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Vigilància ambiental de metil *tert*-butil èter (MTBE), un additiu de la gasolina, en aigües i sòls

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2 METODOLOGIA I APLICACIÓ DE P&T-GC/MS PER A L'ANÀLISI D'AIGÜES

2.1 INTRODUCCIÓ

2.1.1 Compostos d'estudi

Segons els objectius inicials del projecte WATCH els compostos objecte d'estudi eren el MTBE, el ETBE i els BTEX ; tot i això, va semblar interessant mirar també els altres èters emprats com a additius oxigenats a la gasolina (TAME i DIPE), així com els principals compostos de degradació d'aquests èters: TBA, TBF i TAA. Els patrons interns (PI) seleccionats van ser el MTBE deuterat (MTBE-d_3) i el fluorbenzè. El primer va ser escollit per la seva especificitat amb el compost d'estudi principal i el fluorbenzè per ser el PI més recomanat (i emprat) per la determinació de barreges de VOCs segons el mètode 524.2 de la USEPA [111].

Més tard, es van incorporar altres compostos a l'estudi: el diciclopentadiè (DCPD), additiu minoritari de la gasolina [112], però que s'havia observat podia produir episodis de males olors a les aigües a concentracions realment baixes (0,01-0,025 μg/L) [56] i que era tant o més recalcitrant que el MTBE [113], per la qual cosa, en cas de trobar-se podria actuar com un nou rastrejador de contaminació per gasolina [112]. I el tricloretilè (TCE) solvent organoclorat d'ús industrial emprat des dels anys 20 als EEUU, també com a desengreixant de metalls a la producció d'automòbils i un dels VOCs més usualment detectat al medi ambient, tant en aire [114] com en aigües superficials [115] i subterrànies [116]. Per tant, es va creure convenient afegir un altre PI, tenint-ne així un per finestra cromatogràfica, i aquest va ser el 1,2-diclorbenzè deuterat (-d_4) que també està recomanat per l'EPA i es troba comercialment en una barreja amb el fluorbenzè, fent-ne més còmode la seva manipulació conjunta. Les estructures de tots aquests compostos es mostren a la *Figura 8*.

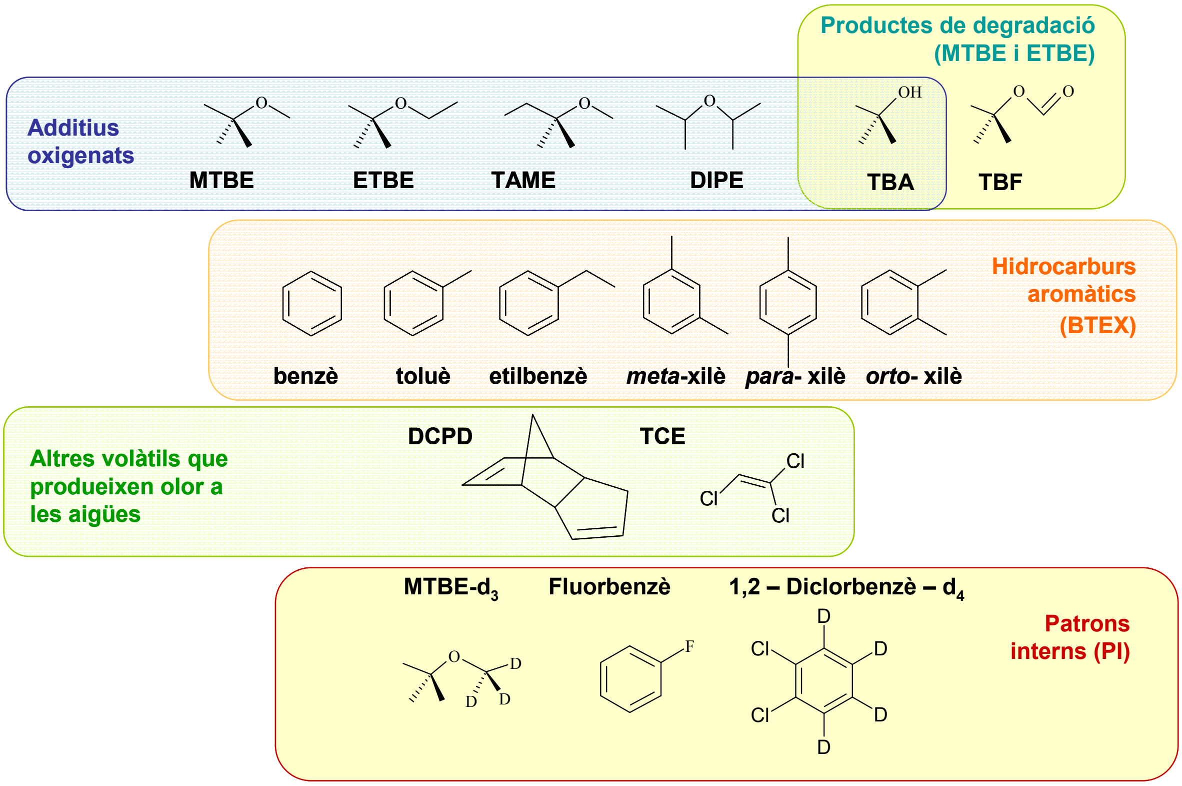

Figura 8.- Estructures dels compostos d'estudi i els patrons interns emprats

2.1.2 La tècnica de Purga i Trampa (o Purga i Captura) - P&T

Recordem que tant el MTBE com la resta d'analits d'aquest estudi són considerats VOCs. Degut precisament a la seva volatilitat, l'extracció d'aquests compostos des de les mostres aquoses a través d'un dissolvent orgànic no és gaire convenient. És per això que la millor manera d'extreure VOCs presents a les aigües a nivells traça o concentracions baixes (ppt – ppb) és portar-los en fase gas fins a un adsorbent sòlid, des d'on seran desorbits per un escalfament ràpid i transferits a un sistema analític (normalment GC o GC-MS) o bé extrets per un dissolvent [117].

Com s'ha vist en el capítol anterior i l'**Art. 1**, pel MTBE i la resta d'analits els mètodes tradicionalment més emprats han estat: HS, P&T, CLSA, deixant enrera els mètodes d'extracció líquid-líquid o de destil·lació. En els últims anys, però, s'han desenvolupat enormement altres tècniques com la injecció aquosa directa (DAI) [37,118] o la SPME [101,119-123]. A la *Taula 7* es mostra a grans trets la comparació entre aquestes tècniques per l'anàlisi d'additius oxigenats, tal i com es troba a l'article de revisió de Schmidt et al. [124]

Taula 7.-Comparació general de tècniques d'injecció o preconcentració per a l'anàlisi de compostos oxigenats en aigües

Tècnica	***P&T***	***HS***	***DAI***	***HS-SPME***	***SPME***
Volum (mL)	5 - 40	5 - 20	0.001 – 0.1	5 - 20	1.5 - 5
Sensibilitat[a] (alcohol/èter)	- /++	--/-	+/+	0/+	+/++
Criteri selectivitat	'purgables'	Constant de Henry elevada	Elució abans H_2O (columna polar)	Constant de Henry mitjana-alta (adsorció al polímer)	Adsorció al polímer
Efectes matriu	Possible contaminació del sistema a elevades concentracions "efecte memòria"	Qualsevol matriu. Addició de sals per compensar dif. matrius	No volàtils o medis agressius poden contaminar la columna	Qualsevol matriu. Addició de sals per compensar dif. matrius	Addició de sals per compensar dif. matrius Vida fibra limitada
Temps requerit (min.)	30	60	0	60	60
Cost[b] (automatitzat/no)	-/--	++/0	++/0	+/-	+/-

Símbols a/b: (++) molt bona/ barat, (+) bona/ no molt car, (0) justa, (-) pobra/ car, (--) molt pobra/ molt car

A la present tesi s'ha desenvolupat una metodologia analítica basada en la utilització de la tècnica d'extracció o preconcentració anomenada P&T, que va ser desenvolupada originàriament per Bellar i Lichtenburg al 1974 [125], i és aplicable, en general, a compostos relativament no polars, de baix pes molecular i baixa solubilitat en aigua [90]. Tot i que una Hc elevada seria desitjable, l'eficient preconcentració d'aquesta tècnica també permet l'anàlisi de compostos amb relativament baixa Hc, com el MTBE.

Bàsicament, els compostos volàtils són purgats o arrossegats directament de la matriu aquosa mitjançant un corrent de gas inert (heli) que passa a través de la mostra en un recipient de vidre amb espai de cap o sistema obert. Una placa porosa o fritat situat a la base de la mostra afavoreix un bombolleig homogeni. Els components purgats passen en fase gas a un adsorbent sòlid o trampa on queden retinguts i posteriorment, un cop finalitzada la purga, són desorbits tèrmicament (a uns 200-250ºC) i transferits amb heli directament a la columna capil·lar del GC-MS. Un esquema del procés es presenta a la *Figura 9*.

Generalment, l'eficiència de la purga depèn del temps i dels coeficients de partició dels compostos, mentre que l'eficiència de l'adsorció depèn de les característiques de l'adsorbent i de la dels compostos que han de ser adsorbits [117]. És per això, que els tubs o **trampes** per aquest tipus d'anàlisi estan fets generalment amb múltiples materials adsorbents, per a que capturin una gran varietat de compostos polars i no polars, amb baix o alt pes molecular en un sol tub. Al seleccionar sorbents, el més important és la capacitat dels materials per atrapar i alliberar eficientment els compostos d'interès, per tal d'assolir una elevada recuperació i bona resolució, que permetrà llur quantificació de forma precisa. A la *Figura 10* es mostra un ampli ventall de trampes amb diferents combinacions d'adsorbents que es poden trobar al mercat, i de les quals, la "C", de Tenax, gel de sílice i carbó actiu és la que s'ha emprat a la present tesi.

Els principals avantatges i inconvenients d'aquesta tècnica analítica es presenten a la *Taula 8*. Amb tot, el P&T ha estat recomanat com a mètode estandaritzat pel control de VOCs per les principals organitzacions americanes com ho mostren el mètode 524.2 de l'EPA [111] o els mètodes del *US Geological Survey* (USGS) junt amb el Laboratori Nacional sobre Qualitat de l'Aigua (NWQL) [126-128] aplicats a nombrosos estudis de control ambiental [6,31,95,129].

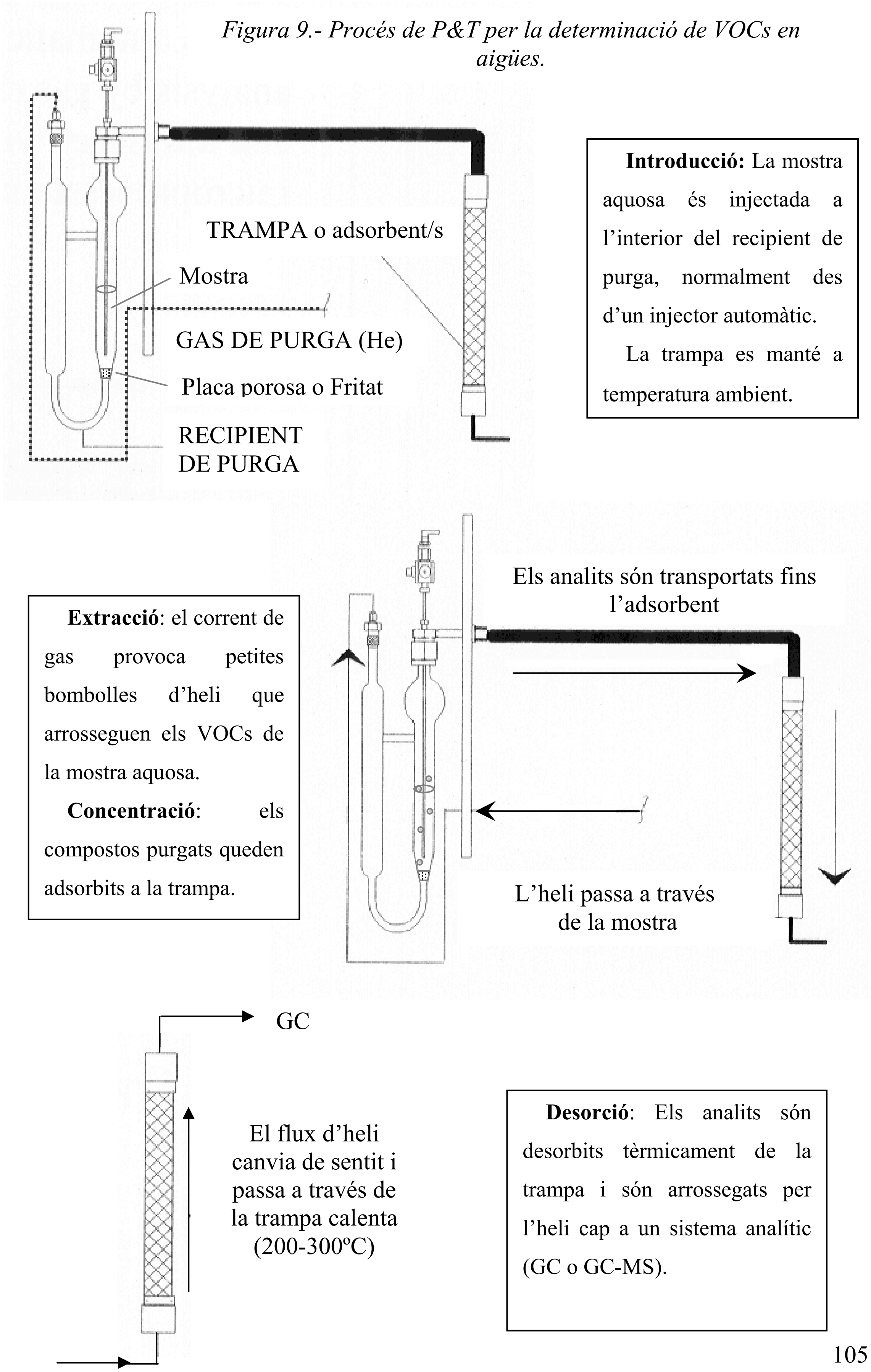

Figura 9.- Procés de P&T per la determinació de VOCs en aigües.

Introducció: La mostra aquosa és injectada a l'interior del recipient de purga, normalment des d'un injector automàtic.

La trampa es manté a temperatura ambient.

Extracció: el corrent de gas provoca petites bombolles d'heli que arrosseguen els VOCs de la mostra aquosa.

Concentració: els compostos purgats queden adsorbits a la trampa.

Desorció: Els analits són desorbits tèrmicament de la trampa i són arrossegats per l'heli cap a un sistema analític (GC o GC-MS).

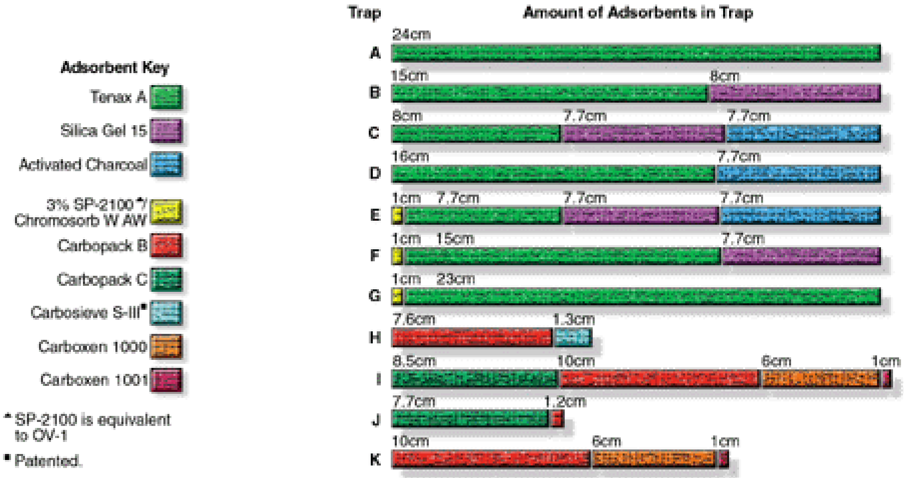

Figura 10.- Trampes i combinacions d'adsorbents per P&T que es poden trobar al mercat (extreta del catàleg Supelco)

Taula 8.-Principals avantatges i inconvenients de la P&T aplicada a l'anàlisi d'aigües

Avantatges	***Inconvenients***
☺ Simplicitat. Mínima preparació i manipulació de la mostra.	☹ Preu de l'equip elevat
☺ Rapidesa (10-15 minuts de purga).	☹ Requereix de la utilització de gas de la màxima puresa.
☺ Extracció selectiva. Els compostos no volàtils no arribaran a la columna cromatogràfica.	☹ Hi ha risc de contaminació del sistema quan s'analitzen mostres molt concentrades.
☺ Un ampli ventall d'aplicació.	☹ Risc de formació d'escumes.
☺ Bona precisió.	☹ Possibilitat de pèrdua dels compostos més volàtils (depenent del tipus de trampa).
☺ Nivells de detecció fàcilment situats en els ppt (ng/L), enfront el HS que és menys adequat per a l'anàlisi de traces.	☹ Possibilitat de degradació dels compostos tèrmicament inestables.
☺ No necessita de la utilització de dissolvents tòxics o inflamables.	☹ Incompleta eliminació o neteja de compostos al llarg del sistema quan una mostra està molt concentrada, passant a contaminar la següent (anomenat *efecte memòria*).
☺ No es veu tan influenciat per la salinitat o l'acidesa de la mostra com ara les fibres del SPME	☹ Les mostres només poden ser analitzades un cop.
☺ Possibilitat d'acoblament directe amb un sistema GC-MS.	
☺ Fàcil automatització.	

2.1.3 Material

Els patrons comercials (purs –d'1 a 5 g- o en disolució en metanol -de 2000 a 5000 ppm) s'han triat en la puresa més elevada disponible al mercat (preferentment de la casa Sigma-Aldrich que inclou actualment Supelco, Fluka, etc.).

Per tal de realitzar les dilucions dels estàndards comercials i posterior anàlisi per P&T-GC/MS, així com per la neteja del material de vidre s'han emprat els dissolvents (metanol, acetona) d'alta puresa o qualitat GC i aigua de qualitat cromatogràfica de Merck (Darmstadt, Alemanya).

Pel que fa a material, bàsicament, s'utilitzen vials de vidre (ambres o blancs) de 40 mL amb tap de rosca i sèptum de silicona/tefló, prerentats de qualitat EPA de la casa Tekmar–Dohrmann (Mason, OH, EEUU) i/o Wheaton (EEUU) compatibles amb l'injector automàtic de la mateixa casa comercial.

Per la preparació dels patrons en aigua, i en un principi la injecció dels patrons interns dins els vials s'han fet servir xeringues especials per gasos (punta bisellada) de 10, 25, 50, 100, 250, 500, 1000 i 2500 σL de SGE (Austràlia) i/o Hamilton (Suïssa).

Un cop oberts, els patrons comercials es transvasen a vials de vidre ambre roscats de 2 mL, que degudament etiquetats, es conserven a –20ºC. Dels patrons purs, es preparen dilucions per pes en metanol a concentracions properes als 2000 ppm i s'emmagatzemen també al congelador. Cal destacar que el TBA i el DCPD en estat pur requereixen una especial atenció, ja que a temperatura ambient, tenen una consistència gelatinosa que en dificulta la manipulació, fent necessari un escalfament lleuger en un bany d'aigua previ al trasvassament o a la dilució.

A partir de les solucions concentrades es preparen dissolucions *de treball* en metanol i el mateix dia de la injecció es prepara la recta de calibració i patrons de control en aigua de qualitat cromatogràfica (també anomenada HPLC) procurant no deixar espai de cap.

Les solucions en metanol es conservaran a –20ºC, mentre que les d'aigua ho faran a 4ºC per un període no més llarg de 14 dies (així com les mostres).

2.1.4 Neteja del material

Un cop utilitzats, els vials de 40 mL són degudament buidats als bidons de residus (diferenciats per residus clorats o no clorats), es llencen el sèptums (si estan punxats no es poden reutilitzar per evitar pèrdues) i es passa a la neteja de vials i taps de rosca.

Quan s'han passat per aigua de l'aixeta, els vials es posen a un bany d'ultrasons amb una mica de detergent en pols (Extran, Merck) durant 15 minuts, posteriorment s'esbandeixen amb aigua de l'aixeta, aigua destil·lada i acetona; i finalment es posen a muflar coberts amb paper d'alumini a l'estufa (a 250ºC) fins la seva propera utilització. Els taps es netegen manualment i s'assequen a temperatura ambient. I pel que fa a les xeringues, cada cop que es fan servir, es netegen abans i després amb metanol.

2.1.5 Instrumentació

Unitat de Purga i Trampa: Fins gener de 2003, es va emprar un *Purge & Trap concentrator Tekmar 3100* connectat a un injector automàtic *Aquatek 70* per vials de 40 mL, ambdós de Tekmar-Dohrmann (Mason, OH, EEUU), vegeu fotografia a la *Figura 11*.

Posteriorment, es va instal·lar un *SOLATek 72 Multi-Matrix Vial Autosampler* de la mateixa casa comercial. A més de fer possible l'anàlisi de matrius sòlides, aquest equip va millorar les prestacions de l'anterior per l'anàlisi de mostres líquides amb la possibilitat de dilucions automatitzades de les mostres més contaminades (permet dilucions de fins 1:250) amb l'aigua HPLC emmagatzemada en un tanc pressuritzat, realitzar blancs automàtics des d'aquest mateix tanc sense necessitat de vial, i sobretot un sistema per la incorporació automàtica dels PI's de 5-25 µL des de fins a tres dipòsits diferents de 20 mL amb protecció ultraviolada (UV) tancats sota pressió per major estabilitat dels compostos. L'aigua de neteja del sistema (a 90ºC per tal minimitzar l'anomenat "efecte memòria"), així com la requerida pels blancs automàtics, prové del tanc i es fa passar a través d'un filtre de GAC per assegurar-ne l'eliminació de compostos aliens (*Figura 12*).

