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Determination of chlorinated toluenes in raw and treated water samples from the Llobregat river by closed loop stripping analysis and gas chromatography–mass spectrometry detection

Isabel Martí, Roger Lloret, Jordi Martín-Alonso, Francesc Ventura *

AGBAR, Societat General d'Aigües de Barcelona, Passeig de Sant Joan 39, 08009 Barcelona, Spain

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Abstract

A study of the occurrence of chlorinated toluenes in Llobregat river (NE Spain) has been carried out. These compounds are currently being used in local textile industries as dye carriers and have replaced the common trichlorobenzene mixtures. Closed loop stripping analysis (CLSA), routinely used to monitor the quality of river water for a broad range of volatile compounds, has been employed as an analytical tool to determine them at ng/L levels in wastewater and textile industry effluents and also in raw and treated water from two drinking water treatment plants situated in the river course. The CLSA extracts were analyzed by HRGC/MS. Ring halogenated dichloro- and, to a lesser extent, mono- and trichlorotoluenes have been identified. These compounds have not been reported to our knowledge as common water pollutants.

Keywords: Closed loop stripping analysis; Extraction methods; Halogenated toluenes; Water analysis

1. Introduction

Chlorinated solvents are among the most frequently observed water pollutants due to their worldwide production and use. As an example, trichloroethylene, perchloroethylene and trichlorobenzenes are usually detected in river waters with textile industries along its banks [1]. Trichlorobenzenes (mainly 1,2,4- and 1,2,3-isomers) are employed as synthetic transformer oils, dielectric fluids and other uses but their main application is as dye carriers. These compounds can be analyzed either by headspace (HS), purge and trap (PT), closed loop stripping analysis (CLSA) or solid-phase microextraction (SPME) [2–5], among other methods.

Barcelona's drinking water is supplied from surface water of the Llobregat (45%) and Ter rivers (55%) (NE Spain). Llobregat river crosses dense industrialized areas (i.e. salt mining activities and textile industries) along its course. Our laboratory routinely analyzes volatile organic compounds (VOCs) in Llobregat river by CLSA, which covers a broad range of compounds, to control the quality of raw water entering the water treatment plant (WTP-2). For many years, trichlorobenzenes have been permanently found at medium levels in wastewaters from textile industries and low μg/L concentrations in the river water entering the WTP [1]. However, we have observed that the concentration levels of trichlorobenzenes have declined in raw water and another group of pollutants—bromochloromethane; *n*-propylbromide and mainly halogenated toluenes—have risen in concentration. These compounds, especially dichlorinated and to a lesser extent mono- and trichlorinated toluenes, have probably replaced the trichlorobenzene mixtures. Halogenated toluenes, surprisingly, have been scarcely reported as water pollutants and only very few references deal with these compounds [2,6]. According to the literature, monochloro toluenes are used among other applications as carrier dyeing (*o*- and *p*-isomers) and in the manufacture of benzyl butyl phthalate and triphenylmethane dyes (α isomer), and also as precursors in the production of pharmaceuticals, optical brighteners and fungicides. Some dichloro- and trichloro-

* Corresponding author.
E-mail address: fventura@agbar.es (F. Ventura).

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toluenes are used as dyestuff intermediates or in the manufacture of benzyl alcohol and benzyl chloride derived quaternary ammonium compounds, etc. [7,8]. Side chain chlorinated compounds (chloro-, dichloro- and trichloromethyltoluenes) have been classified by IARC as group 2A carcinogen on the basis of combined exposures, but toxicity data of ring halogenated toluenes is not available to the best of our knowledge.

In view of the sparse data found in the literature, the aims of this study were as follows: (i) to take advantage of the routine CLSA method used in our laboratory for the analysis of VOCs, to quantitatively determine chlorinated toluenes at ng/L levels and (ii) to provide data of the occurrence of chlorinated toluenes in river water and treated water.

