On-Line Purge and Trap GC–MS for Monitoring 1,3-Dichloropropene in Agricultural Water and Soil Samples

Antonia Garrido Frenich[1,*], Salvador Cortés Aguado[2], José Luis Martínez Vidal[1], and **Francisco Javier Arrebola[1]**

[1]Research group "Analytical Chemistry of Contaminants", Department of Analytical Chemistry, University of Almería 04120 Almería (Spain), and [2]Pesticide Residue Laboratory C.U.A.M. – Council of El Ejido, Paraje "El Treinta", 5, 04700 El Ejido, Almería (Spain)

Abstract

A simple and reliable method using on-line purge and trap gas chromatography mass spectrometry has been developed for the determination of the fumigant 1,3-dichloropropene (1,3-DCP) in agricultural water and soil samples. The proposed analytical methodology was validated in the target environmental matrices by the analysis of spiked blank matrix samples. Limit of detection values of 0.05 µg/L for water and 0.005 µg/Kg for soils were obtained, while limits of quantitation were of 0.1 µg/L for water and 0.01 mg/kg for soils. Good recoveries (93–104%) and precision values (< 6%) were obtained for the target compound in the studied matrices. This methodology has been successfully applied to the analysis of incurred groundwater samples from an agricultural area, The Campo de Dalías (Almería, South Spain), although 1,3-DCP was not detected. The method was also applied to soil samples from greenhouse treated with a soil fumigant containing 1,3-DCP.

Introduction

The 1,3-dichloropropene (1,3-DCP) is a halogenated fumigant, which can exist in either *cis* (Z) and *trans* (E) isomeric forms. The two isomers have very similar, but not identical, properties, and both are generally present as a racemic mixture in commercial formulations. 1,3-DCP is widely used in agriculture, on both food and feed crops, to control nematodes and fungi. In the last years, its use as a pre-plant fumigant has increased in response to the ban of methyl bromide (1). It is injected directly into soil or sprayed on the ground, and hence released directly to the environment. In consequence, 1,3-DCP can enter as pollutant in soil and groundwater indirectly from drainage of agricultural lands. In soil, it can exist in solution or as a gas, with different mobility for each one. In the aqueous phase, 1,3-DCP presents a relatively high mobility because its adsorption capacity is low. However, it is adsorbed more strongly to soil particles when it is in the vapour phase, increasing its adsorption with the presence of high organic matter content and at low temperature. All of this generates an increasing need for monitoring soil and groundwater quality with respect to content of 1,3-DCP, especially in areas with intensive agriculture and/or mainly relying on groundwater for drinking water supply.

Sensitive and reliable analytical methods are required to monitor 1,3-DCP residues in water and soil samples. Given the relatively low boiling points and high vapour pressures of the *cis* and *trans* isomers, capillary gas chromatography (GC), using mainly electron capture detector (2–12) or mass spectrometry (MS) detector (13–16), has been the technique more frequently used. However, GC still shows low limits of detection (LOD) in order to reach the trace levels of residues in environmental samples, and appropriate extraction and preconcentration steps are required prior to the instrumental analysis. For that, analytical procedures based on headspace (3–6,9,13,14), solid phase microextraction (2,8), and purge and trap (P&T) (12,15,16) approaches have been proposed for the extraction of 1,3-DCP from water and soil samples. Also, the isolation of the target compound from soil samples has been carried out with organic solvents, such as hexane (10) or ethyl acetate (3,7,11).

P&T technique purges volatiles from water or soil onto an adsorbent trap, followed by thermal desorption of the analytes with GC carrier gas onto the GC column for separation and detection. P&T has the advantage of providing clean samples, free from matrix interferences, and as a consequence low detection limits are obtained. In addition, the P&T extraction is automated, and for that it is a useful option when high precision and high sample throughput are required. Among different types of P&T systems for analysis of volatile organic chemical compounds, the Velocity XPT is directed to ensure the highest sample throughput, as well as the highest chromatographic resolution. The first advantage is obtained by reducing sample cycle times, while the second one is reached placing an expansion chamber after the trap that focuses analytes into a tight band prior to desorption into the GC. In addition, the expansion chamber efficiently desorbs, and this greatly decreases carryover effect from run to run.

