

Continuous chemical monitoring with osmotically pumped water samplers: OsmoSampler design and applications

Hans W. Jannasch¹, C. Geoff Wheat², Josh N. Plant¹, Miriam Kastner³, and Debra S. Stakes¹

¹Monterey Bay Aquarium Research Institute, 7700 Sandholdt Road, Moss Landing, CA 95039, USA

²Institute of Marine Sciences, University of Alaska Fairbanks, P.O. Box 475, Moss Landing, CA 95039, USA

³Scripps Institute of Oceanography, University of California at San Diego, La Jolla, CA 92093, USA

Abstract

Long-term osmotically pumped fluid samplers, or OsmoSamplers, were developed to reliably and autonomously collect continuous small-volume water samples for monitoring aqueous environments in remote locations for up to several years. OsmoSamplers provide sequential milliliter-size samples that, when analyzed, yield high-resolution time-series for a wide range of dissolved components. These instruments fill an important niche that has not been addressed by automated samplers or in situ analyzers. OsmoSamplers can be customized for flow rate and duration for addressing numerous scientific questions. The samplers consist of an osmotic pump that continuously pulls fluid sample into a long small-bore tube. They are thus extremely simple, reliable, and require neither electrical power nor moving parts. Upon recovery, fluid samples are extracted from subsections of the sample tubing, where each subsection integrates a discrete time interval. The time-stamped subsamples are then analyzed for chemical species of interest. Sample smearing due to static and dynamic diffusion and mixing is kept to a minimum by the use of small-bore tubing (0.5 to 1.2 mm inside diameter) and low flow rates (0.1 to 12 mL d⁻¹). Theory and laboratory experiments show that sample smearing is not significantly greater than that calculated from static diffusion alone. OsmoSamplers have been tested in the laboratory and deployed at sea. Results from laboratory tests and field deployments illustrate initial results and potential applications.

Introduction

Most biogeochemical processes vary over a wide range of temporal scales. The lack of instrumentation that can obtain continuous chemical data greatly limits our ability to characterize this natural variability (e.g., Johnson and Jannasch 1994; Dickey et al. 1997). These limitations result in a severe undersampling of the environment, and traditional manual sampling may often completely miss significant episodic events. Long-term, high-resolution sampling and analytical capability are required to understand the driving forces and variability of biogeochemical processes such as nutrient availability to surface ocean or estuarine

productivity, fluid flow-induced geochemical processes on the seafloor, or environmental conditions for aquatic biological communities.

General trends of chemical variability in natural well-mixed systems can be resolved by periodic sampling. Long-term open-ocean time-series are being conducted at the Bermuda-Atlantic Time-series Study site (Michaels and Knapp 1996), the Hawaiian Ocean Time-series site (Karl and Lukas 1996), by the California Cooperative Oceanic Fisheries Investigation (Rebstock 2002), and in Monterey Bay (Chavez et al. 1991). All of these experiments, however, are still limited by approximately monthly availability of sea-going support, proximity to port, and cost.

Automated samplers have been used to monitor lakes and streams (e.g., Amundson et al. 2000), but only a few have been used in the marine environment. Several automated sample collection systems have been developed that can collect up to several dozen samples while deployed on remote moorings, however this is a low number of samples for many long-term studies (e.g., Abbott et al. 1990; Bell et al. 2002; Boyle et al. 1996). Although electromechanical collection systems can have a high temporal resolution, their sample capacities limit their overall duration. Most oceanographic moorings are only

Acknowledgments

We wish to thank the crews of the *ROV Ropos*, *DSV Alvin*, and *JOIDES Resolution* drill ship for their agile work in deploying and recovering the instruments. This paper benefited from helpful comments by A. Fisher and others. The work was supported by the Monterey Bay Aquarium Research Institute through the David and Lucile Packard Foundation, the National Science Foundation (NSF OCE 98–11552 and OCE 98–12121), and the Joint Oceanographic Institutions U.S. Science Support Program (JOI/USSSP 93–20477).

visited every two to twelve months, and thus processes that result in daily to weekly perturbations, and variability that is controlled by periodic and sporadic events, are difficult to constrain or even identify.

