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A portable and autonomous mass spectrometric system for on-site environmental gas analysis

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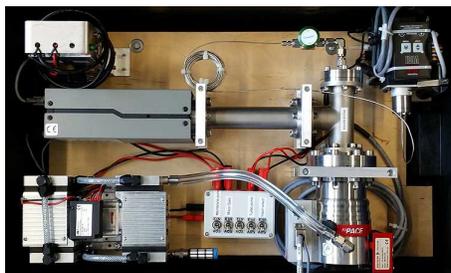
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TOC Art



Abstract

1
2 We developed a portable mass spectrometric system (“miniRuedi”) for quantification of
3 the partial pressures of He, Ne (in dry gas), Ar, Kr, N₂, O₂, CO₂ and CH₄ in gaseous and
4 aqueous matrices in environmental systems with an analytical uncertainty of 1–3%. The
5 miniRuedi does not require any purification or other preparation of the sampled gases and
6 therefore allows maintenance-free and autonomous operation. The apparatus is most suit-
7 able for on-site gas analysis during field work and at remote locations due to its small size
8 (60 cm × 40 cm × 14 cm), low weight (13 kg), and low power consumption (50 W). The gases
9 are continuously sampled and transferred through a capillary pressure reduction system into
10 a vacuum chamber, where they are analysed using a quadrupole mass spectrometer with a
11 time resolution of $\lesssim 1$ min. The low gas consumption rate (< 0.1 ml/min) minimises interfer-
12 ence with the natural mass balance of gases in environmental systems, and allows the unbi-
13 ased quantification of dissolved-gas concentrations in water by gas/water equilibration using
14 membrane contractors (gas-equilibrium membrane-inlet mass spectrometry, GE-MIMS). The
15 performance of the miniRuedi is demonstrated in laboratory and field tests, and its utility is
16 illustrated in field applications related to soil-gas formation, lake/atmosphere gas exchange,
17 and seafloor gas emanations.

18 Introduction

19 The abundances of gas species in environmental systems are controlled by numerous physical,
20 chemical and biological processes and conditions. Gases are therefore highly useful proxies to
21 study the dynamics of environmental processes and can be of great utility to study the interplay
22 of these processes. In particular, chemically inert gases (noble gases; He, Ne, Ar, Kr, Xe) were
23 successfully used to study and quantify physical transport and mixing of fluids as well as the
24 exchange between gas and water^{1–27} or biofluids.^{28,29} Such quantitative information on the physical
25 processes controlling the dynamics of gases in environmental systems is required to quantify and
26 interpret the turnover and the fate of biogeochemically active species (e.g., O₂, CO₂, CH₄, N_xO_x)
27 in terms of chemical and biological processes^{5,21,30–35}

28 The dynamics of gases and the associated processes in environmental systems are often not
29 accessible from “snapshot data” obtained from single samples reflecting the conditions of a system
30 at a unique point in time. In order to capture the complete evolution of the gas species of interest,
31 data series with sufficiently high temporal and spatial resolution are required. Careful optimisa-
32 tion of the sampling strategy in terms of sampling frequency and locations is therefore of utmost
33 importance, but is often very challenging due to the lack of prior knowledge of the gas dynamics
34 within a given system.

35 The currently applied methods for environmental gas analyses are usually targeted at a single
36 gas species or limited set of gases, and are often based on expensive and highly specialised instru-
37 ments and techniques for sampling and subsequent laboratory based quantification.^{36–42} Acquiring
38 data sets comprising a sufficiently complete suite of both inert and active gas species at the re-
39 quired spatial and temporal resolutions therefore poses numerous practical limitations related to
40 field-work logistics, access to specialised laboratories and data turnaround time that often prevent
41 acquisition of suitable data sets.

42 The way forward to overcome these technical and logistical limitations is to simultaneously
43 analyse a sufficiently complete suite of inert and biogeochemically active gas species at the re-
44 quired temporal and spatial resolution directly in the field. On-site and real-time availability of

45 such data avoids the limitations involved with sampling, transport and analysis and would thus
46 considerably improve the quality and utility of the recorded data during fieldwork. For this pur-
47 pose, membrane-inlet mass-spectrometric (MIMS) systems^{43,44} were developed with the aim to
48 reduce their complexity and size.^{42,45-48} However, these MIMS are targeted at limited sets of gas
49 species dissolved in water samples only, and are not suitable for unattended long-term operation
50 in the field, because their gas inlet system is designed for manual sample inlet or requires frequent
51 maintenance of gas-purifying devices. In addition, these instruments rely on a gas-permeable mem-
52 brane to separate the water sample at atmospheric pressure from the vacuum in the MS. The rates
53 by which the gas species diffuse from the bulk water across the membrane and into the vacuum
54 of the MS depend on temperature, water flow along the membrane surface, membrane ageing and
55 fouling, etc. It is notoriously difficult to achieve tight control over these operational parameters and
56 cumbersome to handle water standards with well-known dissolved gas concentrations during field-
57 work. Reliable and accurate calibration and application of such MIMS instruments is therefore
58 challenging.

59 The recently developed gas-equilibrium MIMS (GE-MIMS) method⁴⁹⁻⁵¹ avoids some of the
60 limitations of previous MIMS designs by establishing a solubility equilibrium between the sampled
61 water and a gas phase separated by a gas-permeable membrane. The advantage of the GE-MIMS
62 method is that the gas/water partitioning is hardly affected by the poorly constrained dynamics of
63 the gas-transfer across the membrane, because the partitioning operates at solubility equilibrium.
64 Reliable on-site calibration of such a gas/water equilibration system is therefore straight-forward,
65 and ambient air can be conveniently used as a standard gas for calibration of the partial pressures
66 of the noble gases, N₂, and O₂.

67 For GE-MIMS analysis, a small fraction of the equilibrated gas phase is continuously trans-
68 ferred through a pressure reducing system into the MS vacuum, where the gases are analysed.
69 Recent GE-MIMS instruments for analysis of O₂/Ar ratios⁵⁰ or Ne/Ar, Ne/Kr, and Ne/Xe ratios⁵¹
70 in seawater used very low gas transfer rates ($\lesssim 0.02 \text{ cm}^3_{\text{STP}}/\text{min}$, STP: standard temperature and
71 pressure, $T = 0^\circ\text{C}$, $P = 1013.25 \text{ mbar}$) to avoid deviation from the gas/water equilibrium in the

72 membrane contactor. In contrast, a modified atmospheric-pressure gas analyser targeted for GE-
73 MIMS analysis of absolute He, Ar, Kr, N₂, O₂, CO₂, and CH₄ concentrations (“Ruedi”)⁴⁹ operates
74 at a much higher gas removal rate from the membrane contactor (2 cm³_{STP}/min). However, this
75 gas depletion biases the partial pressures relative to the assumed gas/water equilibrium in the mem-
76 brane contactor. While both approaches have illustrated the great potential of continuous analysis
77 of selected gas species,^{30,32,34,35,52,53} the remaining analytical limitations of these instruments (lim-
78 ited sets of gas species, lack of absolute partial pressure analysis) and their bulkiness and high
79 power consumption (several hundred watts) prevented widespread use in diverse environmental
80 research applications in the field.

