



HAL
open science

Field continuous measurement of dissolved gases with a CF-MIMS: Applications to the physics and biogeochemistry of groundwater flow

Eliot Chatton, Thierry Labasque, Jérôme de La Bernardie, Nicolas Guihéneuf,
Olivier Bour, Luc Aquilina

► To cite this version:

Eliot Chatton, Thierry Labasque, Jérôme de La Bernardie, Nicolas Guihéneuf, Olivier Bour, et al..
Field continuous measurement of dissolved gases with a CF-MIMS: Applications to the physics and
biogeochemistry of groundwater flow. *Environmental Science and Technology*, 2017, 51 (2), pp.846-
854. 10.1021/acs.est.6b03706 . insu-01416090

HAL Id: insu-01416090

<https://insu.hal.science/insu-01416090>

Submitted on 14 Dec 2016

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Field continuous measurement of dissolved gases with a CF-MIMS: Applications to the physics and biogeochemistry of groundwater flow

Eliot Chatton, Thierry Labasque, Jérôme de La Bernardie, Nicolas Guihéneuf, Olivier Bour, and Luc Aquilina

Environ. Sci. Technol., **Just Accepted Manuscript** • DOI: 10.1021/acs.est.6b03706 • Publication Date (Web): 12 Dec 2016

Downloaded from <http://pubs.acs.org> on December 12, 2016

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.

Field continuous measurement of dissolved gases with a CF-MIMS: Applications to the physics and biogeochemistry of groundwater flow

Authors: Eliot Chatton ^{a,*}, Thierry Labasque ^a, Jérôme de La Bernardie ^a, Nicolas Guihéneuf ^{a,b}, Olivier Bour ^a, Luc Aquilina ^a

** Corresponding author.*

^a *Géosciences Rennes, Université de Rennes 1-CNRS, UMR 6118, adress: 263 avenue du général Leclerc, Campus de Beaulieu, bâtiment 15, 35042 Rennes Cedex, France, phone: (+33) 223 233 725, email:*

eliot.chatton@gmail.com, thierry.labasque@univ-rennes1.fr, jerome.delabernardie@univ-rennes1.fr,

olivier.bour@univ-rennes1.fr, luc.aquilina@univ-rennes1.fr.

^b *University of Guelph, 50 Stone Road East Guelph, Ontario, Canada, email: guiheneuf.nicolas@gmail.com*

Keywords: *Dissolved gases, Noble gases, Groundwater, Tracer test, Noble Gas Temperature, Residence time, biogeochemical reactivity, MIMS.*

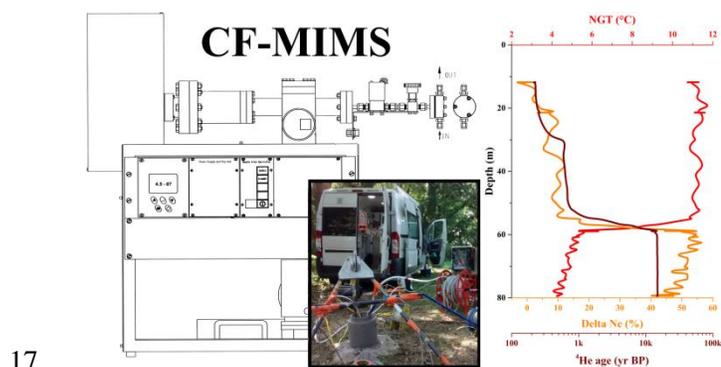
1 **Abstract**

2 In the perspective of a temporal and spatial exploration of aquatic environments (surface and ground
3 water), we developed a technique for field continuous measurements of dissolved gases with a precision
4 better than 1% for N₂, O₂, CO₂, He, Ar, 2% for Kr, 8% for Xe, and 3% for CH₄, N₂O and Ne. With a large
5 resolution (from 1×10⁻⁹ to 1×10⁻² ccSTP/g) and a capability of high frequency analysis (1 measure every 2
6 seconds), the CF-MIMS (Continuous Flow Membrane Inlet Mass Spectrometer) is an innovative tool

7 allowing the investigation of a large panel of hydrological and biogeochemical processes in aquatic
8 systems.

9 Based on the available MIMS technology, this study introduces the development of the CF-MIMS
10 (conception for field experiments, membrane choices, ionisation) and an original calibration procedure
11 allowing the quantification of mass spectral overlaps and temperature effects on membrane permeability.

12 This study also presents two field applications of the CF-MIMS involving the well-logging of dissolved
13 gases and the implementation of groundwater tracer tests with dissolved ^4He . The results demonstrate the
14 analytical capabilities of the CF-MIMS in the field. Therefore, the CF-MIMS is a valuable tool for the
15 field characterisation of biogeochemical reactivity, aquifer transport properties, groundwater recharge,
16 groundwater residence time and aquifer-river exchanges from few hours to several weeks experiments.



18 Introduction

19 Dissolved gas concentrations in groundwater originate mainly from atmosphere-water equilibria existing
20 at the water table during aquifer recharge. These equilibria are governed by physical laws allowing the
21 calculation of dissolved gas equilibrium concentrations (solubilities) as a function of the gas partial
22 pressure in the air (z_i), the atmospheric pressure (P), the water temperature (T) and salinity (S)¹⁻⁸.
23 Therefore, the combined determination of any dissolved gas concentration unaltered from recharge
24 equilibrium enables the reconstruction of recharge conditions (T, S, P) as long as the gas partial pressures

25 at the time of recharge are known. Consequently, several studies have been using dissolved noble gases^{9–}
26 ¹¹ sometimes combined to dissolved nitrogen^{12,13} to derive past and present climatic conditions through
27 the determination of noble gas temperatures (NGTs i.e. recharge temperatures), the extent of the excess air
28 phenomenon (EA) and recharge elevations. Therefore, dissolved noble gases (and dissolved nitrogen) are
29 valuable tools for the study of groundwater origins, paleoclimates and climate changes.

30 Contrary to other noble gases, dissolved ⁴He concentrations in groundwater can increase quite rapidly
31 (over a hundred years) due to *in situ* production by radioactive decay of uranium and thorium rich
32 minerals of aquifer rocks. As a result, dissolved radiogenic ⁴He accumulates over time in aquifers and its
33 production creates an excess He that can be typically quantified for residence time larger than hundred
34 years. The determination of dissolved radiogenic He concentrations enables the characterisation of
35 groundwater residence times as long as ⁴He production rates are known^{14–17}.

36 Dissolved reactive gases (N₂, CO₂, O₂, CH₄, N₂O and H₂) originate initially from atmospheric equilibria.
37 However, their concentrations in natural waters can be significantly altered by biogeochemical reactions
38 that typically occur in aquatic environments¹⁸. Therefore, the measurement of these reactive dissolved
39 gases is critical to the understanding of the biogeochemical reactivity of aquatic environments^{19–25}.

40 All these applications need precise dissolved gas measurements with various requirements in terms of
41 spatial and temporal distribution in the field. Currently, most of the available analytical techniques are
42 based on field sampling and laboratory analysis performed from a few hours or several days after
43 sampling. Therefore, ensuring sample preservation and representativeness is crucial for the determination
44 of accurate actual dissolved gas concentrations. For instance, groundwater sampling in wells is not an easy
45 task due to the risk of sample contamination with atmospheric air, the mixing processes naturally
46 occurring in the well (natural flows) or induced by the sampling process (renewal of the well water,
47 pumping, movement of mobile samplers) that would bias water samples²⁶. Furthermore, preservation of
48 dissolved gas samples is a crucial stake particularly for the measurement of dissolved reactive gases such
49 as O₂, N₂, N₂O and H₂ in reactive environments.

