Simultaneous Quantification of Polar and Non-Polar Volatile Organic Compounds in Water Samples by Direct Aqueous Injection – Gas Chromatography/Mass Spectrometry (DAI-GC/MS)

Christoph Aeppli#, Michael Berg*#, Thomas B. Hofstetter°, Rolf Kipfer#, René P. Schwarzenbach°

Eawag, Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf, Switzerland and °Institute of Biogeochemistry and Pollutant Dynamics (IBP), ETH Zurich, 8092 Zurich, Switzerland

ACCEPTED MANUSCRIPT **JCA-07-1585**

Journal of Chromatography A

December 7, 2007

* Corresponding author. Phone: +41-44-823 50 78; Fax: +41-44-823 50 28

E-mail: michael.berg@eawag.ch

Key words
VOC, analysis, groundwater, environmental aqueous samples, carbon tetrachloride, chlorobenzene, chloroform, 1,2-dichlorobenzene, 1,4-dichlorobenzene, 1,2-dichloroethane, 1,2-dichloropropane, 1,1,1-trichloroethane, 1,3-dichlorobenzene, trichloroethene, 1,1-dichloroethene, *trans*-1,2-dichloroethene, *cis*-1,2-dichloroethene, perchloroethene, vinyl chloride, dichloromethane, benzene, toluene, xylene, methyl *tert*-butyl ether (MTBE), *tert*-butyl alcohol (TBA).

Abstract

A direct aqueous injection – gas chromatography/mass spectrometry (DAI-GC/MS) method for trace analysis of 24 volatile organic compounds (VOCs) in water samples is presented. The method allows for the simultaneous quantification of benzene, toluene, ethyl benzene, and xylenes (BTEX), methyl *tert*-butyl ether (MTBE), *tert*-butyl alcohol (TBA), as well as a variety of chlorinated methanes, ethanes, propane, enthenes and benzenes. Applying a liquid film polyethylene glycol or a porous layer open tubular (PLOT) divinylbenzene GC capillary column to separate the water from the VOCs, volumes of 1–10 µL aqueous sample are directly injected into the GC. No enrichment or pretreatment steps are required and samples volumes as low as 100 µL are sufficient for analysis. Method detection limits determined in groundwater were between 0.07–2.8 µg/L and instrument detection limits of <5 pg were achieved for 21 out of the 24 evaluated VOCs. DAI-GC/MS offers both good accuracy and precision (relative standard deviations ≤ 10% for 19 analytes, comparison with conventional headspace GC/MS). The versatility of our method is demonstrated successfully with applications for contaminant quantification during drinking water disinfection (advanced oxidation treatment of MTBE) and field investigations for VOC analysis in a polluted aquifer. The wide range of detectable compounds and the lack of labor-intensive sample preparation illustrate that the DAI method is robust and easily applicable for the quantification of important organic groundwater contaminants.

1. Introduction

Many semi-polar organic groundwater contaminants such as chloroform (CF), non-polar fuel constituents benzene, toluene, ethylbenzene and xylene isomers (BTEX) or perchloroethene (PCE), or the polar fuel additive methyl *tert*-butyl ether (MTBE) belong to the class of volatile organic compounds (VOCs). VOCs are persistent and toxic, and some are even considered to be carcinogenic, mutagenic, or teratogenic [1]. At industrial or accidental spill sites, VOCs can accumulate in groundwater up to concentrations of several hundred mg/L. Because numerous drinking water supplies rely on groundwater resources, VOC pollution is often a drinking water quality issue. The World Health Organization (WHO) guideline values for VOCs in drinking water are, e.g., 0.3 µg/L for vinyl chloride, 40 µg/L for PCE and 1 mg/L for 1,2-dichlorobenzenes [1]. Various studies have revealed that VOCs are prevalent groundwater contaminants: Chloroform, PCE and MTBE were the most abundant contaminants in wells of the U.S. Geological Survey network at a frequency of 48%, 28% and 14%, respectively [2]. These findings are comparable to Switzerland, where 45% of 413 observation wells of the Swiss groundwater monitoring network show traces of VOCs, mainly PCE or MTBE [3]. Since groundwater safety regulations require systematic monitoring of these substances, accurate, fast, and simple analytical methods are necessary for the quantification of VOCs. Several methods, like purge and trap (P&T), solid phase microextraction (SPME), headspace analysis or liquid-liquid extraction, have been developed for the analysis of VOCs [4]. However, direct aqueous injection (DAI) of water samples in a GC system offers significant advantages. DAI-based methods allow for the quantification of compounds in water samples without discriminating the more polar analytes. Because no enrichment or extraction step is necessary, loss of compounds due to volatilization is minimized and apart from a standard benchtop GC/MS system, this approach does not require specialized equipment.

Injection of water as solvent into a GC system is usually not desired because water commonly degrades coatings of gas chromatography columns and decreases the sensitivity of detectors. These effects can be circumvented if water can be separated from the analytes before the GC column using either pre-column sorbents [5] or a programmable temperature vaporization injector [6-9]. Aqueous samples were successfully injected directly onto a GC column in 1974 for the analysis of aliphatic and aromatic compounds including chloroform, dichloromethane and acetone in the mg/L range using a packed column and a quadrupole MS [10]. The introduction of capillary columns and cold on-column injection (OCI) [11] led to measurements of halogenated methanes, ethanes, and ethenes in the low µg/L range using an electron capture detector (ECD) [12-18]. It was found that liquid film non-polar columns with immobilized coatings were sufficiently resistant towards water injected as solvent [12]. DAI methods using either a flame ionization detector (FID) [19-21], ion trap mass spectrometer (MS, [22,23]) or quadrupole MS [21,24,25] have been reported for analysis of BTEX compounds and MTBE [26] but quadrupole MS is the detector of choice for trace level concentrations in environmental samples (ng to mg per liter range). To overcome the effect of unstable vacuum in the MS during water elution, either a high capacity vacuum pump [24] or a highly polar column that enables analyte elution before the water breakthrough [25] were applied. For the simultaneous analysis of MTBE and its degradation product, *tert*-butyl alcohol (TBA), this setup has become the state of the art [27,28].

Despite these developments, there is no DAI method available for the analysis of a broad range of VOCs of various polarity including BTEX, gasoline oxygenates, and chlorinated compounds that can be applied for the monitoring of groundwater quality. Therefore, we developed a method suited for simultaneous quantification of polar and non-polar VOCs at trace levels in small sample volumes. This DAI-GC method can be used as a routine analytical tool in monitoring programs and investigations that require high throughput and minimum handling of samples at low (ng/L – µg/L)

method detection limits (MDLs) . To this end, we tested the presented method for simultaneous quantification of 24 analytes (Table 1) in a contaminated aquifer at an industrial spill site, and we studied the product formation of MTBE during its drinking water treatment with advanced oxidation processes.

