

Design and deployment of a portable membrane equilibrator for sampling aqueous dissolved gases

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[1] We present designs for a portable trace gas sampler, based on membrane technology, to obtain a gas sample from water in the field. A continuous flow of water is equilibrated with a finite volume of gas until the gas pressure matches the total dissolved gas pressure of the water stream. Samples collected in this manner can be analyzed to determine original water concentrations for potentially any dissolved gas. The sampler requires neither compressed carrier gas nor a vacuum pump to extract the dissolved gas sample; its power consumption is minimal and it fits within a 30 L plastic case. During the development stages, both major atmospheric gases (N₂, O₂, and Ar) and trace gases (CO₂, SF₆, and SF₅CF₃) were measured to confirm the equilibrium condition and to quantify the response time. Equilibration studies were conducted in the laboratory and at the site of a borehole CO₂ injection experiment on the Lamont campus of Columbia University. The time required to achieve solubility equilibrium depends on the dissolved gas content and the water flow rate; we determined an *e*-folding response time of 9–12 min, under air-saturated conditions and with a flow rate of 2 L/min. Typically, equilibrium is achieved within 30–45 min. We compare the system function and analytical results to conventional sampling methods during the recovery phase of a push-pull experiment and find a generally good agreement within 10% of conventional analyses for each of the gases.

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1. Introduction and Motivation

[2] The most well established methods for measuring aqueous trace gases require the collection of water samples for gas extraction under laboratory conditions; often large volumes of water are necessary. The transport and preservation of water samples is cumbersome; samples can be compromised by variations in temperature and pressure, leakage, contamination, or biological activity. These problems can be avoided by extracting the gases in the field. Thin polymer “membranes” are one approach to gas sample extraction from a liquid phase; two phases (liquid/liquid or liquid/gas) are brought into close proximity, separated by the thin membrane wall, and gas transfer is maximized by a large contact surface area. For example, *Sanford et al.* [1996] used gas-filled Silicon and Teflon tubing as a semipermeable membrane for gas sample collection, by immersing the tubing in a dissolved gas solution and allowing the phases to equilibrate by diffusion, within 24 h. Other so-called microporous membranes are

configured as sheets or as tubes with micron-scale openings that permit rapid gas transfer. These membranes can be hydrophilic (wetted) or hydrophobic. Wetted membranes suffer from complications, such as the buildup of foam within the membrane reactor and the separation of the two phases [*Kreulen et al.*, 1993].

[3] Hollow tube hydrophobic (PTFE) microporous membrane contactors, such as the one used in this study, are utilized extensively in industrial applications to degas liquid process streams. The small diameter ($\sim 300 \mu\text{m}$) and relatively large pore openings (40–50 μm) maximize the contact area, in a very compact assemblage, while minimizing the diffusive length scale. By enhancing the concentration difference across the membrane, with a clean sweep gas such as high-purity N₂ or He, or by applying a vacuum, these contactors can be optimized for a specific gas to produce near 100% transfer efficiency in less than a second. As such, they have been successfully applied to yield high spatial resolution measurements of SF₆ [*Ho et al.*, 2002] and CO₂ [*Hales et al.*, 2004] in surface waters and the upper ocean.

[4] In this application, our objective was to develop a portable sampler for surface and groundwater that can produce a representative concentration of all the dissolved gases within a single volume. To achieve this, rather than attempting to quantitatively extract the gases from the sample, we equilibrate a recirculated gas volume, using a membrane contactor, with a continuous stream of water, pumped from surface or groundwater. This configuration is advantageous, because (1) equilibration may begin with any