More recently, several in situ sensors have been developed that, instead of archiving samples, analyze specific dissolved chemical species in situ and store and return only data. Such systems can generally obtain a much better temporal resolution, and are limited mostly by reagent supply and power. In situ analyzers using modified continuous flow analysis techniques have been developed using peristaltic (Johnson et al. 1986; Massoth et al. 1995), osmotic (Jannasch et al. 1994), and solenoid (Weeks and Johnson 1996) pumps. In situ optical sensors have been used extensively for measuring ambient light and fluorescence, but have also been adapted to measure several chemical species by curve-fitting absorption spectra in the ultraviolet spectrum (Johnson and Coletti 2002).

In sum, current remote samplers are limited in temporal resolution (usually to tens of samples), whereas in situ analyzers are limited to, at most, four dissolved constituents that have simple and well-characterized chemistries or optical properties, and generally are not capable of returning archived sample.

This paper describes a new type of long-term high-resolution sampler, the OsmoSampler, which uses osmotic pumps requiring no electrical power to continuously pull sample into a long small-bore tube. OsmoSamplers have the capability to collect samples at a much higher temporal resolution than existing samplers and allow many more analyses to be conducted on the same samples than present in situ analyzers (Jannasch and Kastner 1995). We describe several configurations of OsmoSamplers with complete details of the general concepts, construction techniques, and laboratory tests. We then describe a range of field applications with initial results from marine deployments. The laboratory and field experiments provide a measure of the quality and integrity of samples collected and a range of potential uses. The inherent simplicity of osmotic pumps makes them an excellent replacement for electromechanical pumps, especially for extended sampling periods in harsh aquatic environments.

Materials and procedures

Osmotic pumps—Osmotic pumps consist of a fixed semipermeable membrane separating two chambers (Fig. 1). Flow within the pump is created by the osmotic pressure across the membrane that separates solutions of differing salinity. These membranes allow water to diffuse through the pore space while restricting the passage of dissolved salts. Differences in the salt concentration between the two solutions bounding the membrane drive a net diffusion of water, and thus flow, through the membrane from the fresher to the more saline side. The magnitude of the salt gradient, a function of the concentration difference and membrane thickness, is directly related to the osmotic pressure and resulting flow rate. Rates of water flow across the membrane are dependent only on

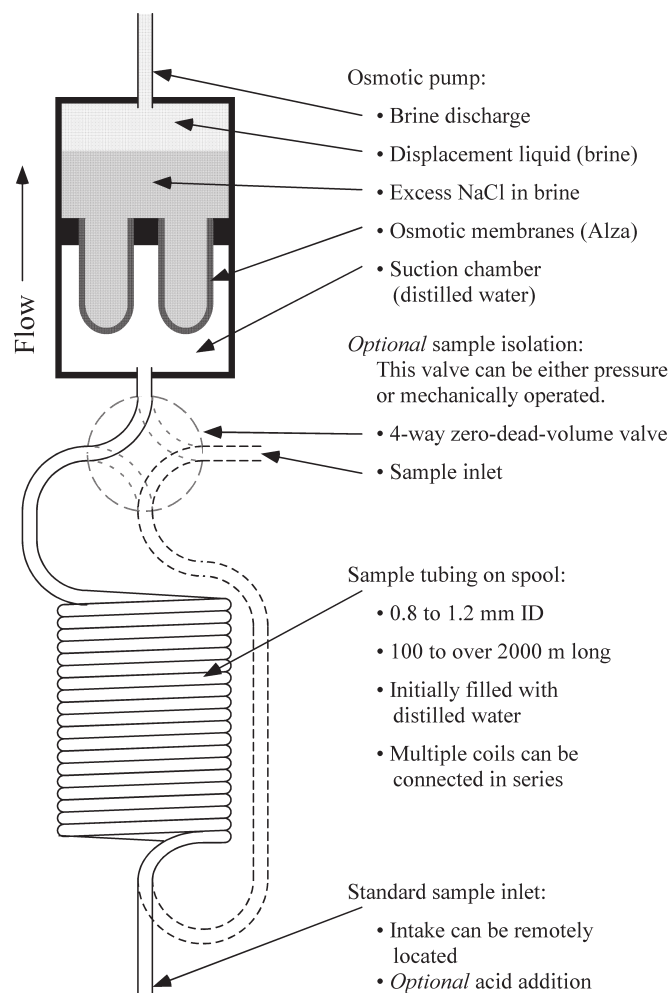


Fig. 1. Schematic of an OsmoSampler. An osmotic pump consists of a rigid semipermeable membrane separating two chambers containing solutions of differing salinity. Flow rates are kept constant by maintaining freshwater and saturated brine with excess salt on either side of the membrane. OsmoSamplers use an osmotic pump to continuously pull fluid into a long micro-bore sample tube (0.5 to 1.2 mm ID). The pumps are attached either directly to a coil of tubing or through a 4-way sampling valve to prevent degassing during recovery. The tubing is initially filled with distilled water and deployed at any depth at ambient pressure.

