

# Simultaneous determination of methyl *tert.*-butyl ether and its degradation products, other gasoline oxygenates and benzene, toluene, ethylbenzene and xylenes in Catalanian groundwater by purge-and-trap-gas chromatography–mass spectrometry

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## Abstract

In Catalonia (northeast Spain), a monitoring program was carried out to determine methyl *tert.*-butyl ether (MTBE), its main degradation products, *tert.*-butyl alcohol (TBA), *tert.*-butyl formate (TBF), and other gasoline additives, the oxygenate dialkyl ethers ethyl *tert.*-butyl ether, *tert.*-amyl methyl ether and diisopropyl ether and the aromatic compounds benzene, toluene, ethylbenzene and xylene (BTEX) in 21 groundwater wells that were located near different gasoline point sources (a gasoline spill and underground storage tank leakage). Purge-and-trap coupled to gas chromatography–mass spectrometry was optimised for the simultaneous determination of the above mentioned compounds and enabled to detect concentrations at ng/l or sub- $\mu\text{g/l}$  concentrations. Special attention was given to the determination of polar MTBE degradation products, TBA and TBF, since not much data on method performance and environmental levels are given on these compounds in groundwater. All samples analysed contained MTBE at levels between 0.3 and 70  $\mu\text{g/l}$ . Seven contaminated hot spots were identified with levels up to US Environmental Protection Agency drinking water advisory (20–40  $\mu\text{g/l}$ ) and a maximum concentration of 670  $\mu\text{g/l}$  (doubling the Danish suggested toxicity level of 350  $\mu\text{g/l}$ ). Samples with high levels of MTBE contained 0.1–60  $\mu\text{g/l}$  of TBA, indicating (but not proving) in situ degradation of parent compound. In all cases, BTEX was at low concentrations or not detected showing less solubility and persistence than MTBE. This fact confirms the suitability of MTBE as a tracer or indicator of long-term gasoline contamination than the historically used BTEX.

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## 1. Introduction

Fuel oxygenates are commonly added to gasoline to increase combustion efficiency and to reduce air pollution. In contrast to the USA, in Europe fuel

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oxygenates are generally used as octane enhancers to increase the oxygen level in gasoline for a cleaner combustion [1]. In particular, since the ban of tetraalkyl lead compounds, methyl *tert.*-butyl ether (MTBE) is by far the most commonly used octane enhancer and one of the organic chemicals with the highest production volume worldwide. Although MTBE is mainly used in the USA with 61% of total use, Europe is another large consumer with 15%. On the other hand, ethanol, the second most-added fuel oxygenate in the USA, is not (yet) widely used as a gasoline additive in Europe, while *tert.*-amyl methyl ether (TAME) and ethyl *tert.*-butyl ether (ETBE) are used in substantial amounts [1].

In European gasoline the average MTBE content is around 2% (v/v), though its use varies considerably between countries. In Spain, MTBE is used in different types of gasoline at levels between 2.8 and 4.3% in 95 unleaded and up to 6.9–10% in 98 unleaded gasoline [2]. In addition, Spanish petrol companies estimate an increase in MTBE content up to a maximum of 12.2% in 2005 due to the application of more restrictive European legislation on the aromatic content of gasolines [3]. MTBE is inevitably released to the environment during the manipulation or storage of petrol fuel and has become a groundwater pollutant due to its chemical and physical properties such as high solubility (25–50 g/l), low octanol–water partition coefficient ( $K_{ow}$ ) (0.94–1.43), Henry's law constant (55.3 Pa m<sup>3</sup>/mol), easy mobility (MTBE moves at about the same rate as groundwater) and limited degradation (practically recalcitrant under anaerobic conditions). Consequently, MTBE has been found to be one of the most frequent groundwater contaminants in recent years [1,4].

Besides health effects [5,6], toxicity [7,8], and carcinogenicity at high concentrations [9–12], there is much interest in the aesthetic implications of MTBE in drinking water. Taste and odour (TO) thresholds for this compound in water have been reported at very low concentrations, approximately 25–60 µg/l for flavour and 40–70 µg/l for odour at 25 °C [13], which is below other gasoline additive thresholds [14], such as ethanol (49 000 µg/l for odour) or benzene (500 µg/l for TO), but in the same order than other oxygenate ethers such as ETBE (13–47 µg/l) or TAME (27–128 µg/l) both for TO. For

this reason, the US Environmental Protection Agency (EPA) established a drinking water advisory for aesthetic concerns at 20–40 µg/l [15–17]. However, a Danish Environmental Protection Agency study resulted in lower TO limits (7 µg/l) than previously reported and thus may be used to justify lower threshold values in the future [18].

To date, there are no regulations for MTBE in water, air or soil in Europe and some countries are establishing their own guidelines. For example, in Denmark a concentration of 350 µg/l as a toxicity water level and 30 µg/l for odour control has been suggested [19] and a stricter Switzerland guideline value for groundwater of 2 µg/l based on precautionary principles (MTBE as a tracer for gasoline presence in water). At present European legislation lacks specific rules but this may change, since in a recent EU document, MTBE was considered one of the five priority substances where action should be taken. The risks associated with MTBE were pointed out and it was indicated that prevention of contamination of groundwater by MTBE should be a key objective of future European Union (EU) legislation [20].