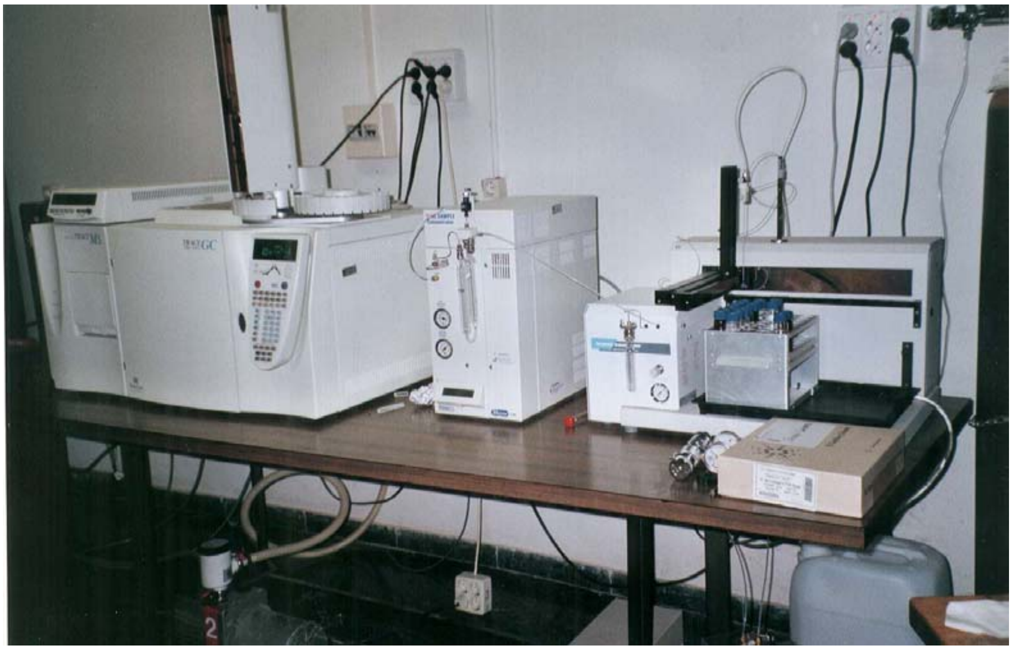

Figura 11.- Equip complet emprat en l'anàlisi inicial, de dreta a esquerra: AutosamplerAquatek 70, P&T concentrator Tekmar 3100 i Trace GC-MS

Figura 12.-Detall del tanc pressuritzat i filtre de GAC pel subministrament d'aigua a l'injector automàtic

El concentrador està equipat amb una trampa de Tenax, gel de sílice i carbó actiu de 8, 7.7 i 7.7 cm respectivament de la casa Supelco (Bellefonte, PA, EEUU) per l'anàlisi multiresidu o de barreges de VOCs tal com recomana el mètode EPA [111]. Normalment aquestes trampes amb barreja d'adsorbents es consideren més efectives, tot i que també s'han descrit bones recuperacions de MTBE amb trampes només de Tenax [99,130]. L'elecció d'un tipus de trampa determina els valors òptims de certs paràmetres com ara la temperatura per a la desorció tèrmica dels compostos, el programa de neteja, etc. i per tant, només es possible experimentar, amb el temps de purga i el temps de desorció. A continuació la *Taula 9* mostra aquests paràmetres per la trampa seleccionada per l'estudi.

Taula 9.- Valors dels paràmetres de P&T predeterminats per la trampa de Tenax, gel de sílice i carbó actiu

Adsorbents de la trampa	*T^a de preescalfament*	*T^a de desorció*	*T^a de neteja posterior*	*Temps de neteja*	*Acondicionament trampa nova*
Tenax, Gel de sílice i carbó actiu	220ºC	225ºC	230ºC	10 – 12 min.	225ºC durant 180 min

Unitat de GC-MS : S'ha emprat un cromatògraf de gasos acoblat a un espectròmetre de masses *Trace GC-MS* de ThermoQuest Finnigan (Austin, TX, EEUU) amb analitzador de tipus quadrupol. Equipat amb una columna capil·lar DB-624 (J&W Scientific, Folsom, CA, EEUU) de sílice fosa, 75 m x 0,53 mm de diàmetre intern i gruix de recobriment de la fase estacionària de 3 µm. Aquesta columna capil·lar, de major diàmetre que les habituals (que són de 0,25 mm), permet un flux de gas portador més elevat (fins a 10 mL/min), mentre que les altres només treballen a menys de 3 mL/min, flux insuficient per a la injecció total dels compostos tèrmicament desorbits.

Software: El programa informàtic de control, registre i tractament de dades del GC-MS és *Xcalibur* (versió 1.2). En els últims anys se n'ha millorat el sistema de quantificació, a través de la utilització del sistema automàtic *XCalibur Quantitative Analysis by Internal Standard Calibration* que permet a través de la injecció d'un patró inicial definir els ions de quantificació i confirmació dels compostos, el temps de retenció, el patró intern de referència, etc., augmentant la fiabilitat de l’anàlisi quantitatiu.

2.2 OPTIMITZACIÓ I APLICACIÓ DEL MÈTODE

2.2.1 Punts destacables del procés d'optimització

Per definició, l'optimització, consisteix en el procés de recerca i localització del conjunt de valors de les variables independents que produeixen el millor resultat possible en el procés de síntesis, mesura o determinació analítica.

En l'acoblament P&T-GC/MS, es poden utilitzar trampes fredes que milloren la resolució i separació cromatogràfica. Una trampa freda o interfase criogènica és una etapa addicional per tal de millorar la transferència dels compostos des de l'aparell de P&T fins el GC i així obtenir una millor resolució. Els VOCs desorbits tèrmicament de la primera trampa passen a una segona de nitrogen líquid a –150ºC, on són desorbits tèrmicament de nou però de forma molt ràpida i amb el menor volum de fase mòbil cap a la columna. Aquesta etapa s'ha calificat d'essencial per l'obtenció d'una bona separació cromatogràfica [124], tot i això, a la literatura es troben estudis per a la determinació de MTBE que no en fan servir [108,131], que ho fan a diferents temperatures que van de -10 a -60ºC [127,130,132] i fins un estudi recent arriba fins els -180ºC [99].

En el nostre estudi, en **absència de trampa freda** i tenint en compte que la línia de transferència entre l'aparell de P&T i el GC és molt llarga, es van utilitzar diferents gradients de flux portador (heli) per tal de preconcentrar els analits a l'entrada de la columna. Partim d'un flux gran (5 mL/min) durant 1 minut, que després disminueix amb un gradient de –2 mL/min^2 fins a 3,5 mL/min, flux que es manté constant fins al final de l'anàlisi.

Per tal d'augmentar la sensibilitat en la detecció dels compostos estudiats es va elaborar un mètode d'adquisició en mode SIM, on es van escollir els tres ions més abundants de cada analit: un de majoritari o diagnòstic (a través del qual es portarà a terme la quantificació) i altres dos de confirmació per identificar, junt amb el temps de retenció, inequívocament cada compost (consultar taula d'ions completa i temps de retenció a la Taula 3 de l'Art. 4). A més, es van elaborar un disseny de 3 finestres cromatogràfiques tenint en compte: espai suficient entre dos pics i similar nombre d'ions a cadascuna d'elles per tenir la mateixa sensibilitat per tots els compostos. Al principi es deixen uns 8 minuts en els quals el MS no adquireix, per tal d'evitar els habituals pics de dissolvent o de diòxid de carboni, a part d'evitar que es faci malbé el filament.

Els compostos que van suscitar més problemes a l'hora d'optimitzar el mètode van ser els compostos degradació i sobretot el **TAA**. Els seus límits de detecció són majors i a concentracions baixes, els espectres són força irregulars. Tot i això, el ió majoritari pels tres compostos, el *m/z* 59, es mantenia constant, així com els temps de retenció fent possible la seva identificació. En el cas del TBF es van poder escollir dos ions addiccionals, el *m/z* 56 i el 57, que encara que amb algunes variacions en l'abundància relativa sempre sortien a l'espectre del compost. El TAA va ser finalment exclòs de l'estudi perquè no es va aconseguir una bona resolució del pic (*m/z* 59) ni una bona separació cromatogràfica (fins i tot amb isoterma) dels seus dos pics veïns (benzè i TAME).

El MTBE es resolia bé a les condicions cromatogràfiques emprades, tot i que al utilitzar el MTBE deuterat com a PI, es produeix la coelució d'ambdós pics. Aquests dos compostos, que només difereixen estructuralment en el canvi de tres hidrogens per deuteris (isòtops de l'hidrogen de massa nuclear igual a 2). Com és habitual, nadius i deuterats coelueixen i es solen separar únicament per la quantificació per diferent ió (o massa). En aquest cas, els pics de **MTBE i MTBE-d$_3$** difereix només en uns pocs segons i es quantifiquen amb els ions 73 i 76, respectivament, com s'observa a la *Figura 13*.

L'optimització dels paràmetres de P&T (temps de purga i temps de desorció) es va realitzar a través del mètode *simplex geomètric*, o simplement, **s*implex***. Des del punt de vista matemàtic, aquest mètode és un algoritme seqüencial de recerca directa que es caracteritza per la no utilització explícita de derivades de la funció objectiu i es basa en un examen seqüencial de respostes [133]. Aquest tipus d'optimització pot ser aplicada quan els paràmetres són variables contínues, com era el nostre cas.

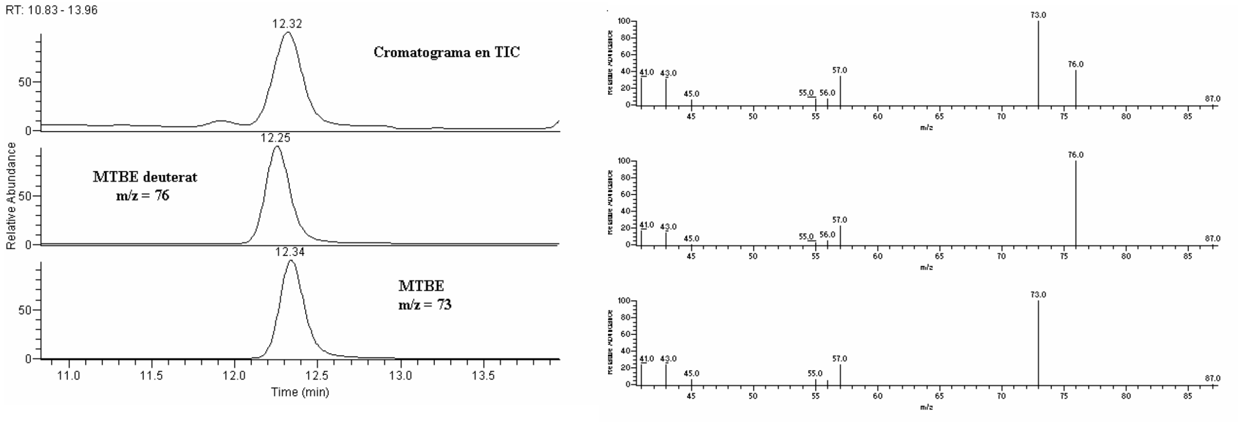

Figura 13.- Separació del MTBE i el MTBE-d_3 per espectrometria de masses (espectre en mode SIM)

Un simplex és una figura geomètrica que té (n + 1) vèrtexs quan la resposta s'optimitza respecte *n* factors, i té la interessant propietat de poder formar un nou simplex sobre qualsevol cara per l'addició, tan sols, d'un nou punt equidistant dels de la cara fixa [134]. En el nostre cas, es tractava de 2 paràmetres i per tant, el simplex formava triangles.

La resposta a maximitzar en aquest cas va ser l'àrea del MTBE. La successió dels diferents experiments realitzats es mostra a la *Figura 14*. Partint dels valors establerts pel mètode 524.2 de l'EPA [111], 11 minuts de purga i 4 de desorció, es van anar elaborant triangles. El simplex es feia cada cop més estret, però no mostrava una tendència clara cap a un valor òptim. En canvi, en la majoria dels casos, l'àrea del MTBE era millor en el punt (13 min. de temps de retenció i 4 min. de temps de purga), present en tots els simplex des de la primera iteració. Per aquesta raó, en el setè experiment es van incloure, a més dels tres punts corresponents, dos d'aleatoris al voltant d'aquest: un al seu centre de gravetat amb el de l'EPA, i un altre una mica més allunyat per l'altra banda. Tots dos van donar menor resposta que el citat valor òptim (13,4).

Per últim, es va escollí el citat punt, el de l'EPA, el punt mig entre aquests dos i l'últim vèrtex del procés. A part de l'àrea del MTBE també es van quantificar les dels altres compostos d'estudi. Es va ratificar que amb l'augment del temps de purga fins a 13 minuts i mantenint el temps de desorció en 4, l'àrea del MTBE era major que a la resta de combinacions. A més, pel que fa a la resta de compostos, es va comprovar que aquest punt era el primer o segon de millor resposta, fet que semblà prou satisfactori com per donar per finalitzada l'optimització.

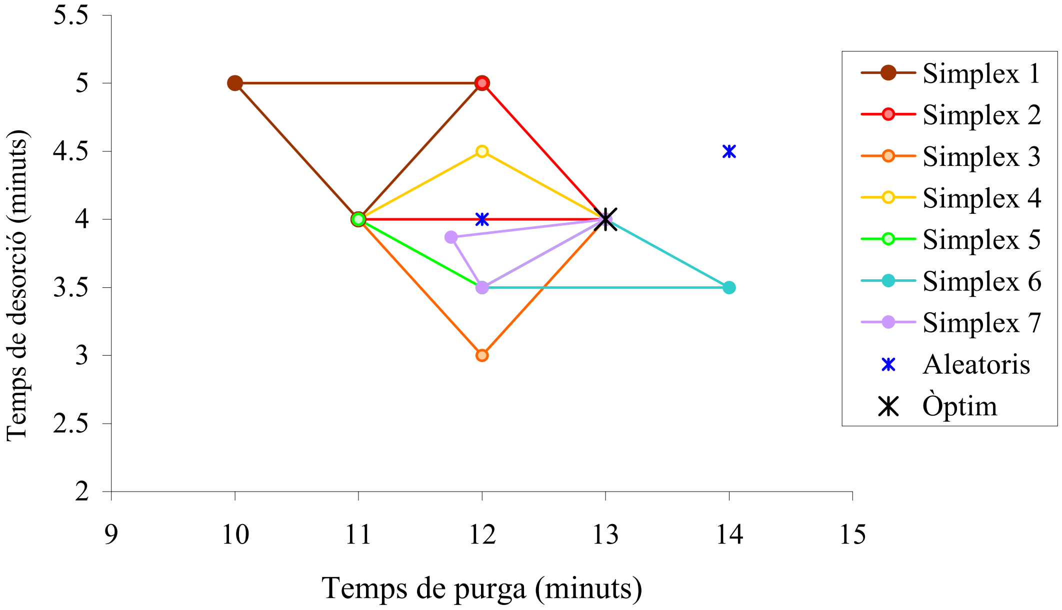

Figura 14.- Optimització dels paràmetres del P&T pel mètode simplex

2.2.2 Estabilitat dels patrons en MeOH a -20ºC

Al maig de 2002, es va realitzar un petit estudi sobre l'estabilitat dels analits (a excepció del DCPD i el TCE) en 7 vials a 10 ppm (en metanol) que havien estat emprats anteriorment i conservats a -20ºC durant un període que anava fins un total de 500 dies. En el moment de l'anàlisi, els vials de 40 mL que contenien les solucions metanòliques presentaven diferents espais de cap, però donaven així una idea sobre la utilització real que se'n podia fer d'aquests. Habitualment, aquestes solucions només s'empraven en un torn d'anàlisi, que en general mai excedia de 45 dies.

Solucions diluïdes de 10 ppb es van preparar en aigua de qualitat per cromatografia. Per cada solució es van preparar dues rèpliques. La recuperació de cada compost es va calcular com la concentració obtinguda dividida entre la concentració teòrica (o esperada) per 100, i es van comparar amb els resultats obtinguts del patró preparat a partir dels patrons comercials aquell mateix dia (temps zero).

Tots els èters presentaven bones recuperacions fins al cap de 300 dies (superiors al 87%), a partir d'aquí començaven a disminuir, observant-se pèrdues d'entre el 25-35 % al cap d'aproximadament 500 dies. Els aromàtics presentaven, en general, recuperacions lleugerament més elevades (els resultats pel benzè i *m*+*p*-xilè es mostren a la *Taula 10* a mode d'exemple), probablement per la seva menor volatilitat.

Taula 10.-Estabilitat d'alguns compostos d'estudi en MeOH a -20ºC

Compost	***MTBE***		***TBA***		***TAME***		***DIPE***		***Benzè***		***m+p-xilè***	
Temps emmagatzemat (dies)	R (%)	± SD (%)	R (%)	± SD (%)	R (%)	± SD (%)	R (%)	± SD (%)	R (%)	± SD (%)	R (%)	± SD (%)
0	**104**	20	**97**	7	**103**	21	**112**	26	**107**	26	**106**	14
96	**91**	15	**73**	2	**89**	14	**85**	18	**93**	16	**93**	11
164	**91**	21	**90**	9	**91**	21	**125**	36	**89**	26	**95**	20
302	**89**	8	**86**	11	**87**	6	**95**	15	**84**	12	**92**	8
417	**97**	9	**78**	6	**98**	7	**41**	6	**99**	13	**95**	6
435	**73**	28	**67**	6	**82**	13	**35**	7	**83**	18	**86**	16
462	**78**	28	**116**	4	**83**	14	**73**	15	**92**	18	**94**	16
477	**65**	25	**108**	8	**75**	7	**73**	10	**77**	11	**84**	11

2.2.3 Protocol per a la presa de mostres d'aigua subterrània

Per la correcta detecció de VOCs en aigües subterrànies, la presa de mostres és un dels punts clau, doncs requereix d'una especial atenció si no es volen contaminar les mostres o perdre els compostos per volatilització o processos de degradació.

Són necessàries les següents precaucions per a la manipulació de VOCs:

Agafar triplicats de les mostres. Segons el mètode 524.2 de l'EPA hi hauria prou amb agafar dues rèpliques de cada punt [111], mentre que el USGS n'aconsella tres [127]. Durant el transport fins el laboratori, o bé per errors humans o instrumentals al llarg del procés analític, podem perdre algunes mostres. Per proporcionar resultats exactes, es requereix almenys de l'anàlisi per duplicat, i encara millor per triplicat. S'ha de tenir en compte, que les mostres només poden analitzar-se un cop per P&T. I que si s'esperen *a priori* mostres molt concentrades, no es poden punxar directament i cal fer-ne dilucions, amb la qual cosa ja utilitzarem com a mínim una de les rèpliques.

Evitar transvasaments innecessaris. Les mostres s'agafen en els vials de 40 mL, nets amb tap de rosca i sèptum de silicona-tefló, que s'incorporaran directament a l'injector automàtic. D'aquesta manera es minimitza la manipulació de la mostra i no es perden VOCs en transvasaments inútils des de ampolles més grans, cosa que també podria provocar la seva contaminació. Normalment, s'utilitzen vials de vidre ambre per preservar de la fotodegradació, tot i que en el nostre cas no sigui gaire important. Una de les rèpliques pot agafar-se en vial de vidre transparent per tal de poder observar l'estat de l'aigua: terbolesa, doble fase, sòlids en suspensió, etc.

Emplenar els vials totalment i tapar-los immediatament. És molt important que no hi hagi espai de cap als vials, per tal de prevenir la volatilització dels compostos en contacte amb la fase gas del recipient durant la recol·lecció, transport i emmagatzematge. També s'ha d'evitar, en la mesura del possible, el pas d'aire o bombolles a través de la mostra.

Bombejar l'aigua del pou fins que els paràmetres físico-químics es mantinguin estables. En el cas que el pou disposi d'una bomba, abans d'emplenar els vials, cal bombejar una estona per tal que surti aigua realment representativa.

No acidificar les mostres. En la majoria dels casos, els VOCs es preserven al camp amb una solució 1:1 d'àcid clorhídric fins a pH = 2 (també es pot fer servir bisulfat de sodi, $NaHSO_4$, o àcid sulfúric, H_2SO_4). En el nostre cas, això no es preferible degut a que un dels analits, el TBF, s'hidrolitza ràpidament sota condicions àcides o alcalines. De tota manera, per l'anàlisi del MTBE no és necessària cap preservació, doncs la seva biodegradació és gairebé inapreciable.

Etiquetatge i codificació. Els vials han d'estar degudament etiquetats amb un codi numèric que eviti la seva pèrdua i faci més senzill el procés d'anàlisi i tractament de dades. Cal anar en compte de no posar les etiquetes a sobre del tap perquè els dissolvents de l'adhesiu podrien contaminar les mostres, com el toluè o l'acetona.

Transport en fred. Els vials es transporten en nevera portàtil amb gel, aproximadament a 4ºC.

Des de la primera campanya de presa de mostres a Catalunya, s'han emprat diferents aparells de presa de mostres o *mostrejadors* d'aigua subterrània (observar fotografies a la *Figura 15*). Des dels més rudimentaris, com són el *mostrejador d'acer* o mètode de "pot i corda", passant pel *mostrejador de plàstic*, o quan ha estat possible, directament de la sortida per una aixeta o mànega connectada al sistema de bombeig del pou. En l'última campanya realitzada a finals de maig de 2006, s'han utilitzat mètodes de bombeig manual (flux ràpid, pel moviment vertical d'una bola a l'interior d'un tub) i un altre de més automatitzat. Aquest últim requeria d'una mini bomba de doble vàlvula assistida per una altra bomba neumàtica que emprava nitrogen com a gas portador. El flux resultant era més lent (200-300 mL/min.), però disminuïa la terbolesa de l'aigua i minimitzava el pas d'aire a través de les mostres. Ambdós sistemes van ser proveïts pel Dr. Weiss (IMW, Tübingen, Alemanya).

Al camp, és habitual mesurar alguns paràmetres de l'aigua subterrània com ara la temperatura, la conductivitat elèctrica, l'oxigen dissolt o el pH, utilitzant preferentment una sonda multiparamètrica. També és força útil la utilització d'un sistema de GPS (*Global Positioning System)* per situar, a través de les coordenades, els pous mostrejats a un mapa o sistema d'informació geogràfica (SIG).