This paper describes the development and validation of a simple analytical method for the determination of trace levels of

* Author to whom correspondence should be addressed: email agarrido@ual.es.

fumigant 1,3-DCP in water and soil samples by P&T coupled to GC–MS using full scan acquisition mode. In order to optimize the method, several parameters were studied, such as purge time and desorption time. Finally, the optimized P&T-GC–MS method was applied to the analysis of 1,3-DCP residues in 10 groundwater samples and in soil samples taken from fumigated greenhouse soil using drip irrigation. In both cases, samples were collected from the main intensive agricultural area in South Spain (El Ejido, Almería).

Experimental

Chemicals and reagents

Standard of 1,3-DCP is a mixture of the *cis* (49%) and *trans* (51%) isomers that were obtained from Dr. Ehrenstorfer (Augsburg, Germany). Acetone of residue analysis grade was supplied by J.T. Baker (Deventer, Holland). A stock solution of 1,3-DCP was prepared by exact weighing of 50 mg of standard and dissolution in 50 mL of acetone; this solution was stored at –18°C. Working standard solutions (10 mg/L) were prepared immediately before use by appropriate dilution of the stock solution with acetone. Spiked water and soil samples were prepared by adding adequate volumes of acetone pesticide standard solution to the matrix. Highly purified (HPLC-grade) water was obtained by ultra filtration of deionized water with a Milli-Q system (Millipore, Bedford, MA).

P&T extraction method

Spiked HPLC-grade water samples were used to optimize the chromatographic conditions. 1,3-DCP extraction was carried out in an accelerated P&T sample concentrator Velocity XPT from Teledyne Tekmark (Mentor, OH), coupled to a fritless glass sparger of 5 mL for water extraction and 25 mL for soil extraction. The Vocarb 3000 trap used from Supelco (Bellefonte, PA) was a commercial mixture of three types of adsorbents, namely Carbopack B, Carboxen 1000, and Carboxen 1001.

For the analysis of water, target compounds were purged at ambient temperature from an aqueous solution for 15 min by administering helium at 40 mL/min. The analytes were dried by a Dryflow process at 175°C for 0.5 min. The helium flowed in this step did not pass through the sample vessel and reduced the moisture before desorbing the analytes. After the analytes were dried and trapped at 0°C onto a Vocarb 3000 sorbent, they were pre-heated at 40°C for 1 min, then baked at 250°C to desorb the compounds, assisted by a helium flow of 200 mL/min for 1 min. They were directly transferred to the GC injector. To avoid carry-over effects, after the transfer of analytes, the trap was cleaned at 235°C and helium was passed through at a flow of 400 mL/min for 2 min.

For the analysis of soils, 5 g of soil sample was mixed with 25 mL of water and pre-heated at 40°C with an external heater. The rest of the process is as described for water samples, except that the trap temperature was 60°C. A sumary of the main parameters is given in Table I.

Table I. Values of Several Parameters used in the P&T Method

Variable	Value
Valve oven temperature	150°C
Transfer line temperature	150°C
Sample mount temperature	90°C
Dryflow stand by temperature	175°C
Standy flow	10 mL/min
Purge time	15.0 min
Purge flow	40 mL/min
Purge temperature	0°C*, 60°C†

* Water analysis; † soil analysis.

GC–MS analysis

GC–MS analysis was performed with a Varian 3800 GC with electronic flow control and fitted with a Saturn 2000 ion-trap mass spectrometer (Varian Inc.; Walnut Creek, CA). The analytical column was a Zebron™ ZB-5ms (30 m × 0.25 mm i.d. × 0.25 µm film thickness) from Phenomenex (Torrance, CA). The initial temperature of the column oven was 35°C (hold for 6 min) and then raised at 50°C/min up to 200°C. For the introduction of the sample into the chromatographic system, a split of 1/20 was used in the injection port. The mass spectrometer was operated in full scan mode, setting the ion trap, manifold, and transfer line temperatures at 200°C, 50°C, and 280°C, respectively. The multiplier voltage (1×10^5 gain) was 1600 V with a multiplier offset of + 100 V. Automatic gain control (AGC) was turned on. The MS was operated in electron ionization (EI) mode at 70 eV. The AGC target value was set at 20,000 counts; the emission current was 30 µA, and the excitation storage level was 40 *m/z*. The mass analyzer was programmed for scanning between 60 and 120 *m/z*. Peak identification and quantitation were carried by the use of VOC TekLink software (Tekmar).