2. Experimental

2.1. Chemicals and materials

Monochlorotoluenes (2,3,4 and α isomers), dichlorotoluenes (2,4; 2,6; 2,5; 2,3; 3,4; 3,5; α,2; α,3; α,4 and α,α isomers) and trichlorotoluenes (α,α,α; α,2,4; α,2,6 and α,3,4 isomers) were purchased from Sigma-Aldrich Chemie (Steinheim, Germany) whereas 2,4,5- and 2,3,6-trichloroluenes were from Supelco (Bellefonte, PA, USA) and Riedel de Haehn (Seelze, Germany), respectively. For CLSA analyses, 1-chloroalkanes (C_5, C_6, C_{12}, C_{16}) were purchased from Fluka (Büchs, Switzerland) and the 1-chloroalkanes (C_8, C_{10}, C_{14} and C_{18}) were from Sigma-Aldrich Chemie. Other reagents used were methanol *purge and trap grade* from Sigma-Aldrich Chemie, and carbon disulfide *for spectroscopy* from Merck (Darmstadt, Germany). Ultrapure water was from Milli-Q® water purification system (Millipore, Bedford, MA, USA).

2.2. Analytical procedure

2.2.1. Geographical situation

Barcelona's drinking water is supplied by Llobregat (45%) and Ter rivers (NE Spain). Two water treatment plants (WTP-1 and WTP-2) are situated on the Llobregat river. The WTP-1 is located approximately 40 km upstream WTP-2, which is situated 7 km from the mouth of the river. The WTP-1, with a treatment process that consists of breakpoint chlorination, clarification, sand filtration, GAC filtration and final postchlorination, supplies water to several cities (0.5 million inhabitants) and also a small part of Barcelona. The WTP-2 follows the same scheme as the other plant but includes an ozonization step between sand filtration and GAC filtration. WTP-2 provides water to the city and surroundings (3 million inhabitants).

2.2.2. Sampling

River and treated water samples were collected in 1 L Pyrex borosilicate amber glass bottles filled without overflow. Previously, the glass bottles had been washed in soapy water, rinsed in tap water, ultrapure water and finally reagent-grade acetone. Then they were air-dried and baked overnight. Sample preservation was accomplished by storing the bottles at 4 °C immediately after sampling. The frequency of sampling during the 2003–2004 period was approximately weekly for river water entering WTP-2 and monthly for treated water, whereas for WTP-1 both raw and treated water samples were collected monthly.

2.2.3. Closed loop stripping analysis (CLSA)

Analyses were carried out in a commercial CLSA apparatus (Brechbüler, Switzerland) according to the method developed by Grob [9]. Water samples (1 L or diluted with Milli-Q) were spiked with 1-chloroalkanes (C_5, C_6, C_{10}, C_{12}, C_{16} and C_{18}) to give a final concentration of 800 ng/L for each compound. We used 5 mg-activated carbon filters for trapping analytes. The samples were stripped for 1 h. Temperatures of 45 and 55 °C were used for water-bath and carbon filter, respectively. After stripping, the carbon filters were spiked with C_8 and C_{14} 1-chloroalkanes at the same concentrations as the spiked water samples in order to control the filter elution. The filters were then extracted with 40 μL of CS_2 (20 μL + 20 μL).

Quantitation was performed by the internal standard method. For each compound, the response is calculated relative to 1-chlorohexane. The calibration analyses were obtained by analyzing Milli-Q water samples spiked with 1-chloro-C_6 and different spiked solutions of chlorinated toluenes (0.25 and 1 μg/L). The unknown concentrations in the sample were then obtained from the mean response factors using the formula $C_z = A_z C_i / R_z A_i$ where C_z; A_z and C_i; A_i are the concentration and peak areas of the unknown compound and the internal standard, respectively, and R_z is the response factor for the target compound.

2.3. Instrumental conditions

Analyses of CLSA extracts were carried out on a Trace GC2000 (Thermo Instruments, USA) mass spectrometer. Injections (1 μL of CS_2 extracts) were made cold "on column" into a 50 m × 320 μm i.d. (0.2 μm film thickness) CP-Sil 19-CB column (Chrompack, The Netherlands). A deactivated precolumn (2 m) was used. The GC temperature program was 30 °C (5 min) to 285 °C (10 min) at a rate of 3 °C/min. Helium was used as the carrier gas (60 kPa). The mass spectrometer was operated in electron impact mode (70 eV). The source temperature was kept at 300 °C. Mass spectra were acquired by scanning from 35 to 450 Da. The chromatographic conditions used gave a complete separation of the nineteen compounds studied except for the pair 2,4- and 2,6-dichlorotoluenes, which eluted as a single peak. Different selected ions were monitored for the identification of each compound. Thus, for monochlorotoluenes, m/z = 91 and 126; for dichlorotoluenes, m/z = 125 and 127; and for trichlorotoluenes, m/z = 159 and 161 were chosen.