Figura 15.-Diferents sistemes de presa de mostres d'aigua subterrània: mostrejador d'acer (A), mostrejador de plàstic (B), bombeig manual (C) o bombeig assistit per nitrogen (D).

2.2.4 Control de qualitat

Al llarg de la seqüència automàtica, es necessari l'intercalament de ***blancs*** (en el nostre cas, aigua de qualitat cromatogràfica sense fortificar) que s'analitzen de la mateixa manera que la resta de mostres o patrons. Serveixen tant per netejar, així com per portar un control del soroll de fons (reflex de l'estat de l'aparell), els possibles contaminants presents al laboratori, així com els nivells d'efecte memòria dels compostos d'estudi.

Així mateix, ***patrons de comprovació*** a diverses concentracions dins del interval de linealitat s'intercalen amb les mostres reals per tal de controlar la sensibilitat de l'equip.

Una altra manera de mesurar la reproductibilitat de l'equip és a través del control de les ***àrees dels PIs***. Com la quantitat afegida d'aquests és la mateixa a totes les mostres, les àrees hauran d'oscil·lar dins un interval de valors constant.

De forma general es segueixen els següents criteris de control:

- Sempre s'inicia la seqüència amb un blanc per controlar que el sistema es troba lliure de contaminants i també s'acaba amb un parell o tres d'ells.
- L'últim blanc es realitza amb un programa de temperatures diferent per tal de deixar el forn a 60ºC, temperatura òptima pel seu bon manteniment.
- Sempre que es punxen patrons seguits, sense blancs al mig, es fa en ordre creixent de concentració.
- Després d'un patró de concentració elevada es segueix amb un blanc.
- Si es dóna el cas, les mostres més antigues tenen prioritat a l'hora de ser analitzades.
- Si es coneix o s'espera un cert estat de contaminació de les mostres, es punxaran primer les menys concentrades per minimitzar l'efecte memòria.

2.2.5 Aplicació a mostres reals

A continuació es presenten tres articles científics referents al desenvolupament i l'aplicació del mètode de P&T-GC/MS optimitzat a l'anàlisi dels compostos d'estudi en aigües subterrànies afectades per fonts de contaminació puntuals de gasolina tant a Catalunya (Art. 2 i 3) com a Düsseldorf, Alemanya (Art. 4).

L'article 2 "*Simultaneous determination of methyl tert.-butyl ether and its degradation products, other gasoline oxygenates and benzene, toluene, ethylbenzene and xylenes in Catalonian groundwater by purge-and-trap-gas chromatography–mass spectrometry*" tenia per objectiu el desenvolupament del mètode automatitzat de P&T-GC/MS que fes possible la detecció dels additius de la gasolina (aromàtics i oxigenats) i els compostos de degradació del MTBE (TBA i TBF) a nivells traça (ng/L o sub-µg/L) en aigües. Es van estudiar els paràmetres de qualitat per tal de demostrar que el mètode era robust i viable. El treball es va realitzar conjuntament amb l'Agència Catalana de l'Aigua (ACA) que es va responsabilitzar de l'elecció de les zones d'estudi (on prèviament s'havien ja detectats problemes de contaminació per MTBE i BTEX [135]) i va aconseguir els permisos i facilitats legals necessaris. Bàsicament es van estudiar dos fenòmens de contaminació per MTBE, un provocat per les pèrdues dels tancs d'emmagatzemat a l'Àrea de Repsol Petroli a Tarragona i un altre, per una fuita accidental a una gasolinera de Sant Celoni, Girona. Es pretenia així, aprofundir en el coneixement de l'estat de contaminació de les aigües subterrànies del nostre país i venia a cobrir el buit d'informació que existia sobre els nivells de MTBE als països del sud d'Europa.

Aquesta campanya va possibilitar també la publicació de **l'article 3**, "*Cross-Validation of Methods Used for Analysis of MTBE and other Gasoline Components in Groundwater*", en el qual es comparaven dues tècniques habituals per a la detecció de VOCs en aigua: el nostre mètode de P&T-GC/MS amb el fet servir per l'ACA, un HS-GC/FID. L'objectiu de l'article era comparar ambdós mètodes per a la detecció de MTBE i BTEX, tant a través dels paràmetres de qualitat (límits de detecció, recuperacions, precisió, etc.) calculats a partir de mostres d'aigua fortificades; com per la comparació o validació creuada dels valors obtinguts per les mateixes mostres d'aigua subterrània. Presenta així, els principals avantatges i inconvenients d'ambdues tècniques i la seva aplicabilitat en mostres reals contaminades.

Per últim, **l'article 4**, "*Fate of gasoline oxygenates in conventional and multilevel wells of a contaminated groundwater table in Düsseldorf, Germany*", compila els resultats de dos anys de vigilància ambiental del MTBE i la resta de compostos d'estudi a un aqüífer contaminat per una suposada fuita accidental de gasolina a Düsseldorf, Alemanya. El article tenia per objectiu determinar la presència, comportament (tant el moviment horitzontal com el perfil vertical en profunditat) de la ploma de MTBE, així com el càlcul de la velocitat de degradació del compost i la identificació dels seus productes en les condicions ambientals de l'aqüífer.

Article científic (Art. 2):

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

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Simultaneous determination of methyl *tert*.-butyl ether and its degradation products, other gasoline oxygenates and benzene, toluene, ethylbenzene and xylenes in Catalonian 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-μg/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 μg/l. Seven contaminated hot spots were identified with levels up to US Environmental Protection Agency drinking water advisory (20–40 μg/l) and a maximum concentration of 670 μg/l (doubling the Danish suggested toxicity level of 350 μg/l). Samples with high levels of MTBE contained 0.1–60 μg/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.

Keywords: Gasoline; Water analysis; Environmental analysis; Purge-and-trap methods; Methyl *tert*.-butyl ether; Benzene; Toluene; Ethylbenzene; Xylenes

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^3/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 carcinogenity 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 degradated 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-μg/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, [$^2H_3$] MTBE (MTBE-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-

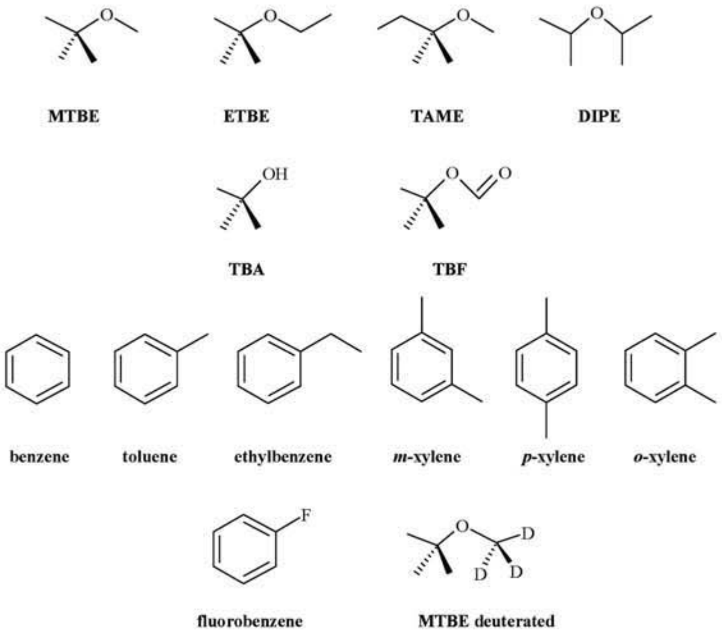

Fig. 1. Chemical structures of fuel oxygenates, MTBE degradation products, aromatic hydrocarbons and internal standards.

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 μg/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-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 devise. VOCs were purged from water samples for 13 min by administering helium at 35 ml/min and absorbed onto a Tenax®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 – Constanti	Oil refinery storage tanks	5	Tarragona Plioquaternary	Plioquaternary	Detritus materials constituted by conglomerates, sands and clays Multilayer aquifer	7–10 m	T=100–500 m^2/day K=1–100 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=460–330 m^2/day K=48–33 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 m^2/day K=300 m/day

[a] 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-µm 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 µA 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 α-cleavage, (M-CH$_3$)$^+$ or (M-CH$_5$)$^+$ 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 µg/l (first sampling in Tarragona only to 3 µg/l) and internal standards MTBE-d$_3$ and fluorobenzene at a constant concentration of 0.5 µg/l. Linear regression of base peak area versus concentration (calculated relative to the nearest internal standard using *m/z* 76 for MTBE-d$_3$ 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$_3$*	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	*m+p*-xylene	106	91	106	77
	33.58	*o*-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 μg/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 μg/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 μg/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 μg/l, but one site had a level of 670 μg/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 μg/l, respectively, and TAME was not detected in any of the samples. BTEX levels were in many cases between 0.02 and 10 μg/l, whereas a couple of samples showed high concentrations, up to 500 μg/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 μg/l, its concentration reached a value of 62 μg/l in the most MTBE contaminated well. It must be taken into consideration that TBF can be hydrolysed to TBA in aqueous phase. Anyway,

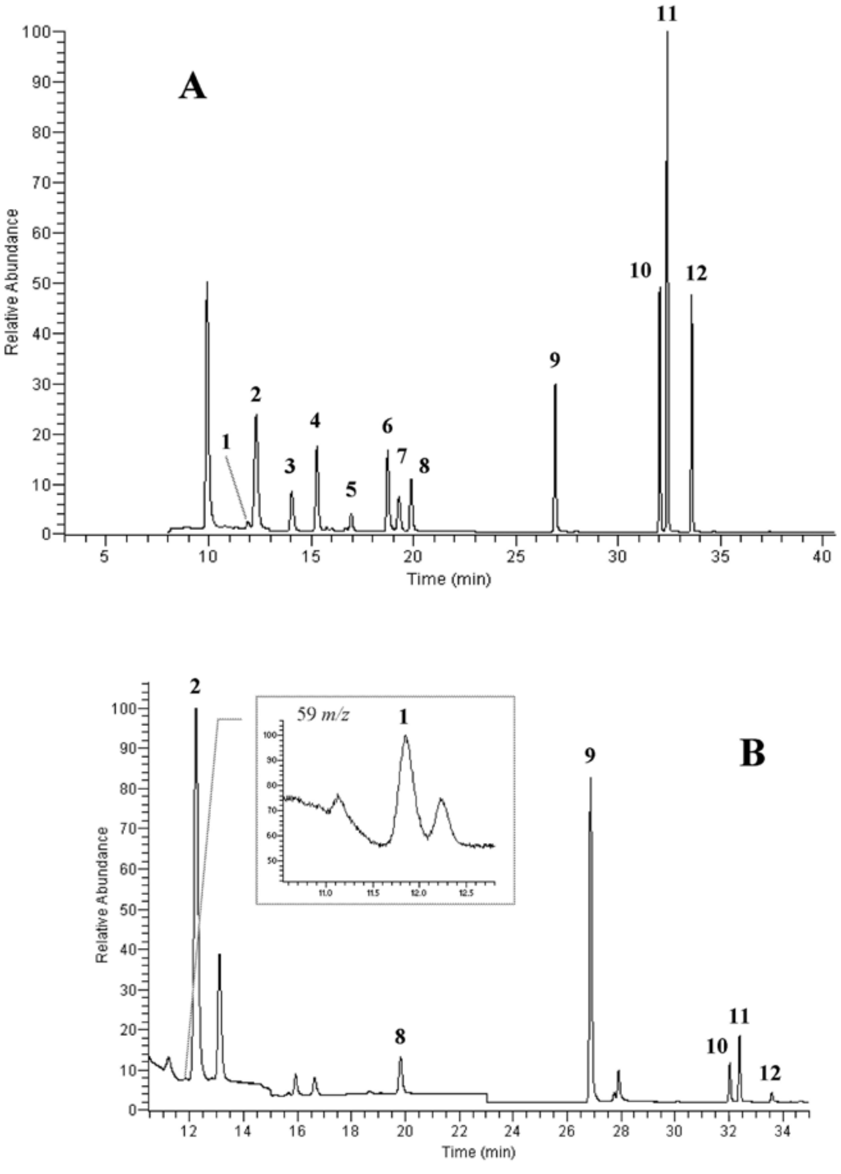

Fig. 3. Total ion chromatogram (TIC, 10^8) in SIM mode for a (A) 10 μg/l standard and (B) detail of groundwater sample. Compound identification number: 1=TBA, 2=MTBE-d_3+MTBE, 3=DIPE, 4=ETBE, 5=TBF, 6=benzene, 7=TAME, 8=fluorobenzene, 9=toluene, 10=ethylbenzene, 11=*m*+*p*-xylene and 12=*o*-xylene.

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 (μg/l)	Repeatability (n=4)		Reproducibility (n=15)		Recoveries±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±5	103±7
MTBE	0.001	7.29	2.13	18.27	10.27	101±4	101±6
DIPE	0.008	5.81	2.96	8.54	9.40	100±3	98±4
ETBE	0.009	7.75	2.49	11.71	14.79	99±3	102±5
TBF	0.034	56.59[a]	5.22	77.16[a]	13.78	55±19[a]	104±7
Benzene	0.002	6.32	3.74	8.66	7.61	99±3	99±5
TAME	0.013	7.41	1.22	13.30	13.56	103±4	106±5
Toluene	0.001	5.56	3.44	7.47	7.15	99±2	97±4
Ethylbenzene	0.001	7.28	3.62	8.81	8.21	98±2	95±6
m+*p*-Xylene	0.001	7.08	2.62	8.66	7.58	99±2	95±6
o-Xylene	0.002	6.47	2.89	9.04	6.79	99±2	96±6

[a] 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 μg/l in 1998 [24] whereas the actual level was 670 μg/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 μg/l and from 0.20 to 1.53 μg/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

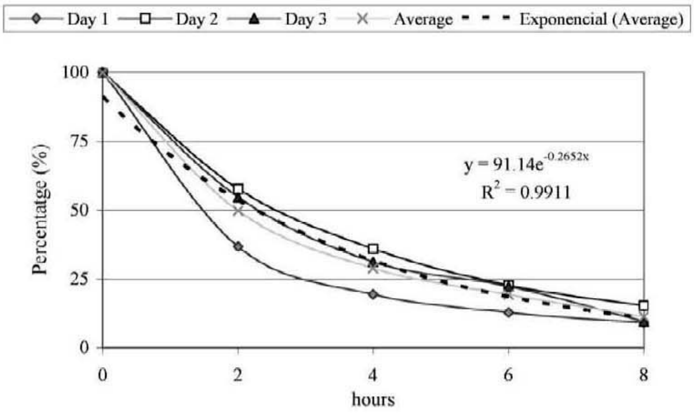

Fig. 4. TBF decreasing curves in organic-free water (HPLC).

Table 4
Concentrations of gasoline additives (μg/l) in monitored groundwater wells in Catalonia

Sample id.	TBA	ETBE	TBF	MTBE	TAME	DIPE	Benzene	Toluene	Ethylbenzene	*m*+*p*-Xylene	*o*-Xylene
Tarragona (pobla Mafumet, Constanti)											
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
Tarragona (La Pineda)											
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
St. Celoni (La Batlloria)											
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.

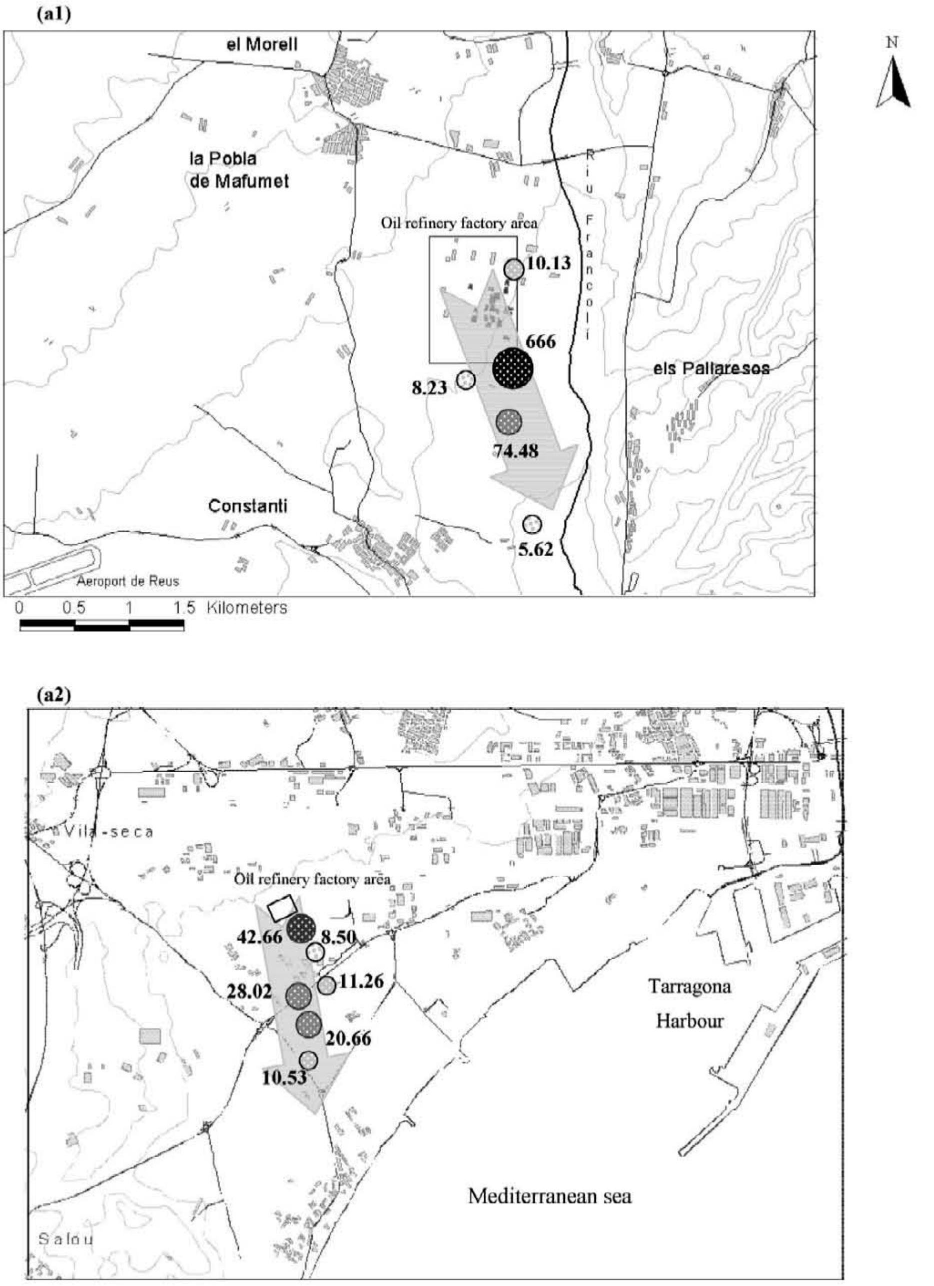

Fig. 5. Maps with MTBE concentrations detected (expressed in µg/l) in the studied wells and hypothetical movement of the plume. Two sites in Tarragona: (a1) Pobla Mafumet–Constanti; (a2) La Pineda and (b) La Batlloria (Sant Celoni, Girona).

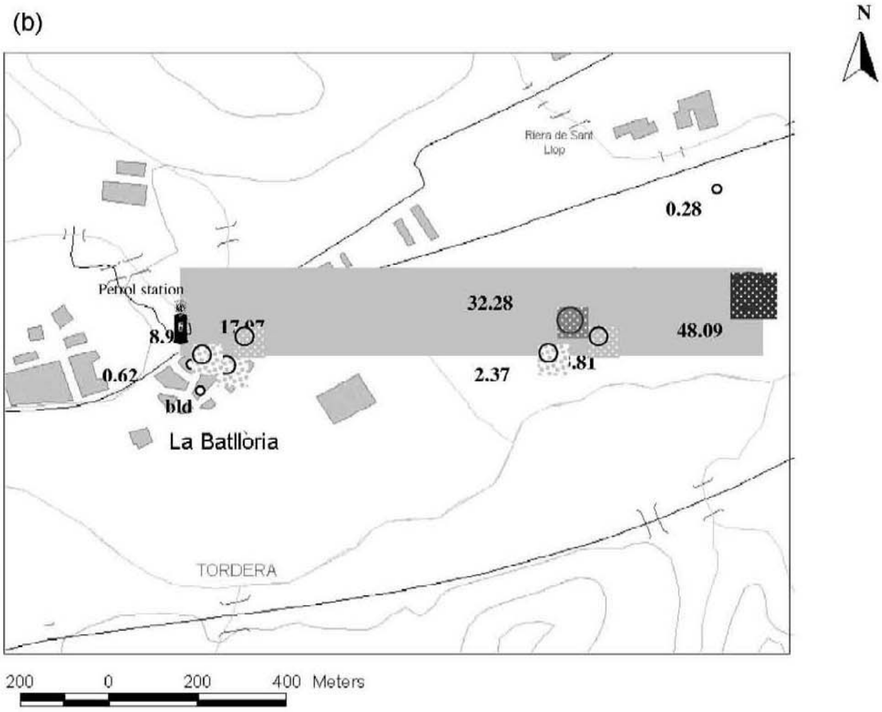

Fig. 5. (*continued*)

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 μg/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 μg/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 μg/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 μg/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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References

[1] T.C. Schmidt, E. Morgenroth, M. Schirmer, M. Effenberger, S.B. Haderlein, in: A.F. Diaz, D.L. Drogos (Eds.), Oxygenates in Gasoline: Environmental Aspects, Vol. 799, ACS Symposium Series, no. 799, American Chemical Society, Washington DC, 2002.

[2] M.A. Pérez Pascual, CEPSA Research Centre director, Personal communication, 2001.

[3] Directive 98/70/EC of the European Parliament and of the Council of 13 October 1998 relating to the quality of petrol and diesel fuels and amending Council Directive 93/12/EEC Official Journal L 350, 28/12/1998, 0058–0068, 1998.

[4] P.J. Squillace, J. S Zogorski, W.G. Wilber, C.V. Price, Environ. Sci. Technol. 30 (5) (1996) 1721.

[5] R. Begley, D. Rotman, Chem. Week 152 (10) (1993) 7.

