoranthene*	202	200, 203	0.10
35	5.337		PCB 101	326	254, 328	
36	5.448	5.42-5.81	*Pyrene*	202	200, 203	0.13
37	5.455		*Endosulfan I*	241	195, 339	
38	5.540		*p,p'*-DDE-D_8 *	254		
39	5.558		*p,p'*-DDE	246	248, 318	
40	5.667		*Dieldrin*	263	79, 277	
41	5.939	5.81-6.03	*Endrin*	263	261, 265	0.16
42	5.875		PCB 118	326	254, 328	
43	5.906		BDE 28	246	406, 408	
44	5.928		*p,p'*-DDD	165	176, 199	
45	5.936		*Endosulfan II*	195	241, 339	
46	6.050	6.03-6.36	PCB 153	360	290, 362	0.10
47	6.219		*p,p'*-DDT	235	165, 237	
48	6.245		Endosulfan sulfate	237	274, 387	

* ILIS used in this work

Table 1. List of compounds studied and GC-MS parameters used (compounds regulated by the Directive 2008/105/CE are shown in italic).

Peak number	t_R (min)	Time window (min) (SIM group)	Compound	Monitored ions in SIM		
				Target ion	Reference ions	Scan time (s)
49	6.260		PCB 138	360	290, 362	
50	6.563	6.36-6.76	Benzo(*a*)anthracene-D$_{12}$	240		0.10
51	6.581		*Benzo(a)anthracene*	228	226, 229	
52	6.612		*Chrysene*	228	226, 229	
53	6.617		BDE 71	326	484, 486	
54	6.659		PCB 180	324	394, 396	
55	6.691		BDE 47	326	484, 486	
56	6.781	6.76-7	BDE 66	326	484, 486	0.10
57	7.205	7-7.3	BDE 100	404	406, 564	0.10
58	7.347	7.3-7.58	BDE 99	404	406, 566	0.10
59	7.395		*Benzo(b)fluoranthene*	252	126, 250	
60	7.412		*Benzo(k)fluoranthene*	252	126, 250	
61	7.661	7.58-7.8	*Benzo(a)pyrene*	252	126, 250	0.10
62	7.677		BDE 85	404	406, 566	
63	7.832	7.8-8	BDE 154	484	482, 486	0.10
64	8.093	8-8.35	BDE 153	484	482, 486	0.10
65	8.527	8.35-8.64	BDE 138	484	482, 486	0.10
66	8.704	8.64-8.9	*Dibenzo(a,h)anthracene*	279	139	0.10
67	8.703		*Indeno (1,2,3,cd)pyrene*	124	272	
68	8.979	8.9-9.6	*Benzo(g,h,i)perylene*	276	138, 277	0.10
69	9.140		BDE 183	562	564, 566	
70	-		BDE 209	799	400, 487	

* ILIS used in this work

Table 2. Average recovery (%) and R.S.D. (in parenthesis) obtained after the application of the GC-MS method to mineral, ground and surface water samples (n=6) fortified at two concentration levels. Detection (LOD) and quantification (LOQ) limits.