81 Here we present a simple, compact, and portable mass spectrometric system with low sample
82 gas consumption (“miniRuedi”). The miniRuedi expands considerably beyond the capabilities of
83 currently available instruments and methods for environmental gas analysis. The system allows
84 quasi-continuous and on-site analysis of the partial pressures of a wide range of environmental
85 gas species at environmental concentrations (He, Ne (in dry gas), Ar, Kr, N₂, O₂, CO₂ and CH₄)
86 and is most suitable for absolute analysis of dissolved gas concentrations in aqueous matrices
87 using the GE-MIMS method. The system does not rely on any gas purification or sample prepa-
88 ration units, which makes it robust and maintenance-free and thus enables autonomous long-term
89 operation in the field. The miniRuedi is built using off-the-shelf parts only. The instrument is
90 portable (60 cm × 40 cm × 14 cm, 13 kg) and consumes only 50 W electrical power, which al-
91 lows straight-forward deployment and operation at remote locations using batteries, solar panels
92 or other off-grid electricity sources. Most importantly, the instrument consumes very little sample
93 gas (0.06 cm³_{STP}/min), which is required for unbiased GE-MIMS measurements of absolute partial
94 pressures, and greatly reduces the interference of on-line gas analysis with the natural dynamics
95 and mass balance of the gases in an environmental system.

96 The utility of the miniRuedi for environmental research is demonstrated in three field-application
97 examples related to soil-gas formation, lake/atmosphere gas exchange, and seafloor gas emana-
98 tions.

99 **Experimental Section**

100 The setup of the miniRuedi system is illustrated in Figure 1. A parts list is given in Table 1.
101 The computer controlled valve (S) is used to select the gas inflow from different gas sources at
102 approximately atmospheric pressure. The capillary (C) controls the gas flow from the gas inlet
103 into the vacuum system. The continuous gas flow from the capillary into the quadrupole mass
104 spectrometer (QMS) is balanced by the turbomolecular pump (TP), which produces a high vacuum
105 in the QMS. The gas species in the QMS are ionised in the open, cylindrically symmetrical ion
106 source by electron impact ionisation (in this work, the ionisation energy was always set to 70 eV
107 unless noted otherwise). The resulting ion beam then passes a quadrupole mass filter set to a
108 specific m/z ratio (m : ion mass number, z : ion charge number), and the ion beam strength at
109 this m/z value is quantified using either a Faraday cup (F) or a secondary electron multiplier (M)
110 detector.

111 **Gas inlet system**

112 The sample gas pressure is reduced from approximately atmospheric pressure to the high vacuum
113 in the QMS using a 10 m long capillary with an inner diameter of 0.1 mm. The rugged 1/16”
114 stainless-steel capillary tubing prevents the leakage of He and other mobile gases through the
115 tubing walls. We empirically determined the gas flow through this capillary to $0.06 \text{ cm}^3_{\text{STP}}/\text{min}$.
116 This gas flow results in a total gas pressure of approximately 2×10^{-8} bar in the MS vacuum
117 chamber, which yields maximum overall sensitivity of the MS while not exceeding the linear
118 operation range of the MS. The observed travel time of the gas from the capillary inlet to the QMS
119 is approximately 80 s. An instantaneous step-like concentration change at the capillary inlet is
120 smeared out over approximately 10 s (50 % rise time) once it reaches the QMS, resulting in an
121 analytical time resolution of $\lesssim 1$ min.

122 Compared to MS systems with a typical two-stage pressure reduction using a capillary fol-
123 lowed by a pinhole/bypass system, the miniRuedi gas consumption is lower by several orders of

124 magnitudes. The system is therefore most suitable for applications where low gas consumption is
125 beneficial, such as the GE-MIMS technique. With a typical total gas concentration in air-saturated
126 water of approximately $25 \text{ cm}^3_{\text{STP}}/\text{L}$, a water flow rate of $\gtrsim 0.1 \text{ L}/\text{min}$ through the membrane con-
127 tactor would provide more than $100\times$ the gas amount consumed by the miniRuedi. This illustrates
128 how the miniRuedi allows unbiased GE-MIMS analysis at low water flow rates. Furthermore, pin-
129 hole/bypass stages or similar flow bifurcations may introduce uncontrollable fractionation of gas
130 species in vacuum systems. Such artefacts are avoided in the miniRuedi by the absence of such a
131 secondary pressure reduction stage.

132 **Data processing and calibration**

133 The peak heights in the m/z spectrum are recorded in a user-defined sequence of the relevant
134 m/z values using the F and M detectors, and repeated readings are averaged over a time interval
135 suitable for a given application. The means ($s_{m/z}$) of the peak heights recorded during each interval
136 at each m/z ratio are used as the raw measurement results of each measurement step. The $s_{m/z}$
137 values obtained from sample or standard-gas analyses are corrected for the instrument blank by
138 subtracting the $s_{m/z}$ values obtained with the inlet valve V closed.

139 The blank-corrected $s_{m/z}$ values are calibrated in terms of the partial pressures of the different
140 gas species in the sampled gas by peak height comparison relative to a reference gas with well
141 known partial pressures of the species of interest. The mixing ratios of the different gas species in
142 the gas are unaffected by the gas passage through the capillary, because the viscous flow regime
143 prevailing throughout most of the capillary prevents fractionation of the gas species. For a given
144 total gas pressure at the capillary inlet, the peak height at a given m/z value is therefore linearly
145 related to the partial pressure of the respective gas species in the sampled gas. Note, however, that
146 the capillary gas flow approaches the molecular flow regime at the outlet to the QMS vacuum. The
147 rate of the total gas flow through capillary is therefore not a perfectly linear function of the total gas
148 pressure at the capillary inlet.⁵⁴ We found this nonlinearity to be negligible for the quantification
149 of the partial pressures (bias $< 1\%$) if the pressure difference between the sample gas and the

150 reference gas at the capillary inlet is $\lesssim 50$ mbar. For larger pressure differences, accurate partial
151 pressures are obtained by normalising their sum to correspond to the true sample gas pressure at
152 the capillary inlet.