[6] R.L. Moolenaar, B.J. Hefflin, D.L. Ashley, J.P. Middaughand, R.A. Etzel, Arch. Environ. Health 49 (5) (1994) 402.

[7] I. Werner, C.S. Koger, L.A. Deanovic, D.E. Hinton, Environ. Pollut. 111 (2001) 83.

[8] G.A. Rausina, D.C.L. Wong, W.R. Arnold, E.R. Mancini, A.E. Steen, Chemosphere 47 (2002) 525.

[9] H.D. Burleigh-Flayer, J.S. Chun, W.J. Kintish, Export, Pennsylvania, Union Carbide, Bushy Run Research Center, BRRC Report 91N0013B, 1992.

[10] J.S. Chun, H.D. Burleigh-Flayer, W.J. Kintish, Export, Pennsylvania, Union Carbide, Bushy Run Research Center, BRRC Report 91N0013B, 1992.

[11] F. Belpoggi, M. Soffritte, C. Maltoni, Toxicol. Ind. Health 11 (2) (1995) 119.

[12] Research Triangle Institute, Draft toxicological profile for methyl *tert.*-butyl ether, Atlanta, GA, U.S. Department of Health and Human Services, Public Health Service Agency for Toxic Substances and Disease Registry, 1994, p. 185.

[13] M.S. Dale, M.S. Moylan, B. Koch, M.K. Davis, MTBE: Taste-and-Odor Threshold Determinations using the Flavor Profile Method, Metropolitan Water District of Southern California, 1997.

[14] EPA 420-R-99-021, Achieving Clean Air and Clean Water: The report of the Blue Ribbon Panel on Oxygenates in Gasoline. Table E1, 1999, http://www.epa.gov/otaq/consumer/fuels/oxypanel/r99021tb.htm

[15] EPA, Health risk perspective on fuel oxygenates, EPA 600/R-94/217, Office of Research and Development, 1994, p. 11.

[16] EPA, Drinking water advisory—Consumer acceptability advice and health effects analysis on methyl tertiary-butyl ether, Washington, DC, Office of Water, EPA 822-B-96-002, 1997, p. 11.

[17] EPA, Drinking water regulations and health advisories, Office of Water, Washington, DC, EPA 822-R-96-001, 1996, p. 16.

[18] Danish EPA, New Taste/Odour Study on MTBE Performed by ISO-Method with Measured Concentrations, Copenhagen, 2002.

[19] P.B. Larsen, Evaluation of Health Hazards by Exposure to Methyl Tertiary-Butyl Ether, International Programme on Chemical Safety, IPCS, 1998.

[20] European Commission, Draft Commission Recommendation of the results of the risk evaluation and the risk reduction strategies for the substances: acrylaldehyde, dimetyl sulphate; nonylphenol; phenol, 4-nonylphenol, branched; *tert.*-butyl methyl ether (MTBE) in the framework of Council Regulation (EEC) 793/93, Brussels, 4-7, Document ENV.C.3/MM/plhD, D/430326 (2001) 35.

[21] P.M. Bradley, J.E. Landmeyer, F.H. Chapelle, Environ. Sci. Technol. 33 (11) (1999) 1877.

[22] J.D. Cirvello, A. Radovsky, J.E. Heath, D.R. Farnell, C. Lindamood, Toxicol. Ind. Health 11 (2) (1995) 151.

[23] C.D. Church, L.M. Isabelle, J.F. Pankow, D.L. Rose, P.G. Tratnyek, Environ. Sci. Technol. 31 (12) (1997) 3723.

[24] J. Fraile, J.M. Niñerola, L. Olivella, M. Figueras, A. Ginebreda, M. Vilanova et al., Sci. World J. 2 (2002) 1235.

[25] J.W. Eichelberger, J.W. Munch, T.A. Bellar, USEPA METHOD 524.2. Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry (Revision 4.0); Environmental Monitoring Systems Laboratory, Office of Research and Development USEPA, Cincinnati, Ohio 45268, August 1992.

[26] T.C. Schmidt, H. Duong, M. Berg, S.B. Haderlein, Analyst 126 (2001) 405.

[27] J.C. Miller, J.N. Miller, in: Statistics for Analytical Chemistry, Ellis Horwood Limited, 1988, p. 184, Chapter 7.

[28] S. Lacorte, L. Olivella, M. Rosell, M. Figueras, A. Ginebreda, D. Barceló, Chromatographia 56 (2002) 739.

[29] L. Zwank, T.C. Schmidt, S.B. Haderlein, M. Berg, Environ. Sci. Technol. 36 (2002) 2054.

[30] EPA, Oxygenates in Water: Critical Information and Research Needs, EPA/600/R-98/048, Office of Research and Development Washington, DC 20460, December 1998.

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Erratum

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

[J. Chromatogr. A 995 (2003) 171–184][☆]

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Page 182, Fig. 5b should read as follows:

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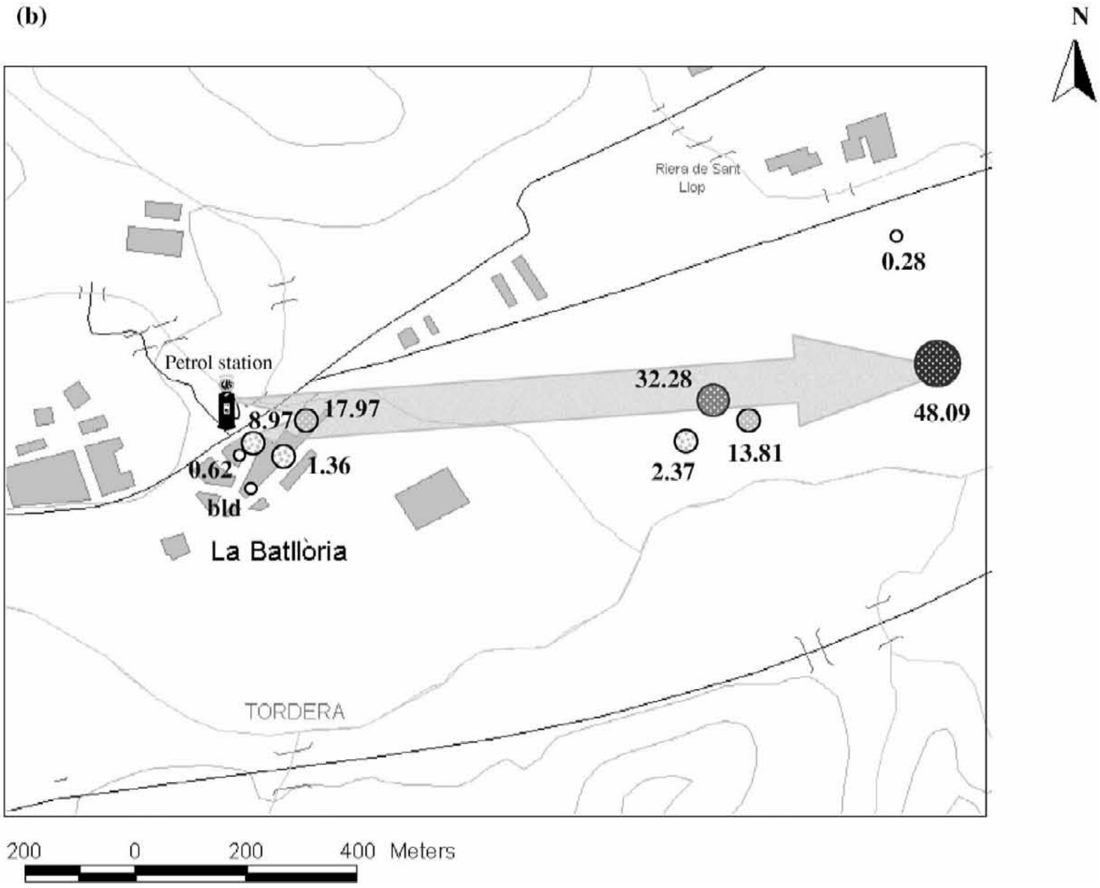
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Fig. 5.

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"Cross-validation of methods used for analysis of MTBE and other gasoline components in groundwater"

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Cross-Validation of Methods Used for Analysis of MTBE and other Gasoline Components in Groundwater

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Key Words

Gas chromatography
Headspace sampling
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Summary

Head space gas chromatography with flame-ionization detection (HS-GC-FID), and purge and trap gas chromatography-mass spectrometry (P&T-GC-MS) have been used to determine methyl-*tert*-butyl ether (MTBE) and benzene, toluene, and the xylenes (BTEX) in groundwater. In the work discussed in this paper measures of quality, e.g. recovery (94 – 111%), precision (4.6 – 12.2%), limits of detection (0.3 – 5.7 µg L^{-1} for HS and 0.001 µg L^{-1} for PT), and robustness, for both methods were compared. In addition, for purposes of comparison, groundwater samples from areas suffering from odor problems because of fuel spillage and tank leakage were analyzed by use of both techniques. For high concentration levels there was good correlation between results from both methods.

Results from P&T analysis showed that 20 of the 21 samples from the vulnerable areas contained MTBE at concentrations up to 666 µg L^{-1}. Levels in seven samples exceeded maximum permissible levels for odor and taste set by the USEPA (20 – 40 µg L^{-1}); for thirteen of the samples levels were between 0.28 and 17.9 µg L^{-1}. The sensitivity of HS-GC-FID was, however, two to three orders of magnitude lower and concentrations of 6 – 10 µg L^{-1} could not always be detected, leading to false negatives. The same behavior was observed for analysis of BTEX – the lower sensitivity of HS-GC-FID and coelution of peaks led to results of poor reliability, and confirmation by GC-MS was always necessary. The applicability of two analytical methods widely used for routine monitoring of VOC thus depends on the organoleptic thresholds of MTBE and BTEX in groundwater (20 µg L^{-1}) and the need to survey trace concentrations of persistent MTBE in vulnerable aquifers.

Introduction

In order to replace antiknock leaded derivatives in gasoline which caused toxic emissions towards the atmosphere, oxygenates derivatives such as alcohols and aliphatic ethers are utilized as octane boosters [1]. Methyl *tert*-butyl ether (MTBE) is currently the most widely used ether oxygenate and is added to gasoline at concentrations up to 30% by volume, depending on national policies [2]. MTBE enters the environment during all phases of the petroleum fuel cycle (e.g. auto emissions, evaporative losses from gasoline stations and vehicles, storage tank release, pipeline leaks, accidental spills, and refinery stock release) [3]. An extensive monitoring study conducted in the US revealed that as a result of the high usage of the compound more than 10% of groundwater samples in urban areas contained MTBE at levels of 0.2–23000 µg L^{-1} [4]. MTBE has also been detected in lakes [5], in stormwater [6], in run-off water [7], and in the atmosphere [8]. A comprehensive review of the environmental behavior and fate of MTBE indicates that partition of the compound between different compartments depends on their physicochemical properties [9]. In short, because of the high solubility of MTBE (25–50 g L^{-1}), low octanol-water partition coefficient (*K*ow; 0.94–1.43), and low Henry's Law constant (55.3 Pa m^3 mol^{-1}), it remains dissolved in surface water from where it can be volatilized to the atmosphere. A small fraction can partition into soil and eventually reach ground water where it is slow to biodegrade and can persist for a long time [10]. Even at very low concentrations it is responsible for taste and odor problems in groundwater [11].

A threshold of 20–40 µg L^{-1} MTBE has recently [12] been imposed in the US. As a result of its persistence and increasing presence in the environment, a major aspect of the monitoring of MTBE is its detection at low levels in different environmental compartments, from water to

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the atmosphere. A recent review indicates that different sampling and analytical techniques are used for its analysis in a wide range of environmental matrices [13]. The analytical approach needed for its unequivocal determination – sampling and preservation of samples, preparation of standard solutions, extraction and analysis, and final quantification procedure – is, however, somewhat complex. These aspects of the analysis are, in general, the main sources of error in all laboratories involved in the monitoring of MTBE, especially in groundwater, because of the combination of high volatility and low concentration levels.

The objective of the work discussed in this paper was to determine quality data for analysis of the gasoline additive MTBE and the volatile aromatic compounds benzene, toluene, ethylbenzene, and the xylenes (BTEX), constituents of petrol commonly used as indicators of contamination, by use of the two methods most commonly used for analysis of VOC – static headspace sampling then analysis by gas chromatography with flame-ionization detection, and purge-and-trap extraction coupled with gas chromatography with mass spectrometric detection, according to EPA method 624 [14]. This paper reports the detection limits, recoveries, and reproducibility obtained by use of both methods. In addition, cross validation was performed by analysis of real groundwater samples; this report indicates the main advantages and disadvantages of each method, and its applicability to real water samples.

Levels of MTBE and BTEX in two aquifers contaminated by tank leakage (Tarragona) and a gasoline spill (La Batlloria) are also reported.

Experimental

Chemicals and Reagents

A standard mixture of benzene, toluene, ethylbenzene, *m* + *p*-xylenes, *o*-xylene, and methyl *tert*-butyl ether (MTBE) was obtained from Supelco (Barcelona, Spain). The mixture was dissolved in methanol and this solution was added to organic-free water. All preparation of standards (dilution, spiking, etc.) was performed over solid carbon dioxide to avoid losses of any of the compounds of interest.

For static headspace GC-FID analysis, α,α,α-trifluorotoluene was used as internal standard. For P&T-GC-MS, deuterated MTBE was used, and fluorobenzene for BTEX analysis. Acetone used for cleaning glassware was from Merck (Darmstadt, Germany).

Sampling Procedure

For the comparison exercise, 21 groundwater samples were taken from two "hot spot" areas in Catalonia in which:

(i) an accidental gasoline spill at a petrol service station (La Batlloria) had occurred in 1997; and
(ii) oil refinery storage tanks had leaked (Tarragona).

These areas had been monitored since these problems occurred and residue levels between 10 and 600 μg L^{-1} were still being encountered [15]. Groundwater samples were collected by use of a Niskins bottle. Samples were transferred to 500-mL amber glass bottles, avoiding passage of air bubbles through the sample and leaving no headspace volume, which could cause losses of the target analytes. For P&T analysis samples were transferred directly to similar 40-mL Tekmar amber glass vials (EPA Method 524.2), which were thereafter used for analysis. Each sample was placed in three such vials which were then immediately placed in a portable freezer and transported to the main laboratory where they were stored at 4 °C. Samples were not acidified but care was taken to ensure samples were analyzed within seven days of collection.

Headspace Analysis with GC-FID

Water samples (10 mL) were sealed in 22-mL headspace vials with an open-center aluminum cap and PTFE-faced butyl rubber septum and, after spiking with 10 μL of 100 μg mL^{-1} solution of the internal standard α,α,α-trifluorotoluene, analyzed by static headspace analysis and gas chromatography with flame ionization detection [16].

Headspace analysis was performed with a Varian Genesis headspace autosampler connected to a Varian Star 3600 gas chromatograph. Samples were equilibrated at 70 °C for 4 min, mixed at 80% of full power for 7 min, and, after mixing, stabilized for 1 min. The sample loop volume was 1 mL, line and valve were maintained at 150 °C, and vials were pressurized at 7 psig. These conditions resulted in the highest sensitivity and reproducibility. Compounds were separated on a 75 m × 0.53 mm × 3 μm film DB-624 fused-silica column from J&W. The GC operating temperatures were: injector 160 °C, detector 300 °C, oven 40 °C (5 min) programmed at 5° min^{-1} to 250 °C. Helium, at 9 psig, was the carrier gas.

Purge and Trap and GC-MS

Tenax-silica gel-charcoal cartridges of the Tekmar 3100 purge and trap concentrator were used. An Aquatek 70 liquid autosampler (Tekmar-Dohrmann) was used to dispense 13-mL samples automatically into a 25-mL purging device. The sample was purged with helium gas at 35 mL min^{-1} for 11 min at ambient temperature. After sample loading the trapped sample components were desorbed by heating the Tenax cartridges at 225 °C and passing helium gas at 3 mL min^{-1} for 3 min, with the injector in splitless mode. These conditions were chosen because they resulted in the maximum response to a large number of volatile organic compounds [17]. GC-MS was performed by means of a Trace GC coupled to a Voyager (ThermoQuest, UK) MS in electron-impact (EI) mode at an electron energy of 70 eV. Compounds were again separated on a 75 m × 0.53 mm × 3 μm film DB-624 fused-silica column from J&W. Helium, at 3.5 mL min^{-1}, was used as carrier gas and the column was programmed from 35 °C (5 min) to 70 °C at 3° min^{-1} (5 min) and then to 210 °C at 6° min^{-1}. The final temperature was maintained for 5 min and the total run time was 50 min. The source and GC interface temperatures were 200 and 250 °C, respectively. The emission current was 100 μV and the detector potential 380 V. Acquisition was performed in time scheduled selected-ion monitoring mode using three ions per compound: MTBE (*m*/*z* 73, 57, and 43), benzene (*m*/*z* 78, 77, and 52), toluene (*m*/*z* 91, 92, and 65), ethylbenzene (*m*/*z* 91, 106, and 77), and the xylenes (*m*/*z* 91, 106, and 77). The internal standard (IS) ions monitored were *m*/*z* 76, 57, and 43 for deuterated MTBE and *m*/*z* 96, 70, and 50 for fluorobenzene.

During GC-MS acquisition the trap was cleaned by baking at 230 °C for 10 min; system blanks were obtained by use of these conditions.

Table I. Quality data obtained from analysis by static HS-GC-FID and P&T-GC-MS.

Compound	Range*		R^2		%*RSD*		Std devn (%)		*LOD* (µg L^{-1})	
	HS	P&T	HS	P&T	HS	P&T	HS	P&T	HS	P&T
MTBE	15000	10.0	0.999	0.9954	102.4	101.0	7.9	11.0	5.7	0.001
Benzene	1000	10.0	0.999	0.9991	95.1	97.7	12.2	10.6	0.6	0.002
Toluene	1000	10.0	0.999	0.9901	100.6	111.8	11.7	4.6	0.6	0.001
Ethylbenzene	1000	10.0	0.999	0.9992	100.4	94.1	8.2	8.1	0.4	0.001
m- + *p*-Xylenes	1000	10.0	0.999	0.9992	99.9	96.0	4.8	10.6	0.3	0.001
o-Xylene	1000	10.0	0.999	0.9967	101.2	96.6	6.3	7.8	0.4	0.002

* Upper limit of the linear range (µg L^{-1}).

Calibration and Quantification

For both types of analysis internal standard calibration was used. For headspace-FID analysis a calibration plot was constructed in the range 1 to 1000 µg L^{-1}; α,α,α-trifluorotoluene was used for quantification. For P&T GC-MS calibration plots were constructed by spiking HPLC water with the test compounds at concentrations from 0.02 to 10 µg L^{-1}. Deuterated MTBE and fluorobenzene (each 1 µg L^{-1}) were added to the sample before extraction.

Recovery studies were performed by spiking HPLC water at a concentration of 10 µg L^{-1} for GC-FID analysis and at 1 µg L^{-1} for GC-MS. These samples were processed automatically as described above. Precautions that must be taken in the analysis of VOC are detailed elsewhere [17].

Results and Discussion

Quality Data

The two methods most commonly used for extraction of MTBE from water are headspace (HS) and purge and trap (P&T) enrichment, although new methods such as solid-phase microextraction are becoming more popular [13]. Basically HS is rather suitable for highly polluted samples which can cause matrix and carry-over problems. P&T enrichment, in accordance with EPA method 624 [14], is the most widely used method for analysis of MTBE and volatile organic compounds in general, because of the large number of compounds that can be analyzed simultaneously and the easy automation. Table I reports quality data obtained for both methods. For HS-GC-FID, calibration equations obtained for each analyte were determined by using of α,α,α-trifluorotoluene at 100 ppb as internal standard. *LOD* were calculated from the standard deviations (S_c) obtained from seven replicate analyses of BTEX at 1 µg L^{-1} and MTBE at 14 µg L^{-1}, by use of the equation [18]:

$$\text{LOD} = t_{(N\text{-}1,1\text{-}\alpha\,=\,0.99)} \times S_c$$

SD% was obtained from the means of 13 replicate analyses at three different concentrations (1, 50, and 500 µg L^{-1}) over the entire linear range. The linear range of HS-GC-FID enables detection of MTBE and BTEX from the limit of detection to 15 mg L^{-1} and 1 mg L^{-1}, respectively. The linear range of P&T-GC-MS is from the limit of detection to 10 µg L^{-1}. When this concentration is exceeded the system suffers from memory effects and poor linearity; highly polluted samples should, therefore, be diluted before analysis. Recoveries and intra-day variation were, on the other hand, excellent for both methods, as indicated by a maximum standard deviation of 12.2%. Recoveries were satisfactory for both methods. The main difference between the methods was, however, their sensitivity. Whereas for P&T the limit of detection was 0.002 µg L^{-1} for all the analytes studied, that for HS was much lower – up to 5.7 µg L^{-1} for MTBE and 0.3–0.6 µg L^{-1} for BTEX. From the results reported it is clear that either HS or P&T is sufficiently sensitive for determination of MTBE at levels higher than 10 µg L^{-1} and will obviously be adequate as an alarm technique for detection of samples containing 20–40 µg L^{-1}, the threshold for odor and taste problems [16]. HS might not, however, be sufficiently sensitive for trace-level determination of MTBE in groundwater, in which residues might be encountered at the low µg L^{-1} level. An additional problem of HS-GC-FID is the need for confirmatory analysis of all positive samples. As a result, P&T-GC-MS is highly recommended for low-level determination of MTBE and BTEX, because of the high sensitivity and reproducibility obtained, the possibility of automation which enables high sample throughput, and quantitative and confirmatory analysis in a single run, with no need for further confirmation. HS-GC-FID is, however, an appropriate option for the direct analysis of highly polluted samples. Both techniques are highly precise and easy to use.