Furthermore, whether the resulting contamination will become an important environmental issue depends, in part, on the rates and products of MTBE degradation. Although MTBE is generally described as a recalcitrant compound, there are some conditions under which the molecule can be degraded due to the presence of an oxidant (such as hydrogen peroxide) or highly active microbial communities [21]. The rates are generally slow, but the major products of its degradation are in all cases, *tert.*-butyl formate (TBF) by atmospheric photooxidation and *tert.*-butyl alcohol (TBA) in the aqueous phase, but this compound can also be found as a gasoline component. The presence of TBA in drinking water merits similar consideration than its parent compound due to its complete water solubility and demonstrated toxicity and carcinogenicity in rats and mice [22]. On the other hand, the accumulation of TBF in aqueous phase is not usually observed because it is readily hydrolysed to TBA [23]. Up to now, in a single analysis, these resulting compounds have not been easily detected or not with suitable sensitivity due to their higher polarity than the other gasoline components.

Overall, the present work had the following objectives: first, the development of a fully automated purge-and-trap-gas chromatography–mass spectrometry (PT-GC–MS) method that enables the detection of MTBE and its main degradation products TBA and TBF; other fuel additives such as oxygenate dialkyl ethers ETBE, TAME and diisopropyl ether (DIPE); and the aromatics benzene, toluene, ethylbenzene and xylene (BTEX), at ng/l or sub- $\mu\text{g/l}$  concentrations. Second, the study of parameters such as limit of detection (LOD), recoveries, repeatability, reproducibility and stability. Finally, the application of this method to the analysis of spiked and real groundwater samples.

The present work completes and expands, with more compounds and data, the previous and first study on the levels of MTBE and BTEX in Catalonian groundwater wells reported by the Catalan Water Agency [24]. This study also fills the gap indicated in a recent overview paper [1] that pointed out that no data on MTBE levels in the environment were available for southern and eastern European countries.

## 2. Experimental

### 2.1. Chemicals and reagents

Standards were made up from 2000 mg/l or neat stock solutions containing TAME, ETBE, DIPE and a mixture of BTEX and MTBE (Supelco, Bellefonte, PA, USA); TBA and TBF (Fluka, Bucks, Switzerland). Fluorobenzene (Supelco) and deuterated methyl *tert.*-butyl ether, [ $^2\text{H}_3$ ] MTBE (MTBE- $\text{d}_3$ ; Aldrich, Germany) were used as internal standards. The chemical structures of target compounds are given in Fig. 1. Each compound was obtained in the highest purity that was commercially available (98.3–99.7%) and used as received within 4 weeks. Working standard solutions (studied compounds and internal standards) were prepared in ultra pure methanol and added on organic-free water (Merck, Darmstadt, Germany).

### 2.2. Study sites

In Catalonia (northeast Spain), a monitoring pro-

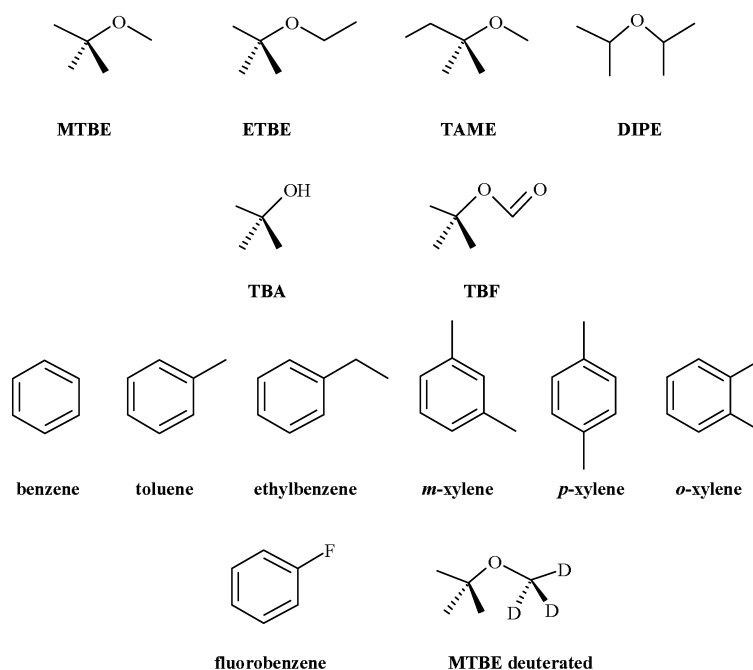


Fig. 1. Chemical structures of fuel oxygenates, MTBE degradation products, aromatic hydrocarbons and internal standards.



Fig. 2. Map of the studied areas.

gram was carried out to determine gasoline pollutants in 21 groundwater wells that are located near different gasoline point sources: (a) in a refinery industry with leaking storage tanks (Tarragona); and (b) close to a petrol service station (La Batlloria, St. Celoni) where there had been an accidental gasoline spill in 1997. These areas have been monitored since then and residue levels between 10 and 600  $\mu\text{g}/\text{l}$  are still being encountered. Sample points are shown in Fig. 2. The description of the MTBE contaminated sites is given in Table 1 based on Catalan Water Agency dates [24]. The groundwater samples were collected in the spring of 2001.