Results and Discussion

Optimization of P&T extraction

Purge and desorption times were the main parameters optimized for the P&T extraction process before the validation step. Purge time influenced the quantity of helium (inert gas used) that bubbled through the aqueous sample, and, in consequence, the quantity of analytes moved from the liquid to the vapour phase. Four different purge times were tested: 5, 10, 15, and 20 min. For each time, three water samples spiked at 1 µg/L were analyzed, and the mean and relative standard deviation (RSD) were calculated. In order to compare the results obtained, the following relationship (equation 1) at variable purge time (R_{pt}) was estimated, maintaining constant desorption time (1 min):

$$R_{pt}\,(\%) = \frac{\text{peak area at variable purge time}}{\text{peak area at final purge time}}\,100 \qquad \text{Eq. 1}$$

An increase of the 1,3-DCP signal can be observed when increasing purge time (Table II). The application of the Student's *t*-test showed no significant differences for R_{pt} ($P > 0.01$) between

15 and 20 min; significant differences between 5 and 10 min, and 10 and 15 min, respectively. It can be also observed that the increase of purge time improved precision values (RSD). In consequence, a purge time of 15 min was selected in order to reduce extraction time and maximize sensitivity.

The second parameter optimized, the desorption time, was tested at 1, 2, 3, and 4 min. For each time, three water samples spiked at 1 µg/L were analyzed, and the mean and RSD were calculated. Also, the relationship (equation 2) between peak areas at different desorption times (R_{dt}) was estimated, maintaining constant purge time (15 min):

$$R_{dt}\ (\%) = \frac{\text{peak area at variable desorption time}}{\text{peak area at final desorption time}}\ 100 \qquad \text{Eq. 2}$$

The application of the Student's *t*-analysis showed no significant differences between each pair of consecutive times, and in consequence the effect of this parameter was smaller than the effect of increasing purge time. As with time purge study, precision values were always below 10%. Therefore, a desorption time of 1 min was selected.

The chromatogram of a water sample extracted with the optimized method is shown in Figure 1. The two chromatographic peaks observed (retention times 4.36 and 5.25 min) corresponding to the *cis* and *trans* 1,3-DCP were used for quantitation purposes as sum of their areas.

Quality parameters of the method

The optimized GC–MS method was validated in terms of linearity, accuracy (trueness and precision), lower limits (detection and quantification limits), and selectivity. The validation was carried out in two different matrices: water and soil. All validation experiments were performed using an uncontaminated environmental groundwater or soil sample.

In groundwater samples, the linearity of the method was tested in a low concentration range (0.1–1.0 µg/L), because such trace levels of 1,3-DCP are expected in real samples. Three calibration points (0.1, 0.5, and 1.0 µg/L) were used with two replicated for each level. The calibration equation was $y = 13286x - 1867$ with a determination coefficient, r^2, of 0.9914. The accuracy of the method was obtained from results from the analysis of five independent samples on the same day at two different concentration levels, 0.1 and 1 µg/L. The trueness, expressed as % recovery, was of 98% and 97% for the low and high concentration levels respectively, while the precision, expressed as %RSD, was 6% and 5%, respectively. The limit of detection (LOD) and quantitation (LOQ) were estimated according to IUPAC recommendations (17,18). LOD calculations were based on the theory of hypothesis testing and the probabilities of false positives ($\alpha = 0.05$) and false negatives ($\beta = 0.05$), whereas the LOQ was established as the lowest concentration tested which gave acceptable recoveries (between 70 and 110%) and precision (RSD lower than 20 % (18). Good values were obtained, with LOD and LOQ values of 0.05 and 0.1 µg/L, respectively.

