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Multicomponent analysis of volatile organic compounds in water by automated purge and trap coupled to gas chromatography–mass spectrometry

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Abstract

The performance of an automated purge and trap concentrator coupled to gas chromatography–mass spectrometric detection was evaluated by analyzing 40 volatile organic compounds of different chemical families. Compounds chosen defined as toxic for the environment and for human health were selected according to Directive 76/464/CEE. The present work includes: (i) the optimization of the purge and trap conditions, (ii) the establishment of quality parameters and in last instance (iii) the analysis of surface waters. The analytical method consisted of a modification of the EPA Method 524.2 in which water was pumped, via an automated AquaTek 70 Liquid Autosampler to a 25-ml purging device, where samples were purged and trapped in a Tenax or Tenax-Silica and Charcoal column. Afterwards, helium was used to desorb the trapped analytes that flow directly into the GC column. Mass spectrometric analysis was carried out in selected ion monitoring and scan modes to ensure quantification and confirmation of the results. Parameters optimized were the sample volume analyzed, bubbling flow-rate and time and temperature of desorption. Optimal conditions lead to mean recoveries of 80%, limits of detection between 0.002 and 0.1 µg/l, linearity from 0.01 to 2.5 µg/l and maximum standard deviation of 10%, using a Tenax trap. This protocol permitted a high precision and sample throughput and was used to determine volatile organic compounds in surface river, effluents and coastal waters of Portugal, on a routine basis. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Monitoring of volatile organic compounds in the environment has become a subject of concern due to the fact that many of these compounds are toxic and persistent [1,2] and in addition, are responsible for

odor and taste problems in different types of waters [3]. Their presence in waters is mainly associated with industrial [4] and urban discharges [5], although biological degradation of natural or anthropogenic substances can also lead to the formation especially of light halocarbons [6]. Several different chemical types of volatile organic compounds (VOCs) have been detected in environmental waters. Alkylbenzenes, alkyl-naphthalenes and chlorobenzenes were encountered in surface waters at levels up to 8 µg/l

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in highly polluted rivers close to Barcelona, where a high level of industrial activity is present [7]. Another study indicated that benzene, toluene, chloroform and dichloromethane were the major contributors of industrial discharges of different categories and were detected in 30% or more of the analyzed samples [8]. Recently, more than 50 VOCs were reported in effluents of high-tech industries, leading to pollution of surrounding river waters and inducing poor atmosphere odor [9]. Agricultural practices can also contribute to the input of VOCs, due to the common addition of solvents in pesticide formulations [10]. The physico-chemical properties of these compounds cause dispersion and mobilization, leading to a natural attenuation of VOCs in surface waters. Mobilization of VOCs to the atmosphere can occur and different studies have shown the presence of VOCs in air [11] and surface snow [12]. In addition, groundwater is a stable reservoir of some VOCs, which can persist for a long time due to the anaerobic, cold and dark conditions of aquifers [13]. In this line, an extensive monitoring study carried out in the USA revealed that 7% of the ambient groundwaters resources of the USA contain at least one VOC at levels of 0.2 $\mu\text{g}/\text{l}$ and in urban areas, 47% of the sampled wells were positive [14].

This growing tendency to monitor the levels of VOCs in different environmental matrices requires the use of techniques that provide low detection limits and high robustness [15]. Several methods have been described in the literature for the analysis of VOCs in water [16,17]. Most established is the preconcentration of the analytes using purge and trap, which after being described and developed [18,19] was rapidly adopted by the EPA in its series of methods 500 and 600. Other techniques are headspace [20], closed loop stripping analysis [21,22], liquid–liquid extraction [23] or solid-phase microextraction [24]. Depending on target analytes to be determined, different detectors can be used, e.g. electron-capture detector offers a high sensitivity and selectivity for halogenated compounds [10], flame ionization detector permits the analysis of a high number of compounds [25] or atomic emission detector [26] has been used for the analysis of environmental samples. However, a precise application of such techniques for monitoring purposes needs to accomplish three basic requirements: (i) detection of a large number of analytes within one