3. Results and discussion

3.1. Study of recovery efficiencies

A study of the recovery efficiencies of chlorinated toluenes was performed by CLSA in order to get an accurate determination of concentration levels and the feasibility of the method to analyze these compounds at the ng/L level. Recovery experiments were performed by spiking Milli-Q water at two concentrations (0.25 and 1 μg/L; $n = 3$ for monochlorotoluenes and $n = 4$ for dichloro- and trichlorotoluenes) and submitting the samples to the whole analytical procedure. Recovery studies were performed using only new carbon filters.

Table 1 displays the recovery efficiencies of the studied chlorinated toluenes. For ring substituted monochlorotoluenes, they ranged from 93% to 104% for different compounds and RSD values ≤ 10%, whereas for α-chlorotoluene both the recovery (84%) and the RSD value (23%) were worse. All dichlorinated toluenes gave recovery values between 84% (α,4-dichloro-) and 103% (α,2-dichloro-) and acceptable RSD values (4–13%). Only one compound of this group, α,α-dichlorotoluene, was not recovered to any extent. Similar recovery efficiencies (89–103%) and RSDs (4–14%) were observed for all trichlorinated toluenes studied.

Matrix effect was carried out by spiking the compounds in river water. The obtained results, data not shown, did not present significant differences with the values displayed in Table 1 for Milli-Q water.

3.2. Chlorinated toluenes in river and treated water

The origin of halogenated toluenes in Llobregat river by dumping of textile industries and inefficient treatment of local wastewater plants was already demonstrated in 1999, when a sampling campaign showed the presence of halogenated toluenes, mainly ring dichlorinated (2,4 + 2,6-; 2,5-; 2,3- and 3,4-derivatives), and to a lesser extent mono- (2- and 4-) and trichlorinated toluenes (2,3,4-; 2,4,5- and 2,3,6- and one unidentified compound) in effluents of wastewater plants and textile industries [10]. Table 2 shows for informative purposes the concentration values measured in that study in effluents from two wastewater treatment plants (WWTP-A and WWTP-B) and a textile industry (TXT), all located upstream WTP-1. Both WWTPs mainly treat domestic and industrial wastewaters (40%) particularly from textile industries. The concentration levels of halogenated toluenes were in the mg/l range in the effluent of the textile industry, whereas μg/L levels were reached in wastewater effluents.

Table 1
Recovery efficiencies for halogenated toluenes by CLSA

Compound	Recovery ± RSD
2-Chlorotoluene	99 ± 10
3-Chlorotoluene	93 ± 6
4-Chlorotoluene	104 ± 10
α-Chlorotoluene	84 ± 23
2,6-Dichlorotoluene	95 ± 6
2,4-Dichlorotoluene	99 ± 8
2,5-Dichlorotoluene	98 ± 8
2,3-Dichlorotoluene	94 ± 4
3,4-Dichlorotoluene	94 ± 13
α,α-Dichlorotoluene	nr
α,2-Dichlorotoluene	103 ± 11
α,3-Dichlorotoluene	102 ± 10
α,4-Dichlorotoluene	88 ± 9
2,4,5-Trichlorotoluene	100 ± 14
2,3,6-Trichlorotoluene	104 ± 4
α,α,α-Trichlorotoluene	93 ± 9
α,2,4-Trichlorotoluene	nc
α,2,6-Trichlorotoluene	89 ± 6
α,3,4-Trichlorotoluene	89 ± 8

Average of $n = 3$ (for monochlorotoluenes) and $n = 4$ determinations (for di- and trichlorotoluenes) at 1 μg/L level. nr, not recovered; nc, not calculated.

Table 2
Concentration levels (in μg/L) of chlorinated toluenes in effluents of wastewater treatment plants (A and B) and textile industries (TXT) (year 1999)

	WWTP-A	WWTP-B	TXT
2-CT	nd	5.21	15.3
4-CT	0.28	7.78	15.2
2,4 + 2,6-DCT	28	37	1171
2,5-DCT	20.4	10.9	968
2,3-DCT	9.32	79.5	1058
3,4-DCT	10.9	9.47	338
2,3,4-TCT	nd	2.10	43.3
2,4,5-TCT	0.34	6.34	108
2,3,6-TCT	0.34	9.94	139
Unidentified TCT	nd	0.50	22.3

nd < 0.10 μg/L.