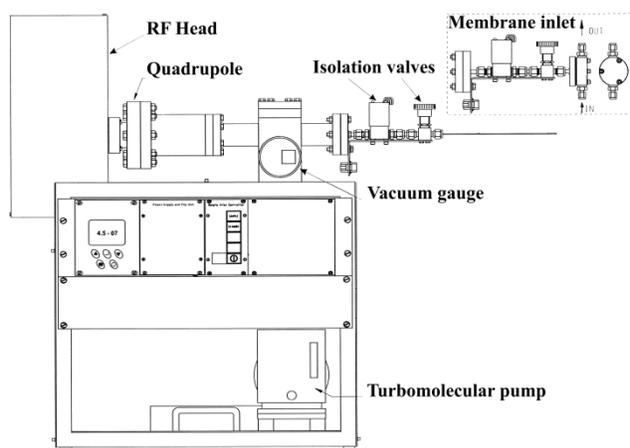
50 In order to solve the issues related to sampling, field measurement techniques such as Membrane Inlet
51 Mass Spectrometers (MIMS) received great attention from environmental scientists for their capacity of
52 rapid evaluation of dissolved gases in water ^{27–32}. MIMS technology was first developed for the
53 measurement of organic compounds in environmental water samples ^{33,34}. Later, Ketola et al ³⁵ proposed a
54 review of the applications and improvements of this technique. Kana et al ³⁶ optimised a MIMS for quasi-
55 continuous determination of major dissolved gases (O₂, N₂, Ar) in water samples in order to study
56 biological activity ^{37–40}. MIMS systems were also miniaturised for oceanographic studies in order to create
57 dissolved gas profiles in seawater ^{41–44}. Recently, developments of MIMS have been realised for
58 groundwater studies. Mächler et al ⁴⁵ developed a portable GE-MIMS for field and laboratory
59 measurements. This stand-alone system allows the quasi-continuous monitoring of dissolved He, Ar, Kr,
60 N₂ and O₂ every 12 minutes over several days. Similarly, Visser et al ⁴⁶ developed also their own portable
61 NG-MIMS for quasi-continuous measurements of the whole suite of dissolved noble gases. However, the
62 NG-MIMS remains sensitive to the sampling conditions as it requires the collection of water samples that
63 are sequentially analysed (every 5 minutes). Furthermore, the available field quasi-continuous techniques
64 (GE-MIMS and NG-MIMS) do not allow so far the measurement of all major dissolved gases.

65 We propose here a new approach for the continuous field measurement of dissolved gases in aquatic
66 environments with a CF-MIMS (Continuous Flow Membrane Inlet Mass Spectrometer). Through this
67 technique, natural waters (surface water or groundwater) are directly brought to a semi-permeable
68 membrane at a constant flow rate for the continuous measurement of dissolved gases. With an original
69 calibration procedure, the CF-MIMS allows the continuous monitoring of dissolved noble and reactive
70 gases (He, Ne, Ar, Kr, Xe, N₂, CO₂, O₂, CH₄ and N₂O) over a large concentration range. After presenting
71 the details of the analytical development, the capabilities of the CF-MIMS are evaluated through two field
72 applications: two groundwater tracer tests with dissolved ⁴He and a well-logging of dissolved gases.

73 Method

74 System description

75 Many MIMS systems are currently available on the market for different applications. The design and
76 conception of the CF-MIMS (HPR-40) was carried out by the private supplier Hiden Analytical.
77 According to the specification requirements, the instrument dimensions (0.150 m³), weight (55 kg) and
78 shielding (reinforced frame mounted on Silent Bloc[®]) make the CF-MIMS a mobile and resistant tool
79 designed for field experiments.



80

81 **Figure 1: Representation of the CF-MIMS adapted from Hiden Analytical HPR40 manual.**

82 Although its robustness, the CF-MIMS consists in a leading-edge analytical instrument for dissolved gas
83 measurements. Equipped with a membrane inlet connected to the vacuum of a Quadrupole Mass
84 Spectrometer (QMS around 10⁻⁵ Torr), the CF-MIMS shown in figure 1 allow the direct permeation of
85 dissolved gases from liquids to the mass spectrometer. Inside the QMS, dissolved gases are ionised using
86 an oxide coated iridium filament allowing the selection of ionisation energies (between 4 and 150 eV) and
87 emission intensities (between 20 and 5000 μA). Once ionised, dissolved gases are separated by the
88 quadrupole according to their mass to charge ratios (m/z ratios). Then, the detection of dissolved gases is
89 performed either by a Faraday cup or a single channel electron multiplier (SCEM). Finally, the CF-MIMS

90 allows a direct and continuous measurement of dissolved gases at the high frequency of 1 dissolved gas
91 measurement every 2 seconds.

92 **Optimisation techniques**

93 **Membrane**

94 The originality of MIMS systems lies in the inlet that uses a semi-permeable membrane to measure
95 directly the dissolved gases of the water. The choice of a suitable membrane is therefore essential to
96 ensure the maximal permeation of the targeted dissolved gases. Laboratory experiments have been carried
97 out at Hiden Analytical to select or create the best membrane for our purposes by comparing different
98 types of membrane (PDMS, Biaxially oriented PET, X44[®] polymer). With an enhanced noble gas
99 permeability and a suitable gas exchange surface (16 cm²), the membrane X44[®] has been selected for our
100 CF-MIMS. This membrane inlet system (figure 1) allows a continuous flow measurement of dissolved
101 gases.

102 **Water vapour entrapment**

103 In order to enhance the sensitivity of MIMS systems to low abundant gases a water trap can be installed
104 just between the membrane inlet and the mass spectrometer ⁴⁶. However, the water trap requires a long
105 stabilisation time to remove the totality of the water vapour from the signal and uses lots of electrical
106 power that is hardly available in the field. Since this water entrapment did not significantly enhance
107 signal/noise ratios in our CF-MIMS we chose not to use it.

108 **Ionisation**

109 Inside the mass spectrometer, optimisation of ionisation procedures can be performed to improve the
110 signal/noise ratio by optimisation of the emission intensity (flow of ionising electrons) or, to a lower
111 extent, by experimental determination of optimal ionisation energies. In the CF-MIMS, the standard
112 ionisation procedure (250 μ A, 70 eV) has been optimised by increasing the emission intensity in order to
113 enhance the sensitivity to low abundant gases such as Kr and Xe (see Supporting Information).

114 **Calibration**

115 In order to convert the partial pressures measured by the CF-MIMS into gas concentrations it is necessary
116 to define a proper calibration procedure. In order to account for the different membrane interactions with
117 dissolved gas concentrations, the system is directly calibrated on water flows of known concentration. For
118 the purpose, a calibration chamber has been built in order to saturate a water volume with different
119 standard gas mixtures of known composition while preventing from any atmospheric exchange (see
120 Supporting Information). The Standard Gas Equilibrated Water (SGEW) is continuously brought from the
121 calibration chamber to the membrane using a low voltage impeller pump allowing the monitoring of water
122 saturation until equilibrium is reached.

123 Measured partial pressures for each gas can be converted into gas concentrations using either an internal
124 or external calibration procedure. The internal calibration consists in the calculation of dissolved gas
125 equilibrium concentrations of different SGEWs using the laws of gas solubility in water¹⁻⁸. The
126 parameters required for the calculation of equilibrium concentrations such as air pressure, water
127 temperature and salinity are continuously monitored in the calibration chamber. In addition, the calibration
128 chamber includes an outlet valve allowing an external calibration by sampling each SGEW for control
129 analysis using classical gas-chromatography techniques (GC-TCD or GC-MS).

130 The calibration procedure is performed after connecting the membrane inlet to the mass spectrometer and
131 should be implemented when the partial pressure baselines are stable (requiring almost 2 hours to establish
132 an equilibrium between the permeation of gases through the membrane and the mass spectrometer
133 vacuum). Calibration temporal stability has been investigated through a laboratory test that did not
134 indicate any sign of instrumental drift over the 38 hours experiment. Therefore, when the calibration is
135 achieved and as long as the membrane inlet remains connected, the CF-MIMS does not require any
136 additional calibration. Nevertheless, regular sampling (for analysis with classical techniques) always
137 ensures the validity of the calibration for long-term monitoring experiments.

138 The CF-MIMS calibration is performed at the same flow and temperature as the measurements because
139 membrane permeability to dissolved gases depends on water temperature and flow. Water flow is
140 controlled by an impeller/submersible pump serving the membrane (Q: 4L/min). Calibrations and
141 measurements are performed in a mobile laboratory conditioned at a controlled temperature close to the
142 temperature of the monitored water. However, when natural waters (in a river or in a borehole) show
143 temperature variations while monitoring, the signals measured with the CF-MIMS must be corrected from
144 temperature effects on the membrane permeability.