single run, to be cost-effective and efficient; (ii) to detect all compounds with limits of detection at $\mu\text{g}/\text{l}$ levels, with high intra-day precision and (iii) avoid false positives/negatives by unequivocally assuring the presence of analytes. Purge and trap (PT) coupled to gas-chromatography with mass spectrometric detection (GC–MS) permits the achievement of such requirements. In addition, when an automated purging device is connected, it allows a high sample throughput without losses in any of the quality parameters. The system is especially suitable for routine monitoring programs, where normally a high amount of samples have to be analyzed monthly. The present paper is aimed to provide an overview of the advantages and problems of the performance of the automated PT–GC–MS directed to the analysis of halogenated, hydroxylated and aromatic priority VOCs. Although the system does not involve any sample preparation, the optimization of several analytical parameters is required in order to obtain optimal performance. Optimization has been carried out in three steps and this paper reports: (i) optimization of the purge parameters, e.g. sample volume, gas flow and trap column, (ii) studying the quality parameters of automated purge and trap coupled to gas chromatography and mass spectrometric detection for a high number of compounds, giving at the same time emphasis of the robustness of the system in relation to automation and (iii) determination of priority volatile compounds in a large number of surface and coastal waters. In this work, special emphasis was given to quality controls in order to provide fully reliable and comparable results, which is of prime importance in monitoring surveys, where in the last instance, correlations and distribution of compounds, within or between different laboratories is performed. All the compounds included in this work are priority according to the 76/464/CEE Directive of the European Union on dangerous substances which can be discharged to the environment.

2. Material and methods

2.1. Chemicals and reagents

Pure standards (99%) used are listed in Table 1 and were purchased from Mix EPA Appendix IX-A

Table 1

Compounds studied ordered by elution time, identification number, retention time window used for time-scheduled SIM and GC–MS spectral information

Compound	Id. no.	t_R (min)	Retention window	M_r	Ion 1	Ion 2	Ion 3
Vinyl chloride	1	5.88	0–15.9	62	62	64	–
1,1-Dichloroethene	2	9.44		96	96	61	63
Allyl chloride	3	9.58		76	76	49	–
Dichloromethane	4	10.76		84	84	86	49
<i>trans</i> -1,2-Dichloroethene	5	11.15		96	96	98	61
1,1-Dichloroethane	6	12.58		98	63	65	83
<i>cis</i> -1,2-Dichloroethene	7	14.05		96	96	98	61
Chloroform	8	14.60		118	83	85	–
1,1,1-Trichloroethane	9	15.29	15.9–20.5	132	97	99	61
Carbon tetrachloride	10	15.68		152	117	119	–
1,2-Dichloroethane	11	16.22		98	62	98	64
Benzene	12	16.22		78	78	77	52
Trichloroethene	13	17.75		130	130	95	60
1,2-Dichloropropane	14	18.27		112	63	112	76
Dibromomethane	15	18.57		172	174	93	95
Toluene	17	20.99	20.5–24	92	91	92	65
<i>trans</i> -1,3-Dichloropropene	17	21.48		110	75	110	–
1,1,2-Trichloroethane	18	21.95		132	97	83	61
Tetrachloroethene	19	22.41		164	166	129	94
Chlorobenzene	20	24.63	24.0–28.5	112	112	77	114
1,1,1,2-Tetrachloroethane	21	24.82		166	131	117	95
Ethylbenzene	22	24.90		106	91	106	77
<i>m</i> + <i>p</i> -Xylene	23	25.21		106	91	106	77
<i>o</i> -Xylene	24	26.30		106	91	106	77
Bromoform	25	26.84		250	173	91	252
Isopropylbenzene	26	27.31		120	105	120	77
1,1,1,2,2-Tetrachloroethane	27	28.09		166	83	131	85
2-Chlorotoluene	28	28.74	28.5–35.2	126	91	126	–
3+4-Chlorotoluene	29	29.03		126	91	126	–
1,3-Dichlorobenzene	30	30.89		146	146	148	111
1,4-Dichlorobenzene	31	31.17		146	146	148	111
Benzyl chloride	32	31.56		126	91	126	–
1,2-Dichlorobenzene	33	32.33		146	146	148	111
Bis(2-chloroisopropyl)ether	34	32.96		170	45	121	–
Hexachloroethane	35	33.17		234	117	119	201
1,2,4-Trichlorobenzene	36	37.39	35.2–46	180	180	182	145
Hexachlorobutadiene	37	37.95		258	225	260	190
1,2,4,5-Tetrachlorobenzene	38	42.35		216	216	214	218
1-Chloronaphthalene	39	44.85		162	162	164	127
2-Chloronaphthalene	40	45.05		162	162	164	127

Volatile Calibration Mix B (Supelco) or bought individually from J.T. Baker or Sigma–Aldrich. Internal standards used were fluorobenzene and 4-bromofluorobenzene. All standard preparations (dilutions, spiking, etc.) were performed over a carbonic ice atmosphere to avoid losses of any of the considered compounds.