Once the quality parameters of the P&T method were estimated in groundwater samples, the method was also validated for soil samples. The linearity of the method was tested in a wide range (0.01–1.00 mg/Kg) by spiking blank soil samples at seven concentration levels (0.01, 0.05, 0.10, 0.20, 0.25, 0.50, and 1.00 mg/Kg), and applying P&T to each of them (two replicates for each concentration). The calibration range was set considering the expected concentrations to be found in the analysis of real soil samples. However, the linearity in the whole selected range was not adequate, with r^2 values lower than 0.98. In order to maintain this wide range, calibration was made considering two different linear ranges: the first one was set from 0.01 to 0.25 mg/Kg, and the second one from 0.25 to 1.00 mg/Kg. The calibration equation obtained was $y = 778795x - 396$ (r^2, 0.9996) in the lower range, and $y = 104230x + 2089$ (r^2, 0.9912) in the

Table II. Relation at Different Purge Time (R_{pt}) and Desorption Time (R_{dt}) for 1,3-DCP when Purge Time Increased from 5 to 20 min and Desorption Time from 1 to 4 min, Respectively

Purge time (min)	R_{pt} (%)	RSD_{pt} (%)	Desorption time (min)	R_{dt} (%)	RSD_{dt} (%)
5	28	8	1	116	6
10	59	6	2	109	8
15	99	5	3	107	7
20	100	5	4	100	6

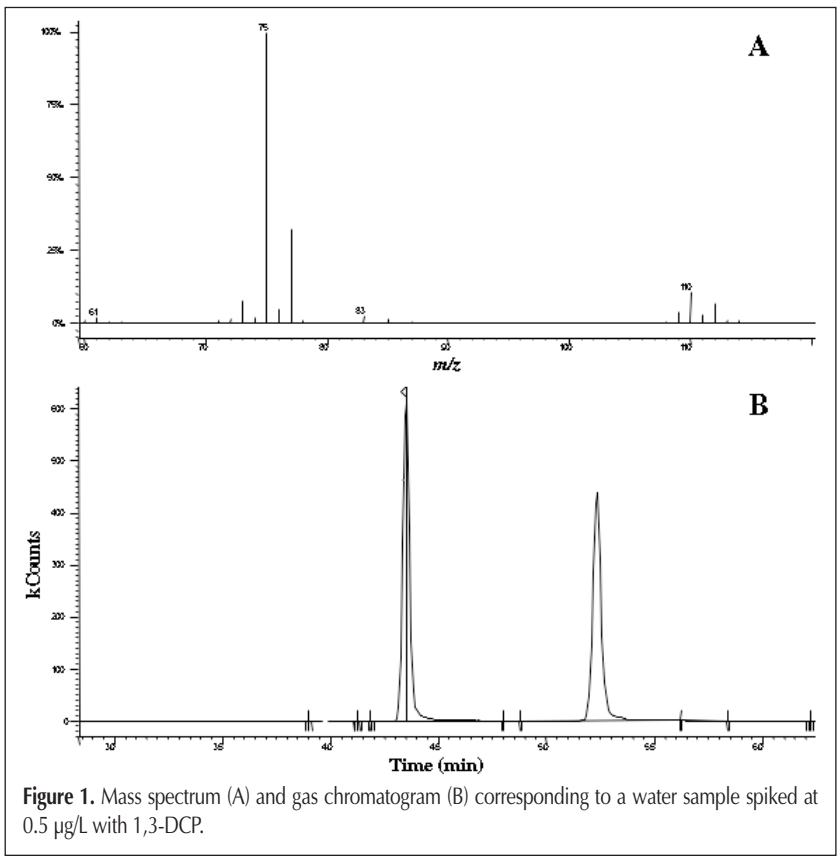

Figure 1. Mass spectrum (A) and gas chromatogram (B) corresponding to a water sample spiked at 0.5 µg/L with 1,3-DCP.