2. Experimental

2.1 Chemicals

Table 1 lists the names, abbreviations and relevant parameters of the analytes and internal standards used in this paper. Methanol (>99.9%), used to prepare stock solutions, was obtained from Scharlau S.A. (Barcelona, Spain). Benzene (≥99.9%), benzene-d_6 (>99.95 atom% D), *tert*-butanol (≥99.7%), carbon tetrachloride (≥99.5%), chlorobenzene (≥99.5%), chloroform (≥99.5%), 1,2-dichlorobenzene (≥99%), 1,4-dichlorobenzene (≥99.0%), 1,2-dichloroethane (≥99.9%), 1,2-dichloropropane (≥99.0%), ethylbenzene (≥99.5%), MTBE (≥99.5%), 1,1,1-trichloroethane (≥99.8%), toluene (≥99.9%), *o*-xylene (≥99.5%), *m*-xylene (≥99.5%) and *p*-xylene (≥ 99.5%) were purchased from Fluka (Buchs, Switzerland). 1,3-Dichlorobenzene (99.4%) was purchased from Riedel-de Haën (Seelze, Germany). Trichloroethene (≥99%), 1,1-dichloroethene (99%), *trans*-1,2-dichloroethene (98%), *cis*-1,2-dichloroethene (97%), MTBE-d_3 (>99 atom% D) and perchloroethene (99%) were obtained from Sigma-Aldrich (Steinheim, Germany). Chloroform-d (99.8 atom% D), chlorobenzene-d_5 (98.5 atom% D), 1,2-dichlorobenzene-d_4 (98 atom% D) and 1,2-dichloroethane-d_4 (99 atom% D) were purchased from Aldrich Chemicals (Milwaukee, USA). Vinyl chloride solution (2 g/L in Methanol, 99.9%) was from Supelco (Bellefonte, USA), and dichloromethane (≥99.8%) from Merck (Darmstadt, Germany).

122 *2.2 Preparation of Standard Solutions*

123 All stock solutions were prepared in methanol. The VC standard solution (2,000 mg/L) was used as
124 obtained. A solution of 14DCB (7,200 mg/L) was prepared by dissolving 180 mg of analyte in 25
125 mL methanol using a volumetric flask. The other stock solutions (0.4% v/v) were prepared as
126 mixtures of 4 to 6 similar compounds (i.e., BTEX or chlorinated compounds) by dissolving 100 µL
127 of each analyte in 25 mL methanol in volumetric glass flasks.To avoid loss due to volatilization, the
128 methanolic stock solutions were prepared once per month and were stored in screw cap glass vials
129 without headspace at 4 °C.
130
131 Aqueous standard solutions of the 24 target compounds (labeled 'S_1'), containing the 24 target
132 compounds in concentrations between 11.9 to 26.0 mg/L (16 ppm v/v), and of the six internal
133 standards (denoted as 'IS_1') were prepared by adding 100 µL of the corresponding methanolic stock
134 solutions (250 µL for VC) to approximately 24 mL fresh tap water in a volumetric flask using glass
135 syringes. The flasks were then filled to 25 mL with fresh tap water, closed, turned upside down
136 three times and transferred in screw cap glass vials to achieve minimal headspace volume. A second
137 dilution series of aqueous analyte standards (denoted as 'S_2', concentrations between 119 and 260
138 µg/L corresponding to 160 ppb v/v) and of the six internal standards ('IS_2') were prepared by
139 diluting 100 µl of S_1 or IS_1, respectively, in 10 mL volumetric glass flasks. For the five-point
140 calibration, aqueous calibration standards were prepared in two concentration ranges (0.30 to 13
141 µg/L and 3.0 to 520 µg/L) as dilutions from S_1 or S_2 in 10 mL volumetric flasks. The same amount
142 of internal standard was added to every flask. All aqueous standard solutions were prepared daily.

143 *2.3 Field Sampling and Sample Preparation*

144 Loss of analytes due to volatilization was minimized during sampling and transport as follows:
145 Groundwater wells were pre-pumped (five time the volume of the well) and sampled with a
146 submersible pump. Water samples were collected in 120 mL glass bottles and sealed with PTFE-

147 lined screw caps. The bottles were slowly filled, sealed without headspace and stored in the dark at
148 4 °C until analysis, which was performed not later than one week after sampling. Sample
149 preparation just required the addition of internal standards by spiking 50 µL of aqueous stock from
150 internal standard solution IS_1 or 100 µL from IS_2, depending on the concentration range of the
151 external calibration). Samples were immediately transferred into 1.8 mL glass autosampler vials
152 and sealed without headspace with a PTFE/silicon septum and a screw cap. To avoid analyte loss
153 through punctured septa, several auto-sampler vials per sample have to be prepared for replicate
154 measurements. Minimum sample needs for DAI-GC/MS were 100 µL (achieved with glass inserts).
155

156 *2.4 DAI-GC/MS Analysis*

157 Aqueous samples were quantified using a gas chromatograph (CG 8000, Fisons, Manchester, U.K.)
158 coupled to a quadrupole mass spectrometer detector (MD 800, Fisons). For separation of the
159 analytes, the gas chromatograph was equipped with a 10 m OV-1701 deactivated guard-column
160 (0.53 mm I.D., BGB Analytik, Böckten, Switzerland) and a 60 m Rtx-Stabilwax® fused silica
161 capillary column (0.32 mm I.D., 1.0 µm cross-bonded polyethylene glycol film, Restek, Bellefonte,
162 PA, USA). Alternatively, separation was also achieved with a Supel-Q® porous layer open tubular
163 (PLOT) capillary column (30 m length, 0.32 mm I.D., Supelco, Bellefonte, PA, USA).
164

165 Volumes of 1 to 10 µL were injected at an injection speed of 1 µL/s to a cold on-column injector
166 using an autosampler (AS 800, Fisons) and a 10 µL glass syringe. The following temperature
167 program was applied for the Rtx-Stabilwax® column, resulting in analysis times (injection to
168 injection) of 45 minutes: 10 min. at 60 °C, 5 °C/min. to 100 °C, 30 °C/min. to 200 °C, hold 10 min.
169 When using the Supel-Q® column, the temperature program was: 60°C, 10 °C/min to 200 °C, hold
170 15 min. Helium (purity 99.999%) was used as carrier gas at a constant column head pressure of 100
171 kPa. Detection and quantification of the analytes was performed in the electron impact positive ion

mode (ionization: 70 eV electron energy, 150 µA emission current, 200 °C source temperature; detection: 450 V detector voltage) using selected ion monitoring (SIM) of compound-specific target and qualifier ions given in Table 1. To achieve minimum dwell times of 0.03 s per mass, four separate retention windows were programmed.

2.5 Determination of Absolute and Relative Recoveries, Method Detection Limits (MDLs) and Instrument Detection limits (IDLs)

Recoveries and MDLs were evaluated for two types of natural waters: Uncontaminated groundwater and river water samples were spiked with the aqueous standards S_1 or S_2 to two analyte concentrations given in Table 2 and five replicates of each spike level and water type were analyzed. Quantification was performed using a five-point calibration curve and absolute recoveries, that is the ratio of measured to spiked concentration, were determined. Whereas absolute recoveries were quantified by absolute peak areas only, relative recoveries were obtained by referring the signals of all analytes and calibration standards to the signal of one of the internal standards given in Table 2. MDLs were calculated as three times the standard deviation determined from five subsequent measurements of a sample spiked to the low analyte concentration. Recoveries and MDLs were evaluated for injection volumes of 1 µL and 10 µL in separate runs. Instrument detection limits, corresponding to the sample amount required on column to produce an MS signal three times higher than the noise, were determined by measuring average analyte S/N ratios of three 1 µL injections of samples containing the low spike concentrations.