Cross-Validation Studies with Real Environmental Water Samples

For purposes of comparison twenty-one groundwater samples were analyzed in parallel by use of HS-GC-FID and P&T-GC-MS. Figure 1 shows an HS-GC-FID chromatogram obtained from a groundwater sample; a typical degraded gasoline profile is seen with dicyclopentadienes, cyclopentadienes and derivatives, and branched aliphatic hydrocarbons [19]. If standards are available GC-FID is a good means of determination of such compounds, although GC-MS confirmation is always necessary because of coelution problems. Figure 2 shows a typical P&T-GC-MS chromatogram obtained by SIM. The advantage of the latter technique is that with SIM acquisition a neater chromatogram is obtained; this makes identification and quantification easier at even very low concentration levels. The MTBE and BTEX levels found are reported in Table II. For each experiment quality control and blank analyses were included, with the intention of monitoring time variations. All the samples analyzed came from areas in which a fuel spill or tank leakage had occurred during 1997. These areas had been surveyed since the accidents and levels of MTBE and other fuel additives had been encountered at levels up to 300 µg L^{-1} [15]. In this work, a larger number of wells was monitored and of the compounds studied, MTBE was found in 20 of 21 wells sampled, at higher concentrations than discovered in previous work. This is attributed to the long half life of the compound in groundwater compared with BTEX, which can undergo degradation [20].

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Table II. Cross-validation of results from static HS-GC-FID and P&T-GC-MS analysis of oxygenate additives. Concentrations are given in μg L^{-1}.

Sample	MTBE	Benzene	Toluene		Ethylbenzene		*m*- + *p*-Xylenes		*o*-Xylene			
	HS	P&T	HS	P&T	HS	P&T	HS	P&T	HS	P&T	HS	P&T
Tarragona												
Sevil-Caseta	<l.d.*	8.50	<l.d.	1.47	<l.d.	8.89	<l.d.	2.53	<l.d.	1.76	<l.d.	1.30
Sevil-road	n.a.**	28.02	n.a.	1491	n.a.	1351	n.a.	312.0	n.a.	508.5	n.a.	454.9
Sevil-sinia	<l.d.	11.26	<l.d.	1.59	<l.d.	10.18	<l.d.	3.15	<l.d.	2.10	<l.d.	1.58
Gate-well	12.7	20.66	<l.d.	1.71	<l.d.	9.05	<l.d.	2.55	<l.d.	1.79	<l.d.	1.28
Sorts	610	666.3	<l.d.	5.88	<l.d.	3103	<l.d.	25.94	<l.d.	24.05	<l.d.	5.47
Ferrerota	65	74.48	<l.d.	4.60	<l.d.	30.31	<l.d.	7.76	<l.d.	4.43	<l.d.	2.77
Tarragonins	<l.d.	5.62	<l.d.	1.74	<l.d.	8.30	<l.d.	2.18	<l.d.	1.59	<l.d.	1.08
Pineda-2	115	42.66	35.0	8.75	8.0	269.4	<l.d.	36.07	50	31.23	65	43.12
Camping	6.0	10.53	<l.d.	1.96	<l.d.	9.88	<l.d.	2.74	<l.d.	2.02	<l.d.	1.34
Repsol-73	<l.d.	10.13	1.6	1.53	<l.d.	9.52	0.7	3.25	13	2.15	<l.d.	1.58
Repsol-83	<l.d.	8.23	<l.d.	1.84	<l.d.	11.08	<l.d.	3.60	<l.d.	2.24	<l.d.	1.57
La Batlloria												
Formigueta	<l.d.	0.28	<l.d.	<l.d.	<l.d.	0.03	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.
Comptesa	20.0	48.09	<l.d.	<l.d.	<l.d.	0.13	<l.d.	0.04	<l.d.	<l.d.	<l.d.	<l.d.
Ferreria 1	11.0	13.81	<l.d.	0.02	<l.d.	0.37	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.
Ferreria 2	57.0	32.85	<l.d.	<l.d.	<l.d.	1.43	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.
Ferreira 3	<l.d.	2.37	<l.d.	<l.d.	<l.d.	0.05	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.
Xemani	5.4	8.97	<l.d.	0.09	<l.d.	0.14	<l.d.	0.06	<l.d.	<l.d.	<l.d.	<l.d.
Xemani 2	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	0.07	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.
Auladell	<l.d.	0.62	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.
Vias	15	17.97	<l.d.	0.02	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.
Blancher	<l.d.	1.36	<l.d.	<l.d.	<l.d.	0.09	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.	<l.d.

* below the detection limit for the compound, see Table I; ** not analyzed.

styrene) in HS-GC-FID and to the matrix itself, because no filtration of the sample could be performed.

Conclusions

These data clearly reveal that contamination of groundwater by MTBE is a problem and that regular monitoring is needed to determine the extent of the contamination and then start remediation. Appropriate tools are thus necessary. In the work discussed in this paper the two methods most widely used for the analysis of gasoline oxygenates have been compared by analysis of groundwater samples which reflect real problems of analysis from sampling to the final results. Both HS-GC-FID and P&T-GC-MS are suitable for detection of MTBE and BTEX in groundwater. Whereas the former lacks sufficient sensitivity for detection of trace amounts, it is easier to use, has a wider linear range, and it is especially applicable to the determination of high concentrations of MTBE without the need for sample dilution. For positive samples, however, P&T GC-MS must be used for confirmatory purposes, with previous dilution of the sample when concentration levels are too high. The use of P&T-GC-MS, an EPA standard method, enables more precise and unequivocal measurement.

To avoid poor reproducibility care should be taken during sampling to prevent collection of samples containing two phases. The choice of proper surrogate compounds to enable verification of the entire analytical procedure and for use in quantification might also enhance the quality of the results. In this sense the use of deuterated MTBE is specially suitable for quantification of MTBE when MS detection is used whereas α,α,α-trifluorotoluene is appropriate for the determination of MTBE and BTEX by HS-GC-FID, and results in high-quality data for all the compounds.

In future work other fuel oxygenates, e.g. ethyl *tert*-butyl ether (ETBE), di-isopropyl ether (DIPE), *tert*-amyl methyl ether (TAME), *tert*-butyl formate (TBF), and *tert*-amyl methyl alcohol (TAA), will be included in the analysis. The new method will be used for routine monitoring of MTBE and related fuel oxygenates in our current monitoring programs.

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References

[1] Begley, R.; Rotman, D. *Chem. Week* **1993**, *152*, 7–14.

[2] US Environmental protection Agency, **1994**, Health Risk Perspectives on Fuel Oxygenates. EPA 600/R-94/217, Washington, DC.

[3] Squillace, P.J.; Zogorski, J.S.; Wilber, W.G.; Price, C.V. *Environ. Sci. Technol.* **1996**, *30*, 1721–1730.

[4] Squillace, P.J.; Moran, M.J.; Lapham, W.W.; Price, C.V.; Clawges, R.M.; Zogorski, J.S. *Environ. Sci. Technol.* **1999**, *33*, 4176–4187.

[5] Reuter, J.E.; Allen, B.C.; Richards, R.C.; Pankow, J.F.; Goldman, C.R.; Scholl, R.L.; Seyfried, J.S. *Environ. Sci. Technol.* **1998**, *32*, 3666–3672.

[6] Delzer, G.C.; Zogorski, J.S.; Lopes, T.J.; Bosshart, R.L. **1996**. Occurrence of the Gasoline Oxygenate MTBE and BTEX Compounds in Urban Stormwater in the United States 1991–95, Report 96-4145, US Geological Survey Water-Resources, Rapid City, SD.

[7] Pankow, J.F.; Thomson, N.R.; Johnson, R.L.; Baehr, A.L.; Zogorski, J.S. *Environ. Sci. Technol.* **1997**, *31(10)*, 2821–2828.

[8] Kirshtetter, T.W.; Singer, B.C.; Harley, R.A.; Kendall, G.R.; Chan, W. *Environ. Sci. Technol.* **1996**, *30*, 661–670.

[9] Squillace, J.P.; Pankow, J.F.; Korte, N.E.; Zogorski, J.S. *Environ. Toxicol. Chem.* **1997**, *16(9)*, 1836–1844.

[10] Borden, R.C.; Daniel, R.A.; LeBrun, I.; Davis, C.W. *Water Resour. Res.* **1997**, *33*, 1105–1115.

[11] Young, W.F.; Horth, H.; Crane, R.; Ogden, T.; Arnott, M. *Water Res.* **1996**, *30(2)*, 331–340.

[12] Drinking Water Advisory: consumer acceptability advise and health effects analysis on methyl tertiary butyl ether (MtBE);

U.S. Environmental Protection Agency, Office Water, **1997**, EPA-822/F-97-008.

[13] Schmidt, T.C.; Duong, H.A.; Berg, M.; Haderlein, S.B. *Analyst* **2001**, *126*, 405-413.

[14] US Environmental Protection Agency. 1984. Method 624 – Purgeables. 40 CFR Part 136, 43373; Federal Register 49, No. 209.

[15] Fraile, J.; Niñerola, J.M.; Olivella, L.; Figueras, M.; Ginebreda, A.; Vilanova, M.; Barceló, D. *The Scientific World Journal* **2002**, *2*, 1235-1242.

[16] Stuart, J.D.; Roe, V.D.; Lacy, M.J.; Robbins, G.A. *Anal. Chem.* **1989**, *61*, 2584-2585.

[17] Martinez, E.; Lacorte, S.; Llobet, I.; Viana P.; Barceló, D. *J. Chromatogr. A* **2002**, *959*, 181-190.

[18] Glaser, J.A.; Foerst, D.L.; Mckee, G.D.; Quave, S.A.; Budde, W.L. *Environ. Sci. Technol.* **1981**, *15(12)*, 1427-1435.

[19] Ventura, F.; Romero, J.; Pares, J. *Environ. Sci. Technol.* **1997**, *31*, 2368-2374.

[20] Johnson, R.; Pankow, J.; Bender, D.; Price, C.; Zogorski, J. *Environ. Sci. Technol.* **2000**, *34*, 210A-217A.

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"Fate of gasoline oxygenates in conventional and multilevel wells of a contaminated groundwater table in Düsseldorf, Germany"

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FATE OF GASOLINE OXYGENATES IN CONVENTIONAL AND MULTILEVEL WELLS OF A CONTAMINATED GROUNDWATER TABLE IN DÜSSELDORF, GERMANY

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Abstract—In a gasoline-contaminated site in Düsseldorf, Germany a two-year monitoring program was carried out to determine the presence, behavior, and fate of 12 gasoline additives in a total of 96 samples from 14 groundwater wells. The origin of contamination was suspected to be a gasoline spill at a gas station. Target compounds were methyl-*tert*-butyl ether (MTBE), its main degradation products, *tert*-butyl alcohol (TBA) and *tert*-butyl formate (TBF); other gasoline additives, oxygenate dialkyl ethers: Ethyl-*tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME) and diisopropyl ether (DIPE); aromatics: Benzene, toluene, ethylbenzene and xylenes (BTEX), and other compounds causing odor problems: Dicyclopentadiene and trichloroethylene. Purge and trap coupled with gas chromatography-mass spectrometry permitted detection of ng/L concentrations. Ninety of the 96 samples analyzed contained MTBE at levels varying between 0.01 to 645 μg/L. Five contaminated hot spots were identified with levels up to U.S. Environmental Protection Agency (U.S. EPA) drinking water advisory values (20–40 μg/L) and one of them doubling Danish suggested toxicity level of 350 μg/L at a depth of 11 m. No significant natural attenuation was found in MTBE degradation, although samples with high levels of MTBE contained 0.1 to 440 μg/L of TBA. These levels were attributed to its presence in the contamination source more than MTBE degradation. *tert*-Butyl alcohol was found to be recalcitrant in groundwater. In all cases, BTEX were at low concentrations or not detected, showing less persistence than MTBE. The monitoring of the contamination plume showed that the distribution of the MTBE and TBA in the aquifer formed a similar vertical concentration profile that was influenced by the groundwater flow direction.

Keywords—Methyl-*tert*-butyl ether Degradation products Aromatic hydrocarbons Purge/trap Groundwater

INTRODUCTION

Contamination of groundwater by motor vehicle fuels and fuel additives is not a new problem, given the history and pervasive use of fuels in the last centuries. Against this background of experience, recent events have focused attention on fuels containing chemicals known as oxygenates [1]. Many case studies of groundwater contamination have been completed in the United States [2–5], and many others have been carried out in Europe in the last five years [6–10].

Fuel oxygenates are added to gasoline to increase combustion efficiency and to reduce air pollution. Since the ban of tetraalkyl lead compounds, methyl *tert*-butyl ether (MTBE) is the most commonly used octane enhancer and one of organic chemical with the highest production volume worldwide [11]. In Europe, large amounts (several million tons) of MTBE are manufactured and used each year, which puts it into the category of high production volume chemicals [12]. Several other ethers and alcohols also serve as oxygenates and could become prevalent, depending on various factors such as cost, ease of production and transfer, and blending characteristics. These additives include methanol, ethyl-*tert*-butyl ether (ETBE), *tert*-amyl methyl ether (TAME), diisopropyl ether (DIPE), and *tert*-butyl alcohol (TBA), but except for ethanol its use is, in general, secondary.

In European gasoline the average MTBE content is approximately 2% volume although the percentage varies considerably between countries and commercial types of gasoline [13]. In Germany, where this average was calculated at 1.35%, MTBE is used at different concentrations in regular (0.4%), eurosuper (0.4–4.2%), super premium unleaded (9.8%), and Optimax (11.9%) gasoline [14]. Beginning in 1985, MTBE was added to gasoline in Germany. Since then, the use of MTBE in this country has increased significantly and reached approximately 450,000 to 500,000 tons in 1997 [15,16]. Inevitably, some of this MTBE is released to the environment during the manipulation or storage of petrol fuel and becomes a groundwater pollutant due to its high solubility, high mobility, and slow degradation [17]. However, in Germany, contamination sources are being minimized by improved technology, such as the use of doubled-sided tanks at gasoline stations [18].

Information on the specific contents of other oxygenates in gasoline and their impact on the environment are very scarce. In Europe, ETBE and TAME also are used in substantial amounts [13] and in France, Italy, and Spain, the consumption of ETBE probably will increase even more rapidly than the use of MTBE due to tax incentives for the application of ethanol which is used to produce this compound [13]. Also, approximately 0.1 million tons annually of TAME are used as a fuel oxygenate in Finland [16].

Maximum permissible levels of MTBE in groundwater have not yet been established in Europe. Instead of health effects concerns (low acute and probably also chronic toxicity), there is much interest in the esthetic implications of MTBE in water resources used for the production of drinking water. Taste and odor thresholds for this compound in water have been reported at very low concentrations, approximately 25 to 60 μg/L for

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flavor and 40 to 70 μg/L for odor at 25°C [19]. For this reason, the U.S. EPA established a drinking water advisory for esthetic concerns of 20 to 40 μg/L in 1997 [20]. However, while a phase-out of MTBE in gasoline finds increasing support throughout the United States, in Germany, authorities only recently began to evaluate the MTBE situation in the country and decided not to implement a drinking water and surface water standard because MTBE concentrations in Germany are believed generally to be low [18] (www.umweltbundesamt.de/verkehr/kraftubst/additiva/mtbe.htm). Nevertheless the German Environment Agency (UBA) recommended a maximum permissible concentration of 0.1 μg/L to reduce the occurrence of anthropogenic compounds with unknown toxicity or unspecific regulation in the environment [21].

Furthermore, whether the resulting contamination will become an important environmental issue depends, in part, on the degradation rates and transformation products of MTBE. Although the rates generally are slow, the major products of its degradation are *tert*-butyl formate (TBF) by atmospheric photooxidation and *tert*-butyl alcohol (TBA) in the aqueous phase [22,23]. Among other methods, these products can be monitored by fully automated purge and trap coupled to gas chromatography–mass spectrometry (GC/MS) [24]. In Catalonian groundwater samples, the abovementioned compounds and other fuel additives such as oxygenate dialkyl ethers were detected at ppb concentrations in groundwater after a fuel spill or an underground storage tank leakage [24]. Other target compounds that can cause odor problems in groundwater are dicyclopentadiene (DCPD), present at trace levels in gasoline formulation and with a very low odor threshold of 0.025 μg/L [25], and trichloroethylene (TCE), an industrial organochlorinated solvent used as a metal degreaser in automobile production.

The objectives of the present study were to monitor a MTBE-contaminated groundwater in Düsseldorf, Germany, that was suspected to have originated after a gasoline spill episode in a neighboring service station. The monitoring data of the two years of surveillance were used to determine the presence of MTBE, behavior (horizontal movement and vertical profile) of the MTBE-contamination plume, and identification of degradation products and their degradation rate in the aquifer.

To achieve such objectives, the sampling protocol included conventional and multilevel wells to have a deeper insight into the contamination plume, which in most occasions are reported as thin and highly stratified [26]. Conventional monitoring wells, with screened intervals of 3 m or more, blend the groundwater over the entire length of the screen. This can mask the true concentrations and distribution of contaminants. Multilevel wells with short-screened intervals overcome this problem and offer more precise identification with a better understanding of the three-dimensional groundwater flow and distribution of contaminants. Compared to multiple individual wells, these are low cost and easy use [27].

This study also fills the gap indicated in a recent overview paper [28], which pointed out that no data on TBA levels at MTBE-contaminated sites were available due to the difficulty of TBA analysis at trace concentrations. In addition, no previous studies include data on potential MTBE degradation products, importance of the depth-oriented sampling, and fate within the aquifer.

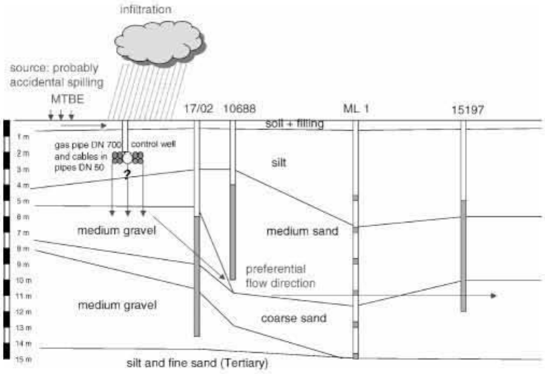

Fig. 1. Hypothetical model for the flow path of methyl-*tert*-butyl ether under the model site in Düsseldorf, Germany. The different monitoring wells are given in dark gray. The filters of the wells are marked in gray. The horizontal distance from the theoretical source to well 15197 is 160 m.

MATERIALS AND METHODS

Reagents and materials

Standards were prepared from methanolic solutions at 2,000 mg/L (TAME and benzene, toluene, ethylbenzene, and xylens [BTEX]/MTBE mix) and 5,000 mg/L (TCE) or single compound neat stock solutions (ETBE, DIPE, TBA, DCPD) purchased from Supelco (Bellefonte, PA, USA) and TBF from Aldrich (Steinheim, Germany). Deuterated methyl *tert*-butyl ether, MTBE-d_3 (Aldrich, Germany), fluorobenzene, and 1,2-dichlorobenzene-d_4 (U.S. EPA 524 Internal Standard Mix from Supelco) were used as internal standards. Each compound was obtained in the highest purity that was available commercially (98.3–99.7%). Working standard solutions were prepared in ultrapure methanol and added on organic-free water (Merck, Darmstadt, Germany).

Study site

A two-year monitoring program had been carried to determine 12 gasoline additives in 96 samples from 14 groundwater wells located in the east of Düsseldorf (Germany).

The altitude in the contaminated area is between 41.6 and 43.2 m mean sea level. The quaternary deposits mostly consist of fine sand, coarse sand, and gravel in a depth of 3.0 to 6.5 m to 14 m below the ground. The altitude of the tertiary clay and fine sands is between 28.0 and 30.0 m mean sea level (see Fig. 1). The aquifer has a thickness of about 7.5 to 11.0 m (groundwater level around 38–39 m mean sea level). Above the aquifer is a layer of silt and clay that is more or less watertight. This layer is overlain by a layer about 1 m thick consisting of filling material, such as soil and bricks.

As a result of odors detected in this area since 1999, nine sampling campaigns have been conducted since November of 2001. The horizontal movement and vertical profile of contamination plumes (basically MTBE and TBA) have been studied following levels found in 11 conventional monitoring wells that have a continuous filter between 4 and 5 m and 11 to 12 m depth. These wells provide data on the average concentration of the whole aquifer. Three new wells built in November 2002 were installed in the line between older ones (10688 and 10979) to find the center of the contamination plume. Two of these new wells (called ML1 and ML2) were multilevel wells,

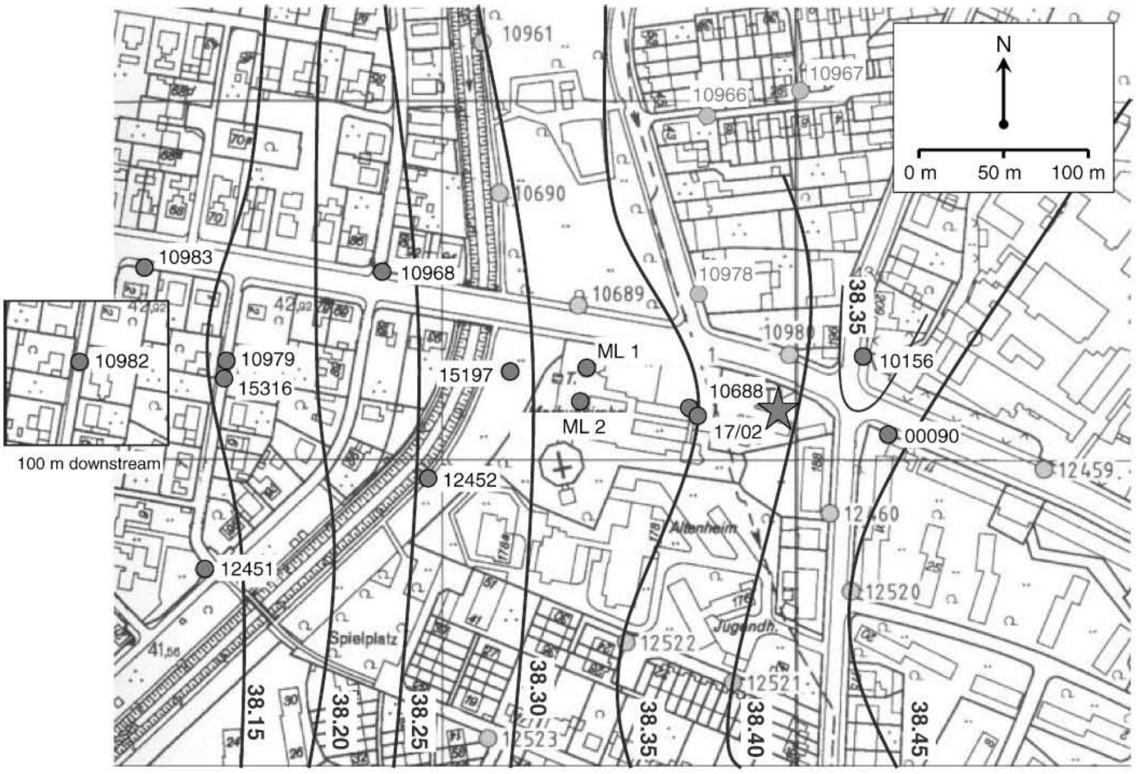

Fig. 2. Map of methyl-*tert*-butyl ether–contaminated site in Düsseldorf, Germany. The monitoring wells are marked with dark gray points and the suspected source of contamination with a star. The lines of equal groundwater level measured in August 2003 are given with the height in meters above mean sea level.

with filters installed at different depths. A map of the study site with the location of the monitoring wells, distribution of the groundwater level according to measurements performed in August 2003, and the derived isohypses is given in Fig. 2. The sampling periodicity of these wells depended on the significance of the levels found in previous campaigns (see Table 1). Physicochemical properties of the groundwater were elucidated in June 2003 (Table 2) to assess the potential biological or chemical degradation of the pollutants.