153 In many environmental applications, ambient air can be used as a well-defined and convenient
154 gas standard for noble gases, N_2 and O_2 . A dedicated standard-gas mixture is only required for
155 species with unknown or variable atmospheric partial pressures, or if the sampled partial pressures
156 are vastly different from those in air, for example in systems with high abundances of CO_2 , CH_4 or
157 (non-atmospheric) He.

158 In order to account for drifts in the instrument sensitivity resulting from changes in the flow
159 resistance of the gas inlet or the sensitivity of the mass spectrometer, the standard gas is analysed
160 periodically in between sample gas analyses. The $s_{m/z}$ values obtained in a given sample-gas
161 analysis step are then calibrated using the $s_{m/z}$ values of the standard-gas analysis steps interpolated
162 to the analysis time of the sample gas step. Finally, the standard error of the sample gas analyses
163 is estimated from the standard deviation of replicate analysis results obtained from standard gases.

164 Results and Discussion

165 Laboratory tests

166 To test the linearity of the $s_{m/z}$ values in response to variations in the partial pressures of the
167 gas species at the capillary inlet, we prepared a gas mixture with mixing ratios of approximately
168 7.0% He, 0.24% CH_4 , 16% O_2 , 72% N_2 , 1.8% Ar, and 3.1% CO_2 . This test gas was kept in a
169 gas sampling bag (Linde, Plastigas) and was incrementally diluted with 99.999% pure N_2 . The
170 dilution factor was determined by quantifying the CO_2 and CH_4 mixing ratios of the dilution using
171 a cavity ring-down spectroscopy analyser (Picarro G2201-i). Figure 2 shows the peak heights
172 obtained from analyses of each test gas dilution step, whereby the total pressure of the gas mixture
173 and its dilutions in the sample bag was always kept at ambient pressure (960 hPa). This dilution
174 test confirms that the F and M peak heights at a given m/z value are linear functions of the partial

175 pressure of the respective gas species at the capillary inlet.

176 To assess the drift of the F and M sensitivity over time, the instrument was set to continuously
177 analyse an air sample during 70 h in a laboratory with stable ambient temperature. Figure 3 shows
178 the Allan deviations⁵⁵ of the resulting F and M signals. The Allan deviations reflect the errors of
179 the means of the F and M signals as a function of the averaging time. Both the F and M Allan
180 deviations exhibit a minimum at an averaging time of approximately 1 h. For shorter averaging
181 times, the uncertainties of the F and M signal means are dominated by random noise, whereas
182 for longer averaging times the uncertainties of the means are dominated by instrument drift. To
183 minimise the effects of drift on the measurement results, peak-height readings should therefore
184 not be averaged for longer than 1 h, and drift calibrations should be run at least hourly. However,
185 changes in ambient temperature will affect the sensitivity of the instrument, mainly because the
186 flow resistance of the capillary decreases with increasing temperature. Averaging time and drift
187 calibration intervals therefore need to be adapted to changes in the ambient conditions. In addition,
188 the choice of the averaging time and the drift calibration intervals will also need to be adapted to
189 the time resolution of the measurement results required to assess the gas dynamics of the system
190 being studied.

191 The Allan deviation corresponds to the resolving power of the measurement and hence indi-
192 cates the analytical precisions and the limits of detection⁵⁵ that can be achieved with the F and M
193 detectors at any given m/z value. The minima of the relative Allan deviations for He (M, $m/z = 4$),
194 Ne (M, $m/z = 20$), N₂ (F, $m/z = 28$), O₂ (F, $m/z = 32$), Ar (M, $m/z = 36$; F, $m/z = 40$), and
195 Kr (M, $m/z = 84$) all correspond to 0.3–0.6% of the respective partial pressure in the atmosphere.
196 The typical limits of detection are therefore estimated to approximately 1% of the partial pressure
197 of the respective gases in the atmosphere.

198 The absence of any gas purification stage requires special attention to avoid matrix effects
199 related to ions of different gas species that contribute to the same signal at a given m/z ratio, e.g.,
200 due to multiple ionisation of gas species or isobaric gas molecules.⁵⁶ Multiple ionisation can be
201 reduced substantially by reducing the electron impact energy in the ioniser unit in the QMS.⁵⁷

202 In particular, the interferences occurring at $m/z = 16$ ($^{12}\text{CH}_4^+$ and $^{16}\text{O}_2^{2+}$ ions) and at $m/z = 20$
203 ($^{20}\text{Ne}^+$ and $^{40}\text{Ar}^{2+}$ ions) may be of special relevance for the targeted applications of the miniRuedi.
204 Figure 4-A shows the F peak heights obtained from analysis of pure Ar at $m/z = 40$ ($^{40}\text{Ar}^+$) and
205 $m/z = 20$ ($^{40}\text{Ar}^{2+}$) as a function of the electron energy. For electron energies below 50 eV, the
206 $^{40}\text{Ar}^{2+}/^{40}\text{Ar}^+$ ratio is less than $3 \cdot 10^{-5}$, which is approximately two orders of magnitude lower
207 than the $^{20}\text{Ne}/^{40}\text{Ar}$ ratio in air ($1.77 \cdot 10^{-3}$). Using electron energies of 50 eV or less will therefore
208 reduce the $^{40}\text{Ar}^{2+}$ interference to a level where it can easily be compensated or even neglected for
209 ^{20}Ne analysis in air-like gases (Figure 4-B). However, we observed that $^{20}(\text{H}_2\text{O})$ molecules may
210 contribute up to $\sim 50\%$ to the $m/z = 20$ signal in moist air-like gas matrices (such as in GE-MIMS
211 analyses). ^{20}Ne quantification is therefore recommended in dry gases only and requires careful
212 compensation of the residual $^{20}(\text{H}_2\text{O})$ contribution, which may be estimated from the the $m/z = 18$
213 signal and by assuming a typical $^{20}(\text{H}_2\text{O})/^{18}(\text{H}_2\text{O})$ ratio. Apart from these interferences, we did not
214 observe any significant interferences that would affect the gas analysis on the m/z values shown in
215 Figure 2. Nevertheless, it is important to note that such interferences may become relevant in gas
216 matrices that are very different from the air-like gas assessed in this work.