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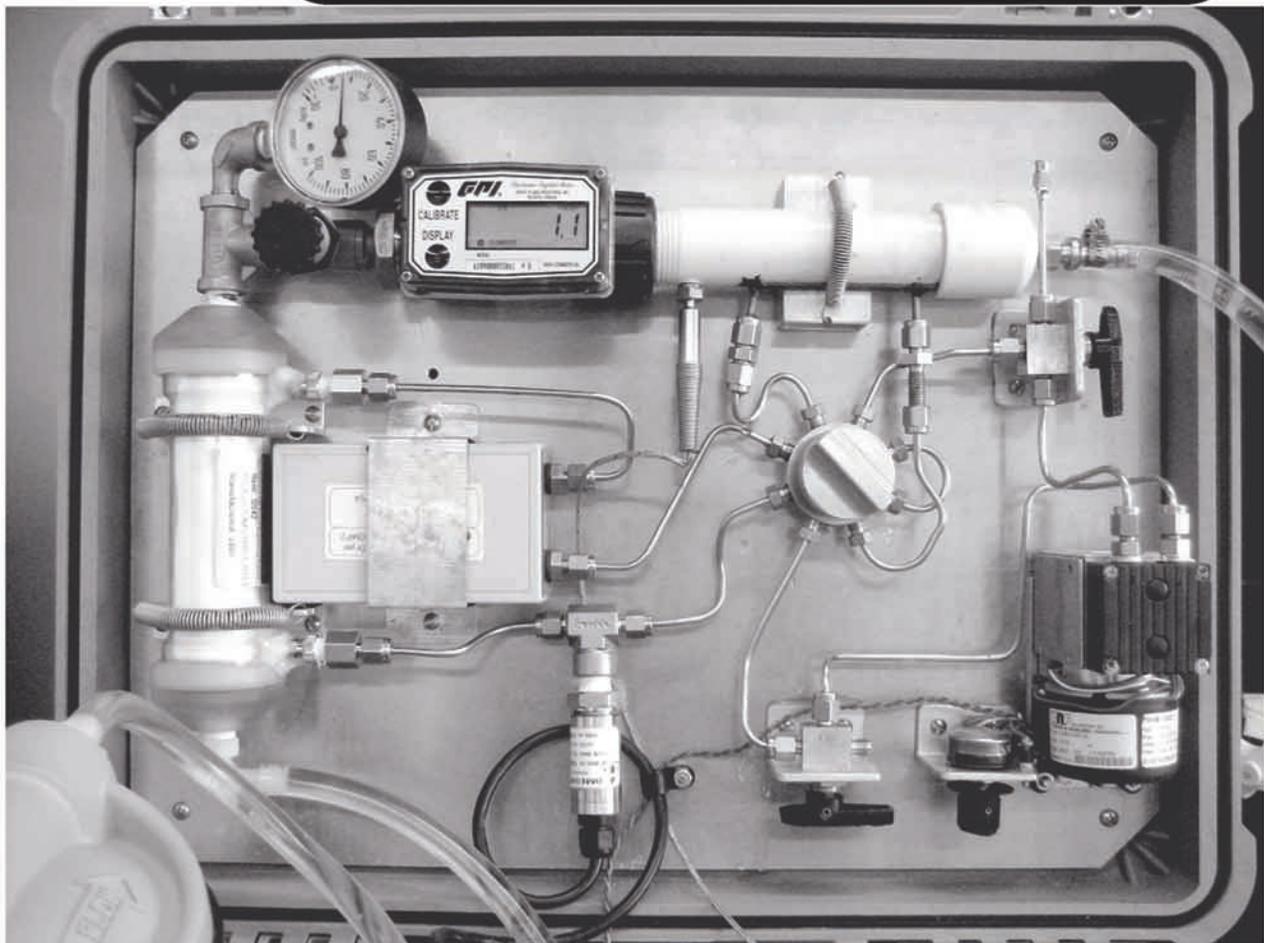
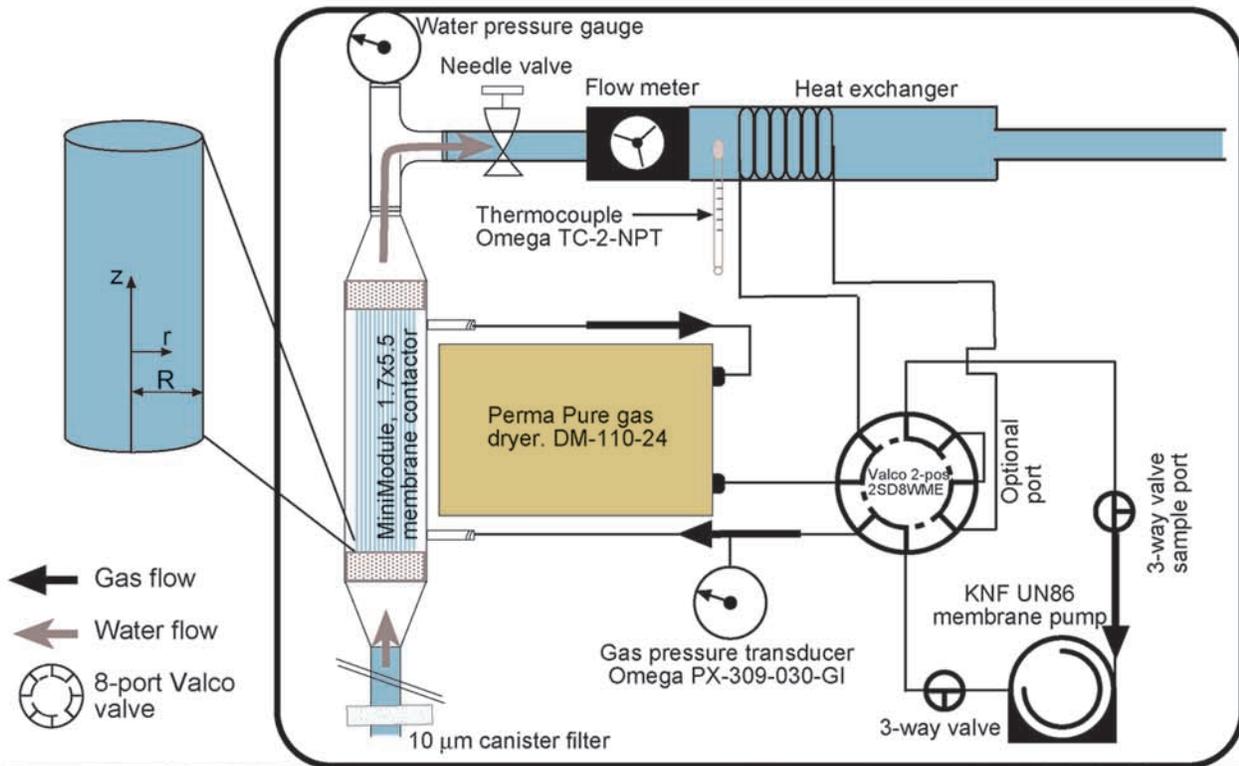