2.2. Sampling strategy

Samples were collected from the river and from the sea using a Niskins bottle. Afterwards, they were transferred to homologated 40-ml Tekmar amber glass vials (EPA Method 524.2), avoiding air bubbles passing through the sample and no headspace

volume was left, which could induce losses of the target analytes. Three vials were taken per sample. Immediately after, samples were placed inside a portable freezer and were transported to the main laboratory and were used directly for analysis. All samples were analyzed within 15 days after collection to avoid sample losses during storage.

2.3. Purge and trap conditions

Tenax[®] and Tenax[®]-SilicaGel-Charcoal cartridges of the Purge and Trap Concentrator Tekmar 3100 were used. An Aquatek 70 Liquid Autosampler (Tekmar-Dohrmann) was programmed to automatically dispense 5- to 15-ml sample aliquots into a 25-ml purging device. The sample was purged with a stream of He at 30–45 ml/min for 10–15 min at ambient temperature. Optimum conditions were: sample volume of 13 ml, flux of He at 35 ml/min and purging time 11 min.

2.4. Desorption conditions

After sample loading, the trapped sample components were desorbed by heating the Tenax[®] cartridges at 225 °C and passing He gas at 3 ml/min during 3 min. Since cryofocusing was not used, the desorption flow-rate was optimized to a minimum value so that it ensured the total desorption of the analytes from the cartridge without affecting the vacuum requirements of the MS. The injector was set in the splitless mode, and He flow-rate was decreased from 3 to 1 ml/min in 1 min. This flow-rate was kept during the MS analysis since better performance of the equipment was obtained (GC–MS equipped with a 250 l/s pump). By using such mode of injection, it was possible to obtain sharp peaks throughout the chromatogram, and no losses appeared during injection. After desorption, bake condition were programmed at 230 °C during 10 min. Using these conditions, system blanks were attained.

2.5. Chromatographic and MS conditions

A Trace GC coupled to a Voyager MS (ThermoQuest, UK) was used in electron impact mode

(EI). A 75 m×0.53 mm I.D. DB-624 (J&W Scientific, Inc.) fused-silica capillary column with a 3- μ m film thickness was used. He was used as carrier gas at 1 ml/min. The oven was set at 35 °C (5 min) and raised to 160 °C at 5 °C/min, letting it stay for 1 min and to 210 °C at 5 °C/min. The final temperature was maintained for 5 min and the total run time was 46 min. Electron ionization was carried out at 70 eV, the source temperature and GC interface temperature were set at 200 and 250 °C, respectively. The emission current was 100 μ V and the detector voltage was set at 380 V. Acquisition was performed in scan mode from 35 to 300 a.m.u. and in time scheduled selected ion monitoring using the retention windows indicated in Table 1. Table 1 also reports the elution time of these compounds, and their mass spectral characterization at three different ions.

2.6. Calibration and quantification

Calibration curves were performed by spiking ground water samples with a mixture of 40 compounds and processing the spiked samples as depicted before. Internal standard quantification was carried out using a six-point calibration at concentrations of 0.01, 0.05, 0.1, 0.5, 1 and 2.5 μ g/l, corresponding to 0.13–32.5 ng injected. In addition, a sample sequence included a blank sample, the two lowest points of the calibration curves, five samples, blank, 3rd calibrant, five samples, and so on, until the 6th calibrant was injected. By doing so, it was possible to have quality controls and draw the calibration curve reflecting exactly the same analytical conditions as for the water samples. It was crucial to produce chromatograms with a very neat baseline, in order to have an unequivocal identification and precise quantification. This was only possible if blanks were intercalated in the sequence, to avoid carryover effects. In addition, precaution had to be taken in cleaning the glass material, which was carried out in an ultrasonic bath for 10 min followed by rinsing with acetone and afterwards with distilled water. All sample preparation had to be done in a laboratory free of solvents in the atmosphere. The 40-ml vial septum should be discarded once used otherwise it produced contamination and problems of unreproducible pumping of an exact sample volume.