properties of the membrane (total area, thickness, and porosity), the osmotic pressure gradient, and the diffusion coefficient of water. The osmotic pressure is maintained by keeping a brine solution saturated with an excess salt (NaCl) on one side of the membrane while maintaining a solution void of salt on the other side. Once constructed, variations in flow rates of osmotic pumps are primarily dependent on temperature (diffusion of water), which is discussed below. Theeuwes and Yum (1976) originally described the technology for an osmotic pump for use as a medical implant.

We used commercially available osmotic membranes from Alza Inc., which were removed from model 2ML1 pumps, and Dow Corning (FilmTec RO, Type 55101). The Alza membranes

consist of a rigid ~1-mm-thick cellulose acetate membrane. Individual ~10-mm-diameter by 30-mm-long sleeves have flow rates of about $4 \mu\text{L h}^{-1}$ at 20°C . We have described the use of these membranes for in situ nitrate and iron analyzers previously (Jannasch et al. 1994; Chapin et al. 2002). Dow Corning membranes are made for reverse osmosis (RO) applications and their flexibility requires a rigid support for positive displacement pumping. These membranes are approximately 3 μm thick and have flow rates of about $16 \mu\text{L h}^{-1} \text{cm}^{-2}$ at 20°C .

Housings for the osmotic pumps are made of acrylic, polycarbonate, or translucent polyvinyl chloride (PVC). Acrylic is preferable because the thermal expansion coefficient of acrylic is most similar to that of water. Membranes are either attached with an O-ring seal (RO) or potted in place (Alza membranes) with a 2-part polyurethane compound (Fluid Polymers, HMP-60). The upper compartment of the osmotic pump is filled with saturated brine and enough excess salt (NaCl, commercial grade) to keep the solution saturated throughout the duration of the experiment. The membrane is allowed to saturate overnight before the lower compartment is filled with distilled water. When flow begins, the under-pressure created in the lower compartment then draws water into this compartment, which is attached to a sample tube. The outflow from the saturated brine reservoir is generally pumped out to the surrounding environment through a 30-cm length of 0.8-mm-inside diameter (ID) tubing to avoid excess loss of salt. An optional modification to the pump includes use of a flexible impermeable membrane to contain the saturated brine thus eliminating salt contamination to the surrounding environment when sampling in confined areas. All of the pumps were tested with a positive pressure head to ensure reliable and smooth rates of pumping.

We have built pumps with flow rates ranging from about 1 to $500 \mu\text{L hr}^{-1}$ (about 10 to 5000 mL y^{-1}). For example, osmotic pumps with 12 Alza pump membranes (model 2ML1) flow at approximately $48 \mu\text{L h}^{-1}$ ($\sim 1 \text{ mL d}^{-1}$) at 20°C . Fitted with a salt reservoir large enough to maintain excess salt throughout the experiment, Alza membranes have pumped continuously for more than 3 y. Although RO membranes pump much faster per membrane area, the significantly thinner and more flexible membranes need to be held rigidly in place. The life of RO membranes is about several months and is limited by a slow leakage of salt across the membrane. These membranes also show a significant pressure effect that is described below.

Sample tubing—OsmoSamplers consist of an osmotic pump that is directly connected to a continuous length of small-bore sample tubing (Fig. 1). Lengths of up to 2400 m of 0.8-mm- or 1.2-mm-ID fluorinated ethylene propylene tubing (FEP Teflon, Atlantic Tubing or Zeus Industrial Products) were carefully coiled onto spools. A 300-m spool of 0.8- or 1.1-mm-ID tubing holds about 150 or 300 mL of water, respectively. An OsmoSampler can have one or more spools attached in series with zero-dead-volume fittings. The pressure drop due to flow resistance does not affect flow rates, because with the slow

flow rates described here, the osmotic pressure that can be generated by these membranes greatly exceeds any normal pressure drop in the sample tube. By example, flow rates of 10 mL d^{-1} within 0.8-mm-ID tubing 300 m in length produce a pressure drop less than 0.03 bars.