Figure 1

gas (usually air) inside the gas volume, (2) an arbitrarily large volume of gas can be collected for injection into multiple analytical instruments, and (3) the low-solubility gases such as SF₆ are amplified in comparison to their concentration ratios in the liquid phase. In the sections that follow, we describe the design and function of the Membrane Equilibrator for Aqueous Gas Samples (MEAGAS), and demonstrate its application to groundwater sampling, using measurements of N₂, O₂ and Ar as major atmospheric gases, as well as CO₂ and SF₆, as trace gases. We test the system response to an instantaneous change in concentration of SF₆, discuss the response time and present a model solution of the kinetics governing the time to equilibration. During a borehole push-pull experiment, we measured the same atmospheric gases, as well as SF₆ and SF₅CF₃ as time-varying tracers of mixing. We find that the MEAGAS produces accurate, reproducible results, in comparison with samples analyzed using the “headspace method” and water samples analyzed on a purge and trap system, and that the membrane equilibrator is capable of reproducing the time-varying breakthrough of groundwater tracers, as compared with conventional analyses for these gases.

2. Methods

[5] The sampler works by recycling a volume of gas (initially air) through the membrane contactor (Liquicel[®] MiniModule 1.7 × 5.5), at the same time that a constant flow of water is pumped through the hollow fibers inside the contactor. Achievement of solubility equilibrium is judged by watching the time rate of change of the total pressure in the gas loop (Figure 1), which typically ranges within 20% of atmospheric pressure, depending on the gas composition. Flow rate, temperature and pressure are measured at the outlet of the membrane contactor. The temperature inside the gas loop is regulated by a heat exchanger and by temperature equilibration with the water phase inside the membrane contactor. When pressure has stabilized, the gas pump is turned off, and the membrane is isolated from the sample loop to avoid a pressure drop (i.e., mass transfer) while filling the sample container (e.g., syringe or mylar bag, Calibrated Instruments, Inc., Maryland).

[6] During the development stages we equilibrated a 100 L tank of water with atmospheric gases in the laboratory by bubbling air through the tank for 12 h. Water from the equilibrated tank was pumped through the membrane and samples were collected as the pressure stabilized in the gas loop. Each sample collected produces a pressure drop in the gas loop so that it is necessary to wait 5 to 10 min for reequilibration between samples. As a means of comparison, water samples were collected from the 100L tank in

glass syringes, coincident with samples from the MEAGAS. By introducing high-purity nitrogen or helium into the syringe and agitating vigorously for 30 min, one can obtain a representative measure of the water concentration. This headspace method has been used extensively in tracer studies [e.g., Wanninkhof *et al.*, 1987; Ho *et al.*, 1997, 2004]. Gas samples from both methods were analyzed using gas chromatography. Ar, N₂ and O₂ were separated using an Alltec CTR-3 coaxial packed column and analyzed on a GC (8610C, SRI Instruments, California) with a thermal conductivity detector (TCD), CO₂ was analyzed using a flame ionization detector (FID), and SF₆ was analyzed using a GC with electron capture (ECD) detector (GC-8A, Shimadzu, Maryland). The measurement precision was estimated by repeat analysis of gas standards during sample measurement (1σ); precision for N₂ and Ar was 5%, O₂, and CO₂ were 7 and 10%, respectively, and SF₆ measurements on the GC-8A was less than 1%.

[7] A groundwater push-pull experiment [Istok *et al.*, 1997] was conducted in a test well [Matter *et al.*, 2006] at the Lamont-Doherty Earth Observatory (LDEO), Columbia University, in November 2007. In total, 2.2 m³ of water were injected into the borehole during a 3-hour period and the dispersed tracer was pumped back over the course of 88 h. SF₆ and SF₅CF₃, as well as bromide, were mixed into the injected water, with an initial concentration of 12.5 and 2.29 pmol/kg for SF₆ and SF₅CF₃, respectively. Water samples for SF₆ and SF₅CF₃ were collected in 250 mL biochemical oxygen demand (BOD) bottles and analyzed using an automated purge and trap system connected to a gas chromatograph equipped with an electron capture detector (GC-17A, ECD, Shimadzu, Maryland) [Smethie *et al.*, 2000]. We used this opportunity to collect samples with the portable membrane sampler and compare them with those analyzed by the purge and trap method.