Compounds	Mineral water				Groundwater				Surface water			
	Fortification levels (ng/L)		LOD (ng/L)	LOQ (ng/L)	Fortification levels (ng/L)		LOD (ng/L)	LOQ (ng/L)	Fortification levels (ng/L)		LOD (ng/L)	LOQ (ng/L)
	10	100			10	100			10	100		
Naphthalene[1]	89 (14)	70 (11)	0.1	0.3	101 (4)	39 (14)	0.2	0.8	52 (30)	14 (0)	0.4	n.e.
Acenaphthylene[1]	94 (2)	13 (28)	1	4	30 (12)	26 (18)	0.1	n.e.	60 (12)	15 (43)	0.1	n.e.
Acenaphthene[1]	101 (18)	78 (18)	0.1	0.4	92 (20)	65 (14)	0.6	3	88 (19)	38 (35)	0.,5	2
Pentachlorobenzene[2]	86 (5)	88 (4)	0.1	0.3	92 (9)	83 (11)	0.1	0.2	89 (6)	76 (20)	0.2	0.6
4-t-Octylphenol[3]	124 (2)	113 (10)	5	10	79 (9)	83 (4)	0.6	2	102 (25)	83 (8)	2	7
Fluorene[1]	51 (25)	74 (17)	0.5	2	74 (19)	65 (13)	0.4	2	69 (11)	38 (49)	0.2	0.6
Chlorpropham[4]	-	100 (8)	10	15	-	67 (8)	32	100	-	71 (3)	17	60
Trifluralin[3]	101 (11)	80 (8)	0.7	3	95 (21)	78 (4)	0.6	2	74 (14)	66 (11)	0.4	2
alpha-HCH[3]	78 (8)	131 (5)	2	5	89 (21)	93 (7)	2	6	108 (16)	82 (16)	3	9
Simazine[4]	-	79 (13)	10	15	107 (12)	76 (6)	2	6	120 (5)	64 (6)	2	4
Atrazine[4]	105 (12)	74 (13)	0.8	3	97 (13)	77 (6)	0.1	0.5	95 (8)	67 (8)	0.4	2
4-n-Octylphenol[3]	26 (30)	91 (11)	5	15	95 (14)	67 (13)	2	6	99 (10)	74 (9)	3	9
Hexachlorobenzene[2]	69 (10)	109 (3)	0.1	0.2	109 (6)	109 (1)	0.1	0.3	101 (3)	108 (4)	0.1	0.5
Terbuthylazine[4]	104 (13)	72 (14)	0.5	2	85 (18)	74 (9)	0.2	0.8	97 (10)	67 (7)	0.4	2
beta-HCH[3]	-	119 (4)	10	15	-	108 (7)	19	64	-	109 (8)	10	26
Propyzamide[4]	80 (20)	73 (12)	2	6	89 (17)	43 (19)	2	6	117 (5)	64 (4)	2	4
Lindane[3]	113 (14)	117 (7)	3	9	112 (18)	90 (4)	2	6	95 (12)	85 (12)	2	6
Phenanthrene[1]	72 (17)	71 (5)	0.1	0.5	96 (14)	71 (19)	0.1	0.3	66 (20)	68 (22)	0.1	0.3
Anthracene[1]	70 (11)	69 (20)	0.2	0.6	75 (20)	77 (14)	2	5	68 (13)	63 (19)	0.2	0.8
4-n-Nonylphenol[3]	102 (14)	76 (8)	1	4	31 (25)	48 (14)	0.3	n.e.	94 (7)	80 (10)	0.6	3
Metribuzin[4]	-	66 (11)	10	15	-	70 (9)	27	90	-	135 (18)	10	n.e.
Endosulfan ether[3]	170 (5)	119 (5)	2	5	156 (9)	90 (5)	9	30	92 (22)	87 (12)	2	6
PCB 28[3]	101 (8)	89 (8)	0.2	0.8	92 (17)	83 (10)	0.2	0.6	87 (6)	74 (15)	0.1	0.5
Alachlor[4]	109 (17)	76 (12)	2	6	93 (18)	75 (10)	2	6	84 (12)	63 (4)	2	6

[1,2,3,4] indicates the internal standard used for quantitative purposes: [1] benzo(a)anthracene-D$_{12}$, [2] hexachlorobenzene-^{13}C$_6$, [3] p,p'-DDE-D$_8$, [4] terbutylazine-D$_5$.
Underlined, not acceptable results.
n.e., LOQ not estimated as validation parameters at both fortification levels were not satisfactory.

Table 2 (cont.). Average recovery (%) and R.S.D. (in parenthesis) obtained after the application of the GC-MS method to mineral, ground and surface water samples (n=6) fortified at two concentration levels. Detection (LOD) and quantification (LOQ) limits.