### 2.3. Sampling

Standard water sampling techniques for volatile organic compounds (VOCs) were used according to the EPA [25] except that samples were not preserved by acidification (to avoid hydrolysis of TBF) [23]. In fact, for MTBE analysis, samples do not have to be preserved as biodegradation is very slow [26]. Special precautions have to be taken in the VOC analysis to avoid losses and prevent contamination. Samples from different wells were collected in triplicate after water had run off the well for several minutes in order to eliminate the stagnant water. Amber glass vials (40 ml, EPA quality, Tekmar) with PTFE-faced silicone septa were filled, avoiding air bubbles

passing through the sample, until overflow to prevent volatilisation during sampling and storage. Immediately after, samples were placed inside a portable freezer and were transported to the laboratory where they were refrigerated at 4 °C and analysed in less than 2 weeks. These same vials were used for posterior analysis, so they were never opened during the process. Just before extraction, internal standards (MTBE- $\text{d}_3$  and fluorobenzene) were injected into the sample vials. If samples were suspected of being highly polluted, a diluted sample was analysed first to avoid contamination of the system.

Besides, all standard preparation (dilutions, spiking, etc.) was performed in a cold atmosphere to avoid losses of any of the considered compounds.

### 2.4. PT method

A commercial Tekmar 3100 purge-and-trap concentrator coupled to an Aquatek 70 liquid autosampler (Tekmar-Dohrmann, USA) was used, which automatically dispensed 15-ml aliquots into a 25-ml purging device. VOCs were purged from water samples for 13 min by administering helium at 35 ml/min and absorbed onto a Tenax<sup>®</sup> silica gel-charcoal trap (Supelco) at room temperature. After sample loading, the trapped sample components were desorbed at 225 °C for 4 min and transferred directly to the GC-MS system.

Table 1  
Description of MTBE contaminated sites

Town	Source of contamination	No. wells	Aquifer	Geology	Lithological characteristics	Piezometric level	Hydraulic parameters
Pobla de Mafumet – Constantí	Oil refinery storage tanks	5	Tarragona Plioquaternary	Plioquaternary	Detritus materials constituted by conglomerates, sands and clays Multilayer aquifer	7–10 m	$T=100\text{--}500\text{ m}^2/\text{day}$ $K=1\text{--}100\text{ m/day}^a$
La Pineda	Oil refinery storage tanks	6	Tarragona Depression	Plioquaternary	Detritus materials constituted by conglomerates, sands and clays Multilayer aquifer	8–11 m	$T=460\text{--}330\text{ m}^2/\text{day}$ $K=48\text{--}33\text{ m/day}^a$
St. Celoni (La Batlloria)	Accidental spill in a petrol service station	10	Tordera alluvial	Quaternary	Detritus materials constituted of gravels and slimes Free aquifer	2–3 m	$T=630\text{ m}^2/\text{day}$ $K=300\text{ m/day}$

<sup>a</sup> Lithological local variations result in significant differences in either transmissivity ( $T$ ) and/or permeability ( $K$ ) values among nearby points.

### 2.5. GC–MS conditions

A Trace GC system coupled to a Voyager MS instrument (ThermoQuest Finnigan, USA) was used. Extracts were transferred onto a 75 m×0.53 mm I.D. DB-624 (J&W Scientific, USA) fused-silica capillary column with a 3- $\mu$ m film thickness. The column was set at 35 °C (5 min) to 70 °C at a rate of 3 °C/min, oven temperature was held at 70 °C for 5 min and then increased again to 210 °C at 6 °C/min. This final temperature was maintained for 5 min and the total run time was 50 min. The injection was operated in splitless mode for 2 min and helium was used as the carrier gas, the first minute at 5 ml/min and afterwards it was decreased to 3.5 ml/min in 45 s. The mass spectrometer was operated in EI mode at 70 eV. The source temperature and GC interface temperature were kept at 200 and 270 °C, respectively. The emission current was 150  $\mu$ A and the detector voltage was set at 350 V.

The mass spectrometer acquisition was performed in full-scan from 35 to 250  $m/z$  to determine the characteristic ions and the retention times used for identification of selected analytes. Calibration, standards and samples were injected in time scheduled selected ion monitoring (SIM) mode as reported in Table 2 using three ions for each compound (except TBA). Due to the rather high energy transfer in the EI ionisation mode, fuel oxygenates do not yield

molecular ions. Instead, after  $\alpha$ -cleavage, (M-CH<sub>3</sub>)<sup>+</sup> or (M-CH<sub>5</sub>)<sup>+</sup> fragments were obtained as base peaks in the mass spectra.

Simultaneous to GC–MS acquisition, bake conditions were programmed at 230 °C during 10 min to clean the trap. Using these conditions, system blanks were attained.

### 2.6. Identification and quantitation

Peak detection and integration were carried out using the XCalibur software (version 1.2, GC–MS).

External standard quantitation was used to calculate recoveries and LODs. Quantitation of samples was performed by internal standard procedures. The calibration equations were obtained by analysing organic-free water samples spiked with target compounds in the range 0.02–10  $\mu$ g/l (first sampling in Tarragona only to 3  $\mu$ g/l) and internal standards MTBE-d<sub>3</sub> and fluorobenzene at a constant concentration of 0.5  $\mu$ g/l. Linear regression of base peak area versus concentration (calculated relative to the nearest internal standard using  $m/z$  76 for MTBE-d<sub>3</sub> and  $m/z$  96 for fluorobenzene) gave a good fit (typically,  $R^2 > 0.990$ ) for all compounds. Exceeding the linear range concentration, the system can suffer from memory effects and poor linearity, and therefore, highly polluted samples should be diluted prior to analysis.