3. Results and Discussion

3.1. Response Time

[8] The time required achieving solubility equilibrium between the water stream and the recycled gas loop is an important parameter, both for determining the wait time between successive samples, and for constraining the ability of the sampler to resolve a time-varying dissolved gas concentration. During equilibration, an individual gas can transfer in both directions, according to the concentration gradient. As the gradient diminishes, so does the mass transfer, and thus the concentration in the gas volume tends asymptotically toward equilibrium. To quantify the response time under these conditions, we simulated a step increase and decrease in dissolved gas concentration. We used two

Figure 1. Diagram of the portable membrane sampler for aqueous dissolved gases (MEAGAS). Water flows through a 10 μm canister filter (nominal pore size), vertically upward through the lumen side of the MiniModule[®] (Liqui-Cel, Inc.) and laterally through the heat exchanger before exiting the system. Gas is recirculated through a gas dryer and a Valco[®] two-position valve using a KNF UN86 membrane pump. By rotating the Valco valve to the alternate position, the contactor is isolated from the sample loop. This avoids a pressure drop (rapid mass transfer) when filling a sample container, e.g., syringe and/or mylar bag. The membrane pump can be used to evacuate the sample container by turning both three-way valves. Temperature, pressure, and the membrane pump are powered by a 12 V battery and are displayed by an Omega DPS-3204 four-channel scanner. The pump and scanner are secured in the lower half of the case (not pictured). Both the water flowmeter and external canister filter are available through McMaster-Carr. At the top left, a breakout diagram indicates the coordinate system used in defining equation (1) for gas transfer across a hollow lumen.

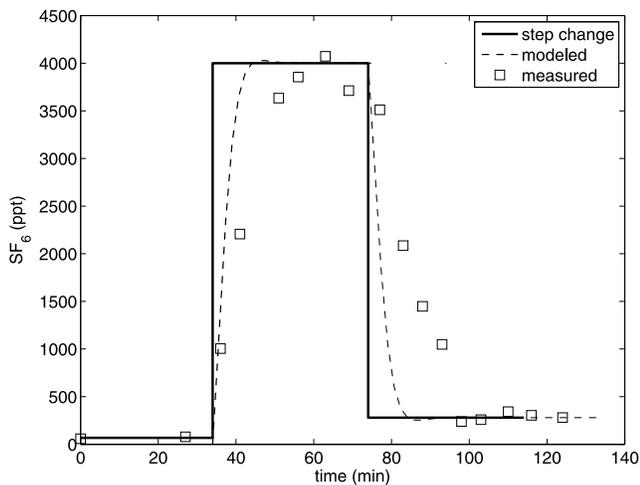


Figure 2. The response time and system memory to a step change in the concentration of SF_6 in the water stream. The dashed lines indicate the discrete solution to the advection-diffusion equation for dissolved gas inside a hollow fiber. The solid black line indicates the change in concentration, and the squares are the concentration that was measured using MEAGAS.

buckets, one filled with tap water and a background SF_6 concentration equivalent to 67 parts per trillion (ppt) partial pressure, and another spiked to a concentration of 4072 ppt partial pressure. By transferring the intake hose from the tap water to the spiked water, we induced an instantaneous increase in SF_6 concentration, and collected regular gas samples to measure the response time. The opposite was done to observe the system memory, as the concentration is instantaneously decreased. An exponential fit to the results (Figure 2), indicates an e -folding response time of 9 min ($r^2 = 0.918$) for the rising limb and 8 min ($r^2 = 0.995$) for the falling limb.

[9] To reproduce the observed response time, we simulated the process of mass transfer that is thought to occur inside the membrane contactor. Gas transferring from one phase to the other must overcome three barriers: diffusion through the water, diffusion across the membrane, and finally diffusion through the gas phase. When the gas volume is well mixed, it is thought that the rate-limiting step is gas diffusion through the water, and that the other barriers can be neglected. Therefore, the membrane response can be adequately simulated as an aqueous diffusive process [Gabelman and Hwang, 1999]. We have solved the equation for laminar diffusion through water inside a hollow fiber, similar to Kreulen *et al.* [1993]:

$$\begin{aligned} \frac{\partial c}{\partial t} + v_r \frac{\partial c}{\partial z} &= D \frac{\partial^2 c}{\partial r^2} \\ c([z, r], 0) &= \text{SF}_6 \text{ in air} \\ c(z = 0, t) &= \text{inflow concentration (4072 ppt)} \\ c(r = R, t) &= (c(t-1) + \bar{F})/V \\ \left. \frac{\partial c}{\partial r} \right|_{r=0} &= 0 \end{aligned} \quad (1)$$