217 To test the miniRuedi performance as a GE-MIMS with miniature membrane contactors at low
218 water flow, we compared GE-MIMS measurements using miniature membrane contactors (Liqui-
219 Cel G591, 11 cm³ external volume) with measurements using the large membrane contactor as used
220 with our original GE-MIMS⁴⁹ (Liqui-Cel G542, 260 cm³ external volume). The miniature contac-
221 tors were operated either as a single unit or as a parallel combination of two units. Groundwater
222 was pumped through the membrane contactors, and tee branches were used to split the water flow
223 among the membrane contactors for parallel operation of the miniature and the large contactors.
224 The flow rates were 0.4 L/min through each miniature contactor and 2 L/min through the large
225 contactor. 10 measurements were made with each miniature contactor setup (single or two parallel
226 contactors). Each miniature-contactor measurement was bracketed with a measurement using the
227 large contactor. Figure 5 shows that using a single miniature contactor may result in a small bias
228 of the gas partial pressures relative to those observed in the large contactor. For the tested gas

229 species shown in Figure 5, the bias is largest for CO₂ (approximately 8%), but much smaller for
230 the remaining gases (He, Ar, Kr, N₂). However, using two miniature contactors removes the bias
231 for all gases. The low gas consumption of the miniRuedi therefore obviates the compensation for
232 gas depletion in the membrane contactor and allows absolute GE-MIMS measurements with much
233 smaller membrane contactors and water flows than the previous GE-MIMS instrument⁴⁹, which
234 requires a water flow of ≥ 2 L/min.

235 **Field test (accuracy and precision)**

236 To quantify the accuracy and precision of the miniRuedi with the GE-MIMS method, we carried
237 out a series of 42 GE-MIMS measurements (using a Liqui-Cel G542 contactor) of the ⁴He, N₂, ⁴⁰Ar
238 and ⁸⁴Kr concentrations in a small creek (Chriesbach, Switzerland). The concentrations of these
239 inert atmospheric gases in the creek are in equilibrium with their atmospheric partial pressure and
240 therefore serve as a well defined reference for comparison with the measured concentrations. In
241 addition, 29 air replicates were analysed to determine the precision of the miniRuedi measurements
242 without the GE-MIMS contactor. Air standards for drift calibration were carried out in between the
243 sample analyses. For each measurement, the peak heights at $mz = 4, 28, 40$ and 84 were integrated
244 for 10 min.

245 The residuals $r_i = (C_{m,i} - C_{e,i})/C_{e,i}$ of the measured concentrations in the water ($C_{m,i}, i =$
246 $1 \dots 42$) relative to the atmospheric equilibrium concentrations ($C_{e,i}$) were computed from the sol-
247 ubility of the respective gas at the water temperature that prevailed at the time of the corresponding
248 measurement (13.4 °C to 15.7 °C). The means of the r_i (μ in Table 2) indicate that the accuracy
249 of the miniRuedi analysis with the GE-MIMS method was 0.9 % or better for all gases. The stan-
250 dard deviations of the r_i (σ) indicate that the overall precision of the miniRuedi analysis with the
251 GE-MIMS method ranged from 1.2 % to 3.3 %. The standard deviations of the air replicates anal-
252 ysed without the GE-MIMS contactor (σ_{air}) are only marginally smaller. The loss of precision
253 associated with the addition the GE-MIMS contactor to the miniRuedi is therefore small.

254 **Application examples**

255 In the three application examples below, we demonstrate the utility of the miniRuedi for the anal-
256 ysis of the gas dynamics in different environmental systems and field settings. The examples were
257 chosen to cover both gaseous and aqueous matrices and to span a wide range of processes and rates
258 controlling the natural gas dynamics.

259 **Soil gas formation**

260 Figure 6 shows the concentrations of Ar, N₂, O₂, CO₂, and CH₄ determined with the miniRuedi
261 in the soil gas of a bioreactor landfill located in north-eastern Switzerland. The landfill is being
262 prepared for active aerobisation by technical means in order to foster aerobic decomposition of the
263 mostly organic wastes to CO₂ in favour of anaerobic decomposition to the more potent greenhouse
264 gas CH₄. To this end, the landfill has been sealed at the top. The ongoing production of landfill
265 gases therefore results in a steady gas outflow from the 5 observation wells, where the gases were
266 sampled in gas-tight 500 mL stainless-steel flasks. We connected the flasks to the miniRuedi gas
267 inlet to determine the concentrations of the various gas species in these samples. The concen-
268 trations of Ar, N₂, and O₂ were calibrated using ambient air, whereas gas mixtures of 10% CO₂
269 in N₂ and 10% CH₄ in N₂ were used for CO₂ and CH₄ calibration. As expected, the observed O₂
270 concentrations are low in all 5 observation wells (0.5–2 %). The concentrations of the remaining
271 gases indicate a binary mixture of landfill gas (CO₂, CH₄) and oxygen-depleted air (N₂, Ar). The
272 Ar concentration yields a direct quantification of the relative proportions of these two endmembers
273 and hence allows quantification of the air-derived O₂ that has been transformed within the landfill.
274 In addition, the N₂/Ar ratio is elevated in one well by approximately 30% relative to the atmo-
275 spheric ratio, which points to N₂ production by denitrification. Such combined analyses of inert
276 and active gas species are therefore highly beneficial to quantify the turnover of O₂ and other gases
277 and thus allows assessing the efficiency of landfill aerobisation.

278 Lake/atmosphere gas exchange

279 Figure 7 shows the partial pressures of Ar, N₂, O₂, CO₂, and CH₄ in a floating chamber deployed
280 on the water surface of Lake Soppensee (central Switzerland). Such floating chambers are used to
281 isolate a section of the water surface (0.126 m²) from the atmosphere in order to study CO₂ and CH₄
282 fluxes across the water surface using a CO₂ / CH₄ analyser.⁵⁸ The mass balance of the gas species
283 in the chamber is controlled by the gas exchange across the isolated section of the water surface.
284 We connected the gas inlet of the miniRuedi to the floating chamber and recorded the change in the
285 partial pressures in the headspace after deployment on the lake during 12 min. The volume of the
286 gas transferred into the miniRuedi gas inlet during this period corresponds to less than 0.05% of
287 the floating chamber volume (19.1 L). The effect of the gas consumption of the miniRuedi on the
288 mass balance of the gas species in the floating chamber is therefore negligible. After deployment
289 of the floating chamber, the CH₄ and CO₂ partial pressures showed a marked increase relative
290 to the atmospheric background, because the surface water of the hypertrophic lake was strongly
291 supersaturated with these gases. In contrast, the surface water was undersaturated in O₂ relative
292 to the atmospheric equilibrium (30% saturation) due to aerobic respiration and possibly also CH₄
293 oxidation, rapid cooling of the surface water, and mixing with O₂-depleted deep water. Despite
294 the large atmospheric O₂ background of the initial air trapped in the floating chamber, the decrease
295 of the O₂ partial pressure due to O₂ transfer to the water is small, but quantifiable. In contrast,
296 the Ar and N₂ concentrations in the water were closer to saturation (both at 75% saturation), and
297 no systematic changes in the Ar and N₂ partial pressures in the float chamber are observed. The
298 miniRuedi thus allows expanding the float chamber method for quantification of CO₂ and CH₄
299 fluxes to Ar, N₂, O₂, and possibly also other gas species. In particular, the gas consumed for
300 miniRuedi analysis does not interfere with the mass balance of the gas species in the floating
301 chamber. The miniRuedi might thus provide new insights into the rates and physical processes
302 controlling gas/water exchange, such as enhanced air/water exchange mediated by microbubbles
303 present in the water body.⁵⁸