Sampling and sample preparation

The U.S. EPA water sampling techniques for volatile organic compounds were used [29], except that samples were

Table 1. List of monitored wells (from east to west), sampling dates, and the total concentration of all target oxygenates (including *tert*-butyl alcohol) expressed in μg/L. Blank cells indicate that no sample was taken. In the multilevel (ML) wells, the maximum concentrations of the profile are reported

	Nov. 28, 2001	Feb. 14, 2002	Apr. 18, 2002	Jun. 26, 2002	Nov. 21–27, 2002	Mar. 7, 2003	Jun. 2–3, 2003	Aug. 12–13, 2003	Nov. 3–4, 2003
00090	0.59	1.84							
10156							0.53		
17/02			4.24		5.56				
10688	232	48.73	30.87	23.84	20.14	7.55	10.53	9.57	4.43
ML1					1,088	385	78.56	74.51	73.52
ML2					608	765	924	187	529
15197					26.34	28.54	74.31	271	214
12452		1.45			0.75				
10968							0.44		
10979	16.46	15.20	9.97	7.35	14.46	19.50	25.62	27.43	41.43
15316								3.75	4.99
12451					0.44				
10983	0.31	1.43					0.35		
10982	0.34	1.19							

Table 2. Physico-chemical properties of the groundwater in multilevel wells and ML1 and ML2 on the sampling of June 2003

Well	Depth (m)	pH	Temp. (°C)	O_2 (mg/L)	Conductivity (µS/cm)	Chloride (mg/L)	Nitrate (mg/L)	Nitrite (mg/L)	Ammonia (mg/L)	Sulfate (mg/L)	Sulfide (mg/L)
ML1	7	6.88	16.4	1.0	871	31	<0.25	<0.02	5.4	103	11
	9	7.01	17.6	1.1	877	33	<0.25	<0.02	7.8	113	17
	11	7.03	17.2	1.1	866	34	<0.25	0.05	7.8	110	9
	13	7.12	16.9	0.7	788	30	<0.25	<0.02	5.1	72	7
	15	7.11	18.3	0.9	769	32	<0.25	<0.02	1.1	85	12
ML2	8	6.76	14.2	0.8	856	36	<0.25	<0.02	6.1	84	<5
	10	6.95	14.7	0.7	994	48	<0.25	<0.02	11.3	102	<5
	11	6.90	15.8	0.7	1,107	46	<0.25	<0.02	14.5	119	7
	12	6.94	15.8	0.8	1,070	47	<0.25	<0.02	17.2	113	9
	13	6.93	14.8	0.9	1,155	53	<0.25	<0.02	19.4	121	5
	14	6.99	17.6	0.8	1,086	54	<0.25	<0.02	9.5	117	14

not preserved by acidification because TBF can be hydrolyzed at pH = 2 [22].

Samples from the different wells were collected in triplicate after water had run for several minutes until temperature and dissolved oxygen were constant according to German Technical and Scientific Association for Gas and Water standard techniques [30]. A portable pump, a Danfoss MP1 (Danfoss A/S, Nordborg, Denmark), working at a flow rate of approximately 1.0 m^3/h was used to recover groundwater, except in emergency well 17/02, which has its own pump at 10 m^3/h. Amber glass vials (40 ml, Tekmar, Mason, OH, USA) with Teflon®-faced silicone septa were filled directly, avoiding air bubbles passing through the sample, until overflow to prevent volatilization during sampling and storage. These vials were used for posterior analysis, so they were never opened during the process.

Immediately after collection, samples were placed inside a portable freezer and shipped under cool conditions to Consejo Superior de Investigaciones Científicas laboratory in Barcelona, Spain where they were stored at 4°C and analyzed in less than two weeks. Just before extraction, internal standards (MTBE-d_3, fluorobenzene, and 1,2-dichlorobenzene-d_4) automatically were added to the sample at a concentration of 0.5 µg/L.

Purge and trap GC/MS analysis

A purge and trap concentrator Tekmar 3100 coupled to a SOLATek 72 multimatrix vial autosampler (Tekmar-Dohrmann, Mason, OH, USA) was used, which automatically dispensed 10-ml sample aliquots into a purging device. Volatile organic compounds were purged from water samples for 13 min by bubbling helium (35 ml/min) and absorbed onto a Tenax®-silica gel-charcoal trap (Supelco) at room temperature. After sample loading, the trapped sample components were desorbed at 225°C during 4 min and transported directly to the GC/MS system (Trace GC coupled to a Voyager MS by ThermoQuest Finnigan, Austin, TX, USA).

Extracts were transferred onto a 75- × 0.53-mm i.d. DB-624 (J&W Scientific, Folsom, CA, USA) fused silica capillary column with a 3-µm film thickness where they were separated as described in a preceding study [24]. Detection and quantitation of target compounds were performed as depicted in previous studies [24,31], although TCE and DCPD were added to the acquisition program and another internal standard (1,2-dichlorobenzene-d_4) was used, as reported in Table 3.

Quality assurance/quality control

Fully automated purge and trap and GC/MS permitted to resolve 12 target compounds in groundwater at trace levels

Table 3. Gas chromatography–mass spectrometry (GC–MS) in time-scheduled selected ion monitoring (SIM) acquisition program in three retention time windows: CAS number, retention time (Rt), molecular weight (MW), quantitation, and confirming ions

					Selected ions (*m/z*)	
Compound	CAS no.	Rt (min.)	MW (*m/z*)	Quantitation	Secondary	Tertiary
tert-Butyl alcohol	75-65-0	13.11	74	59		
Methyl-*tert*-butyl ether-d_3[a]	29366-08-3	13.43	91	76	57	43
Methyl-*tert*-butyl ether	1634-04-4	13.51	88	73	57	43
Diisopropyl ether	108-20-3	15.11	102	45	87	59
Ethyl-*tert*-butyl ether	637-92-3	16.30	102	59	87	57
tert-Butyl formate	762-75-4	18.10	102	59	56	57
Benzene	71-43-2	20.02	78	78	77	52
tert-Amyl methyl ether	994-05-8	20.52	102	73	55	87
Fluorobenzene[a]	462-06-6	21.25	96	96	70	50
Trichloroethylene	79-01-6	22.88	130	130	132	95
Toluene	108-88-3	27.97	92	91	92	65
Ethylbenzene	100-41-4	32.96	106	91	106	77
m+*p*-Xylene	108-38-3 106-42-3	33.32	106	91	106	77
o-Xylene	95-47-6	34.51	106	91	106	77
Dicyclopentadiene	77-73-6	39.43	132	66	132	39
1,2-Dichlorobenzene-d_4[a]	2199-69-1	40.35	150	150	152	115

[a] International standards.

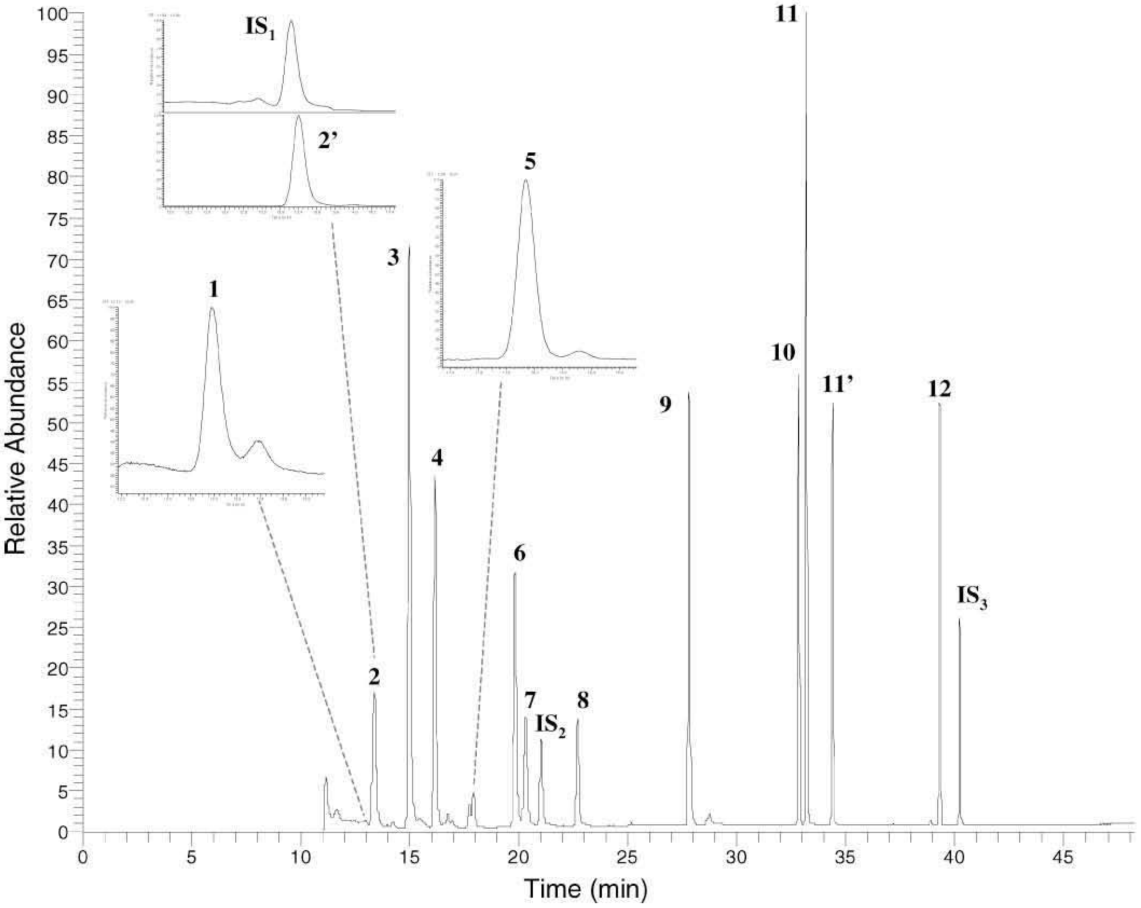

Fig. 3. Total ion chromatogram (TIC) in selected ion monitoring (SIM) mode for a 1-μg/L spiked groundwater. Compound identification number: 1 = *tert*-butyl alcohol (m/z = 59), 2 = methyl-*tert*-butyl ether-d3 (IS1: m/z = 76) + methyl-*tert*-butyl ether (2′: m/z = 73), 3 = diisopropyl ether, 4 = ethyl-*tert*-butyl ether, 5 = *tert*-butyl formate (m/z = 59), 6 = benzene, 7 = *tert*-amyl methyl ether, IS2 = fluorobenzene, 8 = trichloroethylene, 9 = toluene, 10 = ethylbenzene, 11 = m+*p*-xylene, 11′ = *o*-xylene, 12 = dicyclopentadiene, and IS3 = 1,2-dichlorobenzene-d4.

(Fig. 3). Limits of detection were calculated by a signal-to-noise ratio of three, and they are given in Table 4. Special consideration was given to the determination of polar MTBE degradation products, TBA and TBF, because not much data on method performance and environmental levels had been reported on these compounds in groundwater.

Simultaneous to GC/MS acquisition, the trap was programmed at 230°C during 10 min to remove adsorbed compounds (bake conditions). Using these conditions, system blanks were attained. Additionally, each analytical sequence included quality control standards and procedural blanks to check noise and background levels and possible carryover effects and to cover little retention time variations. In all cases, blank concentrations were below limits of quantitation.

The calibration equations were obtained by analyzing blank groundwater samples spiked with target compounds in a range of 0.01 to 10 μg/L and internal standards at a constant concentration of 0.5 μg/L. Linear regression of base peak area versus concentration (calculated relative to the nearest internal standard using m/z 76 for MTBE-d_3, m/z 96 for fluorobenzene, and m/z 150 for 1,2-dichlorobenzene-d_4) gave a good fit (typically, $r^2 > 0.990$) for all compounds. Exceeding the upper concentration range, the system suffered from memory effects and poor linearity. Therefore, in case the samples were suspected of being highly polluted, an automated dilution was analyzed to avoid system contamination. The limits of quantitation were set at the most diluted calibration standard for each compound.

For all groundwater samples, two replicates were analyzed. Different dilution factors were chosen for each sample, taking into consideration MTBE last campaign concentrations. Some of these factors were changed for the second replicate to fit the signal into linear range. Normally the average value between these two replicates is reported in the tables or figures. In all cases, the relative standard deviation was less than 20%.

RESULTS AND DISCUSSION

General remarks

The affected area originated from a leakage in the tanks of a petrol station. Foul-smelling groundwater was detected in the neighborhood and was attributed to the migration of MTBE

Table 4. Minimum, maximum, average, and median of detected levels found in Düsseldorf, Germany, contaminated groundwater samples (Nov. 01–Nov. 03, *n* = 96). The limits of detection (LODs) were calculated by a signal-to-noise ratio of three and the limits of quantitation (LOQs) were set at the most diluted calibration standard for each compound

Compound	LODs (µg/L)	No. of samples ≥LOQs (*n* = 96)	Min. (µg/L)	Max. (µg/L)	Average (µg/L)	Median (µg/L)
Oxygenate additives						
Methyl-*tert*-butyl ether	0.001	91	0.01	645	67.6	8.70
Ethyl-*tert*-butyl ether	0.009	0	—	—	—	—
tert-Amyl methyl ether	0.013	27	0.02	0.15	0.05	0.04
Diisopropyl ether	0.008	37	0.01	0.29	0.07	0.05
Degradation products						
tert-Butyl alcohol	0.110	93	0.18	443	35.1	3.38
tert-Butyl formate	0.034	7	0.08	5.42	1.59	0.49
Aromatic hydrocarbons						
Benzene	0.002	44	0.01	0.64	0.04	0.02
Toluene	0.001	66	0.01	5.52	0.38	0.09
Ethylbenzene	0.001	42	0.01	0.78	0.10	0.02
m+*p*-Xylene	0.001	62	0.01	1.59	0.16	0.03
O-Xylene	0.002	37	0.01	1.35	0.18	0.04
Total BTEX[a]		71	0.01	9.24	0.67	0.14
Other volatile organic compounds						
Trichloroethylene	0.001	28	0.02	0.06	0.04	0.04
Dicyclopentadiene	0.003	17	0.05	1.04	0.26	0.10

[a] BTEX = Benzene, toluene, ethylbenzene and xylenes.

from oil into the aqueous phase. Added to this problem, and taking into account previous knowledge about the site and the aquifer, the groundwater under study was considered to be of poor quality, influenced by former pesticide spills and the run-off from a former rubbish dump. Sulfate-reducing conditions are likely (see Table 2). So, the concentrations of the pollutants should be related to the activity of anaerobic microorganisms.

It is obvious that MTBE poses a problem of groundwater contamination, and detailed monitoring data are needed to determine the magnitude of this contamination to prepare remediation actions. In this study, the results were clear: MTBE was detected in 91 of 96 groundwater samples analyzed at concentrations that varied between 0.01 and 188 µg/L (measured in the conventional monitoring wells as is given in Fig. 4) and a maximum detected level of 645 µg/L at the depth of 11 m (in a multilevel well, ML1, as shown in Tables 4 and 5). Samples with high levels of MTBE contained TBA and TBF at maximum concentration of 440 and 5.42 µg/L, respectively.

To date, neither Europe nor Germany regulates MTBE or implements any MTBE drinking water standard. However, esthetic thresholds can be used for comparison purposes. For example, in view of MTBE values, five monitoring wells were identified as hot spots that exceeded the U.S. EPA maximum permissible levels of taste and odor in water (20–40 µg/L). Maximum detected level practically doubled Danish suggested toxicity level of 350 µg/L in water. Moreover, taking into account stricter measures, such as Swiss guideline value for groundwater of 2 µg/L based on precautionary principle (MTBE as a tracer for gasoline presence in water) 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 risk sites (e.g., 17/02 or 15316).

The detection of high TBA concentrations in the aquifer (up to 443 µg/L) was of environmental concern because it may be as recalcitrant as MTBE. In contrast to MTBE, this main degradation product is a known animal carcinogen [32]. In California, a provisional drinking water action level for TBA of 12 µg/L recently has been set because of its anticipated human toxicity [33] and, in Maine or New York, other thresholds have been established at 25 and 50 µg/L, respectively.

In contrast to MTBE, the other oxygenate additives always were found at lower levels with maximum concentrations of 0.15 and 0.29 µg/L for TAME and DIPE, respectively, and ETBE was not detected in any of the samples. This was expected because they are added to gasoline at lower levels (although the specific contents is not available in the literature), and they have a lower solubility in water (between 3 and 4 times less soluble than MTBE [11]). These values were comparable to the concentrations found in a leakage from corroded,

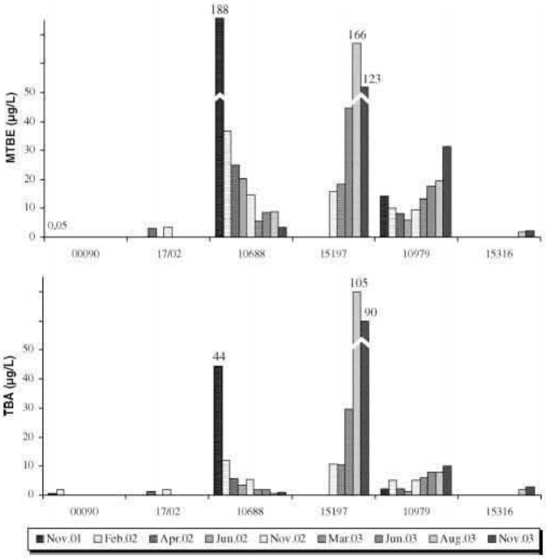

Fig. 4. Methyl-*tert*-butyl ether (MTBE) and *tert*-butyl alcohol (TBA) concentrations found in the conventional monitoring wells located on the line of the plume from east (close to petrol station) to west during two years of study.

Table 5. Methyl-*tert*-butyl ether (MTBE) and *tert*-butyl alcohol (TBA) concentrations (expressed in μg/L) found in multilevel monitoring wells (ML1 and ML2) from November 2002 to November 2003 (the exact number of days between sampling campaigns is reported)

	Days:	0	100	188	259	342
	Depth (m)	Nov. 02	Mar. 03	Jun. 03	Aug. 03	Nov. 03
Methyl-*tert*-butyl ether						
ML1	7	222	138	17.4	47.4	47.6
	9	122	209	40.7	5.44	3.41
	11	645	236	1.31	0.43	1.53
	13	0.07	0.41	0.02	0.03	0.01
	15	0.12	0.01	0.01	0.04	0.01
	Mixed (7–15)					14.7
ML2	8	221	252	40.8	129	126
	10	145	482	591	109	365
	11	414	211	2.26	16.3	117
	12	212	5.21	1.31	6.19	0.62
	13	0.96	0.63	0.19	0.17	0.13
	14	0.86	0.77	0.40	0.85	0.62
	Mixed (8–14)					129
tert-Butyl alcohol						
ML1	7	108	87.5	15.6	27.1	25.9
	9	41.2	116	37.8	3.44	1.74
	11	443	149	1.47	<0.1	1.55
	13	3.34	0.72	0.23	<0.1	0.55
	15	1.16	0.96	0.60	<0.1	0.65
	Mixed (7–15)					5.60
ML2	8	68.2	102	28.3	58.0	74.7
	10	59.0	283	333	48.4	163
	11	194	134	4.79	4.27	70.7
	12	76.0	9.75	1.31	1.46	1.22
	13	3.38	1.07	0.77	0.18	0.97
	14	2.18	1.93	1.41	1.20	2.00
	Mixed (8–14)					79.0

underground storage tanks in two large oil refinery factories in Tarragona (Catalonia, Spain), where concentrations ranged from 0.13 to 0.68 μg/L and from 0.20 to 1.53 μg/L of ETBE and DIPE respectively, but TAME was not detected [24].

The TBF was found in a total of seven samples during the whole monitoring study. In November 2003, it was detected at 5.42 μg/L in well ML2 at 10 m depth. However, it is not usual to detect this compound in aquatic environment. Church et al. [22] indicated that TBF was formed as an MTBE degradation product by atmospheric photooxidation due to the attack of hydroxyl radicals. Although this reaction is also possible in aqueous phase, TBF accumulation was not found in water because it was hydrolyzed readily to TBA [22]. In other studies, TBF was observed as an intermediate and it was suggested that *tert*-butoxymethanol (compound proposed as a first intermediate in the oxidation of MTBE but not yet observed directly) preferentially might be oxidized rapidly to yield TBF [34] and formic acid, thus excluding the formation of formaldehyde [28].