Table 2

GC-MS in time scheduled Selected Ion Monitoring (SIM) acquisition program: Retention time window, retention time (Rt), molecular weight (MW), quantitation and confirming ions

Retention window (min)	Rt (min)	Compound	MW ( $m/z$ )	Selected ions ( $m/z$ )		
				Quantitation	Secondary	Tertiary
8.00–17.80	11.90	TBA	74	59		
	12.23	MTBE-d <sub>3</sub> *	91	76	57	43
	12.31	MTBE	88	73	57	43
	14.00	DIPE	102	45	87	59
	15.23	ETBE	102	59	87	57
	16.89	TBF	102	59	56	57
17.80–23.00	18.70	benzene	78	78	77	52
	19.25	TAME	102	73	55	87
	19.83	fluorobenzene*	96	96	70	50
23.00–45.00	26.94	toluene	92	91	92	65
	32.01	ethylbenzene	106	91	106	77
	32.40	<i>m</i> + <i>p</i> -xylene	106	91	106	77
	33.58	<i>o</i> -xylene	106	91	106	77

\*Internal Standards

### 3. Results and discussion

#### 3.1. Method performance

From EPA method 524.2 (purgeable organic compounds by PT technique), optimisation of purge and desorption times were performed by the simplex [27] statistical method. Varying the purge time from 10 to 14 min and desorption time from 3 to 5 min the MTBE area response was maximum at 13 and 4 min, respectively. These conditions showed the first or second highest area for the rest of the compounds. Typical chromatograms of standard at 10  $\mu\text{g/l}$  and an example of a real groundwater sample are shown in Fig. 3.

The LODs of selected compounds in organic-free water were calculated by a signal-to-noise ratio of 3. The LODs obtained were from 0.001 to 0.1  $\mu\text{g/l}$  lower than using other techniques [28,29]. Thus, it is clear that automated PT-GC-MS is suitable for simultaneous trace determination of all target compounds that permit an environmental survey of both parent and degradation products.

Repeatability (as relative standard deviation (RSD) for four consecutive replicates in the same day) and reproducibility (as RSD for 15 analysed replicates over a period of 5 days) were evaluated by spiking organic-free water and groundwater at a concentration of 1  $\mu\text{g/l}$ . Also, the mean accuracy or recovery and the standard deviation were calculated for three replicates. All these parameters are reported in Table 3. Satisfactory recoveries were provided in both matrices, except for TBF in organic-free water. Repeatability was below 8% and lower results were found for groundwater. For most of the compounds, there were no significant differences between reproducibility values in the two matrices (from 7 to 23%), but MTBE and TBA gave better results in spiked groundwater samples.

Going back to TBF, a particular behaviour was observed during quality parameter experiments, which must be taken into consideration. After simultaneous replicates preparation, TBF response decreased during the analysis period of time between consecutive HPLC water-spiked samples whereas it was constant for groundwater. This practically exponential reduction of signal in organic-free water (half-life time of 2.26 h, see Fig. 4) might be explained due to its lower pH (pH 6–6.5) and buffer

capacity than groundwater (pH 8.85), which enhances the TBF degradation. Therefore, the pH of organic-free water should be measured or a better option is to perform calibration curves using a similar matrix than the sample, in this case, groundwater. Additionally, each analytical sequence included quality control standards and blanks to check noise and background levels, possible carryover effects and to cover little retention time variations.

In fact, in a previous study in collaboration with the Catalan Water Agency, PT-GC-MS was compared with headspace gas chromatography with flame ionization detection (HS-GC-FID) for the determination of MTBE and BTEX in these same groundwater samples. In general, satisfactory results were obtained, especially for high concentration levels, where a good correlation between both methods was achieved. However, care should be taken in the sampling procedure to avoid samples with double phases [28].

#### 3.2. Application and levels

The optimised method was applied to the analysis of a total of 21 groundwater samples from Catalonia. Target compounds were unequivocally identified by matching retention times and mass spectrums in SIM mode. Table 4 reports the concentration of studied gasoline additives in the different monitored sites.

MTBE was detected in all monitored wells at concentrations that mainly varied between 0.3 and 70  $\mu\text{g/l}$ , but one site had a level of 670  $\mu\text{g/l}$  exceeding/doubling the Danish suggested toxicity level for groundwater. In contrast, as it was expected due to their minor use in gasoline composition, the other oxygenate additives were always found at lower concentrations, for instance ETBE and DIPE were detected below 1 and 2  $\mu\text{g/l}$ , respectively, and TAME was not detected in any of the samples. BTEX levels were in many cases between 0.02 and 10  $\mu\text{g/l}$ , whereas a couple of samples showed high concentrations, up to 500  $\mu\text{g/l}$  due to the probable presence of a double phase (gasoline or gas-oil) in the water sample vial. On the other hand, TBF was never detected, whereas TBA levels varied from 0.1 to 10  $\mu\text{g/l}$ , its concentration reached a value of 62  $\mu\text{g/l}$  in the most MTBE contaminated well. It must be taken into consideration that TBF can be hydrolysed to TBA in aqueous phase. Anyway,