304 **Seafloor gas emanation**

305 Figure 8 shows the concentrations of He, CO₂, and CH₄ observed in deep-water samples taken
306 in the Gulf of California (Mexico). These gases are associated with hydrothermal fluids released
307 from black smokers or other fluid vents at the seafloor.⁵⁹ At each sampling location, replicate deep-
308 water samples were collected in 10 L Niskin samplers. Immediately after retrieval of the Niskin
309 samplers, one replicate was screened for the dissolved-gas concentrations with the miniRuedi using
310 the GE-MIMS method. To allow GE-MIMS analysis with such a limited amount of water, two
311 parallel miniature membrane contactors (Liqui-Cel G591) were used with a total water flow of
312 0.5 L/min from the Niskin samplers. The small gas volume of the miniature membrane contactors
313 facilitates fast gas/water equilibration within approximately 3 min after starting the water flow.
314 Therefore, more than 15 min were left for GE-MIMS analysis of the water flowing from the Niskin
315 samplers. The dissolved-gas concentrations obtained from the GE-MIMS screening were used
316 to optimise the the selection of subsamples from the remaining Niskin samplers for after-cruise
317 laboratory-based analyses of ³He/⁴He and δ¹³C of the fluids emitted from the black smokers.⁵⁹ The
318 new possibility for rapid on-board GE-MIMS screening of relatively small sample volumes (10 L)
319 proved to be highly beneficial for identifying target samples for post-cruise analyses in specialised
320 labs. In addition, data turnaround time was reduced and the quality of the ³He/⁴He and δ¹³C data
321 set used for detailed characterisation of the hydrothermal fluids was optimised.

322 **Assessment**

323 Our laboratory tests and field applications demonstrate the performance and flexibility of the
324 miniRuedi for on-site gas analysis in a wide range of environmental systems and applications.
325 The miniRuedi provides real-time partial pressure measurements of He, Ne (in dry gas), Ar, Kr,
326 N₂, O₂, CO₂ and CH₄ both in gaseous and aqueous matrices. The low gas consumption opens
327 up new possibilities for unbiased GE-MIMS quantification of dissolved gas concentrations at low
328 water flow, gas analysis in flux chambers, and other systems with low gas throughput where sample
329 gas consumption must be minimised to avoid interference with the natural gas dynamics. In con-

330 trast to earlier systems aimed at environmental gas analysis, the miniRuedi is highly suitable for
331 on-site gas analysis in various environmental systems and at remote locations due to its portability,
332 low power requirements, and maintenance-free operation. The on-site data availability and the
333 high temporal resolution of time-series data are crucial benefits over conventional methods based
334 on expensive and often laborious laboratory analyses of single samples. The miniRuedi therefore
335 opens new opportunities for the combined analysis of inert (He, Ne, Ar, Kr, N₂) and reactive gases
336 (O₂, CO₂, CH₄, etc.), which provides the basis for quantitative studies of environmental processes
337 and their interplay in terms of physical, chemical, and biological mechanisms.

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Tables

Table 1: Parts list (see also Figure 1).

Part	Description
S	6-port inlet selector valve (VICI C5-2306EMHY)
C	10 m stainless steel tubing with 0.1 mm inner diameter (VICI TSS104)
V	Inlet valve (Swagelok SS-4H)
QMS	Quadrupole mass spectrometer with Faraday cup and secondary electron multiplier detectors (Stanford Research Systems RGA-200)
TP	Turbomolecular pump with 70 L/s pumping speed (Pfeiffer HiPace 80)
DP	Diaphragm pump for < 20 mbar forevacuum (KNF N 813.4 ANDC-B)
Power supply	24 VDC power supply (max. 5 A during turn on) for S, QMS, TP, and DP, for instance 2×12 V ‘car batteries’ or mains voltage converter (e.g., Mean Well SP-240-24)

Table 2: Field test results for accuracy and precision of the miniRuedi analysis and the GE-MIMS method (see text). Means (μ) and standard deviations (σ) of the residuals of the observed concentrations relative to the atmospheric equilibrium concentrations, and standard deviations of replicate air analysis results (σ_{air}).

Species	μ (%)	σ (%)	σ_{air} (%)
^4He	-0.5	2.5	1.9
N_2	-0.3	1.2	0.9
^{40}Ar	0.8	2.3	1.1
^{84}Kr	0.9	3.3	3.2

Figures

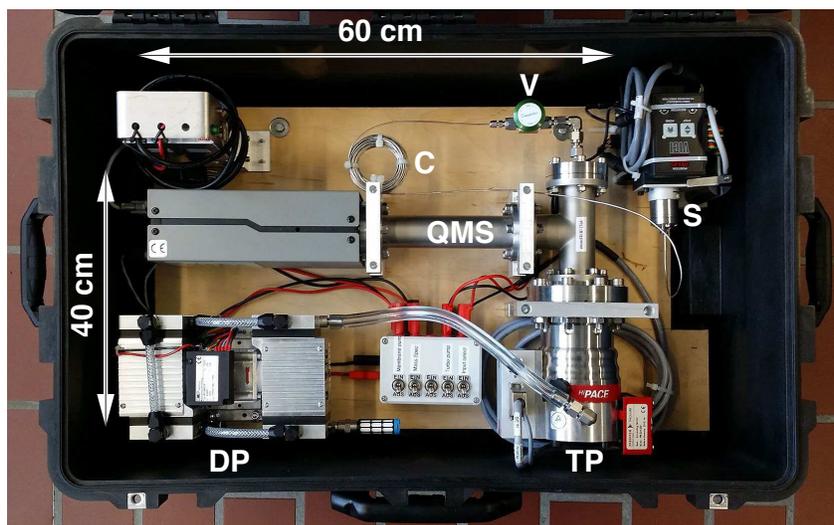
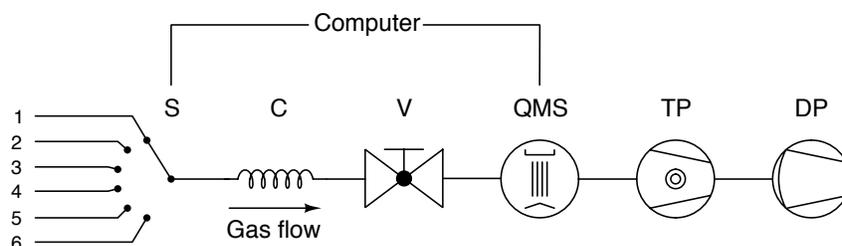