3. Results and discussion

3.1. Method performance

By automating PT with GC–MS, it was possible to detect 40 compounds within 105 min, corresponding to a separation of 46 min and the rest was needed for the purging device (purging itself, clean and transfer time between samples). Fig. 1 shows a chromatogram with all compounds corresponding to a 1 µg/l spiked groundwater sample where 13 ml of sample were purged at a flux of He at 35 ml/min during 11 min. The chromatographic column and ramp permitted to detect from vinyl chloride (b.p. –13.9 °C and solubility 2700 g/l) up to 2-chloronaphthalene (b.p. 256 °C), being therefore suitable to determine a wide range of compounds of different volatility and polarity. With the fully automated system on which experiments were performed, no background noise was detected since all sample manipulation was carried out in a special laboratory for VOCs, where some safety measures had to be

taken, such as: (i) special isolation of the laboratory to avoid pollution due to benzene and toluene, among others, in the atmosphere of Barcelona and (ii) avoid any solvent entering the room. Method performance and robustness were checked within this atmosphere and all quality parameters involved with the method (limits of detection, recoveries, inter and intra day variation and response factors) were studied within different analytical conditions. In this study, sample volumes of 5, 10 and 15 ml were purged. In the configuration depicted below, volumes of 5 ml lead to poor inter-day variations (up to 30–40%). This was attributed to the small sample volume in a 25-ml vessel. However, there was an increase in sensitivity from 10 to 15 ml and an optimum was found at 13 ml. Keeping the sample volume at 13 ml, the He gas flow was varied from 30 to 45 ml/min and sensitivity and inter-day variation was checked. More water soluble compounds with boiling points above 200 °C were purged from the water with higher efficiencies at 35–40 ml/min. As the former condition is suggested by the EPA method 524.2, it

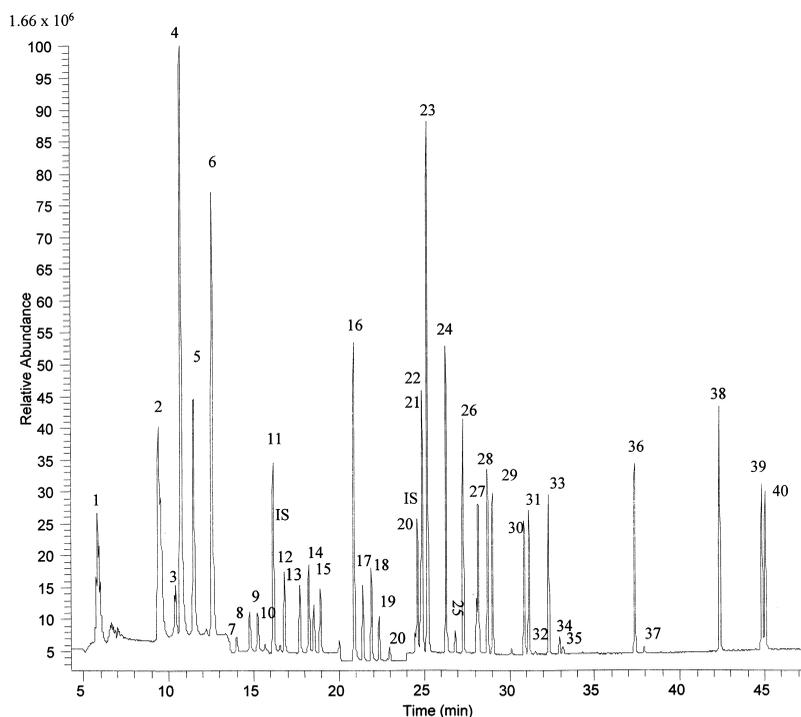


Fig. 1. GC–MS chromatogram in SIM acquisition mode of a groundwater sample spiked at a concentration of 1 µg/l (see Table 1 for peak identification).