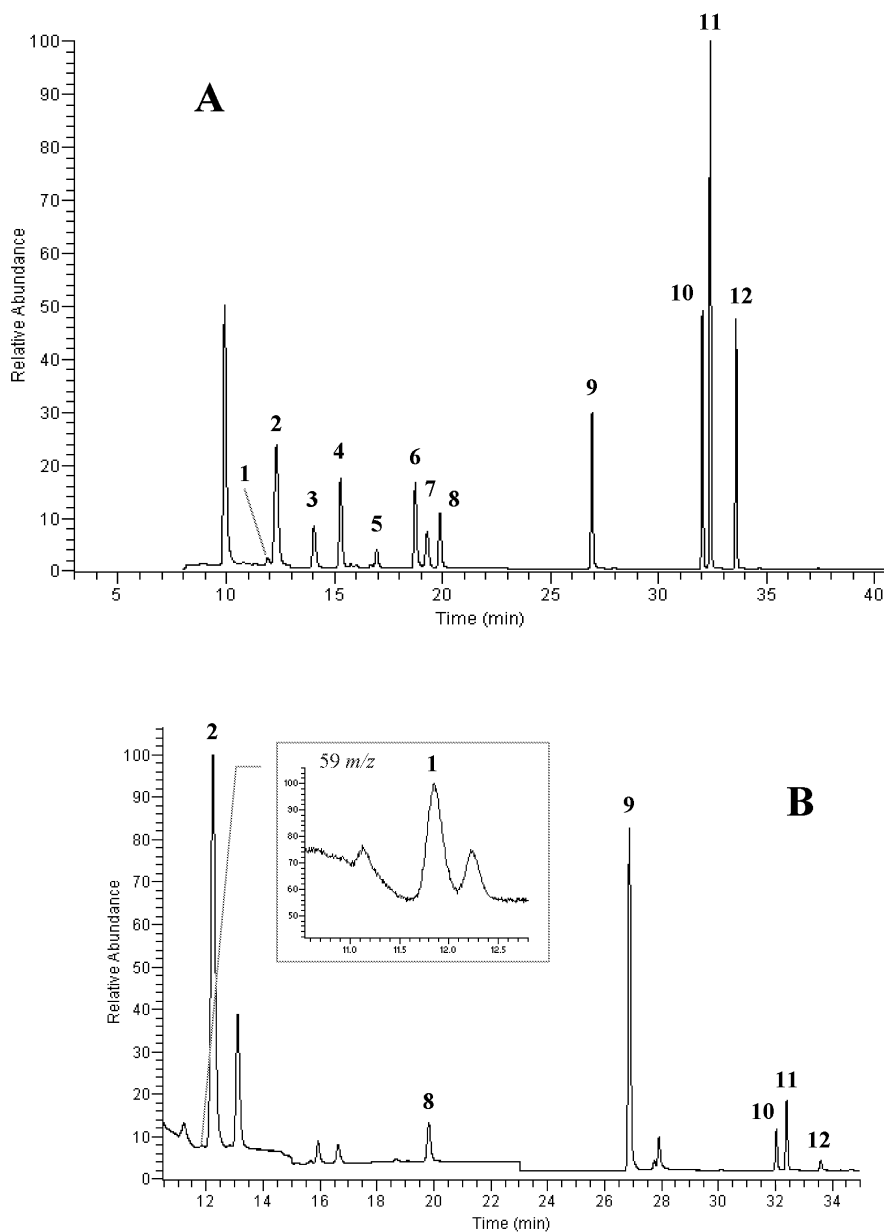


Fig. 3. Total ion chromatogram (TIC,  $10^8$ ) in SIM mode for a (A) 10 µg/l standard and (B) detail of groundwater sample. Compound identification number: 1=TBA, 2=MTBE- $d_3$ +MTBE, 3=DIPE, 4=ETBE, 5=TBF, 6=benzene, 7=TAME, 8=fluorobenzene, 9=toluene, 10=ethylbenzene, 11=*m*+*p*-xylene and 12=*o*-xylene.

although the presence of TBA in groundwater could indicate (but not still prove due to its presence in gasoline) in situ degradation of parent compound, the TBA/MTBE ratio was in all cases below unity, indicating that contamination is still recent in the

study sites in terms of MTBE persistence, thus 5 years is not enough for its degradation.

Two different contamination sources were involved. First was a leakage from underground storage corroded tanks in two large oil refinery factories



Table 3

Quality parameters obtained by PT-GC–MS in SIM mode: limits of detection (LOD), repeatability, reproducibility and recoveries obtained in organic-free water (HPLC) and groundwater

Compound	LOD HPLC water ( $\mu\text{g}/\text{l}$ )	Repeatability ( $n=4$ )		Reproducibility ( $n=15$ )		Recoveries $\pm$ SD ( $n=3$ )	
		HPLC water RSD (%)	Groundwater RSD (%)	HPLC water RSD (%)	Groundwater RSD (%)	HPLC water (%)	Groundwater (%)
TBA	0.110	6.73	5.50	22.70	15.65	98 $\pm$ 5	103 $\pm$ 7
MTBE	0.001	7.29	2.13	18.27	10.27	101 $\pm$ 4	101 $\pm$ 6
DIPE	0.008	5.81	2.96	8.54	9.40	100 $\pm$ 3	98 $\pm$ 4
ETBE	0.009	7.75	2.49	11.71	14.79	99 $\pm$ 3	102 $\pm$ 5
TBF	0.034	56.59 <sup>a</sup>	5.22	77.16 <sup>a</sup>	13.78	55 $\pm$ 19 <sup>a</sup>	104 $\pm$ 7
Benzene	0.002	6.32	3.74	8.66	7.61	99 $\pm$ 3	99 $\pm$ 5
TAME	0.013	7.41	1.22	13.30	13.56	103 $\pm$ 4	106 $\pm$ 5
Toluene	0.001	5.56	3.44	7.47	7.15	99 $\pm$ 2	97 $\pm$ 4
Ethylbenzene	0.001	7.28	3.62	8.81	8.21	98 $\pm$ 2	95 $\pm$ 6
<i>m</i> + <i>p</i> -Xylene	0.001	7.08	2.62	8.66	7.58	99 $\pm$ 2	95 $\pm$ 6
<i>o</i> -Xylene	0.002	6.47	2.89	9.04	6.79	99 $\pm$ 2	96 $\pm$ 6