3. Results and Discussion

3.1 Chromatographic Separation

As can be seen in Figure 1, baseline separation was achieved with a Stabilwax® column for all investigated compounds, except cDCE/TCE, CT/111TCA and TOL/12DCP. Quantification was not

196 compromised by overlapping retention times since compound-specific target ions produced clearly
197 separated signals in the MS. During water elution (retention time 17 to 22 minutes) an elevated
198 baseline was observed. Nevertheless, detection and quantification of analytes was never
199 compromised, neither during nor after this period, and peak areas were in the same order of
200 magnitude for all investigated compounds (Figure 1). Only the sensitivity of CT analysis was
201 hampered because CT was quantified on its minor ion fragment (m/z 82) in order to avoid
202 interference with 111TCA.
203

204 *3.2 Injection volumes*

205 Sample injection volumes were increased from 1 to 10 µL to optimize method sensitivity (Figure
206 2). Different behavior of the analyte peaks was observed, depending on their elution relative to the
207 water peak. For compounds eluting before water, increasing the injection volumes from 1 to 10 µL
208 caused the peak areas to increase by an average factor of seven. However, a decrease in sensitivity
209 was observed for compounds eluting with or after the water peak. oXY and chlorobenzenes peaks
210 vanished at injection volumes of 10 µL. For the highly polar TBA, significant peak broadening
211 occurred already at an injection volume of 3 µL as observed previously [25]. Therefore, we
212 recommend sample injection volumes smaller than or equal to 1 µL if TBA or any compounds
213 eluting with or after the water peak are the primary targets of analysis.

214 *3.3 Calibration, recoveries, precision and detection limits*

215 The linearity of the DAI-GC/MS method was tested for a concentration range of 3 to 520 µg/L
216 using a five-point calibration (1 µL injection volume). All calibration curves were linear ($R^2 \geq 0.99$,
217 relative standard errors of slopes 0.52 – 5.6%, curves forced through origin). Table 2 summarizes
218 the results of the method validation for the 24 investigated analytes. The absolute recoveries of
219 spiked uncontaminated groundwater samples covered a range of 56 – 212% with an average value

of 90%. Whereas for CT, TBA, BENZ and the xylene isomers higher recoveries than 110% were observed, they were significantly lower (66% in average) for the other compounds with retention times below 22 minutes. Chlorobenzenes elute later and were recovered quantitatively (94 – 104%). This variation of absolute recoveries during a GC run reflects effects of water in the MS source: water entering an MS system can cause a discharge of accelerating potentials and degradation of electron multiplier detectors. However, for 1 to 10 µL injection volumes, this effect was found not to deteriorate system stability [10]. Furthermore, due to its high density and low molecular weight, water produces a vapor volume, which is more than seven times larger than that of the same amount of an organic solvent such as hexane. This leads to a significant decrease of the vacuum in the MS, which reduces the ionization efficiency and detector sensitivity (see section 3.4). Since pressure in the MS source the during water elution (retention time 17–22 min.) is not completely reproducible from injection to injection, absolute recoveries for analytes eluting after 17 minutes are compromised.

Using internal standards and calculating relative rather than absolute recoveries, we could correct for the effect of lacking ionization reproducibility. Six deuterated compounds with similar physical-chemical properties to the analytes were used. For each analyte the internal standard leading to best linearity and relative recovery is given in Table 1. Similar elution times relative to water were the only condition for selecting an appropriate internal standard for quantification of a specific analyte. Therefore, for analytes with retention times shorter than 17 min., similar results were obtained with MTBE-d_3, BENZ-d_6 or CF-d as internal standards. However, the use of an internal standard did not improve the recoveries of CT and TBA. Overall, relative recoveries of 83 – 119% were obtained for spiked uncontaminated groundwater. Only the recoveries of ETBENZ (124%), pXY (138%) and oXY (141%) differed more than 20% from unity. This result might be improved by using of a more suitable internal standard, e.g. a deuterated xylene.

245

246 To test the accuracy of the method, relative standard deviations (RSD) of 10 subsequent injections
247 were determined. RSD values below 10% for all analytes except for cDCE (14%), ETBENZ (24%)
248 and the xylene isomers (23, 42 and 16%) demonstrate the high accuracy of measurements by DAI-
249 GC/MS. MDLs of below 1 µg/L were obtained for all compounds except CT (1.3 µg/L), TBA (2.8
250 µg/L) and oXY (2.1 µg/L). The IDLs were ≤5.0 pg of substance on-column for all substances
251 except CT (20 pg), 111TCA (8.5 pg), and PCE (5.7 pg). The higher IDL for CT is a result of
252 compromised quantification on its major mass fragment (see above).

253

254 Different sources of water (e.g., river water vs. groundwater) did not influence the accuracy and
255 reproducibility of the method as shown from a comparison made in Table 2. No significant
256 difference in recoveries, RSDs and MDLs can be observed because most potentially interfering
257 matrix constituents (e.g., salts and dissolved organic matter) are trapped in the guard column.
258 However, to avoid long-term interferences, we recommend using a 10 m long pre-column, which
259 should be shortened by 10 cm after some 100 injections.

260

261 The precision of the presented method was further tested by analyzing 17 groundwater samples
262 from a contaminated field site by DAI-GC/MS and conventional headspace analysis-GC/MS.
263 Figure 3 shows the cross-correlation of the concentrations measured for cDCE, CF, and TCE. The
264 results agreed well with a correlation coefficient of 0.98 (n=41 quantified compounds).

265

266 *3.4 Vacuum in Ion Source*

267 To examine the effect of water vapor on the stability of the vacuum in the MS, the pressure in the
268 ion source was monitored using a high vacuum gage (BOC Edwards, UK). As depicted in Figure 4,
269 the pressure increased from $1.5 \cdot 10^{-2}$ to $3.0 \cdot 10^{-2}$ mbar upon elution of 1 µL water injection, but the

initial conditions were re-established within five minutes. The fact that no drift in baseline vacuum could be observed during 15 consecutive GC runs demonstrates that the water vapor is efficiently removed from the ion source (Figure 4A).

For injection volumes >1 µL, the temporary pressure increase is more pronounced and reached up to $20 \cdot 10^{-2}$ mbar in the case of 10 µL water injection. Figure 4C shows that the vacuum recovered more slowly and, consequently, hampered ionization conditions persisted for a longer time period for higher injection volumes. So, 10 µL injection volumes decreased the sensitivity of analytes eluting between 15–25 min., instead of 17–21 min. in the case of 1 µL injections.

The long-term stability of the GC/MS was evaluated by a sequence of 62 samples using 5 µL injection volumes. No baseline drift from sample to sample was observed during the more than 40 h of consecutive measurements, and the concentrations quantified in 10 aqueous standards containing PCE, TCE, cDCE, 11DCE and tDCE were reproducible (RSD <9%).

3.5 Use of a PLOT column for improved sensitivity of late-eluting compounds

Besides the polar Rtx-Stabilwax® column with a polyethylene glycol stationary phase, apolar capillary columns stationary phase like DB-1 or DB-624 have also been applied for DAI [14-16]. These stationary phases are liquid films that are generally not completely inert to water. A newer type of stationary phase is used in porous layer open tubular (PLOT) capillary columns, which are coated with a porous polymer layer and were originally developed for the separation of gases. To test the applicability of PLOT columns for DAI, we evaluated the Supel-Q® capillary column, a widely used PLOT column that is compatible for aqueous injection and whose stationary phase consists of porous divinylbenzene polymer.

As is shown in Figure 5, the chromatographic separation of 22 VOCs on the PLOT column is comparable to the Stabilwax column. While all chlorinated ethenes were completely baseline-separated, an overlap of DCM/11DCE and of PCE/TOL was observed. An important difference to the Stabilwax® column is the early elution of water at 2 – 5 minutes, which can be monitored by recording the vacuum in the ion source of the MS (see Figure 4B). However, the vacuum in the ion source fully recovers 3-4 minutes later. The PLOT column is therefore ideal for analysis of compounds with retention time above 10 min., particularly if 10 µL injection volumes are required for maximum sensitivity. Average relative recoveries of 105 ± 16% were determined in uncontaminated groundwater spiked with a set of 16 chlorinated VOCs to two concentration levels (4.4 to 6.5 µg/L and 177 to 260 µg/L) using 1 µL injection volume (data not shown).