higher range. This calibration strategy allows the quantitation of concentrated soil samples without prior dilution, and therefore reduces the average time required per sample, as well as the uncertainty of the estimated concentration. The accuracy of the method was obtained from analysis of five independent samples on the same day at three concentration levels, 0.10, 0.25, and 0.50 mg/Kg. The trueness, expressed as % recovery, was of 93%, 102%, and 104% for the low, medium, and high concentration levels, respectively, while the precision, expressed as %RSD, was 4%, 3%, and 2%, respectively. The LOD and LOQ in soil samples were also estimated. Good values were obtained, with LOD and LOQ values of 0.005 and 0.01 mg/Kg, respectively.

In both matrices studied the selectivity of the procedure was evaluated by analyzing control blank samples. The absence of any signal at the same retention time as the target compound indicated that there were no chemical interferences. In consequence, in this study, the combination of selective extraction by P&T and selective determination by GC–MS made possible a selective determination of the target compound in complex environmental samples.

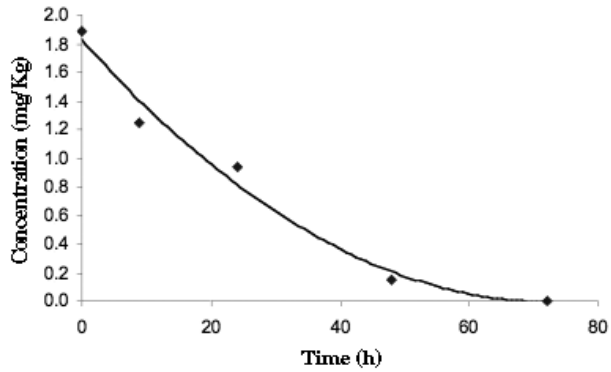

Figure 2. 1,3-DCP concentrations (mg/Kg) found in soil samples after its application (hours).

Identification of 1,3-DCP was done based on the retention time windows, defined as the chromatographic retention time average of the isomers (4.36 and 5.25 min) ± three times the standard deviation of the retention time when 5 blank water samples spiked at 1 µg/L were analyzed. They were 4.05–4.51 min for *cis*-1,3-DCP and 5.05–5.45 min for *trans*-1,3-DCP.

The confirmation of a previously identified compound was performed by the recording of the full scan spectra and checking the presence of all measured diagnostic ions with a relative intensity of more than 10% in the reference spectrum obtained in identical experimental conditions. These characteristic ions must correspond to those of the reference spectrum with a tolerance of 20% (19). Also, abundance of the clusters caused by the presence of two chloride atoms in the structure of the molecule was also considered for the confirmation of the results.

Method application

To assure the quality of results when the proposed procedures are applied to routine analysis, various internal quality criteria have been established. The batch of samples analyzed each day was processed together with: (*i*) a blank sample (water or soil) that eliminates a false positive by contamination in the extraction process; (*ii*) a blank spiked at the concentration of the second calibration level (0.5 µg/L in water and 0.05 mg/Kg in soil) in order to assess the extraction efficiency (recovery rates between 60% and 120% are accepted); and (*iii*) calibration curves prepared daily to check both sensitivity and linearity in the working range of concentrations in order to avoid quantitation mistakes caused by possible matrix effects of instrumental fluctuations ($R^2 > 0.99$ are requested).

The proposed method was applied to the analysis of 10 groundwater samples taken from wells of the Campo de Dalías, the main area of intensive agriculture of Almería (Spain). None of the presented 1,3-DCP were above the stated LOD level. As a consequence of the negative results obtained, and in order to test again the efficiency of the proposed method for the analysis of real groundwater samples, the negative real samples were spiked with 0.1 µg/L of 1,3-DCP and reanalyzed. Now the analyte was positively determined with an average recovery of 96%, and RSD of 7%.