<sup>a</sup> TBF behaviour in HPLC water is described in Fig. 4.

in Tarragona. Supposedly, the gasoline losses might be small but continuous, showing the highest levels of MTBE and the rest of the target compounds in the area closer to the petrochemical industry. A previous study showed that the maximum detected level of MTBE was 340  $\mu\text{g}/\text{l}$  in 1998 [24] whereas the actual level was 670  $\mu\text{g}/\text{l}$ , so it can be supposed that MTBE accumulates due to its physicochemical properties, environmental conditions and is enhanced by a permanent leakage. This event has special importance because MTBE plume arrives to domestic zones as campsites and villages near the Tarragona coast (see Fig. 5 with MTBE concentrations and

hypothetical movement of the plume in each study site map). In addition, other oxygenate additives were found at low concentrations, from 0.13 to 0.68  $\mu\text{g}/\text{l}$  and from 0.20 to 1.53  $\mu\text{g}/\text{l}$  of ETBE and DIPE, respectively. Up till now, no environmental levels of these compounds were available in the literature and neither their use or percentage in gasoline composition. However, in France, Italy and Spain, the consumption of ETBE will probably increase even more rapidly than the use of MTBE due to tax incentives for the use of ethanol, which is used to produce this compound [1]. It is important to mention that ETBE, TAME and DIPE could be possible

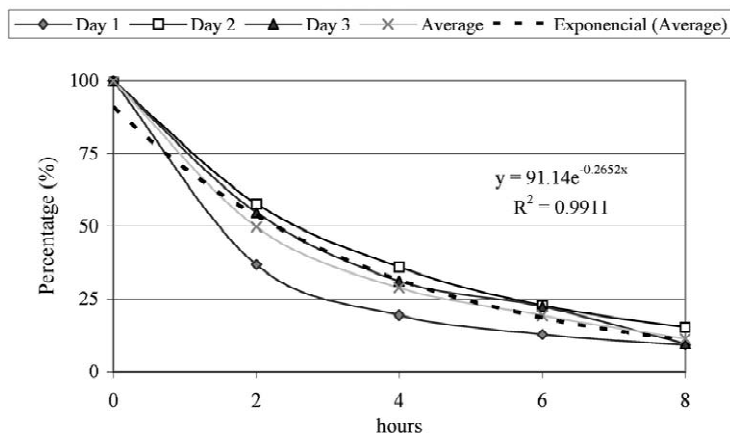


Fig. 4. TBF decreasing curves in organic-free water (HPLC).

Table 4  
Concentrations of gasoline additives ( $\mu\text{g}/\text{l}$ ) in monitored groundwater wells in Catalonia

Sample id.	TBA	ETBE	TBF	MTBE	TAME	DIPE	Benzene	Toluene	Ethylbenzene	<i>m+p</i> -Xylene	<i>o</i> -Xylene
<i>Tarragona (pobla Mafumet, Constanti)</i>											
Sorts	62.23	nd	nd	666.27	nd	1.08	5.88	3103.09	25.94	24.05	5.47
Ferrerota	bld	0.21	bld	74.48	nd	0.78	4.60	30.31	7.76	4.43	2.77
Tarragonins	bld	0.14	bld	5.62	nd	0.20	1.74	8.30	2.18	1.59	1.08
Repsol-73	bld	0.24	bld	10.13	nd	0.36	1.53	9.52	3.25	2.15	1.58
Repsol-83	bld	0.24	bld	8.23	nd	0.43	1.84	11.08	3.60	2.24	1.57
<i>Tarragona (La Pineda)</i>											
Sevil-caseta	bld	0.15	bld	8.50	nd	0.61	1.47	8.89	2.53	1.76	1.30
Sevil-road	bld	0.53	bld	28.02	nd	1.16	1491.56	1351.61	312.02	508.52	454.91
Sevil-sinia	bld	0.17	nd	11.26	nd	0.85	1.59	10.18	3.15	2.10	1.58
Gate-well	bld	0.13	bld	20.66	nd	1.02	1.71	9.05	2.55	1.79	1.28
Pineda-2	18.08	0.68	bld	42.66	nd	0.76	8.75	269.39	36.07	31.23	43.12
Camping	bld	0.35	bld	10.53	nd	1.53	1.96	9.88	2.74	2.02	1.34
<i>St. Celoni (La Batlloria)</i>											
Formigueta	0.10	nd	nd	0.28	nd	nd	nd	0.03	bld	bld	bld
Comptesa	8.86	nd	nd	48.09	nd	nd	nd	0.13	0.04	bld	bld
Ferreria 1	1.51	nd	nd	13.81	nd	nd	0.02	0.37	bld	bld	bld
Ferreria 2	8.42	nd	bld	32.28	nd	nd	nd	1.43	bld	bld	bld
Ferreira 3	0.54	nd	nd	2.37	nd	nd	bld	0.05	bld	bld	bld
Xemani	1.23	nd	nd	8.97	nd	0.03	0.09	0.14	0.06	bld	bld
Xemani 2	0.23	nd	nd	bld	nd	nd	nd	0.07	bld	bld	bld
Auladell	0.16	nd	nd	0.62	nd	nd	nd	bld	bld	bld	bld
Viñas	3.06	nd	nd	17.97	nd	nd	0.02	bld	nd	nd	nd
Blancher	bld	nd	nd	1.36	nd	nd	nd	0.09	nd	nd	nd

bld, below limit of detection of each compound, see Table 3. nd, not detected.