145 **Temperature sensitivity**

146 Laboratory experiments have been carried out to determine the influence of the water temperature on the
147 permeability of the membrane X44[®]. The results (see Supporting Information) show that the membrane
148 permeability to gases increases substantially with temperature. Small temperature variations ($\Delta T \pm 2^\circ\text{C}$)
149 can modify the signal acquired at 17°C from 2.5% to 11.0% depending on the gas considered (He is less
150 sensitive than H_2O to temperature variations). However, the fitted curves allow the calculation of effective
151 permeability coefficients β_T^i of the gas i at the temperature T of measurement expressed in equation (1) as
152 the ratio of the partial pressure of the gas i at the temperature T on the partial pressure of the same gas i at
153 the temperature of calibration (T_{calib}).

$$154 \quad \beta_T^i = \frac{P_T^i}{P_{T_{\text{calib}}}^i} \quad (1)$$

155 The effective permeability coefficients are used when post-processing the data to correct temperature
156 effects on the membrane permeability for the different gases measured with the CF-MIMS.

157 **Spectral Overlaps**

158 In MIMS systems, the simplest case consists in measuring dissolved gases directly at their corresponding
159 m/z . For instance, the partial pressures of He, Ar, Kr, Xe and O_2 can be respectively associated to the m/z

160 at 4, 40, 84, 132 and 32. However, in mass spectrometry, spectral overlaps are issues frequently
161 encountered.

162 The objective of the CF-MIMS is to measure the full suite of noble gases (He, Ne, Ar, Kr, Xe) as well as
163 the most common dissolved gases (N_2 , O_2 , CO_2 , CH_4 and N_2O). These dissolved species coexist in natural
164 waters and unfortunately some of them occur at m/z ratio overlapping with other gases as shown in table
165 1. Most of the time, the overlapping gases are also among the targeted ones which inhibits the use of traps
166 and getters⁴⁶ to remove the overlapping N_2 , CO_2 , CH_4 , N_2O and Ar.

167 **Table 1: Spectral overlaps occurring at measured mass-to-charge ratios.**

| m/z | Targeted gas | Main overlap | Second overlap |
|-----|----------------------------------|----------------------|----------------------|
| 12 | CO_2 | CH_4 | - |
| 14 | N_2 | N_2O | - |
| 15 | CH_4 | N_2 | - |
| 20 | Ne | Ar | H_2O |
| 22 | Ne | CO_2 | N_2O |
| 28 | N_2 | N_2O | CO_2 |
| 44 | $\text{CO}_2/\text{N}_2\text{O}$ | - | - |

168
169 Without traps and getters, the other way to remove overlapping species at a particular m/z ratio is to
170 optimise ionisation energies. For instance, laboratory tests have been carried out to distinguish Ne signals
171 from $^{20}(\text{Ar}_{(\text{II})})$ and $^{20}(\text{H}_2\text{O})$ or from $^{22}(\text{CO}_{2(\text{II})})$ and $^{22}(\text{N}_2\text{O}_{(\text{II})})$ using lower ionisation energies to avoid the
172 second ionisation of overlapping gases at m/z 20 and 22 respectively. Although ^{20}Ne and $^{20}(\text{Ar}_{(\text{II})})$ could be
173 separated from $^{20}(\text{H}_2\text{O})$, the attempts to fully discriminate (with ionisation energies) Ne signals from
174 $^{20}(\text{Ar}_{(\text{II})})$, $^{22}(\text{CO}_{2(\text{II})})$ or $^{22}(\text{N}_2\text{O}_{(\text{II})})$ were unsuccessful despite the information reported in other works on
175 similar QMS systems^{47,48}.

176 Therefore, we choose to overcome the issue of spectral overlaps by calibrating the CF-MIMS with a
177 variety of suitable standard gases allowing the quantification of these overlaps. The idea here is to
178 quantify the distribution of a given gas on the different m/z ratios of interest. For instance, CO_2 is found at

179 m/z 12, 22, 28 and 44 (table 1) and its distribution over each of these m/z ratios can be measured and
 180 expressed as polynomials (see Supporting Information). This is performed by monitoring the partial
 181 pressures at these m/z ratios when saturating a volume of water in the calibration chamber with pure CO₂
 182 and desaturating it with another pure gas (N₂, Ar, He, etc.). The same rationale applies for N₂ at m/z 14,
 183 15, 28 and for Ar at m/z 20 and 40. The polynomials linking the partial pressures P_k^i and P_l^i of the gas i
 184 measured respectively at m/z k and l are expressed in equation 2:

$$185 \quad P_k^i = f(P_l^i) = \sum_{n=0}^N \alpha_n (P_l^i)^n \quad (2)$$

186 Once fitted to the data, the resulting polynomials allow the determination of relationships between each
 187 m/z ratios due to each gas (CO₂, N₂ and Ar) over a large concentration range. As a result, any significant
 188 partial pressure change away from the fitted polynomials indicates an overlap attributable either to Ne,
 189 N₂O or CH₄ depending on the considered m/z. In this case, the partial pressure (P_k^j) attributed to the
 190 overlapping gas j can be calculated as the difference between the total partial pressure (P_k) measured at
 191 m/z k and the partial pressure (P_k^i) of the gas i at m/z k as expressed in equation 3:

$$192 \quad P_k^j = P_k - P_k^i = P_k - \sum_{n=0}^N \alpha_n (P_l^i)^n \quad (3)$$

193 This method relies on multiple measurements at different m/z ratios of the same targeted gas to guarantee
 194 a better precision (the gas is measured twice or thrice) and a better confidence respect to overlaps (the
 195 different m/z ratios of a gas usually do not undergo the same overlap).

196 After calibration and measurement, the data files provided by the CF-MIMS are post-processed using a
 197 data processing program implemented in Matlab[®] that calculates the partial pressure $P_{m/z}^i$ of the gas i at
 198 m/z using the spectral overlap polynomials and the effective permeability coefficients β_T following
 199 equation 4:

$$200 \quad P_{m/z}^i = \beta_T^i * \left[P_{m/z} - \sum_j \left(\beta_T^j * \sum_{n=0}^N \alpha_n (P_{m/z}^j)^n \right) \right] \quad (4)$$

201 Dissolved gases undergoing overlaps are hence calculated as the difference between the measured partial
 202 pressure at a given m/z and the sum of partial pressures produced by the overlapping species j weighted by
 203 their effective permeability coefficients (β_T^j). Therefore, it is essential to properly assess the different
 204 overlap polynomials.

205 Finally, the data processing program calculates and compiles the partial pressures of each gas free from
 206 overlaps, determines internal or external calibration coefficients for each gas and provides the dissolved
 207 gas concentrations that are delivered as a spreadsheet.

208 Analytical performances

209 For each dissolved gas, laboratory experiments have been carried out to evaluate the analytical precisions
 210 of the CF-MIMS (expressed as the relative standard deviation, RSD) and the detection limits (DL) for
 211 reactive (N_2 , O_2 , CO_2 , CH_4 , N_2O) and noble (He, Ne, Ar, Kr, Xe) gases. Table 2 shows the details of the
 212 analytical performances of the CF-MIMS measured from three series of monitoring (2 hours) of an AEW
 213 kept at a constant temperature ($17^\circ C$). The analytical frequency of the instrument allows the measurement
 214 of a m/z ratio every two seconds (the measurement of gas can require more than one m/z measurement).
 215 Therefore, a measurement cycle of the 10 gases listed in the table 2 takes about 26 seconds.