was adopted in this study and permitted recovery of all analytes under study. Finally, two different traps were tested: (i) Tenax[®] which is widely used for the analysis of VOCs in many applications although it may lead to losses of very volatile organic compounds and (ii) a combined phase with Tenax[®]-SilicaGel-Charcoal which allows the retention of a

broader range of chemicals. Table 2 shows the quality parameters of the method using both traps. Calibration curves were constructed from 0.01 to 2.5 µg/l and both systems showed excellent linearity as can be seen by the coefficient of correlation values (Table 2) which were in all cases in the 0.97–0.99 range. This is in line with the results reported earlier

Table 2
Quality parameters obtained using a Tenax and a Tenax-Silica Gel-Charcoal trap

Compound	Id. no.	Calibration equation (TSC)	R^2		Recovery (%)		CV (%)		LOD (µg/l)	
			Tenax	TSC	Tenax	TSC	Tenax	TSC	Tenax	TSC
Vinyl chloride	1	$y=3.1633x+0.091$	n.a.	0.9909	n.a.	62	n.a.	15	n.a.	0.017
1,1-Dichloroethene	2	$y=2.1206x+0.115$	0.9875	0.9969	92	44	7.5	24	0.054	0.038
Allyl chloride	3	$y=9.1659x-0.390$	n.a.	0.9893	n.a.	91	n.a.	16	n.a.	0.001
Dichloromethane	4	$y=1.6402x+7.444$	0.9887	0.8092	105	43	10.2	27	0.062	0.053
<i>trans</i> -1,2-Dichloroethene	5	$y=1.4399x+0.103$	n.a.	0.9859	n.a.	38	n.a.	9	n.a.	0.007
1,1-Dichloroethane	6	$y=0.2607x+0.055$	0.9899	0.9992	99	99	2.9	19	0.017	0.107
<i>cis</i> -1,2-Dichloroethene	7	$y=0.2601x+0.003$	n.a.	0.9999	n.a.	62	n.a.	21	n.a.	0.07
Chloroform	8	$y=0.2262x+0.072$	0.9524	0.9272	93	91	4.2	17	0.002	0.002
1,1,1-Trichloroethane	9	$y=0.4581x-0.023$	0.9842	0.9963	95	51	9.7	18	0.021	0.01
Carbon tetrachloride	10	$y=0.3002x+0.001$	0.9974	0.9965	90	43	4.9	18	0.002	0.012
1,2-Dichloroethane	11	$y=0.4189x-0.0034$	0.9813	0.9997	97	92	7.4	15	0.002	0.012
Benzene	12	$y=0.9635x-0.0903$	0.9901	0.9859	98	113	9.5	12	0.002	0.011
Trichloroethene	13	$y=0.3043x-0.0172$	0.9752	0.9930	97	111	10.5	21	0.010	0.002
1,2-Dichloropropane	14	$y=0.3260x-0.0306$	0.9804	0.9987	99	97	5.7	20	0.011	0.01
Dibromoethane	15	$y=0.0522x-0.0117$	0.9964	0.9137	91	113	3.2	14	0.022	0.121
Toluene	16	$y=1.4605x+0.252$	0.9876	0.9598	93	119	8.4	11	0.007	0.001
<i>trans</i> -1,3-Dichloropropene	17	$y=0.4793x-0.0456$	0.9980	0.9932	98	105	4.7	5	0.010	0.002
1,1,1,2-Trichloroethane	18	$y=0.3196x-0.0439$	0.9825	0.9959	92	104	7.5	7	0.023	0.003
Tetrachloroethene	19	$y=0.1686x-0.0005$	0.9867	0.9847	91	116	3.5	12	0.014	0.09
Chlorobenzene	20	$y=0.9641x-0.0631$	0.9876	0.9951	97	82	9.0	13	0.003	0.008
1,1,1,2-Tetrachloroethane	21	$y=0.293x-0.0139$	0.9919	0.9906	91	103	4.7	21	0.029	0.011
Ethylbenzene	22	$y=1.3321x-0.0057$	0.9901	0.9981	90	111	5.3	21	0.014	0.001
<i>m+p</i> Xylene	23	$y=1.4961x+0.159$	0.9924	0.9948	91	137	2.1	9	0.036	0.001
<i>o</i> -Xylene	24	$y=0.7936x+0.122$	0.9947	0.9783	99	141	2.3	19	0.015	0.002
Bromoform	25	$y=0.1221x-0.0258$	0.9939	0.9875	98	103	2.1	13	0.027	0.059
Isopropylbenzene	26	$y=1.0644x-0.1664$	0.9874	0.9936	94	130	2.4	19	0.058	0.001
1,1,2,2-Tetrachloroethane	27	$y=0.4370x-0.1104$	0.9388	0.9928	98	62	2.1	14	0.02	0.011
2-Chlorotoluene	28	$y=0.835x+0.0692$	n.a.	0.9962	n.a.	109	n.a.	22	n.a.	0.012
3+4-Chlorotoluene	29	$y=0.7287x+0.080$	n.a.	0.9946	n.a.	105	n.a.	23	n.a.	0.008
1,3-Dichlorobenzene	30	$y=0.4525x+0.080$	0.9820	0.9907	96	123	2.3	18	0.014	0.035
1,4-Dichlorobenzene	31	$y=0.5130x+0.009$	0.9812	0.9951	97	140	5.3	25	0.014	0.014
Benzyl chloride	32	$y=0.0245x+0.006$	n.a.	0.9943	n.a.	77	n.a.	8	n.a.	0.246
1,2-Dichlorobenzene	33	$y=0.5766x-0.0094$	0.9802	0.9994	96	124	4.0	19	0.016	0.034
Bis(2-chloroisopropyl)ether	34	$y=0.1260x-0.0185$	n.a.	0.9771	n.a.	114	n.a.	16	n.a.	0.132
Hexachloroethane	35	$y=0.2498x+0.003$	0.9834	0.9992	97	97	4.3	17	0.115	0.024
1,2,4-Trichlorobenzene	36	$y=0.6164x-0.0105$	0.9792	0.9911	99	104	3.4	10	0.009	0.014
Hexachlorobutadiene	37	$y=0.5255x-0.0135$	0.9916	0.9603	97	83	4.2	19	0.061	0.015
1,2,4,5-Tetrachlorobenzene	38	$y=0.8120x+0.079$	0.9895	0.9996	98	78	2.9	12	0.009	0.113
1-Chloronaphthalene	39	$y=0.8204x-0.0468$	0.9678	0.9980	Nc	74	2.6	15	0.014	0.016
2-Chloronaphthalene	40	$y=0.8206x+0.014$	0.9738	0.9997	91	87	4.7	14	0.025	0.014