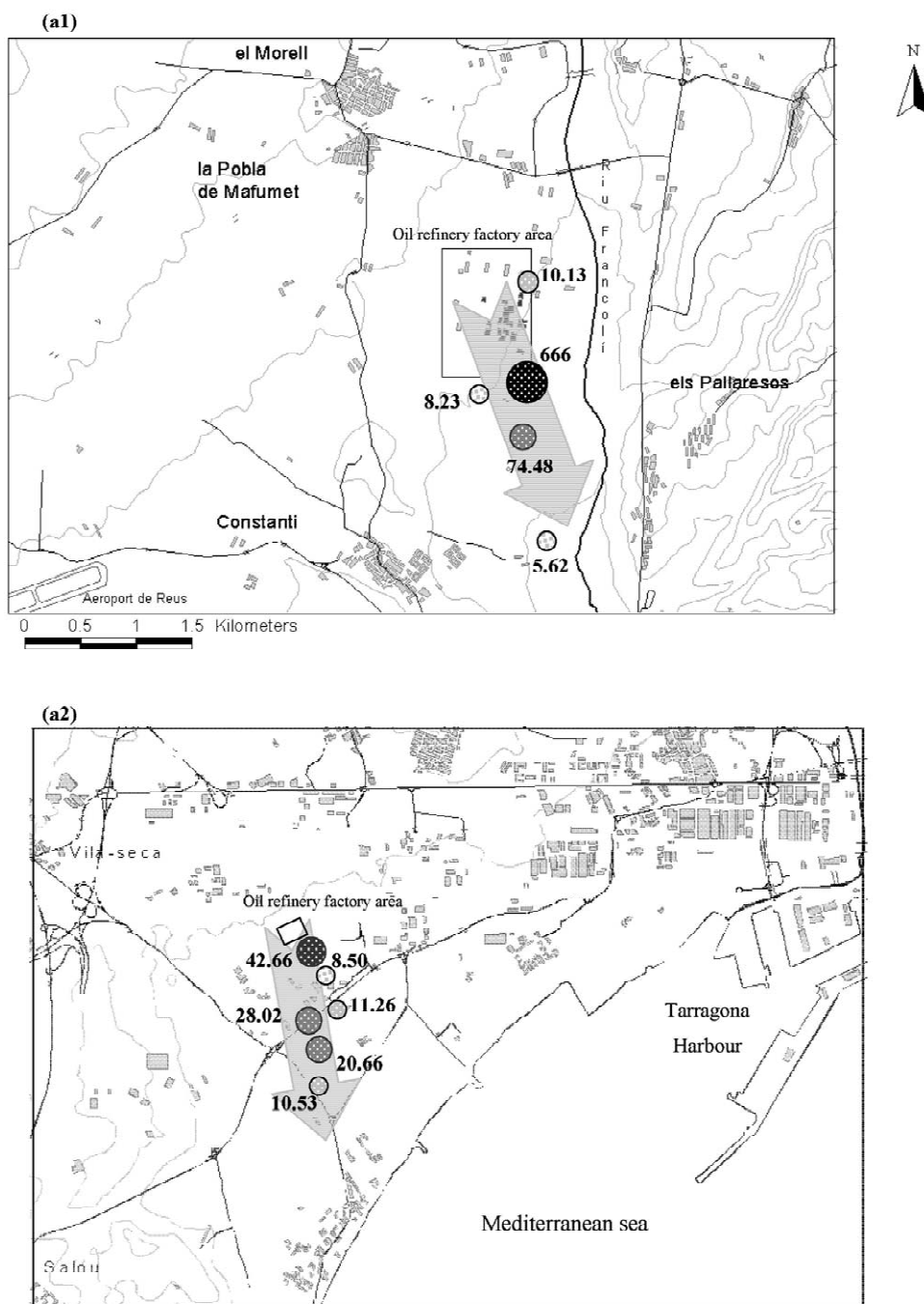


Fig. 5. Maps with MTBE concentrations detected (expressed in  $\mu\text{g}/\text{l}$ ) in the studied wells and hypothetical movement of the plume. Two sites in Tarragona: (a1) Poble Mafumet–Constantí; (a2) La Pineda and (b) La Batlloria (Sant Celoni, Girona).