Compounds	Mineral water				Groundwater				Surface water			
	Fortification levels (ng/L)		LOD (ng/L)	LOQ (ng/L)	Fortification levels (ng/L)		LOD (ng/L)	LOQ (ng/L)	Fortification levels (ng/L)		LOD (ng/L)	LOQ (ng/L)
	10	100			10	100			10	100		
PCB 52[3]	105 (10)	97 (10)	0.3	0.9	101 (11)	88 (10)	0.3	1	86 (8)	85 (12)	0.3	2
Metolachlor[4]	68 (24)	72 (9)	0.6	2	63 (21)	75 (11)	0.3	1	105 (6)	70 (6)	0.3	2
Chlorpyrifos[4]	-	87 (10)	10	19	-	72 (6)	13	44	-	76 (7)	10	15
Aldrin[3]	95 (6)	53 (7)	0.6	3	87 (11)	56 (7)	0.6	2	79 (8)	48 (5)	0.6	2
Pendimethalin[4]	-	67 (10)	10	15	-	69 (9)	10	22	-	50 (10)	10	n.e.
Chlorfenvinphos[4]	-	110 (24)	10	15	-	100 (8)	10	23	-	99 (12)	10	15
Isodrin[3]	70 (9)	50 (11)	2	6	72 (16)	60 (10)	2	5	71 (9)	41 (6)	2	6
Fluoranthene[1]	106 (11)	82 (19)	0.1	0.3	108 (5)	93 (10)	0.1	0.3	93 (5)	75 (19)	0.1	0.4
PCB 101[3]	103 (8)	83 (7)	0.1	0.5	104 (4)	79 (6)	0.1	0.4	96 (4)	79 (4)	0.1	0.4
Pyrene[1]	99 (13)	86 (17)	0.1	0.4	79 (8)	80 (12)	0.1	0.4	95 (5)	82 (19)	0.1	0.5
Endosulfan I[3]	-	112 (6)	10	15	-	98 (5)	10	28	-	97 (9)	10	31
p,p'-DDE[3]	120 (14)	99 (8)	0.2	0.8	113 (3)	95 (2)	0.2	0.8	107 (3)	98 (3)	0.2	0.8
Dieldrin[3]	-	105 (5)	10	15	-	100 (6)	10	33	-	97 (6)	10	8
Endrin[3]	-	115 (10)	10	29	-	108 (9)	33	100	-	115 (9)	10	21
PCB 118[3]	114 (7)	90 (5)	0.3	0.9	118 (2)	82 (3)	0.3	2	104 (5)	87 (2)	0.2	0.8
BDE 28[3]	154 (7)	96 (4)	2	5	130 (5)	104 (6)	1	3	136 (2)	101 (2)	1	3
p,p'-DDD[3]	104 (14)	94 (7)	2	5	126 (6)	102 (2)	10	16	115 (6)	96 (6)	3	9
Endosulfan II[3]	-	115 (11)	10	15	-	104 (7)	21	70	-	113 (6)	10	20
PCB 153[3]	112 (6)	80 (5)	0.2	0.6	111 (4)	78 (4)	0.1	0.4	116 (4)	120 (10)	0.1	0.5
p,p'-DDT[3]	-	109 (9)	10	15	-	118 (6)	18	59	-	119 (15)	10	16
Endosulfan sulfate[3]	-	129 (26)	17	n.e.	-	121 (2)	52	172	-	120 (7)	10	24
PCB 138[3]	102 (10)	87 (5)	1	3	111 (14)	84 (5)	1	3	112 (7)	86 (8)	1	3
Benzo(a)anthracene[1]	124 (6)	96 (3)	0.5	2	112 (3)	99 (2)	0.4	2	104 (2)	95 (2)	0.2	0.7
Chrysene[1]	134 (12)	91 (3)	0.5	2	107 (4)	99 (4)	0.3	1	101 (3)	92 (7)	0.5	2

[1,2,3,4] indicates the internal standard used for quantitative purposes: [1] benzo(a)anthracene-D_{12}, [2] hexachlorobenzene-$^{13}C_6$, [3] p,p'-DDE-D_8, [4] terbutylazine-D_5.
Underlined, not acceptable results.
n.e., LOQ not estimated as validation parameters at both fortification levels were not satisfactory.