3.6 Application to Environmental and Laboratory Samples

The wide range of detectable compounds as well as the simple sample preparation makes DAI-GC/MS a versatile method for the quantification of VOCs in water samples. We tested its applicability in field measurements as well as for drinking water treatment.

1. Assessment of PCE degradation at an industrial spill site. Figure 6 shows a chromatogram of a groundwater sample originating from a mixed PCE and gasoline spill site. The presence of the *cis*-DCE in the aquifer points towards biodegradation of PCE, which can only proceed via TCE to cDCE, usually without significant formation of 11DCE and tDCE. Highly toxic VC at a concentration exceeding more than 300 times the WHO guideline value was also found in this sample. The simultaneous detection of polar and non-polar compounds at very different concentrations demonstrates the eligibility of the presented method field applications.

2. Advanced Oxidation of MTBE during Drinking Water Treatment. The product formation from MTBE oxidation by conventional ozonation and advanced oxidation process applying ozone/hydrogen peroxide was studied in drinking water treatment systems. Therefore, an analytical method that allows for the simultaneous and rapid determination of MTBE, TBA, *tert*-butyl formate, acetone and methyl acetate in small sample volumes is required. These highly polar analytes are hardly extractable from water by conventional pre-concentration techniques such as SPME and P&T. Our DAI-GC/MS method enabled the sensitive and simultaneous quantification of the target analytes. In this study, it was important to process the samples rapidly, to minimize loss of TBF by hydrolysis to TBA. DAI-GC/MS was the only analytical method, which fulfilled all requirements necessary to conduct this study (i.e., fast and sensitive detection of polar analytes in small aqueous sample volumes).

4. Conclusions

The presented DAI-GC/MS-method is an accurate, sensitive, and robust method that is suited for trace level quantification of polar and non-polar VOCs in aqueous matrices. Accurate determinations of analyte concentrations in the ng/L to µg/L range are possible from small sample volumes (≥100 µL). As an alternative to widely used liquid film capillary columns, separation of the analytes can also be achieved with a divinylbenzene PLOT capillary column. Such column types have advantages when analytes of interest are less volatile, that is they elute later than 10 min. and injection volumes of 10 µL are necessary to achieve MDLs as low as 0.5 µg/L. Because no pre-concentration steps are necessary for VOC analysis with DAI-GC/MS and sample preparation is simple (i.e., addition of internal standard), losses of volatile analytes as well as sample contamination can be minimized. The achieved sensitivity is well below EU and US EPA drinking water regulation values. Thus, the presented DAI-GC/MS method is an ideal tool for monitoring of groundwater, drinking water and surface waters. It offers significant advantages over existing methods, such as a large number of detectable analytes, good sensitivity and accurate results, high

343 throughput of small sample volumes, and no need for dedicated equipment. Finally, DAI-GC/MS
344 has the potential to be expanded to other polar compounds such chain alcohols, esters, aldehydes
345 and ketones.
346

347 **Acknowledgments**

348 We gratefully acknowledge financial support from the Swiss Federal Office for the Environment.
349 We thank Jakov Bolotin for technical assistance, Juan Acero for the results on advanced oxidation
350 processes, and Rolf Gloor (Bachema AG) for his cooperation at the contaminated aquifer site.
351

352 **References**

353 [1] WHO, Guidelines for Drinking-water Quality, World Health Organization, Geneva, 2004.
354 [2] P.J. Squillace, M.J. Moran, C.V. Price, Environ. Sci. Technol. 38 (2004) 5327.
355 [3] NAQUA - Grundwasserqualitaet in der Schweiz 2002/2003, National Groundwater Quality
356 Monitoring Network, Swiss Federal Office for the Environment, Bern, Switzerland, 2004.
357 [4] M. Marczak, L. Wolska, W. Chrzanowski, J. Namiesnik, Microchim. Acta 155 (2006) 331.
358 [5] G. Schomburg, E. Bastian, H. Behlau, H. Husmann, F. Weeke, M. Oreans, F. Muller, J.
359 High Resolut. Chromatogr. Chromatogr. Commun. 7 (1984) 4.
360 [6] H.G.J. Mol, H.G.M. Janssen, C.A. Cramers, U.A.T. Brinkman, J. High. Resolut.
361 Chromatogr. 16 (1993) 459.
362 [7] R. Kubinec, J. Adamuscin, H. Jurdakova, M. Foltin, I. Ostrovsky, A. Kraus, L. Sojak, J.
363 Chromatogr. A 1084 (2005) 90.
364 [8] M. Wortberg, W. Ziemer, M. Kugel, H. Muller, H.J. Neu, Anal. Bioanal. Chem. 384 (2006)
365 1113.

[9] J.J. Vreuls, G.J. Dejong, R.T. Ghijsen, U.A.T. Brinkman, J. Microcolumn Sep. 5 (1993) 317.

[10] L.E. Harris, W.L. Budde, J.W. Eichelberger, Anal. Chem. 46 (1974) 1912.

[11] K. Grob, K. Grob, J. Chromatogr. 151 (1978) 311.

[12] K. Grob, A. Habich, J. High Resolut. Chromatogr. Chromatogr. Commun. 6 (1983) 11.

[13] K. Grob, J. Chromatogr. 299 (1984) 1.

[14] D. Carmichael, W. Holmes, J. High. Resolut. Chromatogr. 13 (1990) 267.

[15] I. Temmerman, D.J.M. Quaghebeur, J. High. Resolut. Chromatogr. 13 (1990) 379.

[16] L. Wolska, C. Olszewska, M. Turska, B. Zygmunt, J. Namiesnik, Chemosphere 37 (1998) 2645.

[17] S.K. Golfinopoulos, T.D. Lekkas, A.D. Nikolaou, Chemosphere 45 (2001) 275.

[18] A. Polkowska, Chemosphere 57 (2004) 1265.

[19] B.S. Middleditch, N.J. Sung, A. Zlatkis, G. Settembre, Chromatographia 23 (1987) 273.

[20] T.L. Potter, Ground Water Monit. Rem. 16 (1996) 157.

[21] S. Hong, C.M. Duttweiler, A.T. Lemley, J. Chromatogr. A 857 (1999) 205.

[22] D.F. Gurka, S.M. Pyle, R. Titus, Anal. Chem. 64 (1992) 1749.

[23] S.M. Pyle, D.F. Gurka, Talanta 41 (1994) 1845.

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

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

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

[27] T.C. Schmidt, Trends Anal. Chem. 22 (2003) 776.

[28] L. Zwank, M. Berg, M. Elsner, T.C. Schmidt, R.P. Schwarzenbach, S.B. Haderlein, Environ. Sci. Technol. 39 (2005) 1018.