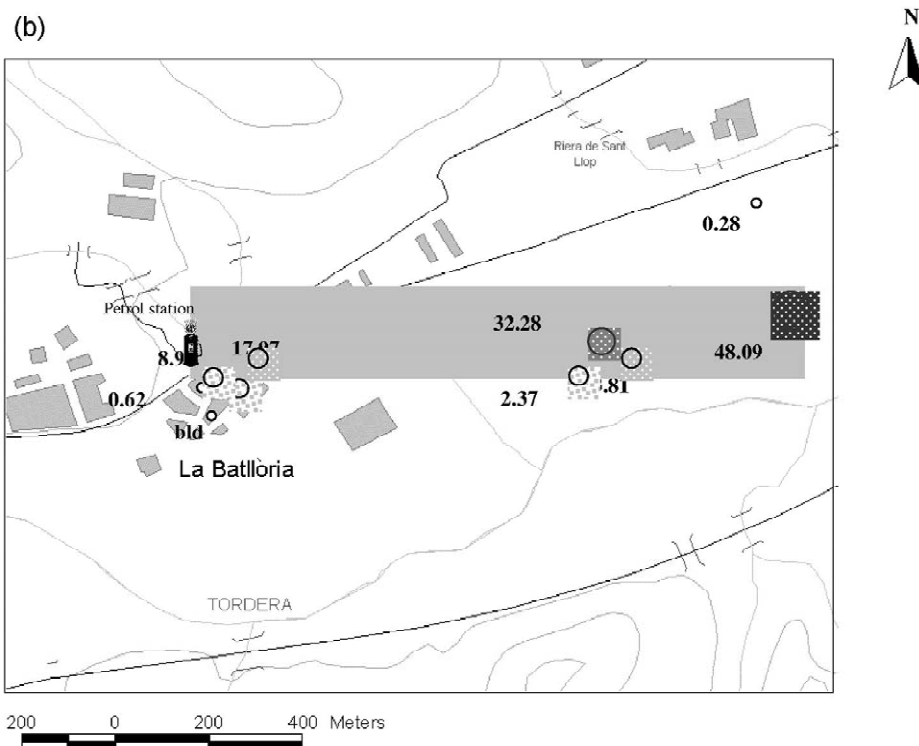


Fig. 5. (continued)

MTBE substitutes due to their higher removal rates from contaminated waters. These compounds have higher Henry's law constants than MTBE (approx. 3–20 times higher), indicating that air stripping would be at least slightly more effective for them. In addition, DIPE can be more easily destroyed by hydroxyl radicals [30].

The second studied contamination episode was a punctual spill from a petrol station that occurred 4 years before the sampling. The service station is situated in the middle of a town so the accidental spill affected the neighbours' private wells. Levels up to 1860 and 830  $\mu\text{g}/\text{l}$  for MTBE and BTEX, respectively, were reported in 1999 [24]. Two years later, the present results still showed traces of MTBE but the highest concentration was found in the most distant monitored well (around 1.2 km from the source) with 48  $\mu\text{g}/\text{l}$ . In addition, although the data are limited and more studies will be needed, it seems that MTBE plume in groundwater is very narrow in the east direction between a stream and the Tordera

river (Fig. 5c). TBA was detected in nine of the 10 wells analysed at concentrations between 0.1 and 8.8  $\mu\text{g}/\text{l}$ . These values correspond to 4 years after the spill, and higher values correspond to the sites where MTBE was found at highest concentrations. The ratios between TBA and MTBE in all sampling points are again below unity (from 0.11 to a maximum of 0.35) indicating partial degradation of the parental compound throughout the plume. In contrast, BTEX compounds were not detected, or were below their detection limits. This is attributed to the higher solubility and longer persistence of MTBE in groundwater than BTEX compounds, which degrades faster. This fact confirms the suitability of MTBE as a tracer or indicator of long-term gasoline contamination than the historically used BTEX.

To summarise, seven of the 21 monitored wells (33% of total) presented a level above 20  $\mu\text{g}/\text{l}$ , the EPA drinking water advisory, so taste and odour problems can be found. For this reason, they were identified as "hot spots" for which a monitoring

program should be required, especially when some of this groundwater needs to be used as domestic water. Moreover, taking into account stricter measures, as Swiss guideline value for groundwater of 2 µg/l or primary and secondary action levels of the state of California, which were fixed at 13 and 5 µg/l, respectively, other wells might be considered as contaminated sites.

In 2000, a comprehensive review with maximum detected levels of MTBE in European groundwater was published by Schmidt [1]. Taking into account that concentrations varied from 120 µg/l in the Netherlands up to 830 mg/l in the UK, the values reported in Catalonia are also within European ranges.

#### 4. Conclusions

A method based on automated purge-and-trap coupled to gas chromatography with mass spectrometric detection was developed to determine MTBE, its main degradation products, BTEX and other gasoline oxygenates. Method detection limits were at the 0.01 µg/l level and a good stability was observed for all compounds except TBF, which degraded in spiked organic-free water. The method developed involves no sample manipulation since samples are collected in 40-ml vials, which are introduced in the sampler unit and losses of volatile compounds are therefore minimised. Automation permitted a high sample throughput with good reproducibility provided groundwater was used. The method was applied to monitor groundwater samples in two sites characterised by a tank leakage and a gasoline spill. In each site, 10–11 wells were monitored and corresponded to the downward movement of the aquifer. Four years after the spills MTBE levels were up to 666 µg/l and TBA, its main degradation product, was found in all sampled wells at levels of 0.1–62 µg/l. DIPE was detected for the first time in groundwater samples at levels of 0.03–1.5 µg/l whereas BTEX were only detected in the tank leakage area. For the levels recorded, it was observed that MTBE moved with the groundwater since highest concentrations were found in the wells situated furthest from the source of pollution. The ratio between TBA and MTBE was always below

unity, indicating that degradation of MTBE is slow and 5 years is not enough to complete elimination. Thus, MTBE can be considered a good indicator of gasoline contamination due to its stability in groundwater.

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