In cylindrical coordinates, r is the radial distance from the axis of the lumen, R is the radius of a hollow lumen fiber

(100 μm), and z is the distance along the length of the lumen (see breakout in Figure 1). \bar{F} is the gas flux during one time step, and V is the volume of the recycled gas loop. To compare with observations, the concentration of SF_6 in the recycled loop, $c(r = R, t)$, was computed by integrating the solution to (1) over the surface area of a cylindrical lumen and multiplying by the number of lumens in the contactor (dashed line in Figure 2). The parameters used in the simulation (and the experiment described above) are listed in Table 1. The solution was calculated numerically using an implicit finite differencing technique. While there is general agreement between our observations and the modeled solution, the modeled concentration in the recycled gas loop appears to slightly lag the observations, during the rising limb, and lead the observations slightly during the falling limb. This may indicate that the effective gas diffusion is greater than the molecular diffusion, perhaps from lateral dispersion due to velocity shear. It may also be evidence of a secondary boundary to mass transfer, such as incomplete mixing within the gas loop. The solution also indicates that decreasing the volume of the recycled gas loop, as well as increasing the flow rate will both reduce the time to equilibration. For example, by decreasing the gas volume by half, equilibrium is achieved in approximately one third of the time. Increasing the flow rate has a diminishing return, as the extraction efficiency also decreases with increasing flow rate.

3.2. Equilibration Experiments

[10] During the laboratory equilibration tests, replicate samples were taken from the 100 L water tank, using both the headspace method and the MEAGAS sampler. Samples were analyzed for Ar, N_2 , O_2 and CO_2 . We present the mean concentration alongside the standard error (σ/\sqrt{n} , $n = 4$) from one of these experiments in Table 2. The first row in Table 1 (“Air-saturated water”) indicates the expected concentration based on equilibration of the water tank with air at 18°C, the water temperature during sampling. The mean concentration from the MEAGAS samples was within 6% of the expected concentration for all gases, except for CO_2 , which was almost double the atmospheric concentration. The measured CO_2 concentration can be attributed to the respiration and combustion in the vicinity of equilibration experiments in a confined lab space with incomplete ventilation. The results are similar for replicates taken with the headspace method. In general, the standard error between replicate gas samples from MEAGAS was 35–65%

Table 1. Values Used in the Laboratory Equilibration Experiment and for the Discrete Solution for the Advection-Diffusion Equation Inside a Hollow Membrane Fiber

	Value
Diffusivity SF_6 in water (cm^2/s) [Koh <i>et al.</i> , 2007]	9.2×10^{-6}
OD/ID membrane fiber (μm) (Membrana, 2007) ^a	300/220
Number of fibers (in $1.7 \times 5.5''$ minimodule) (Membrana, 2007)	7400
Length of fiber (cm) (Membrana, 2007)	9.4
Gas volume (cm^3)	113
Water flow rate (L/min)	2

^aMembrana, 1.7 × 5.5 MiniModule[®] product data sheet, 2007, Charlotte, N. C., available at <http://www.liqui-cel.com/uploads/documents/1.7x5.5-Mini%20Module-D86Rev13-7-07.pdf>.