Figure 1: Schematic overview (top) and photo (bottom) of the miniRuedi mass-spectrometer system (see also Table 1): 6-port inlet selector valve (S), capillary (C), inlet valve (V), quadrupole mass spectrometer (QMS), turbomolecular pump (TP), diaphragm pump (DP). The inlet selector valve and the quadrupole mass spectrometer are controlled by a computer. The photo shows the miniRuedi mounted in a wheeled hardshell suitcase for transport and protection.

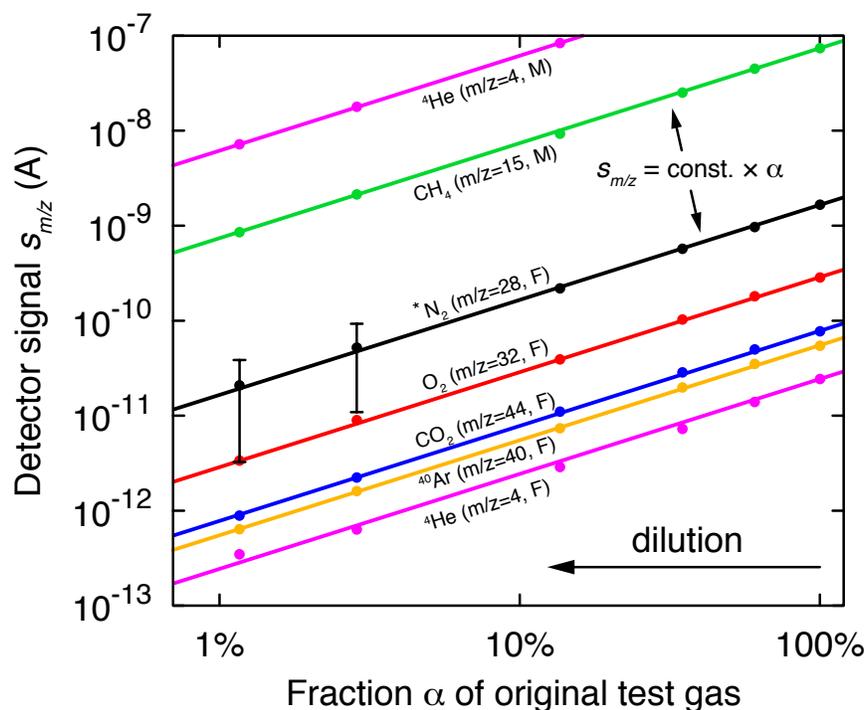


Figure 2: Peak heights $s_{m/z}$ obtained with F and M detectors from a test gas mixture (at ambient pressure) that was incrementally diluted with pure N_2 to reduce the partial pressures of the various gas species (see text). The dilution is quantified as the fraction α of the original test gas remaining in the dilution. The $m/z = 28$ peak heights corresponding to the N_2 of the test gas (denoted by an asterisk, N_2^*) was arithmetically corrected for the contribution of the N_2 added for dilution. The dots show the peak heights at the respective m/z values (mean values of three replicate analyses). Error bars reflecting the standard deviations of the replicate measurements are covered by the plot symbols, except for N_2^* error bars, which reflect the uncertainty of the dilution correction. The best-fit lines are of the form $s_{m/z} = \text{const.} \times \alpha$, with $r^2 > 99.5\%$ for all fits.

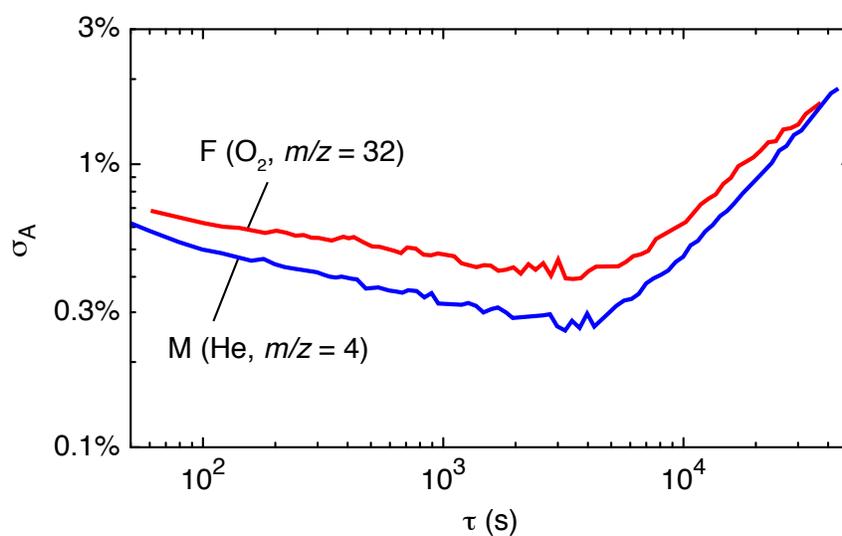


Figure 3: Relative Allan deviations σ_A as a function of the averaging time τ of the F and M signal readings obtained from the analysis of an air sample (see text). The instrument was operated in a laboratory with ambient temperature stabilised to $\pm 1^\circ\text{C}$.