As an example, the single ion chromatogram of chlorinated toluenes present in the effluent of a textile industry (TXT) is depicted in Fig. 1, where dichlorotoluenes represent 88% of the total halogenated toluenes measured, and trichlorotoluenes and monochlorotoluenes, 10% and 2%, respectively.

River water samples from the Llobregat river entering the WTP-1 and WTP-2 and their treated waters are monitored regularly. The data displayed (Table 3) only correspond to the period 2003–2004 and include the concentration range, mean values and frequency of appearance of chlorinated toluenes expressed in ng/L.

The results also show the presence of the same compounds in agreement with those identified in the effluents from the wastewater plants and textile industries. Monochlorinated and trichlorinated toluenes were also identified at concentration levels two orders of magnitude lower. No α-substituted chlorotoluenes were found in any sample.

The concentration levels in the raw water entering WTP-1 are higher than those found in WTP-2 as expected, due to its proximity to the textile industrial area. The average levels of dichlorinated toluenes were several hundreds of ng/L in 2003 and even higher during 2004, when they rose to several μg/L levels with a frequency of appearance of 82–91% of the samples analyzed. Monochlorinated toluenes and trichlorotoluenes median values were <13 ng/L and a frequency rang-

ing from 0% to 36% in these two years. Seasonal variations in concentrations followed the same trend both years with maximum levels monitored from October to March and low levels during summer, probably due to the different dyes and carriers used throughout the year for producing textiles adapted to the different fashion seasons. Fig. 2 shows as an example the presence of chlorinated toluenes in raw water entering the WTP-2.

Treated water from WTP-1 only shows the presence of dichlorinated toluenes at the low ng/L, being the values detected in 2004 significantly lower than those monitored in 2003. The frequency of appearance varies significantly from a range of 32–68% in 2003 to 10–60% in 2004. Taking into account the opposite trend found for raw water median levels, an appreciable improvement is achieved in the treatment process due to shorter regeneration periods of carbon filters.