Recoveries were calculated by spiking groundwater at a concentration of 1 µg/l; n.a., not analyzed.

CV=coefficient of variation.

for 27 VOCs [15]. The recoveries, obtained after spiking groundwater at a level of 1 $\mu\text{g/l}$ were in most cases close to 100%, although somewhat better recoveries were obtained with the Tenax[®] trap. The Tenax[®]-Silica Gel-charcoal did not provide acceptable recoveries for some of the more volatile compounds, where in some instances, values of 40–50% were obtained. This was due to the fact that the Tenax[®]-Silica Gel-Charcoal is designed for compounds with a higher boiling point and high molecular mass, since the charcoal permits a better retention efficiency. However, a 10–20% decrease in recovery in compounds eluting at the end of the chromatogram (from hexachlorbutadiene to the end) was also observed, attributed to a strong retention in this trap. The coefficient of variation of the intra-day assays was calculated by analyzing a spiked groundwater solution during five consecutive days. For the Tenax[®] trap, a very good precision was obtained, where the overall value was between 2 and 5% variation, and in only some cases, a 10% variation was found, which was considered as acceptable. However, for the Tenax[®]-Silica Gel-Charcoal trap, a higher variation was obtained, and values were in the 10–20% range. In relation to the limits of detection with both systems calculated using a signal-to-noise ratio of three, values were at the 0.01 $\mu\text{g/l}$ range, similar to what is described in the EPA method 524.2. However, some compounds exhibited values higher than 0.1 $\mu\text{g/l}$, such as hexachloroethane, with the Tenax[®] trap and 1,1-dichloroethane, dibromomethane, benzyl chloride and 1,2,4,5-tetrachlorobenzene for Tenax[®]-Silica Gel-Charcoal. Since for most of the compounds the Tenax[®] column was more reproducible and gave better limits of detection, it was chosen as more appropriate for the monitoring study that was being performed.