Table 1. Investigated Compounds and Internal Standards, Water Solubility, Air-Water Partitioning Coefficients (K_{iaw}), Densities, Molecular Weights and Monitored Mass Traces

Compounds	abbreviation	water solubility[a,b] [g·L^{-1}]	K_{iaw}[a,c] [mol·L^{-1}/mol·L^{-1}]	density [g·cm^{-3}]	molecular weight [g·mol^{-1}]	target ion [m/z]	qualifier ion [m/z]	retention time [min]	internal standard (IS)
vinyl chloride	VC	2.79[d]	1.08	0.91	62.5	62	27	5.1	1
methyl *tert*-butyl ether	MTBE	48[c]	0.03[f]	0.74	88.2	73	43	5.8	1
deuterated MTBE (IS 1)	MTBE-d_3				91.2	76		5.8	
1,1-dichloroethene	11DCE	2.49	1.06	1.21	96.9	61	96	6.2	1
trans-1,2-dichloroethene	tDCE	6.26	0.03	1.26	96.9	61	96	8.8	1
carbon tetrachloride	CT	0.83	1.21	1.59	153.8	82	117	9.7	-
1,1,1-trichloroethane	111TCA	1.30	0.71	1.34	133.4	97	61	9.7	1
tert-butyl alcohol	TBA	complete[c]	0.0004[g]	0.79	74.1	59	41	10.3	-
dichloromethane	DCM	16.95	0.12	1.33	84.9	49	84	11.6	1
benzene	BENZ	1.75	0.22	0.88	78.1	78	56	12.5	2
perdeuterated benzene (IS 2)	BENZ-d_6				84.2	84		12.5	
cis-1,2-dichloroethene	cDCE	5.09	0.19	1.28	96.9	61	96	14.5	1
trichloroethene	TCE	1.09	0.42	1.46	131.4	130	95	14.6	1
chloroform	CF	8.45	0.17	1.48	119.4	83	85	15.8	3
deuterated chloroform (IS 3)	CF-d				120.4	84	86	15.8	
perchloroethene	PCE	0.14	0.71[h]	1.62	165.8	166	129	16.1	3
toluene	TOL	0.56	0.27	0.87	92.1	91	92	17.1	3
1,2-dichloropropane	12DCP	2.74[c]	0.12	1.16	113.0	63	62	17.1	4
1,2-dichloroethane	12DCA	8.42	0.06	1.25	99.0	62	64	18.1	4
deuterated 1,2-dichloroethane (IS 4)	12DCA-d_4				103.0	65		19.6	
ethylbenzene	ETBENZ	0.17	0.34	0.87	106.2	91	106	19.7	4
p-xylene	pXY	0.18	0.28	0.87	106.2	91	106	19.9	4
m-xylene	mXY	0.16	0.29	0.86	106.2	91	106	20.1	4
o-xylene	oXY	0.19	0.22	0.90	106.2	91	106	21.0	4
chlorobenzene	CB	0.46	0.13	1.11	112.6	112	77	21.9	5
deuterated chlorobenzene (IS 5)	CB-d_5				117.6	117		21.9	
m-dichlorobenzene	13DCB	0.12	0.15	1.29	147.0	146	148	25.9	6
p-dichlorobenzene	14DCB	0.07	0.10	1.25	147.0	146	148	26.4	6
o-dichlorobenzene	12DCB	0.13	0.08	1.31	147.0	146	148	27.3	6
deuterated *o*-dichlorobenzene (IS 6)	12DCB-d_4				151.0	152		27.3	

[a] For T = 25 °C. [b] Reference 29 unless otherwise indicated. [c] Reference 30 unless otherwise indicated. [d] Determined for a partial pressure of VC = 1 bar. [e] Reference 19. [f] Reference 31. [g] Reference 32. [h] For T = 20 °C

Table 2. Relative and Absolute Recoveries with Relative Standard Deviations (RSD), Method Detection Limits (MDL) and Instrument Detection Limits (IDL) Determined with Uncontaminated Groundwater and River Water

			spiked groundwater			spiked river water			
	injection volume	spike levels	relative recovery[a,b]	absolute recovery[c]	MDL[c]	relative recovery[a,b]	absolute recovery[c]	MDL[c]	IDL[d]
Compound	[μL]	[μg/L]	[%] (RSD)	[%] (RSD)	[μg/L]	[%] (RSD)	[%] (RSD)	[μg/L]	[pg]
VC	10	0.50 5.0	99 (6.5)	63 (35)	0.10	92 (6.9)	65 (35)	0.10	0.77
MTBE	10	3.0	102 (8.6)	72 (7.3)[e]	0.76	115 (5.9)[e]	82 (30)[e]	0.52	1.3
11DCE	10	0.49 4.9	90 (8.9)	60 (38)	0.13	84 (11)	60 (38)	0.16	1.8
tDCE	10	0.50 5.0	97 (9.9)	56 (55)	0.15	95 (12)	51 (90)	0.18	3.0
CT	10	3.5	[f]	123 (20)[e]	2.1[g]	[f]	115 (57)[e]	6.0[g]	20
111TCA	10	6.4	83 (3.7)[e]	61 (13)	0.72	73 (17)[e]	59 (43)	3.3	8.5
TBA	1	25	[f]	110 (3.7)[e]	2.8[g]	[f]	113 (0.7)[e]	0.52[g]	2.8
DCM	10	0.53 5.3	102 (6.1)	58 (53)	0.10	83 (27)	58 (51)	0.42	4.1
BENZ	10	3.5	111 (5.7)[e]	212 (10)[e]	0.59	123 (14)[e]	222 (17)[e]	1.4	1.6
cDCE	10	0.51 5.1	104 (14)	63 (36)	0.21	98 (8.7)	65 (38)	0.13	3.4
TCE	10	0.58 5.8	107 (7.8)	62 (35)	0.14	108 (6.1)	68 (33)	0.11	2.6
CF	10	0.60 6.0	113 (3.9)	62 (53)	0.07	123 (7.0)	79 (35)	0.13	2.5
PCE	10	0.65 6.5	103 (10)	58 (53)	0.20	103 (4.0)	63 (48)	0.08	5.7
TOL	10	3.5	119 (9.3)[e]	73 (5.6)[e]	0.98	141 (29)[e]	82 (12)[e]	3.1	0.81
12DCP	10	4.6	97 (5.9)[e]	74 (12)[e]	0.81	110 (14)[e]	75 (30)[e]	2.0	3.3
12DCA	10	0.50 5.0	92 (7.6)	65 (53)	0.11	90 (11)	64 (52)	0.17	4.8
ETBENZ	10	0.35 3.5	124 (23)	100 (21)	0.24	105 (13)	91 (31)	0.14	2.3
mXY	10	0.35 3.5	117 (28)	140 (17)	0.29	101 (35)	128 (19)	0.36	3.0
pXY	10	0.34 3.4	138 (42)	124 (11)	0.43	128 (43)	127 (20)	0.44	2.5
oXY	1	4.4 35	141 (16)	139 (15)	2.1	129 (4.8)	123 (14)	0.63	3.3
CB	1	4.4 35	108 (1.8)	97 (14)	0.23	109 (2.3)	102 (3.3)	0.31	1.6
13DCB	1	5.1 41	106 (3.3)	93 (14)	0.50	104 (2.2)	94 (4.1)	0.33	2.5
14DCB	1	7.2 58	105 (3.0)	93 (15)	0.65	101 (2.6)	91 (3.9)	0.56	2.4
12DCB	1	5.2 42	119 (6.4)	104 (14)	0.99	115 (2.0)	103 (4.9)	0.31	1.9

[a] n=10. [b] Relative to internal standard given in Table 1. [c] Calculated as three times the RSD of relative recoveries multiplied with the lower spike level. [d] Amount of sample necessary to be injected on column to produce a peak with S/N = 3 (1 μL injection volumes). [e] n=5. [f] no suitable internal standard. [g] MDL calculated from RSD of absolute recovery.