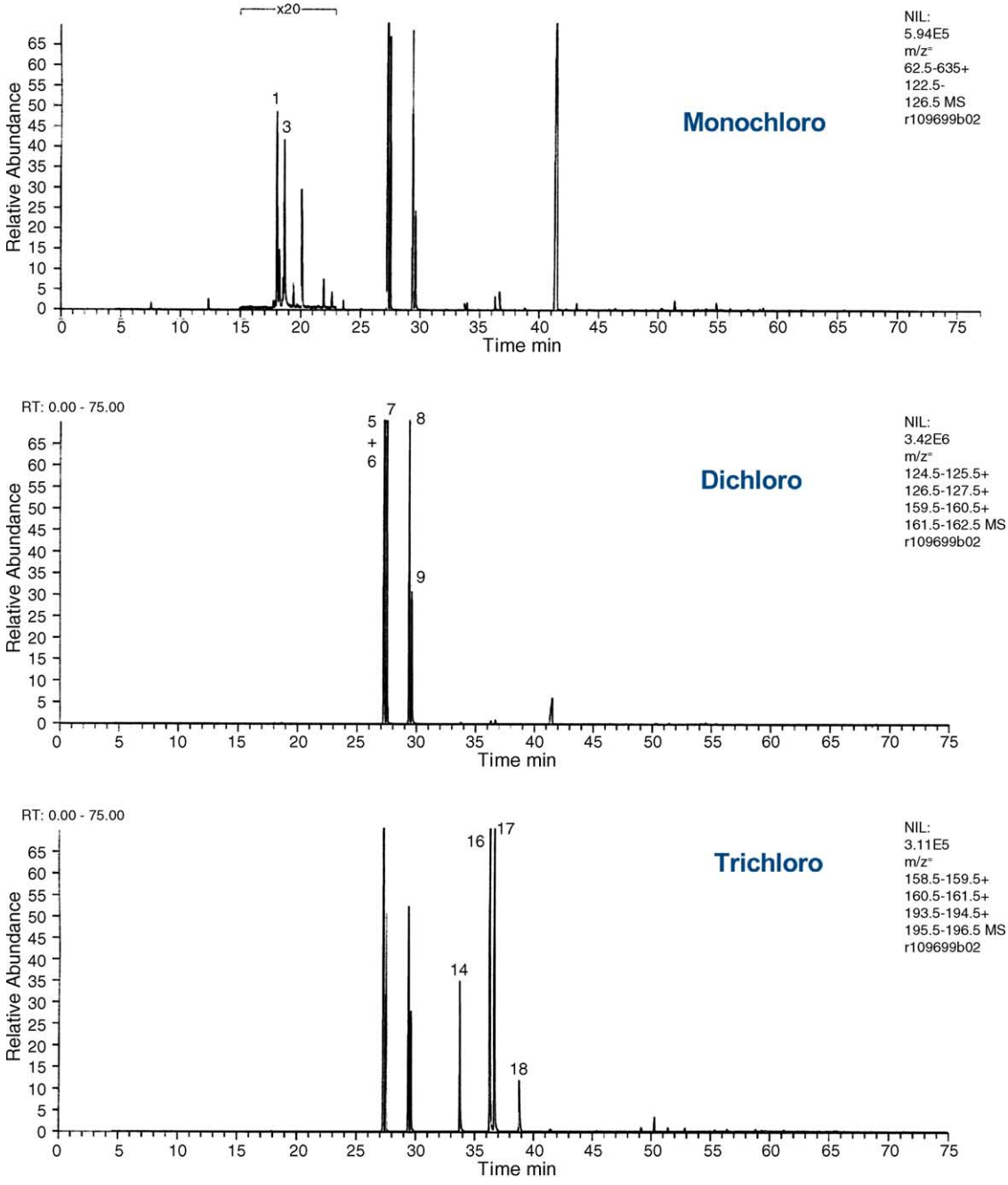

Fig. 1. GC–MS (SIM mode) chromatogram. Effluent from a textile industry. Peak identification: (**1**) 2-chlorotoluene; (**3**) 4-chlorotoluene; (**5** + **6**) 2,4 + 2,6-dichlorotoluene; (**7**) 2,5-dichlorotoluene; (**8**) 2,3-dichlorotoluene; (**9**) 3,4-dichlorotoluene; (**14**) 2,3,4-trichlorotoluene; (**16**) 2,4,5-trichlorotoluene; (**17**) 2,3,6-trichlorotoluene; (**18**) unidentified trichlorotoluene. TIC: total ion current.

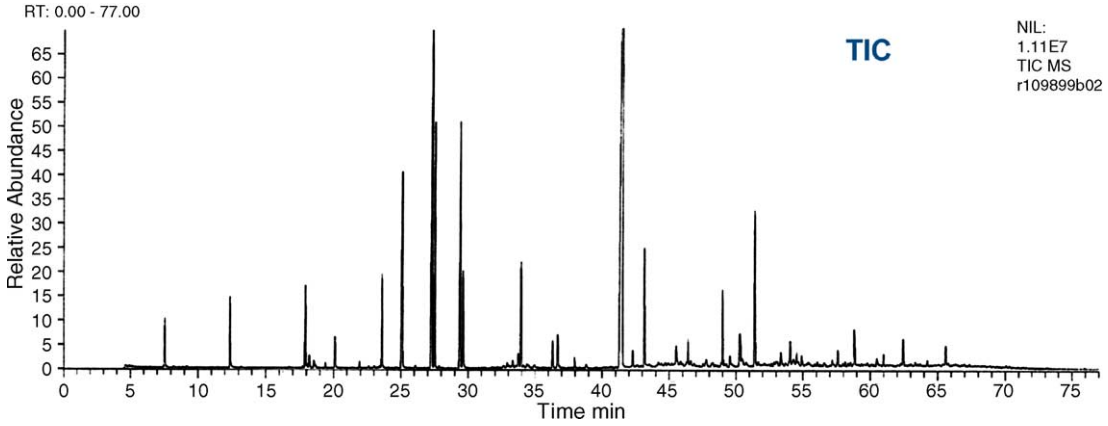

Fig. 1. (*Continued*).

Table 3
Concentration range, mean values and frequency of appearance of chlorinated toluenes in Llobregat river and treated water (in ng/L)