216 **Table 2: Experimental assessment of the CF-MIMS gas measurement precisions (RSD) and estimated detection limits**
 217 **(DL). Asterisks refer to DL estimations performed on the basis of $3 \times RSD$ of the most abundant gas at the measured m/z**
 218 **for typical concentrations obtained with an AEW ($CO_2 = 4.3 \times 10^{-4}$ ccSTP/g; $N_2 = 1.4 \times 10^{-2}$ ccSTP/g).**

| Gas | RSD (%) | DL ($\times 10^{-9}$ ccSTP/g) |
|--------|---------|--------------------------------|
| N_2 | 0.3 | 750 |
| O_2 | 0.3 | 2 |
| CO_2 | 0.3 | 2000 |
| CH_4 | 2.0 | 800* |
| N_2O | 0.3 | 900* |
| He | 1.0 | 0.01 |
| Ne | 2.5 | 6* |
| Ar | 0.3 | 200 |
| Kr | 1.2 | 0.5 |

| | | |
|----|-----|---|
| Xe | 7.5 | 4 |
|----|-----|---|

219 As Ne, CH₄ and N₂O are measured at overlapped m/z ratios, their detection limits depend also on the
220 analytical uncertainty of the main overlapping gas at these m/z ratios (respectively ²²(CO₂), ¹⁵(N₂) and
221 ⁴⁴(CO₂)). Table 2 displays an example of the detection limits calculated for Ne, CH₄ and N₂O for an air
222 equilibrated water ([CO₂]_{atm}=0.04% and [N₂]_{atm}=78.08%) expressed as three RSD of the main overlapping
223 gas. As a result, higher levels of N₂ or CO₂ would increase proportionally the detection limits of Ne, CH₄
224 and N₂O.

225 **Field Applications**

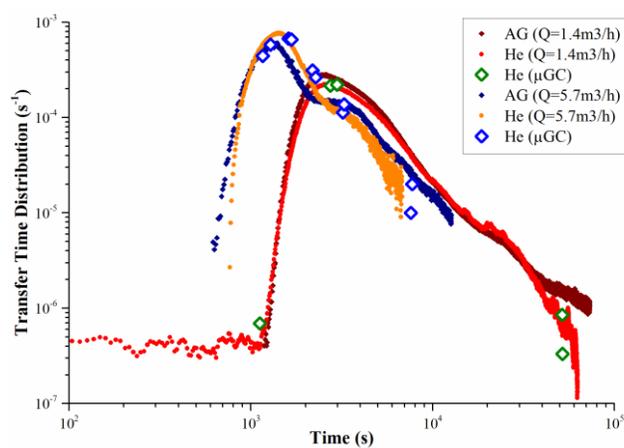
226 **Groundwater tracer test with dissolved ⁴He**

227 In hydrogeology, groundwater introduced tracer tests are usually performed with salts or fluorescent dyes
228 in order to derive the transport properties of aquifers ⁴⁹⁻⁵¹. Although little used so far in tracer tests,
229 dissolved noble gases are inert tracers of the physical processes governing conservative transport in
230 aquifers such as advection, dispersion and diffusion ⁵²⁻⁵⁵. Where classical tracers may possibly entail flaws
231 such as toxicity, sorption, degradation or density effects ⁵⁶⁻⁵⁸, dissolved noble gases can represent a
232 valuable alternative especially when implementing tracer tests in drinking water supply areas ⁵⁹. As a
233 result, we decided to evaluate the potential of the CF-MIMS to perform continuous and field
234 measurements through a groundwater tracer test using dissolved ⁴He.

235 The groundwater tracer test was carried out in a fractured aquifer located at the experimental site of
236 Ploemeur (H+ observatory network, Brittany, France) at the contact zone between a granitic formation and
237 the overlying micaschist ⁶⁰. This vertical tracer test was performed in a single well (B3) and consisted in
238 the combined pulse injection of dissolved ⁴He (60 L of He saturated water) and a fluorescent dye called
239 amino-G acid (7-Amino-1,3-naphthalenedisulfonic acid) in a fracture crossing the borehole at 44.9m
240 (B3.2) while pumping in an hydraulically connected fractured zone (B3.1) found in the same well at

241 34.0m. Tracer path was constrained into the fracture network using low flow injections (6 L/min) below a
242 single packer placed in the borehole between the two connected fractures.

243 Figure 2 shows the ^4He and amino-G acid (AG) breakthrough curves produced respectively by the CF-
244 MIMS and the fluorimeter over two tracer tests performed with two pumping rates (1.4 and 5.9 m^3/h). For
245 these short tracer tests, ^4He and AG show similar breakthrough curves (although ^4He systematically peaks
246 late) as well as similar fitted transport parameters (see Supporting Information) using a semi analytical
247 solution developed by Becker and Charbeneau ⁴⁹. For longer tracer tests, the differences between the two
248 breakthrough curves are expected to increase with time due to a higher He diffusion.



249
250 **Figure 2:** ^4He and AG acid breakthrough curves obtained with two different pumping conditions (1.4 and 5.9 m^3/h). The
251 transfer time distribution curves (s^{-1}) refer to the tracer mass flux (g/s) divided by the recovered mass of tracer (g).

252 This groundwater tracer tests show that the CF-MIMS is able to measure dissolved gas concentrations *in*
253 *situ* over experiments of several hours and to record ~~instantaneously~~ large concentration gradients with
254 high temporal resolution. The CF-MIMS measurements are directly validated by control sampling
255 performed during the two tracer tests and indirectly by AG breakthrough curves produced by the
256 fluorimeter.

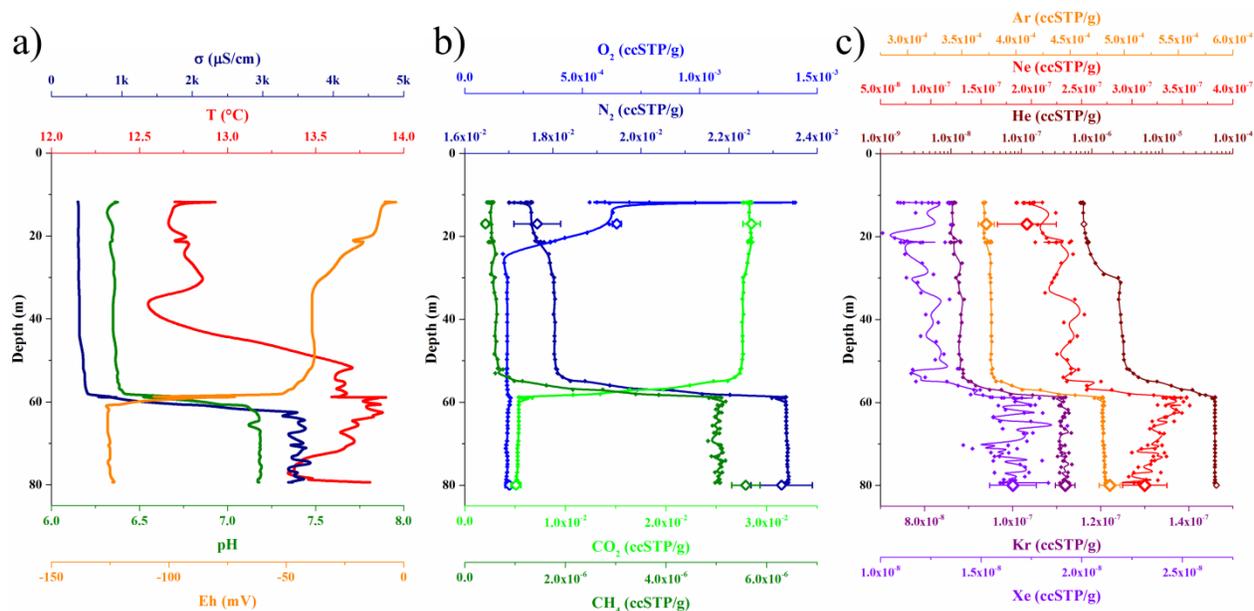
257 **Well-logging of dissolved gases**

258 Classically, a first order characterisation of groundwater geochemistry is achieved using a multi-parameter
259 probe allowing the vertical measurement of the field parameters in wells (temperature, electrical
260 conductivity, pH, redox potential and dissolved oxygen). More detailed investigations require additional
261 measurements that are usually performed through the sampling of targeted dissolved species (gases, ions,
262 stable isotopes, etc.). The results of such geochemical characterisation are hardly available on the field and
263 rely inherently on substantial uncertainties associated to sampling (representativeness, contamination and
264 preservation of the sample). Besides, due to practical constraints the exhaustiveness (number of measured
265 parameters, spatial and temporal distribution) of classical geochemical characterisation is often limited in
266 view of the variety and variability of biogeochemical processes in time and space.