Table 2. Comparison Between the Headspace and Membrane Sampling Method^a

	Ar (mL/L)	N ₂ (mL/L)	O ₂ (mL/L)	CO ₂ (mL/L)
Air-saturated water	0.324	12.34	6.62	0.318
Headspace	0.26 [2.4%]	12.17 [2.5%]	5.84 [2.9%]	0.56 [1.2%]
MEAGAS	0.32 [1.5%]	12.60 [0.9%]	6.20 [1.7%]	0.61 [7.5%]
MEAGAS/ASW	1.03	1.05	0.97	1.89
MEAGAS/Headspace	1.22	1.04	1.06	1.09

^aSamples were drawn from a reservoir of air-saturated water at 18°C using the solubility data of *Weiss* [1974, 1971] and correcting for the difference in vapor pressure. The standard error ($SE = \sigma/\sqrt{n}$, $n = 4$) between sample replicates is provided in brackets as percent of the mean ($(SE/\mu) \times 100$).

less than the headspace method, however, the variability for CO₂ was 83% greater for the membrane replicates. Because CO₂ is buffered by the carbonate system, solubility equilibrium is not uniquely dependent on the partial gas pressure. The water used during the equilibration experiments was tap water (a mixture of surface and groundwater), which may have produced time variations in the carbonate and bicarbonate concentration in the tap water, resulting in incomplete equilibration and greater variability in the CO₂ concentration than for the non-buffered gases. This problem should not exist for a water stream whose carbonate system is in equilibrium. It should also be noted that the headspace method using glass bottles and septa has achieved better precision than what is reported here using syringes (L. N. Plummer, and E. Busenberg, *Dissolved gas analysis*, 2006, U.S. Geological Survey, Reston, Va., available at http://water.usgs.gov/lab/dissolved-gas/lab/analytical_procedures/).

[11] It is known that some plastics have the tendency to emit SF₆ and CFCs, or molecules with similar chromatographic retention time. This results in a nonzero blank

concentration in sampling. To assess the potential for background SF₆ concentration the membrane was flushed with UHP N₂ from the water side to the air side, and subsequently sealed. The membrane was left for 2 h and for 24 h to allow gases to diffuse into the pure N₂. Upon measurement, both samples yielded an SF₆ concentration of 0.1 ± 0.001 ppt, which is nearly 2% of the atmospheric concentration. For sampling old water with trace SF₆ concentrations, more work would be necessary to condition the membrane and remove the blank or establish its consistency over time, to facilitate a correction factor.

3.3. LDEO Borehole Samples

[12] Gas samples were collected with the membrane sampler on days one and three of the recovery phase of the push-pull experiment. The membrane samples capture the decreasing SF₆ and SF₅CF₃ trend that is depicted by water samples collected in the 250 mL BOD bottles (Figure 3). The average difference between SF₆ from the membrane and the BOD samples is 10% with relatively symmetrical scatter above and below the 1:1 line (Figure 4). Samples were not