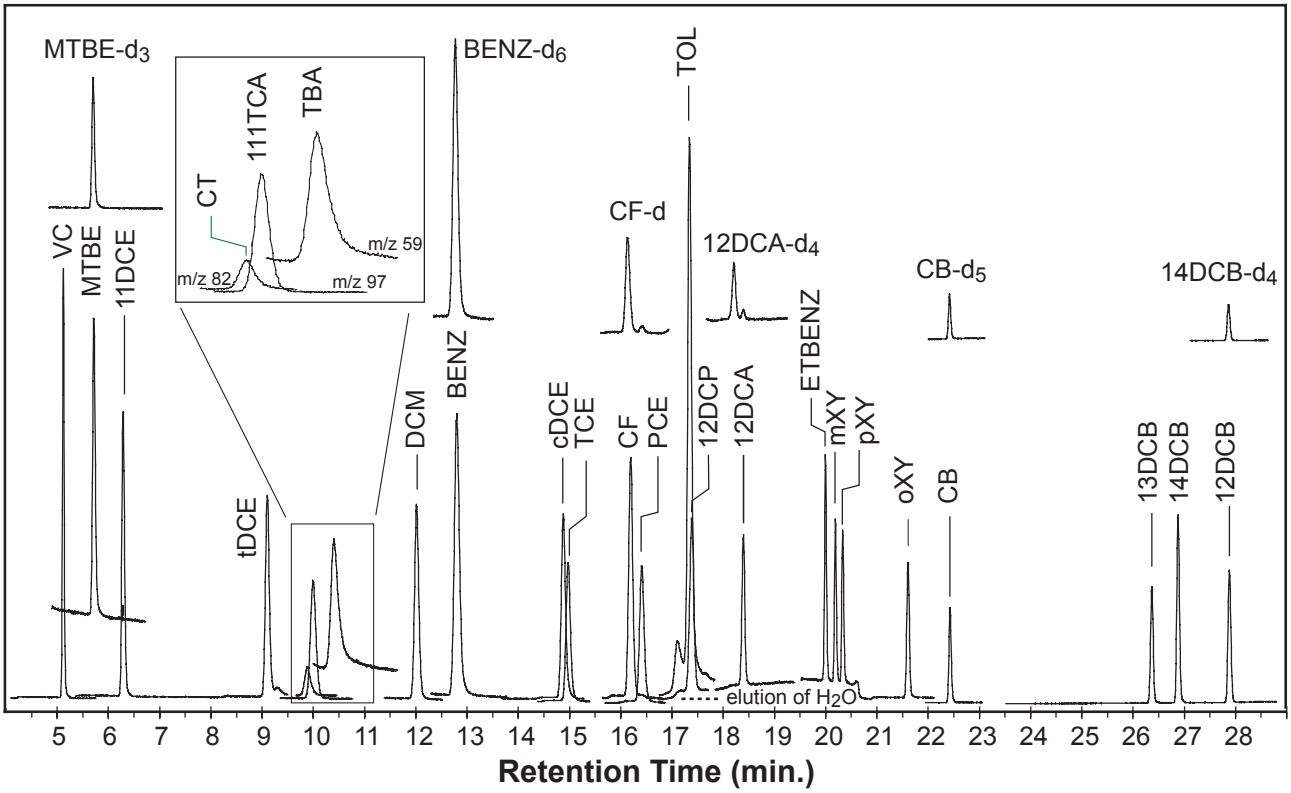

Figure 1. Separation on a Rtx-Stabilwax® capillary column using chromatographic conditions given in section 2.4. SIM chromatogram (mass traces of target ions) derived from 1 µL injection of a standard containing of the 24 analytes (250–520 µg/L) and of the six internal standards (60–105 µg/L, vertically shifted upwards) is shown. The water elutes as a broad solvent peak between 17 and 21 min.

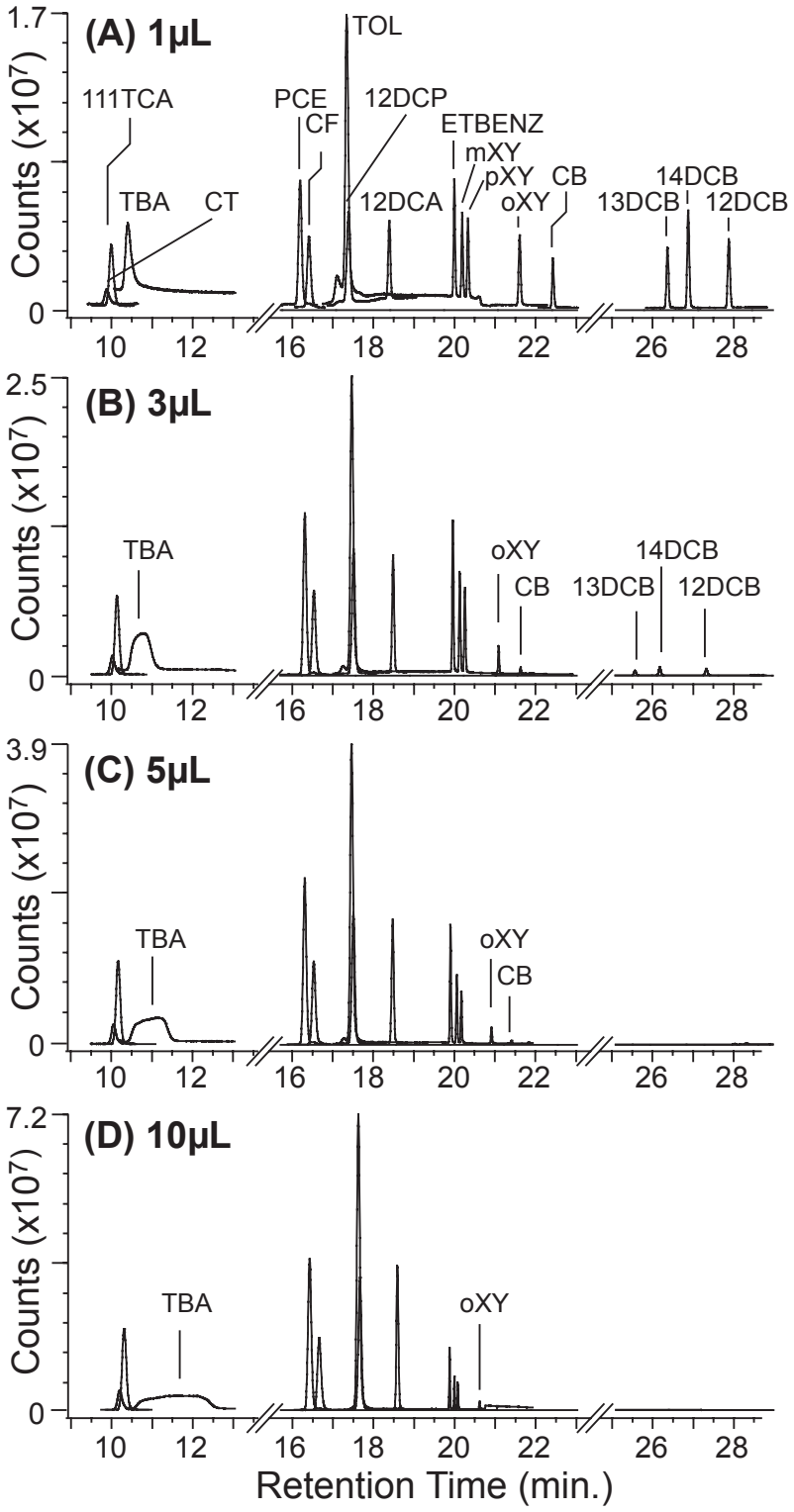

Figure 2. Effect of injection volume on peak intensities, shapes and retention times. Chromatograms derived from injection of (A) 1 µL, (B) 3 µL, (C) 5 µL, (D) 10 µL of a standard containing 250 - 520 µg/L (320 ppm v/v) of each analyte using the chromatographic conditions given in section 2.4.