3.2. Environmental monitoring

Automated purge and trap with a Tenax[®] column was used to determine 40 VOCs in water samples of different origin in a routine basis. In total, 46 samples were analyzed monthly during 7 months and for halogenated compounds during 14 months. Method robustness was guaranteed for surface and coastal waters with a mean TOC level of 5 mg/l, given the

high number of samples analyzed without the need of any sample dilution. Using successive blanks, the automated system was void of external contamination and the use of internal standards throughout the monitoring permitted to ensure an accurate measurement of all VOCs. Out of a total of 40 priority volatile organic compounds investigated in surface and coastal water samples, 36 VOC were detected at least once. According to the concentration values obtained, the global consideration is summarized in Table 3, which includes all the priority compounds studied, the number of positive samples and the minimum and maximum concentration encountered. Table 3 also indicates the main sources of pollution of the compounds included in this work. In general terms, areas with high industrial activity showed the highest levels of VOCs, especially of volatile halogenated compounds which were detected at concentrations up to 15–18 $\mu\text{g/l}$. However, the overall concentrations of VOCs were very low, with median values of 0 or 0.1 $\mu\text{g/l}$ and the dominant class (halogenated and aromatic VOCs) accounted for less than 0.1% of the total dissolved carbon (around 3–5 mg/l). The overall low concentrations found throughout the monitoring highly reflect the capacity of surface water to eliminate VOCs by volatilization, metabolization, photo-induced degradation or in the last instance, adsorption, although this last process seems to play a minor role in surface waters [27]. Highest concentrations, basically of dichlorobenzenes, volatile aromatics, carbon tetrachloride, chloroform 1,1-dichloroethane, 1,2-dichloropropane and tri- and tetrachloroethylene were attributed to local uses or spills of these compounds. Fig. 2 shows the concentration profile of trichloroethene in three sampling sites close to the city of Porto, in which it can be seen that this compound was detected during practically all sample months but with a lack of a clear temporal distribution. 1,2,4,5-Tetrachlorobenzene was the compound detected in the highest percentage of the samples analyzed (75%). However, the median value for this compound was at a concentration of 0.1 $\mu\text{g/l}$, indicating trace level pollution. Compounds detected in more than 20% of the samples were 1- and 2-chloronaphthalene, 1,4-dichlorobenzene, 1,2,4-trichlorobenzene, benzene and toluene, chloroform, *cis*-1,2-dichloroethene, tri- and tetrachloroethylene and allyl chloride. Most of

Table 3

Compounds analyzed classified by chemical classes, uses, number of positive samples out of the total analyzed and minimum and maximum concentration in surface waters (in $\mu\text{g/l}$)

Compounds analyzed	Primary use	Detected/analyzed	Range ($\mu\text{g/l}$)
<i>SVHO</i>			
1-Chloronaphthalene	Solvent (oil, fats, additives)	144/322	0.01–1.15
2-Chloronaphthalene	Impurity of 1-chloronaphthalene	167/322	0.01–0.94
1,2-Dichlorobenzene	Solvent, dye manufacture	63/322	0.01–3.16
1,3-Dichlorobenzene	Solvent, dye manufacture	62/322	0.01–1.01
1,4-Dichlorobenzene	Solvent, fumigant	74/322	0.02–2.23
1,2,4-Trichlorobenzene	Solvent	141/644	0.01–0.81
1,2,4,5-Tetrachlorobenzene	Solvent	243/322	0.1–2.75
Hexachlorobutadiene	Organic synthesis	0/322	0
Hexachloroethane	Solvent, ignition suppressant, polymer additive	5/322	0.1–0.88
<i>Volatile aromatics</i>			
Ethylbenzene	Resin solvent	47/322	0.09–4.75
Isopropylbenzene	Organic synthesis	22/322	0.03–8.08
Toluene	Solvent, industrial manufacturing, gasoline additive	67/322	0.01–4.77
<i>o</i> -Xylene	Solvent, industrial manufacturing	57/322	0.02–2.16
<i>m</i> + <i>p</i> -Xylene	Solvent, industrial manufacturing	43/322	0.01–27.61
Benzene	Solvent, gasoline additive	94/322	0.01–0.70
<i>VHO</i>			
Carbon tetrachloride	Solvent	111/644	0.01–17.55
Chloroform	Solvent	343/644	0.01–15.99
1,1-Dichloroethane	Organic synthesis	14/644	0.01–17.11
1,2-Dichloroethane	Solvent	92/644	0.01–1.40
Dichloromethane	Solvent	0/322	<0.01
1,2-Dichloropropane	Solvent	73/644	0.01–14.34
<i>trans</i> -1,2-Dichloroethene	Solvent	0/322	<0.01
<i>cis</i> -1,2-Dichloroethene	Solvent	98/322	0.02–3.36
1,1-Dichloroethene	Organic synthesis	18/322	0.21–2.37
<i>trans</i> -1,3-Dichloropropene	Fumigant	49/644	0.01–5.27
Chlorobenzene	Solvent	4/322	0.01–0.03
2-Chlorotoluene	Solvent, organic synthesis, dyestuff intermediate	8/322	0.67–4.95
3+4-Chlorotoluene	Solvent, organic synthesis, dyestuff intermediate	1/322	4.45
Bis(2-chloroisopropyl)ether	Solvent	55/322	0.1–10.17
1,1,2,2-Tetrachloroethane	Solvent	77/644	0.01–4.02
Tetrachloroethene	Solvent, dry cleaning	239/644	0.01–13.87
1,1,1-Trichloroethane	Solvent	92/644	0.01–1.63
1,1,2-Trichloroethane	Solvent	35/644	0.05–6.02
Trichloroethene	Industrial manufacturing, solvent, anaesthetic	140/644	0.01–13.07
Benzyl chloride	Perfumes, pharmaceuticals, dyes, resins	16/322	0.01–1.89
Allyl chloride	Synthesis of allyl compounds	80/322	0.1–5.46
Vinyl chloride	Plastic industry, refrigerant, organic synthesis	62/322	0.01–4.68
Dibromomethane	Solvent	14/322	0.07–0.30
<i>Others</i>			
1,1,1,2-Tetrachloroethane	Solvent	22/322	0.1–0.61
Bromoform	Fumigant, solvent, sedative	0/322	0