267 In order to test the method developed here, we have investigated the potential of performing a well-log of
268 dissolved gases with the CF-MIMS in a borehole (Pz6) drilled in a schist bedrock and located nearby our
269 laboratory in Rennes (H⁺ observatory, Brittany, France). The transportation and power supply of the CF-
270 MIMS has been made possible thanks to the mobile laboratory arranged in an all-terrain truck (CRITEX
271 Lab). This simple experiment consisted in coupling a multi-parameter probe (OTT[®] Hydrolab) to the well-
272 pump (Grundfos[®] MP1) serving the CF-MIMS in order to measure the evolution with depth of dissolved
273 gases concentrations (He, Ne, Ar, Kr, Xe, N₂, O₂, CO₂, CH₄), temperature (T), pH, electrical conductivity
274 (σ) and redox potential (Eh). The pumping rate (3 L/min) and the logging velocity (2.5 m/min) have been
275 adjusted to the borehole diameter, the number of measured dissolved gases and hence to the measurement
276 frequency of the CF-MIMS (12 m/z every 24 s for 1 measure every meter).

277 The figure 3 shows the profiles that were obtained at Pz6 for the field parameters (figure 3a), the reactive
278 dissolved gases (figure 3b) and the dissolved noble gases (figure 3c). This well-log consists in two
279 contrasted groundwater bodies and two transition zones: (80-60m) high pH and conductivity, high reactive
280 and noble gas concentrations except CO₂ and low Eh and O₂; (60-55m) a mixing zone where almost all the
281 parameters change; (55-30m) lower pH, conductivity and dissolved gas concentrations except CO₂ that

282 increases, low O₂ and higher Eh. The shallowest part of the well (30-12m) shows a transition towards an
 283 atmospheric dissolved gas composition.



284
 285 **Figure 3: Well-logs performed at Pz6 for (a) water temperature (T), electrical conductivity (σ), pH and redox potential**
 286 **(Eh); (b) reactive dissolved gases (N₂, O₂, CO₂, CH₄); (c) dissolved noble gases (He, Ne, Ar, Kr, Xe). The large dots in b)**
 287 **and c) refer to samples collected at 17m and 80m. Continuous lines refer to a spline fit of the data points shown as small**
 288 **dots in the figure.**

289 During the well-logging experiment discrete samples were collected and analysed using accepted
 290 analytical protocols^{46,61,62}. A comparison of these analyses with the CF-MIMS measurements is shown in
 291 table 3. Both measurements agree for all dissolved gases analysed within the error of the respective
 292 methods.

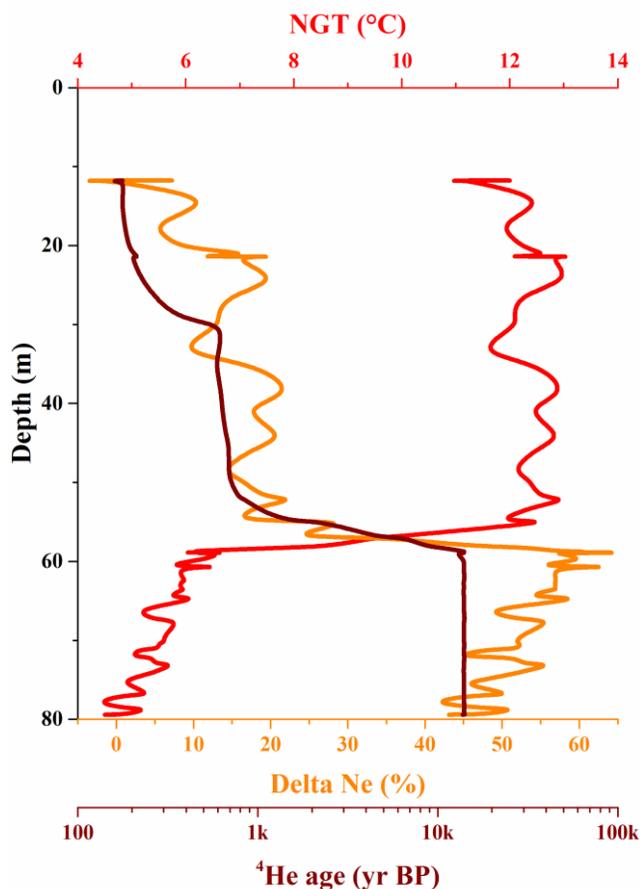
293 **Table 3: Comparison of CF-MIMS measurements with measurements of dissolved gases in Pz6 conducted either (*) at the**
 294 **University of Rennes by gas-chromatography^{61,62} or (#) *in situ* by mass-spectrometry with a NG-MIMS⁴⁶.**

| Depth (m) | Gas ^{*#} | Sample (ccSTP/g) | Sample RSD (%) | CF-MIMS (ccSTP/g) | CF-MIMS RSD (%) | Relative difference (%) |
|-----------|------------------------------|-----------------------|----------------|-----------------------|-----------------|-------------------------|
| 17 | N ₂ [*] | 1.76×10 ⁻² | 3.0 | 1.75×10 ⁻² | 0.3 | 0.5 |
| | O ₂ [*] | 6.48×10 ⁻⁴ | 3.0 | 6.21×10 ⁻⁴ | 1.3 | 3.0 |
| | CO ₂ [*] | 2.85×10 ⁻² | 3.0 | 2.84×10 ⁻² | 0.3 | 0.5 |

| | | | | | | |
|-----------|------------------------|-----------------------|------|-----------------------|-----|------|
| | CH₄* | 4.11×10^{-7} | 15.0 | 5.29×10^{-7} | 3.0 | 17.5 |
| | He* | 7.75×10^{-7} | 3.0 | 1.19×10^{-6} | 3.5 | 1.0 |
| | Ne* | 1.96×10^{-7} | 10.0 | 2.11×10^{-7} | 5.0 | 5.5 |
| | Ar* | 3.73×10^{-4} | 2.5 | 3.71×10^{-4} | 0.1 | 0.5 |
| 80 | N₂* | 2.32×10^{-2} | 3.0 | 2.33×10^{-2} | 0.1 | 0.5 |
| | O₂* | 1.90×10^{-4} | 10.0 | 1.77×10^{-4} | 0.6 | 5.0 |
| | CO₂* | 5.09×10^{-3} | 10.0 | 5.24×10^{-3} | 2.1 | 2.0 |
| | CH₄* | 5.59×10^{-6} | 5.0 | 5.05×10^{-6} | 0.7 | 7.0 |
| | He[#] | 5.88×10^{-5} | 2.0 | 5.82×10^{-5} | 1.3 | 3.0 |
| | Ne[#] | 3.13×10^{-7} | 6.5 | 3.04×10^{-7} | 4.8 | 2.0 |
| | Ar[#] | 4.87×10^{-4} | 2.0 | 4.83×10^{-4} | 0.1 | 0.5 |
| | Kr[#] | 1.12×10^{-7} | 2.0 | 1.12×10^{-7} | 0.7 | 0.5 |
| | Xe[#] | 1.66×10^{-8} | 6.5 | 1.66×10^{-8} | 5.2 | 0.5 |

295

296 The field measurement of dissolved noble gas concentrations allow to derive profiles of groundwater
 297 recharge conditions ⁶³ and the amount of non-atmospheric ⁴He produced by radiogenic U and Th of the
 298 rocks. With no mantle He and using a production rate of 4×10^{-9} ccSTP/g/yr for ⁴He calibrated on ¹⁴C ages
 299 ⁶⁴, the groundwater residence time can be assessed for regional groundwater circulations using ⁴He dating
 300 ¹⁷. Figure 4 shows the field determination of the distribution with depth of noble gas temperatures (NGTs
 301 i.e. recharge temperatures), amounts of excess air (commonly expressed as the $\Delta Ne = ((CNe_{meas}/CNe_{eq}) -$
 302 $1) \times 100$) and ⁴He ages.