On the other hand, levels of 1,3-DCP in soil samples from a greenhouse after its application (Drafol-one, 107% p/v) were studied. Application rate of the commercial product was 110 L/Ha. Concentrations decreased after the compound application, starting with a value of 1.89 mg/Kg immediately after application and decreasing to less than the LOD (0.05 mg/Kg) after three days (Figure 2), which agrees with the DT_{50} values reported in the literature (20). Figure 3 shows the mass spectrum and gas chromatogram obtained from a soil sample obtained 48 h after application.

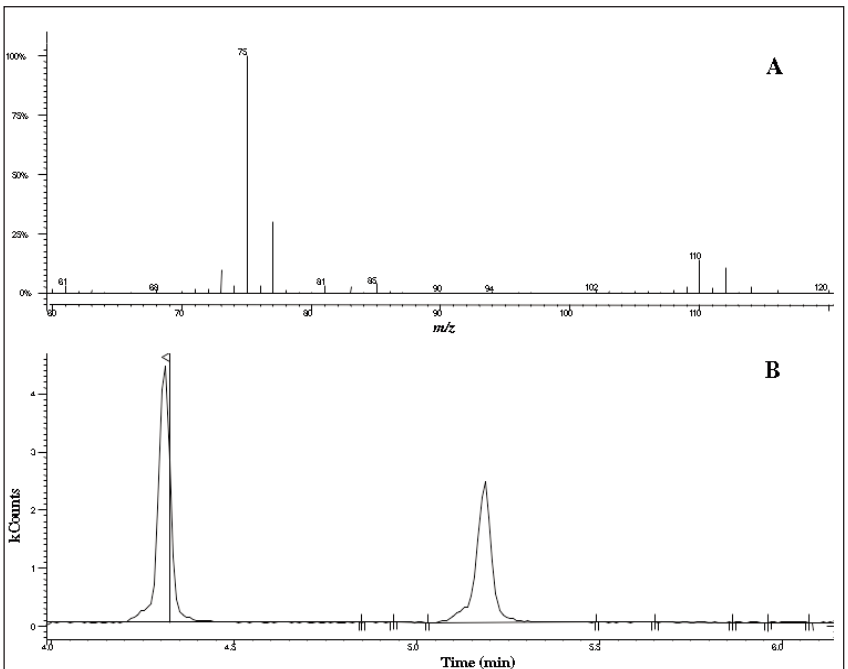

Figure 3. Mass spectrum (A) and gas chromatogram (B) corresponding to a real soil sample containing 0.15 mg/Kg of 1,3-DCP.

Conclusions

P&T extraction method coupled to GC–MS analysis is a useful approach for the determination of 1,3-DCP in groundwater and soil samples. This method is simple, inexpensive, and solvent-free, and in consequence sample preparation or clean-up steps such as extraction, concentration, fractionation, and isolation of analytes, which may result in a loss of volatile compounds, are avoided. This approach also allows the achievement of adequate LOD values in order to detect the target compound at trace levels in the studied agricultural matrices. The proposed method was applied to the determination of 1,3-DCP in 10 real groundwater samples, but the target compound was not present at concentrations above the LOD of the method. Also, a dissipation study of 1,3-DCP was carried out after its application in soil from a greenhouse.

Acknowledgements

The authors gratefully acknowledge the Consejería de Innovación Ciencia y Empresa de la Junta de Andalucía (P05-FQM-0202 and AGR-02922) for financial support.