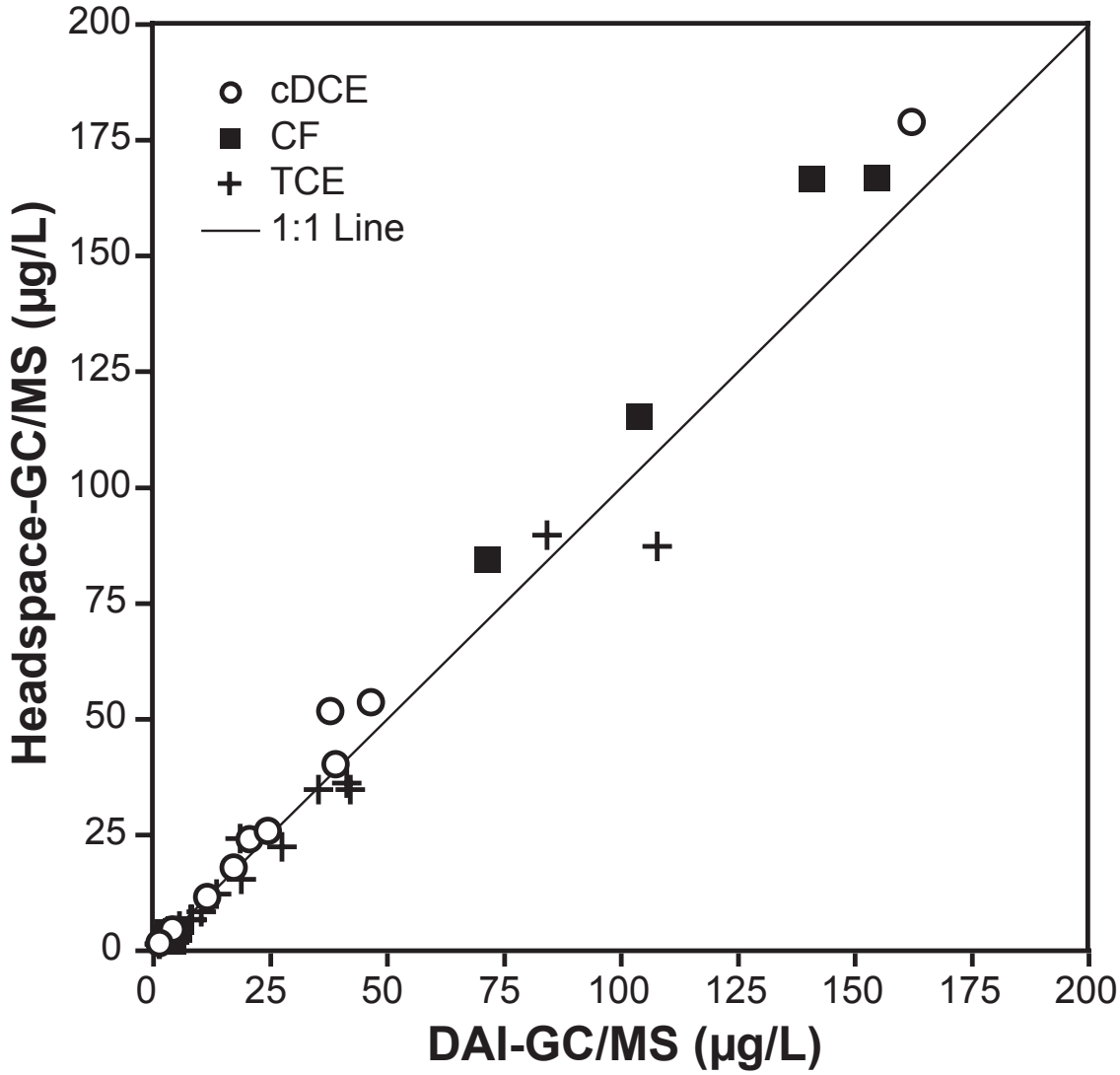

Figure 3. Cross-evaluation of DAI-GC/MS with headspace-GC/MS. Concentrations of cDCE, CF and TCE determined in 17 groundwater samples from a contaminated aquifer using DAI-GC/MS (1 µL injection volume, Rtx-Stabilwax® column) and headspace-GC/MS (50 °C incubation temperature, 1 mL injection volume, Rtx-VMS column) are shown. Correlation data: slope = 1.07, intercept = 0, R^2=0.98, n=41.

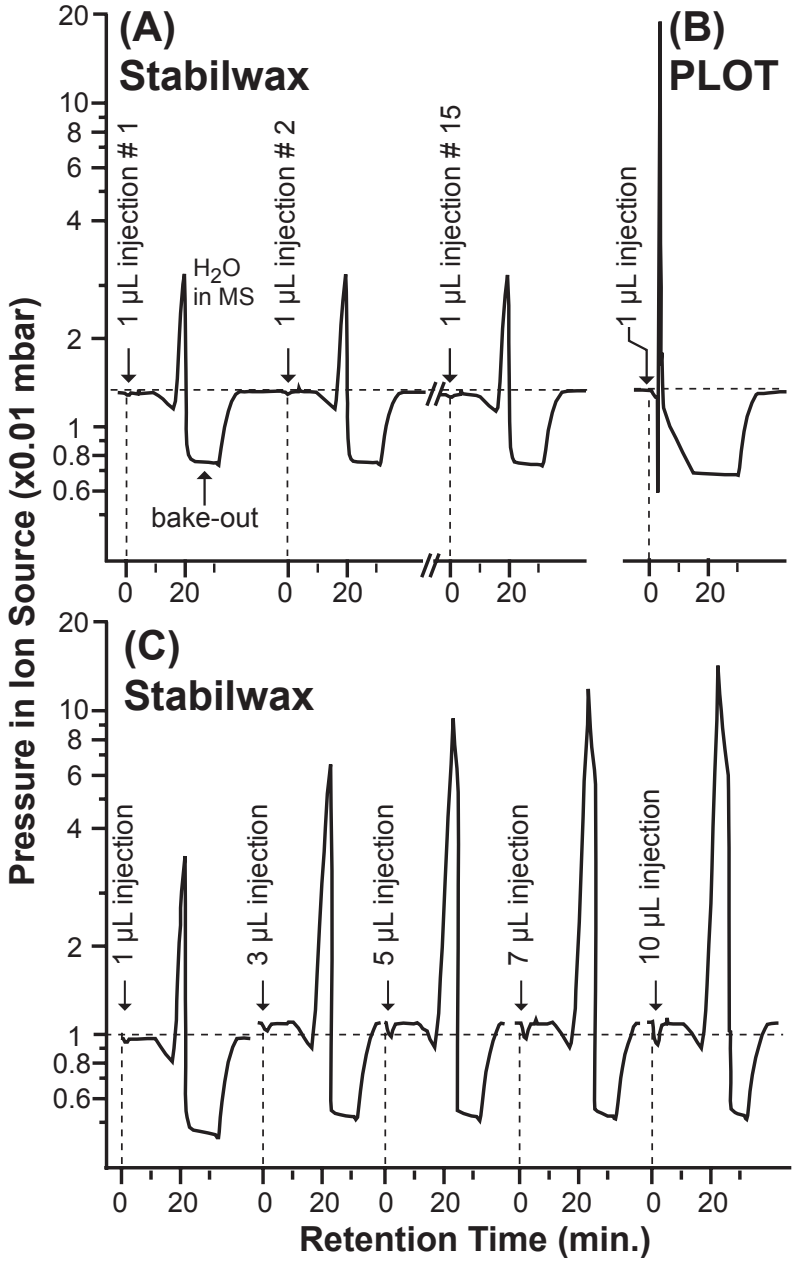

Figure 4. Effect of water vapor on the vacuum in the ion source. (A) Multiple 1 µL injections using a Rtx-Stabilwax® column. (B) 1 µL injection on a Supel-Q® PLOT column. The temperature program is given in Figure 5. (C) Injection of 1 to 10 µL sample volumes on the Rtx-Stabilwax® column. The temperature program is given in section 2.4. The decrease in pressure during bake-out is caused by lower carrier gas velocity at increased temperature due to constant pressure mode.