Table 2 (cont.). Average recovery (%) and R.S.D. (in parenthesis) obtained after the application of the GC-MS method to mineral, ground and surface water samples (n=6) fortified at two concentration levels. Detection (LOD) and quantification (LOQ) limits.

Compounds	Mineral water				Groundwater				Surface water			
	Fortification levels (ng/L)		LOD (ng/L)	LOQ (ng/L)	Fortification levels (ng/L)		LOD (ng/L)	LOQ (ng/L)	Fortification levels (ng/L)		LOD (ng/L)	LOQ (ng/L)
	10	100			10	100			10	100		
BDE 71[3]	131 (3)	102 (6)	1	3	143 (12)	103 (6)	0.7	3	149 (5)	105 (2)	0.8	3
PCB 180[3]	139 (8)	106 (7)	1	3	128 (9)	97 (9)	1	3	116 (11)	102 (14)	1	3
BDE 47[3]	157 (7)	109 (7)	0.8	3	154 (19)	108 (6)	2	6	204 (4)	113 (8)	2	6
BDE 66[3]	120 (7)	104 (7)	0.9	3	153 (14)	100 (10)	0.7	3	176 (4)	114 (3)	0.6	3
BDE 100[3]	94 (14)	101 (7)	1	4	136 (17)	98 (6)	2	6	137 (4)	105 (6)	2	6
BDE 99[3]	-	102 (8)	10	15	-	95 (14)	10	15	-	112 (5)	10	14
Benzo(b)fluoranthene[1]	171 (2)	92 (2)	2	6	117 (7)	88 (8)	2	6	124 (4)	93 (6)	2	6
Benzo(k)fluoranthene[1]	198 (9)	92 (4)	2	6	115 (7)	87 (10)	2	6	104 (8)	89 (5)	2	6
Benzo(a)pyrene[1]	107 (13)	79 (8)	2	6	114 (8)	80 (9)	2	6	106 (7)	78 (11)	2	6
BDE 85[3]	-	96 (9)	10	15	-	98 (15)	10	17	-	105 (7)	10	17
BDE 154[3]	88 (18)	85 (12)	2	4	-	118 (13)	10	15	-	94 (10)	10	15
BDE 153[3]	147 (13)	77 (15)	2	5	-	105 (3)	10	15	-	89 (8)	10	15
BDE 138[3]	-	58 (27)	10	n.e.	-	103 (12)	10	17	-	82 (11)	10	18
Dibenzo(a,h)anthracene[1]	-	106 (11)	10	15	-	59 (50)	10	n.e.	-	55 (26)	10	n.e.
Indeno(1,2,3-cd)pyrene[1]	-	94 (11)	10	30	-	46 (35)	10	n.e.	-	28 (64)	10	n.e.
Benzo(g,h,i)perylene[1]	83(17)	103 (8)	5	15	115 (14)	75 (19)	5	15	152 (6)	80 (10)	10	16
BDE 183[3]	-	-	-	n.e.	-	-	-	n.e.	-	-	-	n.e.
BDE 209[3]	-	-	-	n.e.	-	-	-	n.e.	-	-	-	n.e.

[1,2,3,4] indicates the internal standard used for quantitative purposes: [1] benzo(a)anthracene-D$_{12,}$ [2] hexachlorobenzene-^{13}C$_{6,}$ [3] p,p'-DDE-D$_8$, [4] terbutylazine-D$_5$.

Underlined, not acceptable results.

n.e., LOQ not estimated as validation parameters at both fortification levels were not satisfactory.