References

1. L.O. Ruzo. Physical, chemical and environmental properties of selected chemical alternatives for the pre-plant use of methyl bromide as soil fumigant. *Pest Manag. Sci.* **62:** 99–113 (2006).
2. A. Antelo, M. Lasa, and E. Millán. Use of experimental design to develop a method for analysis of 1,3 dichloropropene isomers in water by HS-SPME and GC-ECD. *Chromatographia* **66:** 555–63 (2007).
3. W. Zheng, J. Gan, S.K. Papiernik, and S.R. Yates. Identification of volatile/semivolatile porductos derived from chemical remediation of *cis*-1,3-dichloropropene by thiosulfate. *Environ. Sci. Technol.* **41:** 6454–59 (2007).
4. D.J. Ashworth and S.R.Yates. Surface irrigation reduces the emission of volatile 1,3-dichloropropene from agricultural soils. *Environ. Sci. Technol.* **41:** 2231–36 (2007).
5. J.E. Thomas, L.-T. Ou, L.H. Allen Jr., J.C. Vu, and D.W. Dickson. Henry´s law constants and mass transfer coefficients for methyl bromide and 1,3-dichloropropene applied to Florida sandy field soil. *Chemosphere* **62:** 980–88 (2006).
6. S. Bondarenko, W. Zheng, S.R. Yates, and J. Gan. Dehalogenation of halogenated fumigants by polysulfide salts. *J. Agric. Food Chem.* **54:** 5503–5508 (2006).
7. W. Zheng, S.R. Yates, S.K. Papiernik, and Q. Wang. Reducing 1,3-dichloropropene emission from soils columns amended with thiourea. *Environ. Sci. Technol.* **40:** 2402–2407 (2006).
8. S. Fuster, J. Beltrán, F.J. López, and F. Hernández. Application of solid phase microextraction for the determination of soil fumigants in water and soil samples. *J. Sep. Sci.* **28:** 98–103 (2005).
9. J.-H. kim, J. Gan, W.J. Farmer, S.R. Yates, S.K. Papiernik, and R.S. Dungan. Organic matter effect on phase partition of 1,3-dichloropropene in soil. *J. Agric. Food Chem.* **51:** 165–69 (2003).
10. N. El Hadiri, M. Ammati, M. Chgoura, and K. Mounir. Behavior of 1,3-dichloropropene and methyl isothiocyanate in undisturbed soil columns. *Chemosphere* **52:** 893–99 (2003).
11. M. Guo, R.S.R. Yates, W. Zheng, and S.K. Papiernik. Leaching of persistent soil fumigant residues. *Environ. Sci. Technol.* **37:** 5181–85 (2003).
12. E. Martínez, I. llobet, S. Lacorté, P. Viana, and D. Barceló. Patterns and levels of halogenated volatile compounds in Portuguese surface waters. *J. Environ. Monit.* **4:** 253–57 (2002).
13. E. Jávorszky, G. Erdoedy, and K. Torkos. The choice of internal standards for measuring volatile pollutants in water. *Chromatographia Supplement* **63:** S55–S60 (2006).
14. V.I. Safarova, S.V. Sapelnikova, E.V. Djazhenko, G.I. Teplova, G.F. Shajdulina, and F.Kh. Kudasheva. Gas chromatogaphy-mass spectrometry with headspace for the analysis of volatile organic compounds in waste water. *J. Chromatogr. B* **800:** 325–30 (2004).
15. S.K. Golfinopoulos, T.D. Lekkas, and A.D. Nikolaou. Comparison of methods for determination of volatile organic compounds in drinking water. *Chemosphere* **45:** 275–84 (2001).
16. H.W. Kuo, F. Chiang, I. Lo, C.C. Chan, J.S. Lai, and J.D. Wang. Exposure assessment of volatile organic compounds from water in Taiwan metropolitan and petrochemical areas.*Bull. Environ. Contam. Toxicol.* **59:** 708–14 (1997).
17. L.A. Currie. Detection and quantification limits: Origins and historical overview. *Anal. Chim. Acta* **391:** 127–34 (1999).
18. D.J. Hamilton, A. Ambrus, R.M. Dieterle, A.S. Felsot, C.A. Harris, P.T. Holland, A. Katayama, N. Kurihara, J. Linders, J. Unsworth, and S.S. Wong. Regulatory limits for pesticide residues in water (IUPAC technical report). *Pure Appl. Chem.* **75:** 1123–55 (2003).
19. Commission Decision 2002/657/EC of 12 August 2002 implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results. Official Journal of the European Union, L 221, 17th August 2002.
20. *Metabolic Pathways of Agrochemicals.* Part 2. Insecticides and Fungicides, Eds, T.R. Roberts D.H. Hutson. The Royal Society of Chemistry, Cambridge 1999.

Manuscript received April 10, 2008;
revision received June 10, 2008.