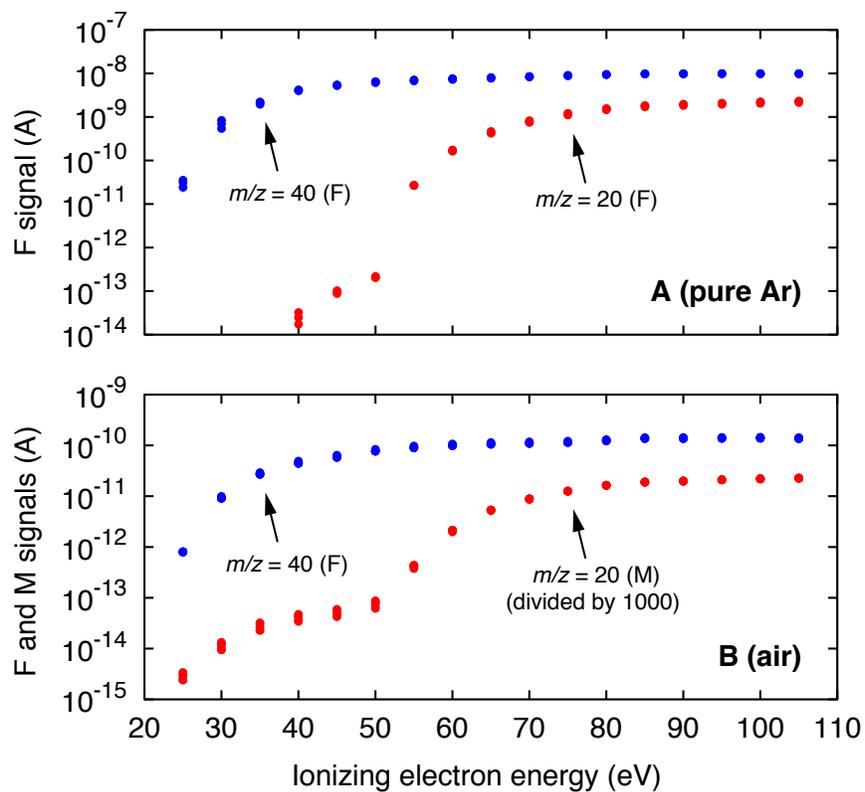


Figure 4: Peak heights at $m/z = 20$ and $m/z = 40$ as a function of the ionising electron energy. A: analysis of pure Ar (99.999%) using the F detector. B: analysis of air, where peak heights at $m/z = 20$ were analysed using the M detector and divided by 1000 to compensate for the higher sensitivity of the M detector relative to the F detector.

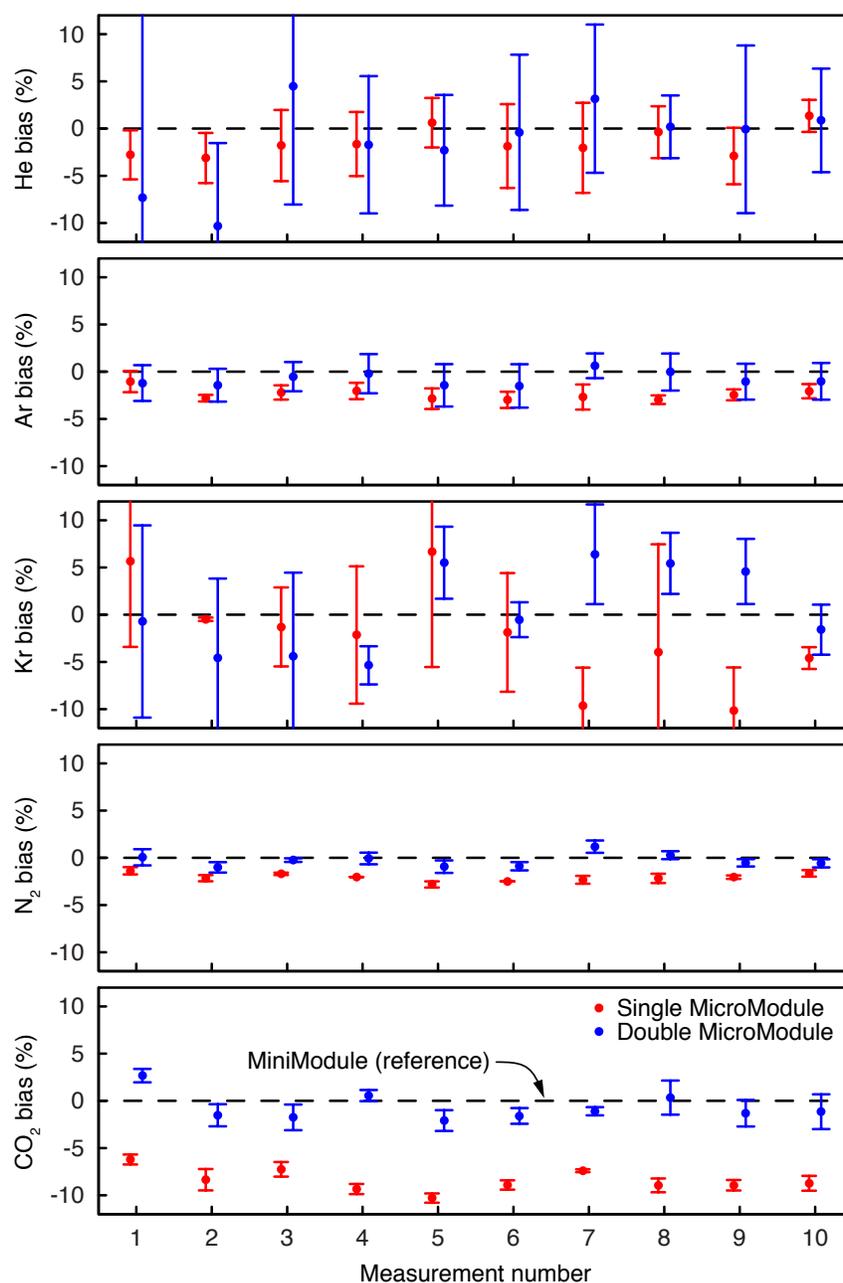


Figure 5: Bias in partial pressures obtained from GE-MIMS measurements in groundwater using miniature membrane contactors (Liqui-Cel MicroModule, type 0.5×1 / G591) relative to partial pressures in larger membrane contactors as required for the original GE-MIMS instrument⁴⁹ (Liqui-Cel MiniModule, type 1.7×5.5 / G542). The miniature contactors were operated either as a single unit or as a parallel combination of two units. Groundwater was pumped through the membrane contactors, and tee branches were used to split the water flow among the membrane contactors for parallel operation of the MicroModules and the MiniModule. The error bars reflect the variability of the gas concentrations in the groundwater flow and the noise in the MS detector signals during each measurement.