303

304 **Figure 4: Profile of noble gas temperature (NGT), Δ Ne and 4 He age distribution with depth.**

305 Similarly to the previous profiles, the figure 4 shows three groundwater layers: (80-60m) low NGTs (\approx
 306 5°C) associated with large Δ Ne ($\approx 50\%$) and 4 He ages ($\approx 14,000$ yr BP); (60-55m) mixing zone; (55-12m)
 307 NGTs around 11°C associated with smaller Δ Ne ($\approx 10\%$) and 4 He ages (≈ 500 yr BP). The shallowest part
 308 of this layer (30-12m) shows decreasing Δ Ne (0% in average) and 4 He ages (≈ 200 yr BP) towards the
 309 water table.

310 This field experiment illustrates the usefulness of field measurements of dissolved gases for the
 311 characterisation of groundwater chemistry and the determination of groundwater origins. The field
 312 continuous measurements performed with the CF-MIMS make available a quantity of valuable distributed
 313 information so far inaccessible during field works.

314 **Discussion**

315 **Calibration**

316 Precise dissolved gas measurements with a CF-MIMS can only be achieved with a proper calibration
317 procedure which is not so trivially accomplished because it is performed on SGEWs (a precise
318 determination of their composition is essential) with a water flow and temperature dependent membrane
319 permeability (a precise determination of these effects is also necessary). In addition, calibration of Ne,
320 CH₄ and N₂O require a special care (use of additional SGEWs) in order to overcome spectral overlap
321 issues.

322 When the calibration procedure is properly achieved and as long as the membrane inlet remains connected
323 to the mass spectrometer, the CF-MIMS allow a continuous monitoring of dissolved gases over relatively
324 long experiments (days or weeks) without additional calibration (standard bracketing). The latter would
325 alter the benefits of the continuous measurements since the CF-MIMS measurements require as much
326 stability as possible. For long monitoring experiments we thus recommend a regular sampling to ensure
327 the validity of the calibration. So far, biogeochemical clogging of the membrane has not been observed
328 which might be explained by the nature of the membrane X44[®].

329 **Capabilities of the CF-MIMS**

330 First, the dissolved gas tracer tests demonstrate the ability of the CF-MIMS to perform field dissolved gas
331 measurements accurate enough to produce appropriate breakthrough curves during groundwater tracer
332 tests. This experiment exhibits the instrument capabilities for high-frequency measurements and its
333 rapidity to quantify large concentration gradients. The CF-MIMS offer new perspectives for groundwater
334 tracer tests enabling the use of new tracers (noble and reactive gases) and allowing a combined injection
335 of several tracers of different nature (salts, fluorescent tracers, dissolved gases, etc.).

336 As for tracer tests, the well-logging experiment demonstrates the ability of the CF-MIMS to work at high-
337 frequency *in situ* and provide accurate environmental measurements allowing in this case the
338 determination of groundwater recharge conditions, groundwater residence time and redox conditions
339 profiles. These field continuous measurements do not only solve the problems associated to sampling
340 (representativeness, contamination or preservation of samples) but also, taken as a whole, improve the
341 quality of the information carried by each value of the dataset (enhanced representativeness with
342 distributed measurements and enhanced precision with several replicates). Therefore, the CF-MIMS gives
343 access to spatially and temporally distributed data of great significance that represents an important
344 breakthrough for environmental measurements.

345 In addition, the CF-MIMS ability to produce field continuous measurements allows the scientist to
346 visualise and interpret the data directly on site allowing a better definition of field experiment strategies
347 and a higher flexibility when implementing them. Finally, the rationale behind the CF-MIMS technology
348 consists in bringing back environmental scientists on the field to get a much more thorough understanding
349 of the site structure and properties all along the experiments.

350 **Potential Applications**

351 Once installed in the mobile laboratory, the CF-MIMS has the required mobility to perform *in situ*
352 measurements in a large diversity of accessible areas (boreholes, rivers, vadose zone, sea or lake shores,
353 wetlands). In these sites, the high-frequency and multi-tracer measurements offered by this instrument
354 allow the observation of a variety of stable to highly-transitory physical, chemical or biological
355 phenomena modifying dissolved gases concentrations (water flow, mixing, degassing, biochemical
356 consumption/production of one or more gas(es)). Therefore, the CF-MIMS is a valuable tool for the field
357 characterisation of biogeochemical reactivity in aquatic systems, aquifer and river transport properties,
358 groundwater recharge conditions, groundwater residence time (^4He , ^{40}Ar) and aquifer-river exchanges.

359 **Associated Contents**

360 **Supporting Information**

361 Measurement settings, Instrumental drift, Temperature Sensitivity, Calibration standard gases, Overlap
362 extents, Tracer test details, Part List. This material is available free of charge via the Internet at
363 <http://pubs.acs.org>.

364 **Acknowledgements**

365 This work is part of the CRITEX project which aims at the study of the Critical Zone and funded the
366 mobile laboratory and the development of the CF-MIMS. The ANR projects CRITEX and Stock-en-Socle
367 also co-provided financial support to fund the PhD of Eliot Chatton. The authors would like to thank
368 Hiden Analytical especially Thomas Gaudy and Peter Hatton for the high quality of their customer
369 service. We are also grateful to Christophe Petton and Nicolas Lavenant for their technical help in the
370 conception and building of the calibration chamber. The authors would like to thank Ate Visser for
371 allowing us to use his data of the G-DAT 2012. We finally thank the two anonymous reviewers for their
372 careful revision of the manuscript.

373 **References**

- (1) Clever, H. L. Helium and Neon - Gas Solubilities. *Solubility data Ser.* **1979**, *1*, 393.
- (2) Clever, H. L. Krypton, Xenon and Radon - Gas-Solubilities. *Solubility data Ser.* **1979**, *2*, 357;
doi:10.1016/0378-3812(80)80030-6.
- (3) Clever, H. L. Argon. *Solubility data Ser.* **1980**, *4*, 331; doi:10.1016/0021-9614(80)90193-7.
- (4) Smith, S. P.; Kennedy, B. M. The solubility of noble gases in water and in NaCl brine. *Geochim. Cosmochim. Acta* **1983**; *41*(1), 503-515.

- (5) Weiss, R. F. The solubility of nitrogen, oxygen and argon in water and seawater. *Deep-Sea Res.* **1970**, *17*, 721-735.
- (6) Weiss, R. F. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar. Chem.* **1974**, *2*, 203-215.
- (7) Weiss, R. F.; Price, B. A. Nitrous oxide solubility in water and seawater. *Mar. Chem.* **1980**, *8*, 347-359; doi:10.1016/0304-4203(80)90024-9.
- (8) Wiesenburg, D. A.; Guinasso, N. L. Equilibrium solubilities of methane, carbon monoxide, and hydrogen in water and sea water. *J. Chem. Eng. Data* **1979**, *24*(4), 356-360; doi:10.1021/je60083a006.
- (9) Aeschbach-Hertig, W.; Peeters, F.; Beyerle, U.; Kipfer, R. Interpretation of dissolved atmospheric noble gases in natural waters. *Water Resour. Res.* **1999**, *35*(9), 2779-2792.
- (10) Aquilina, L.; Vergnaud-Ayraud, V.; Armandine Les Landes, A.; Pauwels, H.; Davy, P.; Petelet-Giraud, E.; Labasque, T.; Roques, C.; Chatton, E.; Bour, O.; Ben Maamar, S.; Dufresne, A.; Khaska, M.; Le Gal La Salle, C.; Barbecot, F. Impact of climate changes during the last 5 million years on groundwater in basement aquifers. *Sci. Rep.* **2015**, *5*, 14132; doi:10.1038/srep14132.
- (11) Stute, M.; Schlosser, P. Principles and applications of the noble gas paleothermometer. In *Geophysical Monograph Series*, **1993**, 78.
- (12) Chatton, E.; Aquilina, L.; Petelet-Giraud, E.; Cary, L.; Bertrand, G.; Labasque, T.; Hirata, R.; Martins, V.; Montenegro, S.; Vergnaud, V.; Aurouet, A.; Kloppmann, W.; Pauwels, H. Glacial recharge, salinization and anthropogenic contamination in the coastal aquifers of Recife (Brazil). *Sci. Total Environ.* **2016**, *569-570*, 1114-1125; doi:10.1016/j.scitotenv.2016.06.180.
- (13) Plummer, L. N.; Eggleston, J. R.; Andreasen, D. C.; Raffensperger, J. P.; Hunt, A. G.; Casile, G. C. Old groundwater in parts of the upper Patapsco aquifer, Atlantic Coastal Plain, Maryland, USA:

- evidence from radiocarbon, chlorine-36 and helium-4. *Hydrogeol. J.* **2012**, *20*(7), 1269-1294; doi:10.1007/s10040-012-0871-1.
- (14) Andrews, J. N.; Davis, S. N.; Fabryka-Martin, J.; Fontes, J. C.; Lehman, B. E.; Loosli, H. H.; Michelot, J. L.; Moser, H.; Smith, B.; Wolf, M. The in situ production of radioisotopes in rock matrices with particular reference to the Stripa granite. *Geochim. Cosmochim. Acta* **1989**, *53*, 1803-1815.
- (15) Méjean, P.; Pinti, D. L.; Larocque, M.; Ghaleb, B.; Meyzonnat, G.; Gagné, S. Processes controlling ²³⁴U and ²³⁸U isotope fractionation and helium in the groundwater of the St. Lawrence Lowlands, Quebec: The potential role of natural rock fracturing. *Appl. Geochem.* **2016**, *66*, 198-209; doi:10.1016/j.apgeochem.2015.12.015.
- (16) Solomon, D. K.; Hunt, A. G.; Poreda, R. J. Source of radiogenic helium 4 in shallow aquifers: Implications for dating young groundwater. *Water Resour. Res.* **1996**, *32*(6), 1805-1813; doi:10.1029/96WR00600.
- (17) Wei, W.; Aeschbach-hertig, W.; Chen, Z. Identification of He sources and estimation of He ages in groundwater of the North China Plain. *Appl. Geochem.* **2015**, *63*, 182-189; doi:10.1016/j.apgeochem.2015.08.010.
- (18) Boisson, A.; De Anna, P.; Bour, O.; Le Borgne, T.; Labasque, T.; Aquilina, L. Reaction chain modeling of denitrification reactions during a push-pull test. *J. Contam. Hydrol.* **2013**, *148*, 1-11; doi:10.1016/j.jconhyd.2013.02.006.
- (19) Abbott, B. W.; Jones, J. B.; Godsey, S. E.; Larouche, J. R.; Bowden, W. B. Patterns and persistence of hydrologic carbon and nutrient export from collapsing upland permafrost. *Biogeosciences* **2015**, *12*(12), 3725-3740; doi:10.5194/bg-12-3725-2015.
- (20) Beaulieu, J. J.; Tank, J. L.; Hamilton, S. K.; Wollheim, W. M.; Hall, R. O.; Mulholland, P. J.;

- Peterson, B. J.; Ashkenas, L. R.; Cooper, L. W.; Dahm, C. N.; Dodds, W. K.; Grimm, N. B.; Johnson, S. L.; McDowell, W. H.; Poole, G. C.; Maurice Valett, H.; Arango, C. P.; Bernot, M. J.; Burgin, A. J.; Crenshaw, C. L.; Helton, A. M.; Johnson, L. T.; O'Brien, J. M.; Potter, J. D.; Sheibley, R. W.; Sobota, D. J.; Thomas, S. M. Nitrous oxide emission from denitrification in stream and river networks. *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*(1), 214-219; doi:10.1073/pnas.1011464108.
- (21) Gardner, J. R.; Fisher, T. R.; Jordan, T. E.; Knee, K. L. Balancing watershed nitrogen budgets: accounting for biogenic gases in streams. *Biogeochemistry*. **2016**, *127*(2-3), 231-253; doi:10.1007/s10533-015-0177-1.
- (22) Kling, G. W.; Kipphut, G. W.; Miller, M. C. Arctic Lakes and Streams as Gas Conduits to the Atmosphere: Implications for the Tundra Carbon Budgets. *Science* **1991**, *251*(4991), 298-301.
- (23) Mächler, L.; Brennwald, M. S.; Tyroller, L.; Livingstone, D. M.; Kipfer, R. Conquering the outdoors with on-site mass spectrometry. *Chimia* **2014**, *68*(3), 155-159; doi:10.2533/chimia.2014.155.
- (24) Peter, S.; Mächler, L.; Kipfer, R.; Wehrli, B.; Durisch-Kaiser, E. Flood-Controlled Excess-Air Formation Favors Aerobic Respiration and Limits Denitrification Activity in Riparian Groundwater. *Front. Environ. Sci.* **2015**, *3*, 75; doi:10.3389/fenvs.2015.00075.
- (25) Riley, A. J.; Dodds, W. K. Whole-stream metabolism: strategies for measuring and modeling diel trends of dissolved oxygen. *Freshw. Sci.* **2013**, *32*(1), 56-69; doi:10.1899/12-058.1.
- (26) Reilly, T. E.; LeBlanc, D. R. Experimental Evaluation of Factors Affecting Temporal Variability of Water Samples Obtained from Long-Screened Wells. *Ground Water* **1998**, *36*(4), 566-576.
- (27) Cowie, G.; Lloyd, D. Membrane inlet ion trap mass spectrometry for the direct measurement of dissolved gases in ecological samples. *J. Microbiol. Methods* **1999**, *35*(1), 1-12;

doi:10.1016/S0167-7012(98)00090-6.

- (28) Kotiaho, T. On-site environmental and in situ process analysis by mass spectrometry. *J. Mass Spectrom.* **1996**, *31*(1), 1-15.
- (29) Lloyd, D.; Scott, R. I. Direct measurement of dissolved gases in microbiological systems using membrane inlet mass spectrometry. *J. Microbiol. Methods* **1983**, *1*(6), 313-328; doi:10.1016/0167-7012(83)90008-8.
- (30) Takahata, N.; Igarashi, G.; Sano, Y. Continuous monitoring of dissolved gas concentrations in groundwater using quadrupole mass spectrometer. *Appl. Geochem.* **1997**, *12*(4), 377-382.
- (31) Virkki, V. T.; Ketola, R. A.; Ojala, M.; Kotiaho, T.; Komppa, V.; Grove, A.; Facchetti, S. On-Site Environmental Analysis by Membrane Inlet Mass Spectrometry. *Anal. Chem.* **1995**, *67*(8), 1421-1425; doi:10.1021/ac00104a019.
- (32) White, A. J.; Blamire, M. G.; Corlett, C. A.; Griffiths, B. W.; Martin, D. M.; Spencer, S. B.; Mullock, S. J. Development of a portable time-of-flight membrane inlet mass spectrometer for environmental analysis. *Rev. Sci. Instrum.* **1998**, *69*, 565; doi:10.1063/1.1148695.
- (33) Hemond, H. F. A backpack-portable mass spectrometer for measurement of volatile compounds in the environment. *Rev. Sci. Instrum.* **1991**, *62*, 1420; doi:10.1063/1.1142461.
- (34) Lauritsen, F. R.; Bohatka, S.; Degn, H. A Membrane-inlet Tandem Mass Spectrometer for Continuous Monitoring of Volatile Organic Compounds. *Rapid Commun. Mass Spectrom.* **1990**, *4*(10), 401-403.
- (35) Ketola, R. A.; Kotiaho, T.; Cisper, M. E.; Allen, T. M. Environmental applications of membrane introduction mass spectrometry. *J. Mass Spectrom.* **2002**, *37*(5), 457-476; doi:10.1002/jms.327.
- (36) Kana, T. M.; Darkangelo, C.; Hunt, M. D.; Oldham, J. B.; Bennett, G. E.; Cornwell, J. C.

Membrane inlet mass spectrometer for rapid high-precision determination of N₂, O₂, and Ar in environmental water samples. *Anal. Chem.* **1994**, *66*(23), 4166-4170; doi:10.1021/ac00095a009.