Generally, BTEX compounds were detected at concentrations <1 μg/L. Their lower solubility and higher degradation rates could explain their low levels in groundwater. For this reason, a single spill event was considered as the main source of MTBE contamination. However, in the last sampling campaign, it was observed that some of these compounds had not been detected previously due to the application of necessary high dilution factors to avoid the MTBE contamination of the analytical system. Total BTEX was up to 9.24 μg/L in some samples from multilevel wells. In all cases, the most abundant compound detected was toluene, with a maximum concentration of 5.52 μg/L, followed by xylenes (m+p-xylene > o-xylene), ethylbenzene, and benzene. This pattern essentially fit with the conventional gasoline contents (% in volume) and their individual solubilities in water from this gasoline at 20°C: 5% toluene (25 mg/L), 10% xylenes (20 mg/L), 1.5% ethylbenzene (3 mg/L), and 1% benzene (18 mg/L) [11].

Once more, MTBE was found to be more suitable than the historically used BTEX as a tracer or indicator of long-term gasoline contamination [24]. As an example, in 2000, Davidson and Creek [35] demonstrated how MTBE played a critical role in the forensic investigation by helping establish the spill source and spill timing.

Traces of the other two volatile organic compound substances were detected at maximum concentrations of 0.06 and 1.04 μg/L for TCE and DCPD, respectively.

Most TCE in air comes from metal degreasing activities associated with tool and automobile production. At the low concentrations detected in the relatively shallow aquifer, the presence of TCE concentrations was explained by diffuse emission via soil air in the vadose zone [36]. It also could enter groundwater from industrial discharges or from improper disposal of industrial wastes at landfills. These low TCE levels did not represent an important contamination problem according to the U.S. EPA drinking water standard set at 5 μg/L (http://www.epa.gov/safewater/dwh/c-voc/trichlor.html).

Dicyclopentadiene is produced by heating crude oil products and it is used as intermediate in the manufacture of a large variety of products such as pesticides, rubbers, flame-retardant resins, etc. Dicyclopentadiene is also a minority compound in gasoline formulations, added at 0.005% v/v in the new unleaded gasoline from CEPSA, one of the first Spanish petrol companies [37]. Although, to our knowledge, DCPD has no drinking water or health-based standards, a threshold odor for this compound was established in the range of 0.010 to 0.025 μg/L [25]. Consequently, the concentrations of DCPD detected in the aquifer (100 times higher than the lower boundary) might increase odor complaints in addition to MTBE and hydrogen sulfide.

Conventional wells

After sampling seven monitoring wells during the year 2002, it was assumed that the contamination plume should be very narrow due to low levels (from 0.05 to 0.38 μg/L for MTBE and from 0.21 to 1.82 μg/L for TBA) detected in the east, northwest, and southwest of the petrol station. For this reason, during year 2003, the contamination plume movement basically was followed by means of five monitoring wells, three of them installed in November 2002 to find the center of the plume at approximately 200 m westerly from the petrol station. Data from well 15197 was very useful to observe the behavior of the pollutants. Until August 2003, MTBE concentration increased up to 166 μg/L in this point and decreased to 123 μg/L in November 2003, as shown in Figure 4. This fact indicated the movement of the MTBE plume center and proved a high persistence of this compound in the groundwater. After two years of monitoring, the MTBE concentration was practically the same as what had been detected at approximately a 100-m distance (188 μg/L in well 10688 in November 2001). Therefore, plume migration rate of the MTBE plume was calculated to be around 55 m/year. This value is not so extraordinarily high if it is compared with flow velocities, between 300 and 400 m/year, measured in a nearby BTEX-contaminated site [38,39]. In addition, this estimation depends on whether or not the center of the plume really was located.

No MTBE mass loss was observed in groundwater. According to its physicochemical properties, MTBE's relatively low partitioning coefficient to organic carbon ($K_{OC} = 41$ vs. $K_{OC} = 191$ for benzene [40]) indicates that it will remain preferentially in the water phase instead of partitioning into soil organic matter [35]. For example, in a sand aquifer with moderate organic carbon content (0.1%), only 8% of the total mass of MTBE was sorbed to the organic matter, whereas 92% remained in solution. By contrast, 39% of the total mass of benzene and 72% of ethylbenzene was sorbed to the organic matter [41].

In addition, in anaerobic groundwater conditions (see Table 2), MTBE is more resistant to degradation than other fuel constituents [42]. Recently, the degradation of MTBE and TBA in laboratory microcosms was described [28]. Although, MTBE and TBA degradation has been reported in the presence of all environmentally relevant terminal acceptors (nitrate, sulphate, Fe[III], Mn[IV], methanogenesis, etc.), except for oxic conditions, results are controversial in literature or very limited studies have been performed so far [43,44].

When the MTBE concentration found in groundwater is between 0.2 and 3 μg/L, the source of contamination can be punctual (such as at the leading edge of the contamination plume), but it normally is considered diffuse due to atmospheric deposition or rain runoff close to urban areas or motorways [13]. This observation is confirmed by a study of the German Technical and Scientific Association for Gas and Water, which considers MTBE concentrations between 0.1 and 0.5 μg/L in groundwater as normal for areas with high motor traffic [8,45]. In fact, these intakes have been calculated recently in urban precipitation of Germany [14]. About 20% of the MTBE detected in urban runoff already is transported in the atmosphere before precipitation, whereas about 80% can be attributed to direct uptake of vehicles emissions and gasoline on road. Therefore, the MTBE concentrations detected from 0.02 to 0.38 μg/L in the most external monitoring wells (00090 and 10156 just upstream of the petrol station in the east; 10968, 10983, and 10982 downstream in the north; and 12452 and 12451 downstream in the south), which are not located in the center of the plume, can be regarded as background levels and not as significant MTBE pollution.

In contrast, the TBA plume origin cannot be clarified easily. This compound showed a similar profile as its hypothetical parental, except that its concentration seemed to be higher after two years. The highest concentration, 105 μg/L found in August 2003, was twice as much as the maximum level detected in November 2001 (44 μg/L). Methyl MTBE degradation was not the main source of TBA. For this reason, its possible presence in the contamination source and its complete solubility in water [13] could explain its occurrence in groundwater similarly to MTBE. Probably, the maximum peak of TBA concentration was not identified at the beginning of the monitoring.

In the literature, TBA is considered to be the key intermediate in the degradation of several dialkyl ethers used as fuel oxygenates, not only MTBE, but also ETBE (as indicated in a biodegradation study in France, where ETBE has been used for several years [46]). However, other authors do report that partitioning of TBA present in gasoline also may contribute to elevated concentrations in groundwater at contaminated sites. These authors concluded that TBA was added intentionally to the fuel because TBA impurities in MTBE should be below 2% [47]; however, in other cases, the low concentrations of TBA in gasoline presumably were due to impurities of fuel-grade MTBE [48]. In both studies, aqueous-phase concentrations of TBA in batch equilibrium experiments reached the high mg/L to low g/L range [28]. For Germany, the use of TBA in mixtures with methanol as fuel oxygenate has been reported at more than 30,000 tons/year in the past [13]. On the other hand and in contrast to MTBE, which almost exclusively is used as a fuel oxygenate, TBA also is a widely used solvent and intermediate in industrial processes [49], so a part of TBA found in the aquifer could have other sources. Once TBA is in groundwater, removal time under anaerobic conditions is relatively long [44,50].

Under anoxic field conditions, MTBE degradation has been shown only a few times. Most of these studies evidenced TBA accumulation in the absence of molecular oxygen [51,52]. Until today, TBA degradation has not been shown under methanogenic conditions, and it currently is accepted widely that TBA is a recalcitrant dead-end product of MTBE under these conditions [28]. Under sulfidogenic conditions, this has not yet been shown unambiguously, although Somsamak et al. [53] found a stoichiometric accumulation of TBA that suggested TBA degradation to be rate-limiting in overall removal of MTBE.

In spite of these uncertainties, it can be concluded that similar behavior of MTBE and TBA was observed in the present study. Specifically, from the beginning of the survey of well 10688, both compounds decreased 70 to 80% in the first 78 d. This drop represents the movement of the pollutants through the aquifer. This means that it takes between 30 and 40 d to sweep away 50% of the initial concentrations. At a second stage, this estimated movement slowed down from February 2002 until the end of the study.

Multilevel wells

The two multilevel wells (ML1 and ML2) installed at the contaminated site permitted the study of the vertical profile and evolution of MTBE and TBA plumes (see Table 5). In addition to confirm how narrow the contamination plume was, two trends have been observed since their installation in November 2002. The center of the plume (the highest detected values) had been moving from the north to the south well and also up toward the surface (from 11 m to 7 and 10 m, respectively). In August 2003, the main part of the contamination had passed through ML1 and ML2 because MTBE concentration decreased 80% (from 645 μg/L in ML1 in November 2002 to 129 μg/L in ML2 in August 2003). In November 2003, higher values were detected again in ML2 (365 μg/L), confirming the movement of the plume to the southwest.

These variations in the distribution of the contamination plume probably were displaced by slight changes in the groundwater flow direction. In August 2003, this fact was attributed to a dryer period in summer time. The Düsseldorf precipitation data from June to August in 2002 (217 mm) and 2003 (139 mm) declined in addition to higher maximum temperatures registered with differences up to 3°C (www.weatheronline.co.uk/Europe.htm).

The same profile was observed for TBA with a maximum detected concentration of 443 μg/L at 11 m for ML1 in November 2002 and a final highest level of 163 μg/L at 10 m for ML2 one year later.

Similar behavior of both compounds can be observed by studying the drop of concentrations in the multilevel well ML1 within one year (342 d). It takes between 44 and 60 d to sweep away 50% of MTBE through the aquifer and 49 to 70 d in the case of TBA.

Differences between MTBE and TBA concentrations in conventional and multilevel wells were evaluated in November 2003. A comparison among the levels obtained in mixed samples (a mixture of water from the different depths), the calculated averages (among concentrations detected in the different depths), and the nearest conventional well (15197) values was done in the last campaign. In three of the four cases, the value of the mixed sample was higher than the calculated average with differences from 25 to 40%; this might be attributed to the fact that the contamination plume is concentrated in the first filters of the well in which the water is extracted more easily than from the deeper ones. On the other hand, the values of ML2 mixed samples fitted better with the concentrations found in the conventional well 15197 (differences of 5 and 13% were calculated for MTBE and TBA, respectively) than with the calculated averages (22 and 47%, respectively), Figure 5 serves as an example.

The knowledge of the setup of the contaminated area, the hydrogeological conditions, the chemical and physical properties of the pollutant, and their spatial distribution is essential to predict the fate of MTBE, degradation products, and other gasoline oxygenates in affected groundwater tables. Selection of appropriate monitoring wells to screen both the horizontal and vertical profiles is necessary to track the contamination plume and to assess the processes (transformation, degradation, and dilution) that determine their final fate. Although MTBE may be detected at values below the odor threshold, more knowledge is needed to assess the stability of their degradation products in groundwater and to explore all contamination sources. Such information is needed for better risk assessment and decision-making.

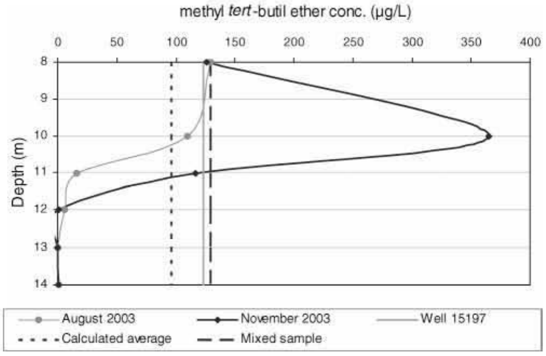

Fig. 5. Methyl-*tert*-butyl ether (MTBE) vertical profile of ML2 in November 2003 in comparison with August 2003, mixed sample concentration, calculated average, and 15197, the nearest conventional well level.

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REFERENCES

1. U.S. Environmental Protection Agency. 1998. Oxygenates in water: Critical information and research needs. EPA/600/R-98/048. Technical Report. Office of Research and Development, Washington, DC.
2. Squillace PJ, Zogorski JS, Wilber WG, Price CV. 1996. Preliminary assessment of the occurrence and possible sources of MTBE in groundwater in the United States, 1993–1994. *Environ Sci Technol* 30:1721–1730.
3. Landmeyer JE, Chapelle FH, Bradley PM, Pankow JF, Church CD, Tratnyek PG. 1998. Fate of MTBE relative to benzene in a gasoline-contaminated aquifer (1993–98). *Ground Water Monit Remediation* 18:93–102.
4. Williams PRD. 2001. MTBE in California drinking water: An analysis of patterns and trends. *Environ Forensics* 2:75–85.
5. Williams PRD, Benton L, Sheehan PJ. 2003. MTBE in California's drinking water: A comparison of groundwater versus surface water sources. *Environ Forensics* 4:175–189.
6. Langenhoff AAM. 2000. Methyl tertiary-butyl ether (MTBE) and its occurrence in The Netherlands. R2000/189. Technical Report. TNO—Milieu, Energie en Procesinnovatie (MEP), Apeldoom, The Netherlands.
7. Dotterridge J, Hall M, Firth S. 2000. A review of current MTBE usage and occurrence in groundwater in England and Wales. Research and Development Technical Report P406. Technical Report. Environment Agency, Bristol, UK.
8. Klinger J, Stieler C, Sacher F, Branch HJ. 2002. MTBE (methyl tertiary-butyl ether) in groundwaters: Monitoring results from Germany. *J Environ Monit* 4:276–279.
9. Juhler RK, Felding G. 2003. Monitoring methyl tertiary butyl ether (MTBE) and other organic micropollutants in groundwater: Results from the Danish National Monitoring Program. *Water Air Soil Pollut* 149:145–161.
10. Morgenstern P, Versteegh AFM, de Korte GAL, Hoogerbrugge R, Mooibroek D, Bannink A, Hogendoorn EA. 2003. Survey of the occurrence of residues of methyl tertiary butyl ether (MTBE)

in Dutch drinking water sources and drinking water. *J Environ Monit* 5:885–890.

11. Johnson R, Pankow J, Bender D, Price C, Zogorski J. 2000. MTBE—to what extent will past releases contaminate community water supply wells? *Environ Sci Technol* 34:210A
12. Ahlberg R, Gennart JP, Mitchell RE, Schulte-Koerne E, Thomas ME, Vahervuori H, Vrijhof H, Watts CD. 2001. An environmental risk assessment of MTBE use in Europe. Technical Report. EFOA/ECETOC Task Force on Environmental Risk Assessment of MTBE, Brussels, Belgium.
13. Schmidt TC, Morgenroth E, Schirmer M, Effenberger M, Haderlein SB. 2002. Use and occurrence of fuel oxygenates in Europe. In Diaz AF, Drogos DL, eds, *Oxygenates in Gasoline: Environmental Aspects*. ACS Symposium Series 799. American Chemical Society, Washington, DC, pp 58–79.
14. Achten C, Kolb A, Puttmann W. 2001. Methyl tert-butyl ether (MTBE) in urban and rural precipitation in Germany. *Atmos Environ* 35:6337–6345.
15. CONCAWE. 1998. A survey of European gasoline qualities—summer 1996. Report 5/98. Technical Report. Automotive Emissions Management Group, Brussels, Belgium.
16. Pahlke G, Leonhard H, Tappe M. 2000. Mögliche Umweltbelastungen durch die Nutzung von MTBE als Kraftstoffzusatz in Deutschland und Westeuropa. *Erdöl Erdgas Kohle* 116:498–504.
17. Squillace PJ, Pankow JF, Korte NE, Zogorski JS. 1997. Review of the environmental behavior and fate of methyl tert-butyl ether. *Environ Toxicol Chem* 16:1836–1844.
18. Achten C, Kolb A, Püttmann W, Seel P, Gihr R. 2002. Methyl *tert*-butyl ether (MTBE) in river and wastewater in Germany. 1. *Environ Sci Technol* 36:3652–3661.
19. Dale MS, Moylan MS, Koch B, Davis MK. 1997. MTBE–taste-and-odor threshold determinations using the flavor profile method. *Proceedings*, American Water Works Association Water-Quality Technology Conference. La Verne, CA, pp. 1–10.
20. U.S. Environmental Protection Agency. 1997. Drinking water advisory: Consumer acceptability advice and health effects analysis on methyl tertiary-butyl ether (MTBE). EPA-822-F-97-009. Technical Report. Office of Water, Washington, DC.
21. Umweltbundesamt. 2003. Bewertung der Anwesenheit teil-oder nicht bewertbarer Stoffe im Trinkwasser aus gesundheitlicher Sicht. Bundesgesundheitsbl—Gesundheitsforsch—Gesundheitsschutz (46). Technical Report. Empfehlung des Umweltbundesamtes nach Anhörung der Trinkwasserkommission beim Umweltbundesamt, Berlin, Germany.
22. Church CD, Isabelle LM, Pankow JF, Rose DL, Tratnyek PG. 1997. Method for determination of methyl tert-butyl ether and its degradation products in water. *Environ Sci Technol* 31:3723–3726.
23. Deeb RA, Scow KM, Alvarez-Cohen L. 2000. Aerobic MTBE biodegradation: An examination of past studies, current challenges, and future research directions. *Biodegradation* 11:171–186.
24. Rosell M, Lacorte S, Ginebreda A, Barcelo D. 2003. Simultaneous determination of methyl *tert*-butyl ether and its degradation products, other gasoline oxygenates, and benzene, toluene, ethylbenzene, and xylenes in Catalonian groundwater by purge-and-trap gas chromatography–mass spectrometry. *J Chromatogr A* 995: 171–184.
25. Ventura F, Romero J, Pares J. 1997. Determination of dicyclopentadiene and its derivatives as compounds causing odors in groundwater supplies. *Environ Sci Technol* 31:2368–2374.
26. Wilson RD, Thornton SF, Mackay DM. 2004. Challenges in monitoring the natural attenuation of spatially variable plumes. *Biodegradation* 15:359–369.
27. Einarson MD, Cherry JA. 2002. A new multilevel groundwater monitoring system using multichannel tubing. *Ground Water Monit Remediation* 22:52–65.
28. Schmidt TC, Schirmer M, Weiß H, Haderlein SB. 2004. Microbial degradation of methyl *tert*-butyl ether and *tert*-butyl alcohol in the subsurface. *J Contam Hydrol* 70:173–203.
29. Eichelberger JW, Munch JW, Bellar TA. 1992. Measurement of purgeable organic compounds in water by capillary column gas chromatography/mass spectrometry. Method 524.2. (Revision 4.0). Technical Report. Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Cincinnati, OH.
30. Deutschen Vereinigung des Gas—und Wasserfaches. 2001. Entnahme von Wasserproben bei der Erschließung, Gewinnung und Überwachung von Grundwasser. Merkblatt W 112. Technical Report. DVGW, Bonn, Germany.
31. Lacorte S, Olivella L, Rosell M, Figueras M, Ginebreda A, Barcelo D. 2002. Crossvalidation of methods used for analysis of MTBE and other gasoline components in groundwater. *Chromatographia* 56:739–744.
32. Cirvello JD, Radovsky A, Heath JE, Farnell DR, Lindamood C. 1995. Toxicity and carcinogenicity of t-butyl alcohol in rats and mice following chronic exposure in drinking water. *Toxicol Ind Health* 11:151–165.
33. Kane SR, Beller HR, Legler TC, Koester CJ, Pinkart HC, Halden RU, Happel AM. 2001. Aerobic biodegradation of methyl *tert*-butyl ether by aquifer bacteria from leaking underground storage tank sites. *Appl Environ Microbiol* 67:5824–5829.
34. Hyman M, Kwon P, Williamson K, O'Reilly K. 1998. Cometabolism of MTBE by alkane-utilizing microorganisms. In Wickramanayake GB, Hinchee RE, eds, *Natural Attenuation: Chlorinated and Recalcitrant Compounds*. Battelle, Columbus, OH, USA, pp 321–326.
35. Davidson JM, Creek DN. 2000. Using the gasoline additive MTBE in forensic environmental investigations. *Environ Forensics* 1:31–36.
36. Pankow JF, Thomson NR, Johnson RL, Baehr AL, Zogorski JS. 1997. The urban atmosphere as a non–point source for the transport of MTBE and other volatile organic compounds (VOCs) to shallow groundwater. *Environ Sci Technol* 31:2821–2828.
37. Olivella L, Figueras M, Fraile J, Vilanova M, Ginebreda A, Barcelo D. 2002. Fate of MTBE and DCPD compounds relative to BTEX in gasoline-contaminated aquifers. *Scientific World Journal* 2:1108–1114.
38. Wisotzky F, Obermann P, Eckert P. 1998. Hydrochemische Reaktionen im Bereich einer Grundwasserbelastung mit monoaromatischen Kohlenwasserstoffen und deren Modellierung. *Neues Jahrb Geol Paläontol Abh* 208:55–72.
39. Eckert P, Appelo CAJ. 2002. Hydrogeochemical modeling of enhanced benzene, toluene, ethylbenzene, xylene (BTEX) remediation with nitrate. *Water Resour Res* 38:1–10.
40. American Petroleum Institute. 1996. *A Guide to the Assessment and Remediation of Underground Petroleum Releases*. Washington, DC.
41. Moran MJ, Zogorski JS, Squillace PJ. 2002. MTBE in groundwater of the United States—occurrence, potential sources, and long-range transport. In Rappont DJ, eds, *Managing for Healthy Ecosystems*. Lewis, Boca Raton, FL, USA.
42. Schmidt TC. 2003. Analysis of methyl *tert*-butyl ether (MTBE) and *tert*-butyl alcohol (TBA) in ground- and surface water. *TRAC Trends Anal Chem* 22:776–784.
43. Mormile MR, Liu S, Suflita JM. 1994. Anaerobic biodegradation of gasoline oxygenates: Extrapolation of information to multiple sites and redox conditions. *Environ Sci Technol* 28:1727–1732.
44. Yeh CK, Novak JT. 1994. Anaerobic biodegradation of gasoline oxygenates in soils. *Water Environ Res* 66:744–752.
45. Deutschen Vereinigung des Gas—und Wasserfaches. 2000. Untersuchungen zur Bedeutung von Methyl-tertiär-butylether (MTBE) für die Trinkwasserversorgung aus Grundwasser. Forschungsvorhaben W08/99. Technical Report. DVGW Technologiezentrum Wasser, Karlsruhe, Germany.
46. Kharoune M, Pauss A, Lebeault JM. 2001. Aerobic biodegradation of an oxygenate mixture: ETBE, MTBE, and TAME in an upflow fixed-bed reactor. *Water Res* 35:1665–1674.
47. Kramer WH, Douthit TL. 2000. Water-soluble phase oxygenates in gasoline from five New Jersey service stations. *Proceedings*, NGWA Conference, Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Detection, and Restoration. Anaheim, California, November 15–17, pp. 283–295.
48. Zwank L, Schmidt TC, Haderlein SB, Berg M. 2002. Simultaneous determination of fuel oxygenates and BTEX using direct aqueous injection gas chromatography mass spectrometry (DAI-GC/MS). *Environ Sci Technol* 36:2054–2059.
49. Clark JJJ. 2002. *tert*-butyl alcohol: Chemical properties, production and use, fate and transport, toxicology, and detection in groundwater and regulatory standards. In Diaz AF, Drogos DL, eds, *Oxygenates in Gasoline: Environmental Aspects*. American Chemical Society, Washington, DC, pp 92–106.
50. Suflita JM, Mormille MR. 1993. Anaerobic biodegradation of potential gasoline oxygenates in the terrestrial subsurface. *Environ Sci Technol* 27:976–978.