these compounds are associated with the chemical industry due to their uses as general, extraction or purification solvents.

4. Conclusions

A fully automated purge and trap system coupled

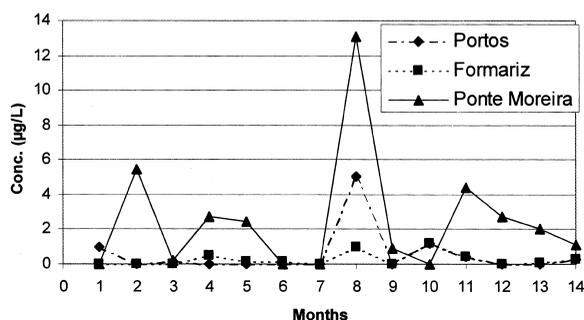


Fig. 2. Concentration profiles of trichloroethene in highly industrialized areas close to the city of Porto during the 14-month survey. Identification codes: Portos (5), Formariz (6) and Ponte Moreira (7).

on-line with GC–MS has been optimized to determine 40 priority VOCs in surface waters. Automation is highly advisable to avoid losses of VOCs since no sample manipulation is carried out and good precision (5–15%) is achieved provided previous optimization of the system is carried out. Quality controls, internal standard calibration and blank analyses are needed to ensure a reliable final quantitative analysis. Quality standards have been set for all compounds studied in final conditions which included a concentration of a sample volume of 13 ml, gas flow at 35 ml/min and a Tenax[®] trap. The automated system permitted a high sample throughput and is especially indicated in routine monitoring programs. This has been demonstrated by the high number samples that have been processed routinely in the monitoring survey carried out to determine VOCs in river and coastal waters in some cases with industrial discharges. Out of 40 compounds monitored on a routine basis, 36 were detected at least once and 24 in more than 10% of the samples, which were considered to be compounds responsible for diffuse pollution. Some compounds, e.g. 1- and 2-chloronaphthalene, 1,2,3,4-tetrachlorobenzene, benzene, chloroform, tetrachlorethylene, allyl chloride and *cis*-1,2-dichloroethylene exhibited concentration levels up to 27 µg/l, attributed basically to local uses or spills.

These preliminary results from the monitoring program are a basis to define the most ubiquitous compounds detected and to establish the ‘hot spots’ as regards contamination by VOCs. Industrialized and highly agricultural areas in the surrounds of

Porto and Lisbon were the main source of water pollution, in relation to the release of volatile organic pollutants into downstream waters.

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