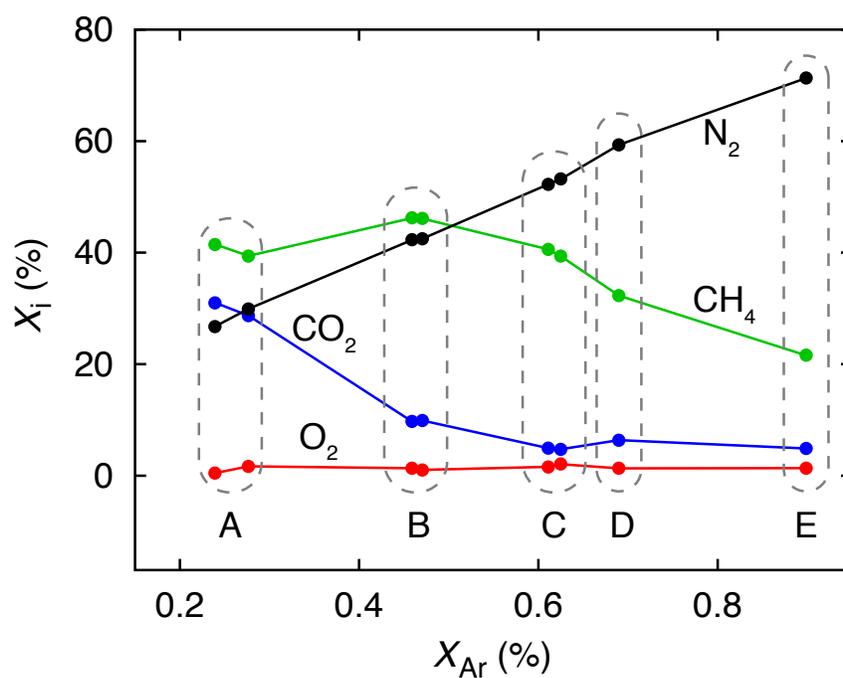


Figure 6: Soil gas composition in a covered landfill: volumetric concentrations of Ar vs. concentrations of $i = N_2, O_2, CO_2, CH_4$ in the five observations wells A–E. Replicate samples were taken in wells A, B and C. Error bars reflecting the standard errors of the measurements are covered by the plot symbols.

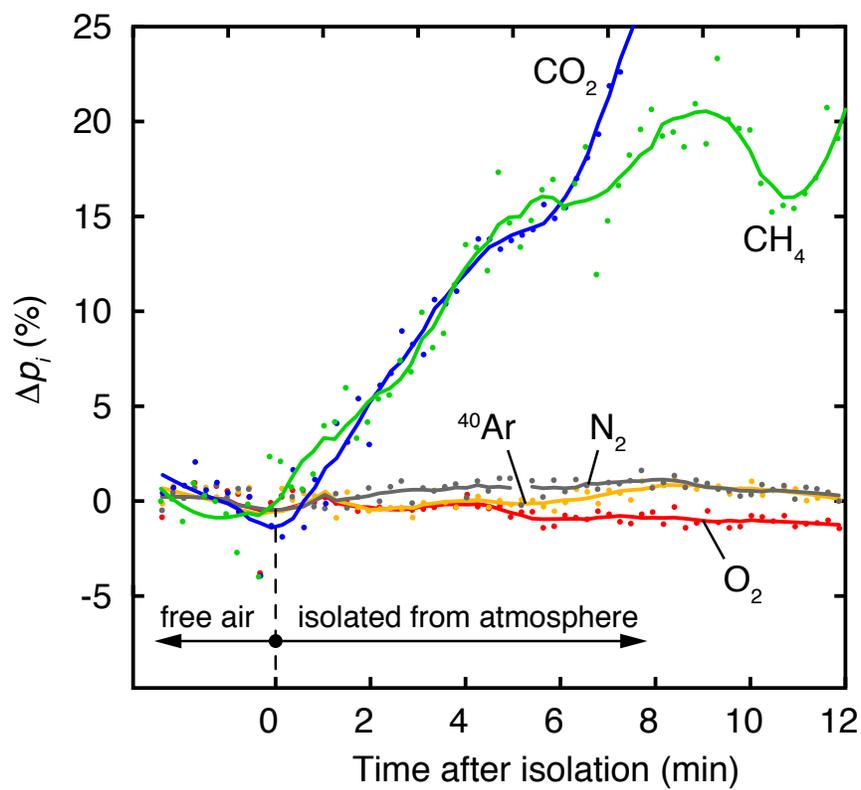


Figure 7: Gas exchange at the water surface of Lake Soppensee: changes of the partial pressures of Ar, N_2 , O_2 , CO_2 , and CH_4 in an air volume above the water surface, before and after isolating the air volume from the atmosphere (Δp_i , change relative to initial partial pressures in free air).

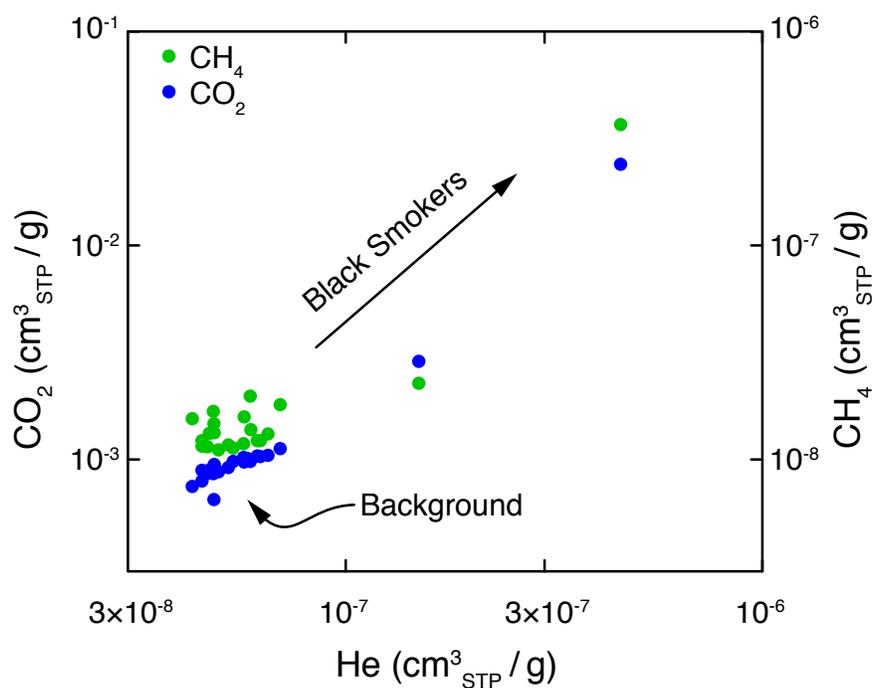


Figure 8: Screening seawater samples for hydrothermal fluids released from black smokers in the Gulf of California: ^3He , CO_2 , and CH_4 concentrations in water samples taken at water depths of up to 2 km (note the logarithmic axis scales).