51. Kolhatkar R, Kuder T, Philp P, Allen J, Wilson JT. 2002. Use of compound-specific stable carbon isotope analyses to demonstrate anaerobic biodegradation of MTBE in groundwater at a gasoline release site. *Environ Sci Technol* 36:5139–5146.
52. Kuder T, Philp P, Kolhatkar R, Wilson JT, Allen J. 2002. Application of stable carbon and hydrogen isotopic techniques for monitoring biodegradation of MTBE in the field. *Proceedings*. Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Assessment, and Remediation. API Petroleum Hydrocarbons and Organic, November 6–8, Atlanta, GA, USA, pp. 371–381.
53. Somsamak P, Cowan RM, Haggblom MM. 2001. Anaerobic biotransformation of fuel oxygenates under sulfate-reducing conditions. *FEMS Microbiol Ecol* 37:259–264.

2.3 DISCUSSIÓ DELS RESULTATS

El mètode P&T-GC/MS desenvolupat permet la identificació d'un total de fins a 14 compostos representatius de contaminació per gasolina i és prou sensible (LODs entre 0,001-0,1 µg/L), precís (variabilitats inferiors al 20%) i permet assolir una elevada recuperació dels analits (entre 94-112%), com per a la seva utilització en la vigilància ambiental dels compostos d'estudi en compliment amb els nivells guia establerts per l'US EPA i que es mostren a la *Taula 5* del capítol 1.

La seva aplicació ha permès la detecció, identificació i quantificació dels compostos en diverses aigües subterrànies europees (a Catalunya, **Art. 2 i 3**, així com Alemanya o Àustria, **Art. 1 i 4**), que en molt casos han superat els nivells recomanats de gust i olor (MTBE o DCPD) i/o toxicitat (per exemple, MTBE > 350 µg/L, TBA >12 µg/L, benzè > 5 µg/L) fent-les inviables pel consum humà.

Les concentracions ambientals més elevades, com era d'esperar, s'han detectat a prop de fonts puntuals de contaminació. L'estudi de la distribució de MTBE i BTEX al llarg de les plomes de contaminació ha permès diferenciar l'origen del problema degut a les seves diferències de comportament i degradació. S'han diferenciat causes puntuals en el temps (fuites accidentals com ara las de les gasolineres de Sant Celoni a **l'Art. 2** o la de Düsseldorf a **l'Art. 4**) envers vessaments més o menys continus (probablement per la corrosió d'un tanc d'emmagatzematge a la refineria de Repsol Petroli a Tarragona, **Art. 2**).

D'altra banda, aquests estudis són dels pocs a Europa que han permès detectar els principals compostos de degradació (TBA i TBF) a llocs contaminats degut a la seva dificultat inherent per a poder ser detectats a nivells traça, tal com indicava Schmidt et al. [47].

Pel que fa a la comparació de mètodes (**Art. 3**), es va provar que tant P&T-GC/MS com HS-GC/FID són adients per l'anàlisi de MTBE i BTEX en aigües subterrànies. Els avantatges i inconvenients de l'aplicació d'aquestes dues metodologies es recullen a la

Taula 11 per facilitar-ne la comprensió. En general, en mostres amb concentracions superiors als 10 µg/L, els resultats obtinguts per ambdues tècniques eren comparables, a excepció de mostres molt contaminades, on es van detectar problemes de reproductibilitat lligades a la presència de dobles fases.

Taula 11.-Avantatges i inconvenients de la utilització de P&T-GC/MS en vers HS-GC/FID

	P&T-GC/MS	**HS-GC/FID**
Avantatges	☺ Bona sensibilitat, nivells de detecció més baixos (0,002 µg/L) ☺ Bona reproductibilitat i precisió ☺ Fàcilment automatitzable ☺ Identificació pràcticament inequívoca, no requereix confirmació posterior ☺ Senzill	☺ Interval de treball més ampli (de ppb a ppm) ☺ No requereix dilució ☺ Bona reproductibilitat i precisió ☺ Adient com a mètode d'alarma (LODs< 20 µg/L) i mostres molt concentrades ☺ Senzill i relativament barat ☺ No tant influenciat per efecte matriu
Inconvenients	☹ Interval de treball més limitat (ppb) ☹ Necessitat de realitzar dilucions de les mostres més contaminades ☹ Problemes reproductibilitat en presència de dobles fases ☹ Possible "efecte memòria" ☹ Relativament car	☹ No adient per la detecció ambiental a nivells traça (LOD: 6 µg/L per MTBE; 0,6 µg/L BTEX) ☹ Requereix anàlisi de confirmació de tots els positius en cas de coelució

En el marc del projecte europeu WATCH, altres validacions dels resultats han estat possibles. A finals de 2001, es va realitzar l'anàlisi de 16 mostres d'aigua subterrània de Salzburg (Àustria), on feia alguns anys hi havia hagut una fuita de gasolina; i van tenir lloc les dues primeres campanyes a Düsseldorf (Alemanya). Alguns dels resultats es van poder comparar amb els d'altres laboratoris com el del grup del Prof. Werner a la Universitat de Dresden amb un HS-GC/FID; i altres dos laboratoris contractats (TZW, Wesslig), dels quals se'n desconeix la ubicació o la tècnica emprada.

Les mostres de Salzburg no van mostrar gairebé rastre de la contaminació per gasolina que s'havia produït en el passat. Es van detectar concentracions baixes de BTEX (0,02-0,45 µg/L), TBA (0,03-0,49 µg/L) i MTBE (0,01-0,56 µg/L). Només un punt a prop d'una gasolinera Shell va donar un nivell de MTBE de 3,32 µg/L comparable amb els 4 µg/L obtinguts per HS-GC/FID. De la resta de valors, tot i que no se'n poden extreure gaires conclusions, es pot considerar els nostres resultats relativament comparables amb els d'altres laboratoris tenint en compte la diferència de dates en la presa de mostres (consulteu *Taula 12*).

Taula 12.-Intercomparació de resultats per MTBE (expressats en µg/L) en aigües subterrànies

Data presa de mostra	***Lab.***	***Codis dels pous***					
		124	***125***	***137***	***Shell***		
20/07/01	**CSIC**	0,05	0,56	0,08	3,32		
13/08/01	**TU Dresden**	<4,0	<4,0	<4,0	4,1		
		00090	***10688***	***12452***	***10979***	***10982***	***10983***
12/11/01	**TZW**	1,80	150	-	6,00	bld	0,52
28/11/01	**CSIC**	0,05	188	-	14,28	0,10	0,09
14/02/02	**TZW**	bld	18,00	0,46	5,90	0,61	0,11
14/02/02	**Wessling**	bld	83,00	bld	9,00	bld	bld
14/02/02	**CSIC**	bld	36,81	0,38	10,15	0,09	bld

Més concloents, van ser els resultats d'una altra comparació per a la determinació de MTBE en mostres reals procedents d'una refineria de l'Alemanya de l'est analitzats pel nostre mètode envers als obtinguts pel grup de Dresden amb HS-GC/FID (*Figura 16*). Les elevades concentracions de les mostres (fins a 200 mg/L) van fer necessari la dilució de la majoria d'elles (fins 1:200.000). Tot i això, en tots els casos, els valors obtinguts van ser del mateix ordre de magnitud. Les diferències estaven al voltant del 14% (mediana), tot i que en el cas de concentracions més baixes la discrepància entre mètodes va arribar al 80% (la mostra *GW2* va donar 8 µg/L per HS-GC/FID, i 2 µg/L per P&T-GC/MS). Això podria ser degut a les pèrdues de MTBE durant el transport a

Barcelona (dues setmanes de diferència entre ambdós anàlisis), més evidents a concentracions baixes, o bé a una sobreestimació per HS-GC/FID més a prop del seu límit de detecció per aquest compost (al voltant de 4 μg/L).

A més, al novembre de 2003, l'anàlisi d'altres mostres procedents de Koblenz (Alemanya) van servir per a la validació de dues metodologies d'immunoassaig per a la detecció de MTBE (a nivells de ppm), en el marc de col·laboració del WATCH i el SENSPOL.

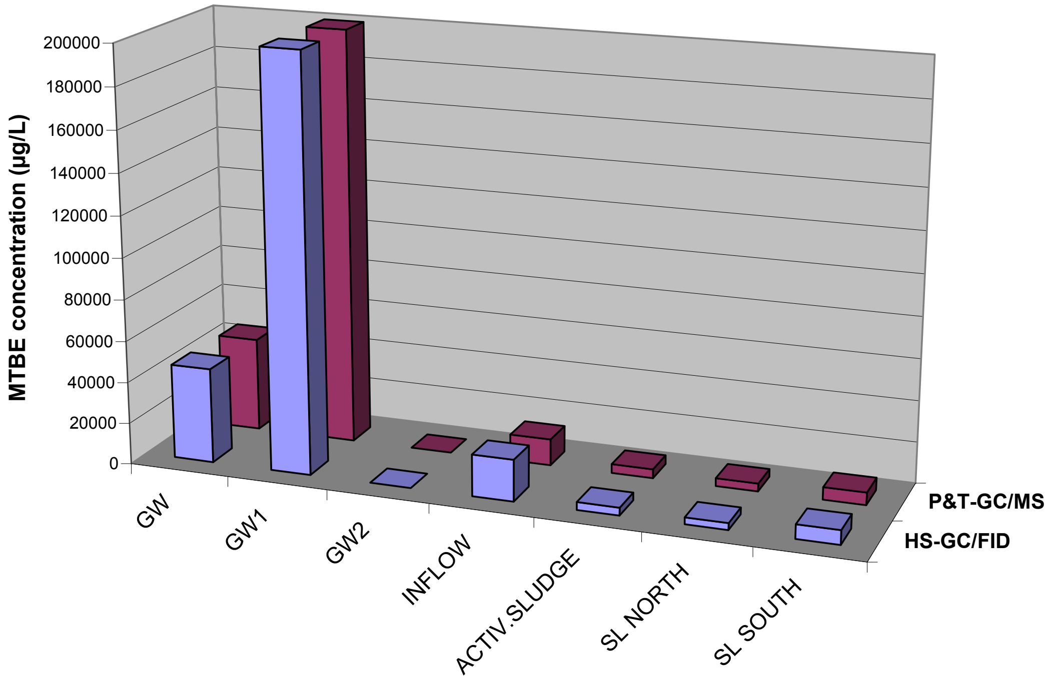

Figura 16.-Comparació de resultats per a la determinació de MTBE en aigües subterrànies (GW) i tractades per fangs actius procedents d'una refineria de l'Alemanya de l'est.

Una altra de les conclusions importants a extreure de **l'article 4** és la importància del seguiment de les plomes de contaminació en profunditat. Per tal fita, va ser necessària la instal·lació de pous multinivell amb filtres a diferents fondàries a través dels quals l'aigua s'extreia de manera independent i donava més informació que no pas "la dilució" obtinguda en un pou convencional. A la *Figura 17* es dona la fotografia del sistema emprat per a la presa de mostra d'aigües subterrànies a diferents fondàries. D'aquesta manera ha estat possible observar un comportament similar de les plomes de contaminació de MTBE i TBA en l'aqüífer, força influenciades per la presència de canals preferents de pas i els fluxos d'aigua subterrània, però que tendeixen amb el temps a situar-se en franges molt estretes, en les capes més superficials de la zona saturada degut a que la seva densitat és menor que la de l'aigua. No s'ha observat una evident atenuació natural dels compostos al llarg dels dos anys de vigilància ambiental, per la qual cosa es suposa que la presència del TBA sigui deguda més a la seva presencia a la gasolina que va produir l'accident que no pas de la posterior degradació del compost.

Figura 17.-Presa de mostres d'aigua subterrània a diferents fondàries a un pou multinivell a Düsseldorf (Alemanya).

A més d'això, altres estudis s'han realitzat en referència als protocols per la presa de mostres. A l'Abril de 2002, es van prendre mostres de tres dels pous estudiats (codis 17/02, 10688 i 10979) amb la combinació de dos sistemes de manipulació (directament dintre del vial d'anàlisi (*A*) o bé prèviament barrejada l'aigua extreta del pou dins una botella o recipient més gros (*B*) i dos mètodes de preservació (acidificant (*acid*) o no amb àcid sulfúric al 0.25%). Com era d'esperar per la seva baixa biodegradació [124], el MTBE no mostrava diferències significatives entre els diferents mètodes. A més els pous estudiats presentaven concentracions mitjanes dels replicats (2,9 / 25 / 7,8 µg/L, respectivament) amb desviacions estàndards relatives (RSD) d'entre el 5 i el 7%. Tot i això, les mostres prèviament barrejades i acidificades presentaven concentracions de MTBE relativament més elevades. D'altra banda, el TBA sí mostrava grans diferències entre tractaments, els valors més alts (1,1 / 6,2 / 2,2 µg/L, respectivament per cada pou) sempre es donaven a les mostres acidificades respecte les que no ho eren. Aquests valors més alts podrien explicar-se en part per la hidrolització del TBF (de 0,2 a 0,7 µg/L) present a les mostres i que no es detectava en condicions àcides, tal i com s'observa als gràfics de la *Figura 18*.

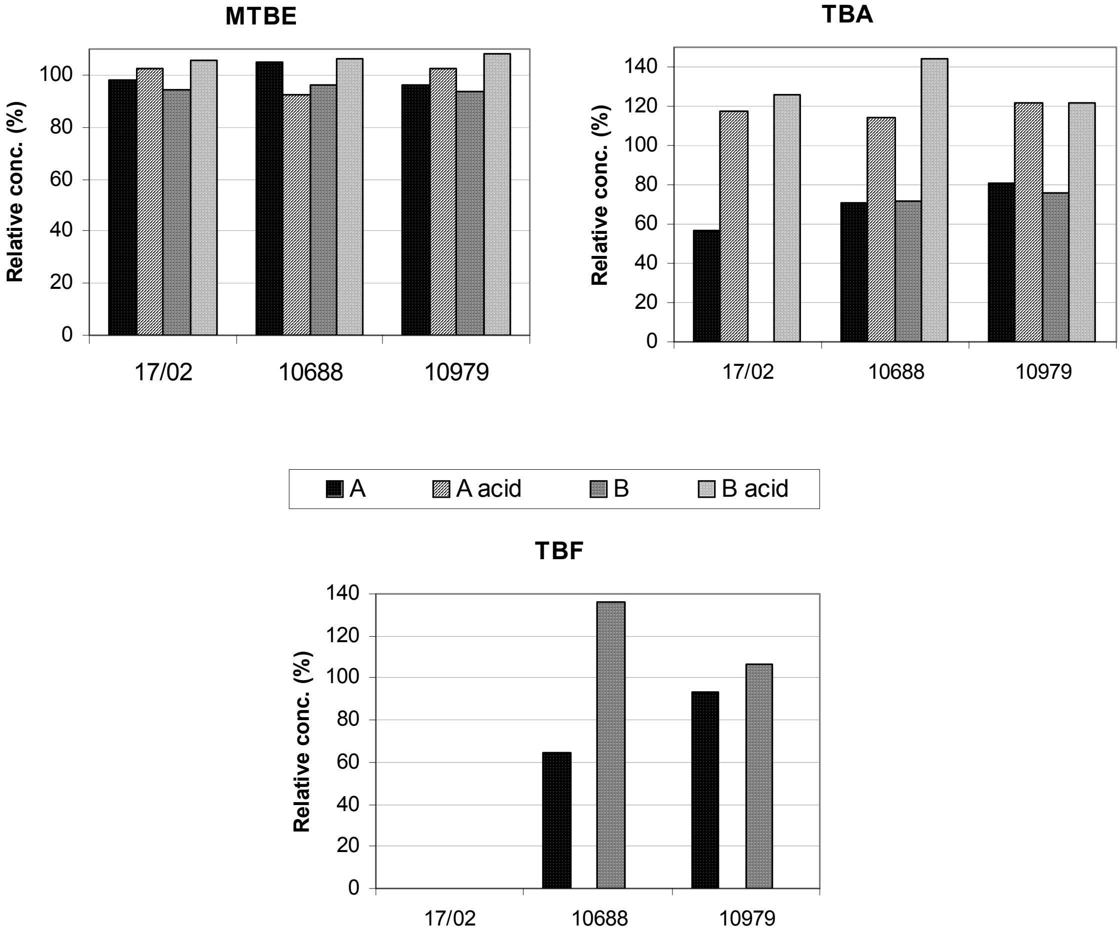

*Figura 18.- Concentracions relatives de MTBE, TBA and TBF expressades com a percentatge envers la mitjana de les mostres (n=4) preses a cada pou: directament al vial (A), prèviament barrejades a una botella (B) amb o sense acidificar * TBA < 0,1 µg/L*

En el marc del projecte ***ARTDEMO***, a l'octubre de 2003, es va realitzar l'anàlisi d'una campanya de 12 mostres procedents de dues plantes de tractament d'aigües amb recàrrega artificial a Göteborg (Suècia) i Copenhaguen (Dinamarca). Bàsicament, aquestes plantes purifiquen l'aigua superficial fent-la passar a través del sòl per injectant-la directament a l'aqüífer i així augmentar les reserves i la qualitat d'aquestes. El projecte pretenia investigar la possible presencia de contaminants emergents a les aigües (antibiòtics, estrògens, progestrògens, plaguicides, així com MTBE o altres volàtils) i la seva eliminació al llarg de les diferents etapes de tractament. No obstant, les concentracions de compostos volàtils van ser molt baixes (només es van detectar alguns BTEX <0.04 µg/L) i en la majoria dels casos per sota dels límits de detecció. Aquests resultats, però, es van veure corroborats per concentracions baixes de la resta de contaminants estudiats. És de destacar que fins i tot la 2,6-diclorobenzamida (també anomenada BAM) es va detectar per sota de 10 ng/L. Aquest producte de degradació del plaguicida diclobenil, que va ser prohibit a Dinamarca a l'any 1997, però que durant molts anys s'havia trobat a concentracions superiors a 100 ng/L. Una segona campanya (19 mostres) al juny de 2004, només va fer que confirmar la bona qualitat de les aigües.

Per últim, també s'ha demostrat la idoneïtat de la tècnica de P&T-GC/MS per l'estudi de diferents matrius aquoses ambientals i la ubiqüitat dels additius de la gasolina en diferents compartiments ambientals, com ara l'aigua de precipitació, de riu, de mar, residual, etc. (com es mostra a l'**Art. 1**). Molts d'aquests valors són comparables amb els obtinguts per altres autors en condicions similars. A la *Figura 19* es presenta un exemple sobre la detecció d'una contaminació puntual deguda a gasolina (probablement per l'ús de motos aquàtiques o embarcacions a motor) al Juliol de 2003 a les aigües costaneres del sud de la Península Ibèrica. Les diferències entre les concentracions detectades a la marea baixa i la marea alta poden ser degudes a multitud de variables ambientals i temporals que queden fora del nostre abast.

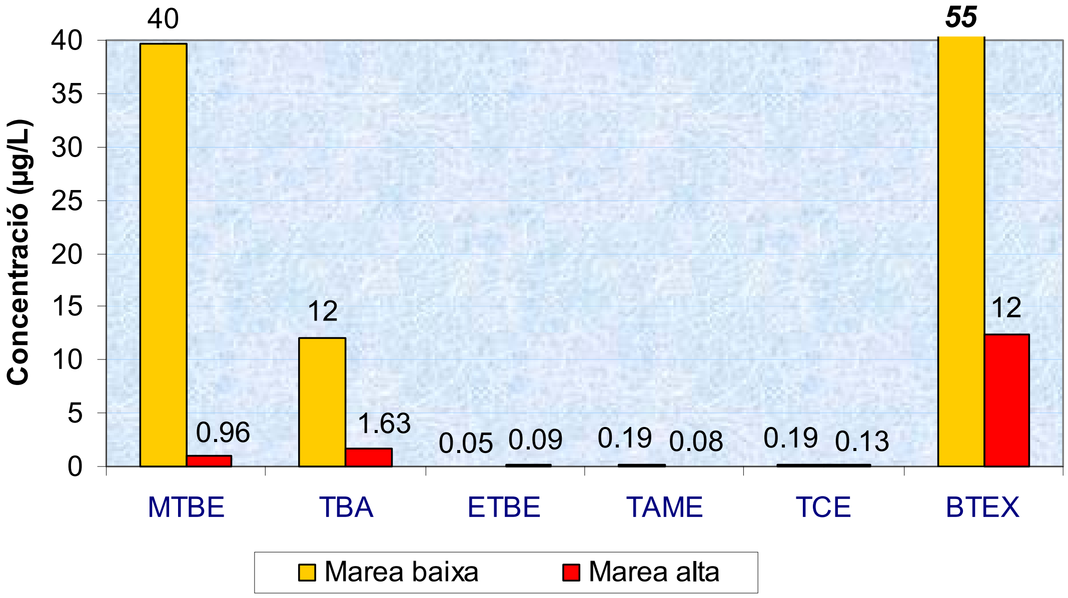

Figura 19.-Contaminació puntual detectada en aigua de mar al sud de la Península Ibèrica