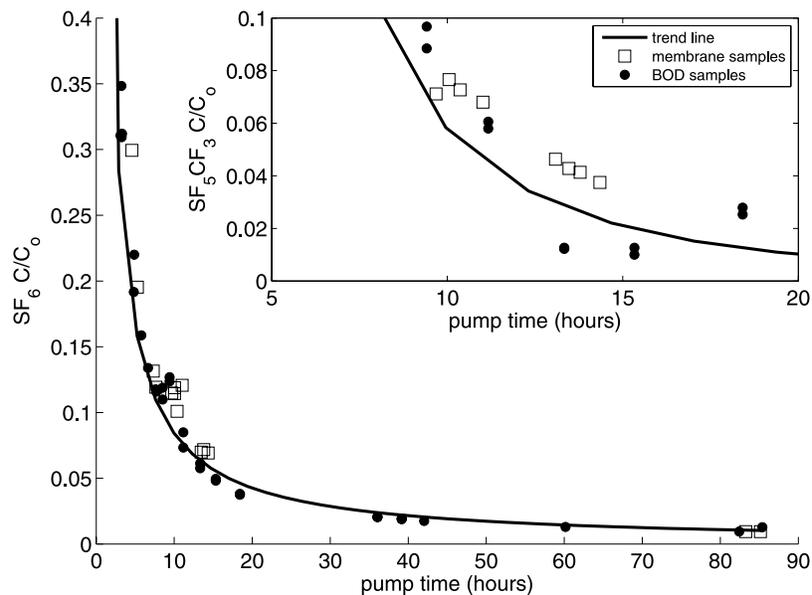


Figure 3. SF₆ and SF₅CF₃ samples collected during the recovery phase of the push-pull experiment. The values are normalized with respect to their initial concentration. Samples were collected using the membrane sampler on the first and third days of recovery. Membrane samples were analyzed for SF₆ on both days and for SF₅CF₃ on day 1 only. SF₅CF₃ was analyzed on a separate machine from SF₆. Biochemical oxygen demand (BOD) water samples were collected in 250 mL glass bottles and were analyzed on a purge and trap system. Membrane samples were collected with the portable membrane equilibrator (MEAGAS) and were measured on a direct injection GC-ECD system.

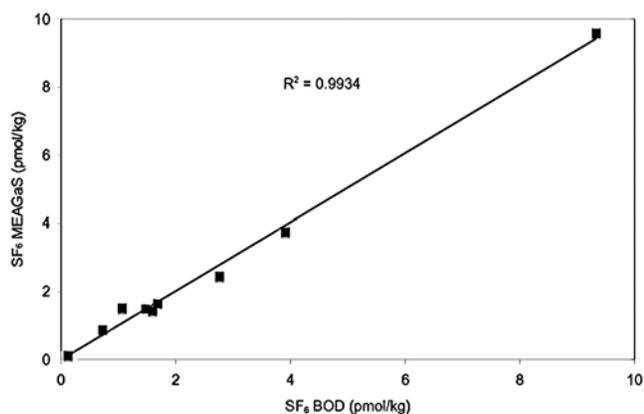


Figure 4. The correlation between near-coincident samples collected from a groundwater injection and pump back at the LDEO borehole. BOD water samples were collected in 250 mL glass bottles and were analyzed on a purge and trap system. Membrane samples were collected with the portable membrane equilibrator (MEAGAS) and were measured on a direct injection GC-ECD system.

always collected at the same moment in time, which may account for some of the observed variability.

4. Conclusions

[13] The analysis of flow and mixing processes in geophysical reservoirs often requires the collection of as many parameters as possible. We have presented a design for a portable dissolved gas sampler (MEAGAS) that is capable of producing a gas volume whose composition reflects the concentration of the major atmospheric gases as well as trace gases. This sampler is ideal for collecting a gas sample to be analyzed for multiple gas parameters. Samples from the portable membrane equilibrator accurately reproduced the gas concentration of water equilibrated with air, as compared with the headspace method, during design studies in the laboratory. The relative standard error of MEAGAS sample replicates was 35–65% of headspace replicates. SF₆ samples collected during the groundwater push-pull experiment were within 10%, of the results measured by purge and trap (measurement error for both GC-ECD systems was better than 1%). The *e*-folding response time of the sampler is ~9 min under typical sampling conditions. At a flow rate of ca. 2 L/min, solubility equilibrium can be achieved within 30–45 min, or 60–90 L of water. Equilibration time is limited by the progressive reduction of the concentration gradient across the membrane, as the concentration increases in the gas loop. This effect was reasonably reproduced through a numerical solution of the advection-diffusion equation inside a hollow microporous fiber.

[14] The portable membrane equilibrator is ideal for remote field studies, or studies where transporting large compressed gas cylinders or large volumes of water can be complicated. The sampler can be powered from a small 12 V battery and requires no extra equipment, save a water pump for extracting groundwater or surface water. The equipment weighs less than 25 pounds and can fit within a medium-sized (14 × 18 × 7") case that can be sent as

checked luggage on air planes. Gas samples can be collected in a variety of vessels, including mylar bags, syringes or copper tubes. In the future, we hope to extend the applicability of the MEAGAS sampler to include measurements of helium isotopes, using mass spectrometry, and evaluate its performance at a higher level of precision.

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