- (37) An, S.; Gardner, W. S.; Kana, T. M. Simultaneous Measurement of Denitrification and Nitrogen Fixation Using Isotope Pairing with Membrane Inlet Mass Spectrometry Analysis. *Appl. Environ. Microbiol.* **2001**, *67*(3), 1171-1178; doi:10.1128/AEM.67.3.1171.
- (38) Bohatka, S.; Futo, I.; Gal, I.; Gal, J.; Langer, G.; Molnar, J.; Paal, A.; Pinter, G.; Simon, M.; Szadai, J.; Szekely, G. Quadrupole mass spectrometer system for fermentation monitoring. *Vacuum* **1993**, *44*(5-7), 669-671; doi:10.1016/0042-207X(93)90121-P.
- (39) Degn, H. Membrane inlet mass spectrometry in pure and applied microbiology. *J. Microbiol. Methods* **1992**, *15*(3), 185-197; doi:10.1016/0167-7012(92)90039-7.
- (40) Eschenbach, W.; Well, R. Online measurement of denitrification rates in aquifer samples by an approach coupling an automated sampling and calibration unit to a membrane inlet mass spectrometry system. *Rapid Commun. Mass Spectrom.* **2011**, *25*(14), 1993-2006; doi:10.1002/rcm.5066.
- (41) Bell, R. J.; Short, R. T.; Van Amerom, F. H. W.; Byrne, R. H. Calibration of an in situ membrane inlet mass spectrometer for measurements of dissolved gases and volatile organics in seawater. *Environ. Sci. Technol.* **2007**, *41*(23), 8123-8128; doi:10.1021/es070905d.
- (42) Gentz, T.; Schlüter, M. Underwater cryotrap-membrane inlet system (CT-MIS) for improved in situ analysis of gases. *Limnol. Oceanogr. Methods* **2012**, *10*, 317-328; doi:10.4319/lom.2012.10.317.
- (43) Short, R. T.; Fries, D. D.; Kerr, M. L.; Lembke, C. E.; Toler, S. K.; Wenner, P. G.; Byrne, R. H. Underwater mass spectrometers for in-situ chemical analysis of the hydrosphere. *J. Am. Soc. Mass Spectrom.* **2001**, *12*(1); 676-682.

- (44) Tortell, P. D. Dissolved gas measurements in oceanic waters made by membrane inlet mass spectrometry. *Limnol. Oceanogr. Methods* **2005**, *3*, 24-37; doi:10.4319/lom.2005.3.24.
- (45) Mächler, L.; Brennwald, M. S.; Kipfer, R. Membrane Inlet Mass Spectrometer for the Quasi-Continuous On-Site Analysis of Dissolved Gases in Groundwater. *Environ. Sci. Technol.* **2012**, *46*, 8288-8296; doi:10.1021/es3004409.
- (46) Visser, A.; Singleton, M. J.; Hillegonds, D. J.; Velsko, C. A.; Moran, J. E.; Esser, B. K. A membrane inlet mass spectrometry system for noble gases at natural abundances in gas and water samples. *Rapid Commun. Mass Spectrom.* **2013**, *27*, 2472-2482; doi:10.1002/rcm.6704.
- (47) Hamme, R. C.; Emerson, S. R. Measurement of dissolved neon by isotope dilution using a quadrupole mass spectrometer. *Mar Chem.* **2004**, *91*, 53-64. doi:10.1016/j.marchem.2004.05.001.
- (48) Manning, C. C.; Stanley, R. H. R.; Lott, D. E. Continuous Measurements of Dissolved Ne, Ar, Kr, and Xe Ratios with a Field-Deployable Gas Equilibration Mass Spectrometer. *Anal. Chem.* **2016**, *88*(6), 3040-3048; doi:10.1021/acs.analchem.5b03102.
- (49) Becker, M. W.; Charbeneau, R. J. First-passage-time transfer functions for groundwater tracer tests conducted in radially convergent flow. *J. Contam. Hydrol.* **2000**, *40*(4), 299-310; doi:10.1016/S0169-7722(99)00061-3.
- (50) Becker, M. W.; Shapiro, A. M. Tracer transport in fractured crystalline rock: Evidence of nondiffusive breakthrough tailing. *Water Resour. Res.* **2000**, *36*(7), 1677-1686; doi:10.1029/2000WR900080.
- (51) Kang, P.; Le Borgne, T.; Dentz, M.; Bour, O.; Juanes, R. Impact of velocity correlation and distribution on transport in fractured media: Field evidence and theoretical model. *Water Resour. Res.* **2015**, *51*(2), 940-959; doi:10.1002/2014WR015799.
- (52) Gupta, S. K.; Stephen Lau, L.; Moravcik, P. S. Ground-Water Tracing with Injected Helium.

Ground Water **1994**, 32(1), 96-102.

- (53) Gupta, S. K.; Moravcik, P. S.; Stephen Lau, L. Use of Injected Helium as a Hydrological Tracer. *Hydrol. Sci. J.* **1994**, 39(2), 109-119; doi:10.1080/02626669409492728.
- (54) Sanford, W. E.; Shropshire, R. G.; Solomon, D. K. Dissolved gas tracers in groundwater: Simplified injection, sampling, and analysis. *Water Resour. Res.* **1996**, 32(6), 1635-1642; doi:10.1029/96WR00599.
- (55) Visser, A.; Singleton, M. J.; Esser, B. K. Xenon Tracer Test at Woodland Aquifer Storage and Recovery Well. *Lawrence Livermore Natl. Lab. Rep.* **2014**.
- (56) Laidlaw, I. M. S.; Smart, P. L. An Evaluation of Some Fluorescent Dyes for Water Tracing. *Water Resour. Res.* **1977**, 13(1), 15-33.
- (57) Magal, E.; Weisbrod, N.; Yakirevich, A.; Yechieli, Y. The use of fluorescent dyes as tracers in highly saline groundwater. *J. Hydrol.* **2008**, 358, 124-133; doi:10.1016/j.jhydrol.2008.05.035.
- (58) Shakas, A.; Linde, N.; Baron, L.; Bochet, O.; Bour, O.; Le Borgne, T. Hydrogeophysical characterization of transport processes in fractured rock by combining push-pull and single-hole ground penetrating radar experiments. *Water Resour. Res.* **2016**, 52(2), 938-953; doi:10.1002/2014WR015716.
- (59) Uddin, M. K.; Dowd, J. F.; Wenner, D. B. Krypton Tracer Test to Characterize the Recharge of Highly Fractured Aquifer in Lawrenceville, Georgia. *Proc. Georg. Water Resour. Conf.* **1999**, 516-519.
- (60) Le Borgne, T.; Bour, O.; Riley, M. S.; Gouze, P.; Pezard, P. A.; Belghoul, A.; Lods, G.; Le Provost, R.; Greswell, R. B.; Ellis, P. A.; Isakov, E.; Last, B. J. Comparison of alternative methodologies for identifying and characterizing preferential flow paths in heterogeneous aquifers. *J. Hydrol.* **2007**, 345, 134-148; doi:10.1016/j.jhydrol.2007.07.007.

- (61) Labasque, T.; Aquilina, L.; Vergnaud, V.; Hochreutener, R.; Barbecot, F.; Casile, G. C. Inter-comparison exercises on dissolved gases for groundwater dating - (1) Goals of the exercise and site choice, validation of the sampling strategy. *Appl Geochemistry*. **2014**, *40*, 119-125; doi:10.1016/j.apgeochem.2013.11.007.
- (62) Sugisaki, R.; Taki, K. Simplified analyses of He, Ne, and Ar dissolved in natural waters. *Geochem J.* **1987**, *21*, 23-27.
- (63) Aeschbach-Hertig, W.; Peeters, F.; Beyerle, U.; Kipfer, R. Palaeotemperature reconstruction from noble gases in ground water taking into account equilibration with entrapped air. *Nature* **2000**, *405*(6790), 1040-1044.
- (64) Ayraud, V.; Aquilina, L.; Labasque, T.; Pauwels, H.; Molenat, J.; Pierson-Wickmann, A. C.; Durand, V.; Bour, O.; Tarits, C.; Le Corre, P.; Fourre, E.; Merot, P.; Davy, P. Compartmentalization of physical and chemical properties in hard-rock aquifers deduced from chemical and groundwater age analyses. *Appl. Geochem.* **2008**, *23*(9), 2686-2707; doi:10.1016/j.apgeochem.2008.06.001.