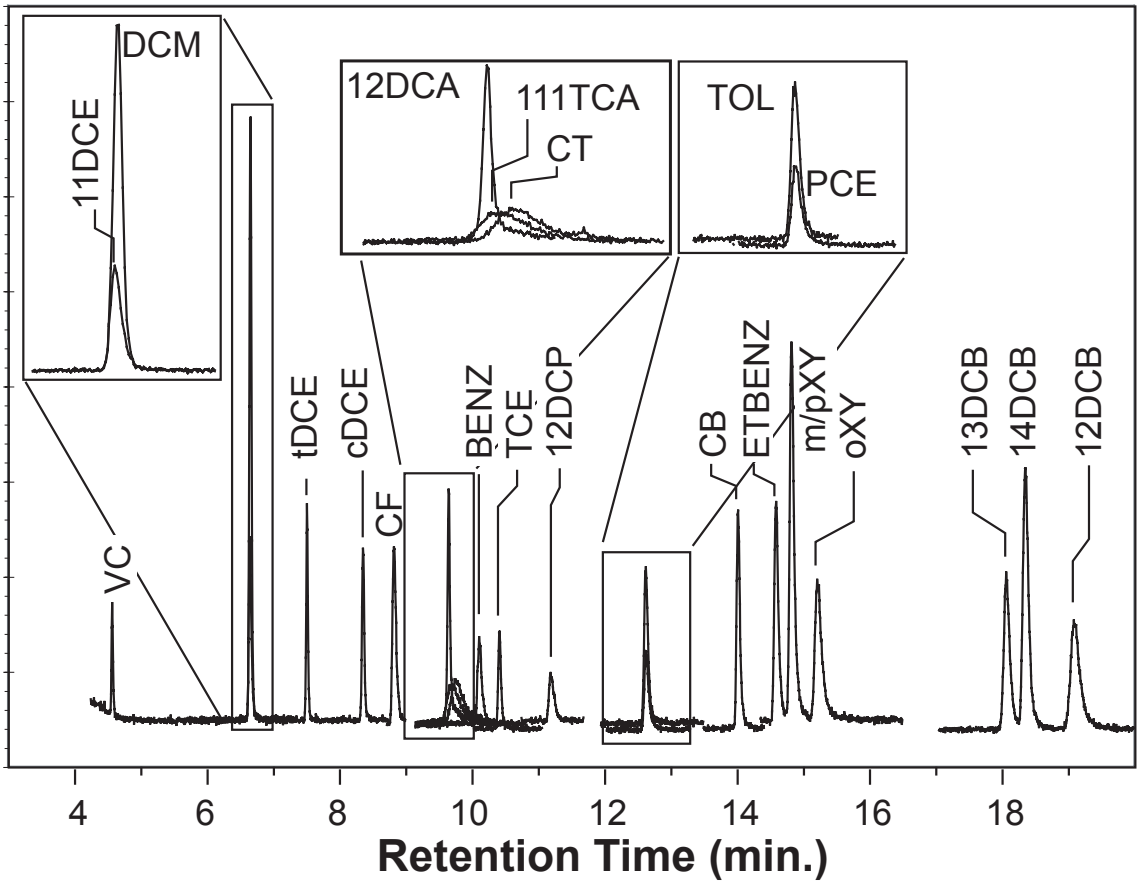

Figure 5. SIM-chromatogram of 22 VOCs using a Supel-Q® PLOT capillary column (30 m length x 0.32 mm i.d.), 9 µL injection volume. The corresponding temperature program is given in section 2.4.

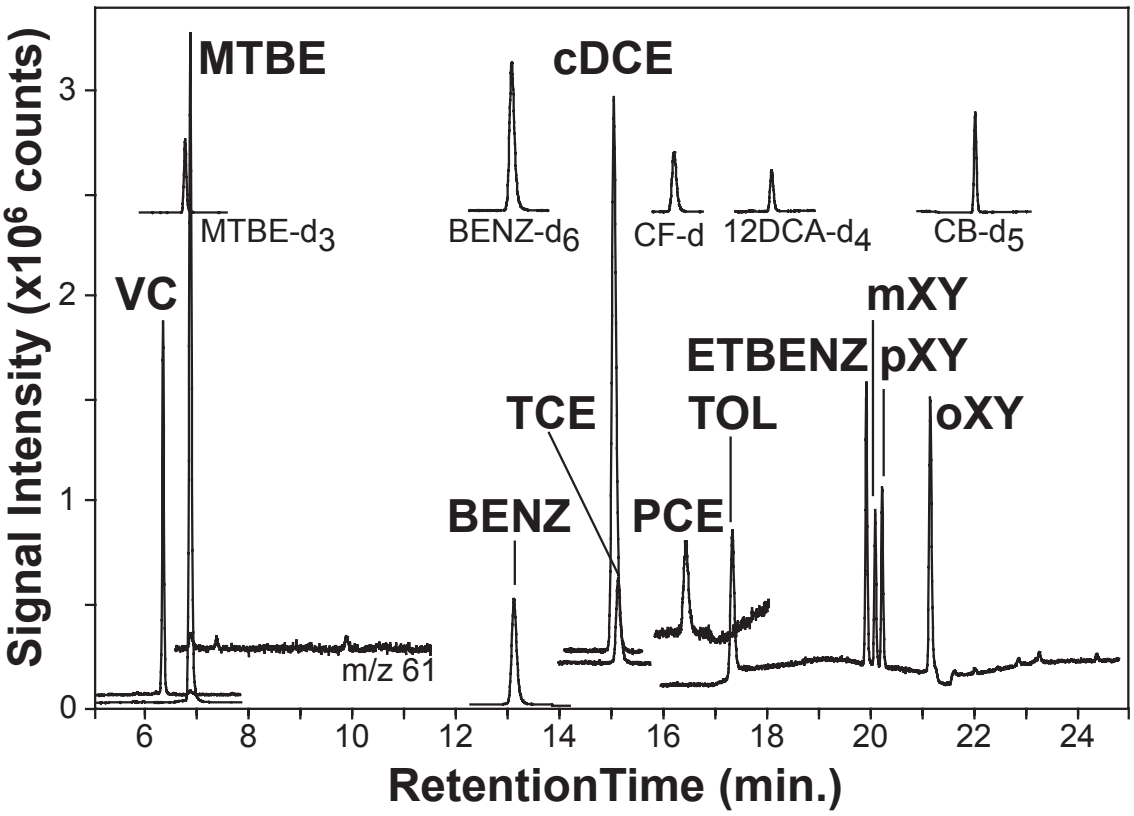

Figure 6. SIM-chromatogram of a groundwater sample from an aquifer contaminated by BTEX, MTBE and chlorinated ethenes (1 µL injection, Rtx-Stabilwax® column, temperature program given in section 2.4). For the purpose of clarity, the following mass traces have been scaled by the indicated factors: Internal standards: 0.1 (shifted vertically upwards); MTBE and BENZ: 0.1; cDCE and TCE: 5; PCE: 10. Identified contaminants and concentrations (in µg/L): VC (98), MTBE (1,100), BENZ (240), cDCE (55), TCE (12.5), PCE (7.7), TOL (21), ETBENZ (62), mXY (46), pXY (57), oXY (126).