	2003			2004		
	Mean	Max to min	Frequency	Mean	Max to min	Frequency
WTP-1 raw						
2-CT	8	33 to <5	27	12	52 to <5	18
4-CT		<5		13	94 to <5	18
2,4 + 2,6-DCT	685	2865 to <5	82	1664	11341 to <5	91
2,5-DCT	390	819 to <5	82	703	2939 to <5	82
2,3-DCT	912	2125 to <5	91	1526	9967 to <5	91
3,4-DCT	630	3401 to <5	82	1610	12388 to <5	91
2,3,4-TCT		<5		tr	10 to <5	9
2,4,5-TCT	10	35 to <5	36	tr	11 to <5	9
2,3,6-TCT	12	64 to <5	18	tr	29 to <5	9
WTP-1 treated						
2-CT		<5			<5	
4-CT		<5			<5	
2,4 + 2,6-DCT	73	337 to <5	58	9	54 to <5	60
2,5-DCT	23	117 to <5	58	tr	16 to <5	10
2,3-DCT	100	391 to <5	68	22	52 to <5	40
3,4-DCT	65	366 to <5	32	6	23 to <5	60
2,3,4-TCT		<5			<5	
2,4,5-TCT	10	58 to <5	21		<5	
2,3,6-TCT		<5			<5	
WTP-2 raw						
2-CT		<5			<5	
4-CT		<5			<5	
2,4 + 2,6-DCT	27	157 to <5	43	35	243 to <5	45
2,5-DCT	27	149 to <5	61	20	135 to <5	35
2,3-DCT	56	309 to <5	73	39	254 to <5	49
3,4-DCT	21	118 to <5	53	32	241 to <5	49
2,3,4-TCT		<5			<5	
2,4,5-TCT		<5			<5	
2,3,6-TCT		<5			<5	
WTP-2 treated						
2-CT		<5			<5	
4-CT		<5			<5	
2,4 + 2,6-DCT	tr	9 to <5	12	tr	17 to <5	16
2,5-DCT		<5			<5	
2,3-DCT	tr	16 to <5	6	tr	17 to <5	16
3,4-DCT		<5			<5	
2,3,4-TCT		<5			<5	
2,4,5-TCT		<5			<5	
2,3,6-TCT		<5			<5	

Number of analyses: $n = 11$, for WTP-1 raw waters; $n = 10$ and 19, for WTP-1 treated, respectively; $n = 49$, for WTP-2 raw waters; and $n = 16$ and 19, for WTP-2-treated, respectively. tr, traces.

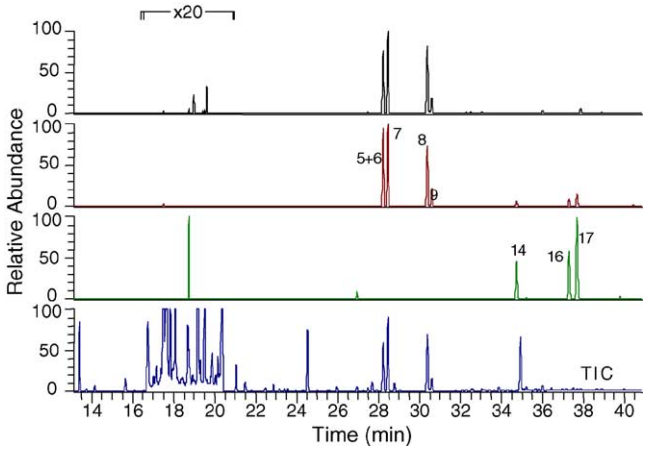

Fig. 2. GC–MS (SIM mode) chromatogram. Raw water entering water treatment plant WTP-2. Peak identification as in Fig. 1.

The only class compounds measured in the raw water entering the WTP-2 are the dichlorinated ones. Dilution along the river course explains the relative low levels measured with a range of 21–27 and 20–39 ng/L in 2003 and 2004, respectively, for all dichlorinated toluenes and frequencies of appearance from 43% to 73% and from 35% to 49%, respectively. Seasonal variations followed the same trend as observed for WTP-1 samples but the maximum levels were monitored from November to March. Only traces of 2,4 + 2,6- and 2,3-dichlorotoluenes were monitored in treated water from WTP-2 showing the effectiveness of the treatment process to eliminate these pollutants. The low concentration levels measured in both treated waters suggest that these compounds do not constitute an environmental risk, but lack of toxicity data is a major drawback to make an assessment of their impact on human health.

4. Conclusions

CLSA is a suitable method to determine chlorinated toluenes at trace levels. The presence of halogenated toluenes, mainly 2,4 + 2,6-; 2,5-; 2,3- and 2,4-dichlorotoluenes, and minor amounts of mono- and trichlorinated species at high ng/L levels in Llobregat river water is due to dumping of textile industries and inefficient elimination in wastewater treatment plants. The treatment processes applied by WTPs situated on the river bank allowed for the reduction of these compounds to trace levels in finished water.

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