Teflon sample tubing can be cleaned with dilute acid if deemed necessary to avoid contamination of samples for trace metal analyses. Due to the high gas permeability of Teflon, the tubing is flushed and filled with degassed, distilled/deionized water and attached to the pumps just prior to deployment. A degassed solution is required because any air bubbles present at deployment will dissolve and compress at depth, thus drawing sample into the sample tubing. This is undesirable because the deionized water-sample interface is used to determine the location (within the sample tubing) and time of the initial sample. While filling the sample tubing, the flow rate ($\sim 1 \text{ mL min}^{-1}$) and inlet pressure (≤ 2 bar) are monitored to ensure that the tubing has no leaks or other defects. When storing sample coils at 1 atm, submerging them in degassed water reduces the chance of forming bubbles within the tube before being deployed.

Although FEP Teflon tubing can readily be cleaned for many trace element analyses, its high gas permeability eliminates its usefulness for collecting samples for dissolved gases such as H_2S , He, CO_2 , O_2 , CH_4 , or the lighter Freons. Other types of less-permeable tubing (e.g., copper, stainless steel, or Teflon-lined stainless steel) can allow sampling of gases and redox sensitive compounds. Such tubing, however, has the potential to corrode and be a source for trace metal contamination. Lupton et al. (1998) has successfully analyzed samples for dissolved He gas and isotopes that were collected by an OsmoSampler fitted with a 0.8-mm-ID copper tube.

Sample recovery—Upon recovery of an OsmoSampler, the sample coil is quickly disconnected from the pump, the ends are sealed, and the coil is refrigerated. As soon as practical, the tubing is pinched and cut into segments of appropriate lengths to provide the necessary volume of sample, beginning at the sample intake (most recent sample). Typically, sections are cut into 1-m lengths, which provide about 0.5 and 1.0 mL of sample from 0.8 and 1.1 mm ID tubing, respectively. Sample is expelled by pushing clean filtered air through subsections of tubing and ejecting the sample into acid-washed microcentrifuge tubes with snap-caps. When sampling brackish water or seawater, a refractometer is used to check for the seawater/distilled water interface. Pumping the sample out of the whole coil and into a fraction collector is not viable because of the dispersion caused by faster pumping rates.

For deployments in environments with stable temperatures ($\pm 1^\circ\text{C}$), samples are time stamped linearly with the sample/distilled water interface and the intake representing the deployment and recovery times, respectively. In areas with more significant temperature variations, such as in estuaries or the surface ocean, it is necessary to calculate flow rate as a function of time and adjust the intermediary time stamps appropriately.

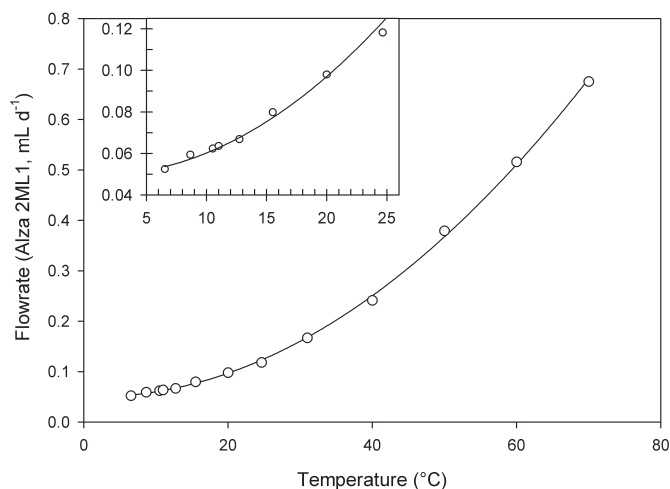


Fig. 2. Flow rates of osmotic pumps with Alza model 2ML1 membranes are mainly a function of temperature. Flow rates are normalized to a single membrane separating distilled water from saturated brine. The inset is an enlargement of the 5°C to 25°C temperature range.

Once samples are extracted, they can be analyzed as desired. Individual 1 mL samples are large enough to allow determination of up to 24 species with a combination of inductively coupled plasma-optical emission spectrometry (ICP-OES), ion chromatography (IC), titration, and standard colorimetric techniques. In this paper we present results from samples that were analyzed for the major ions and trace elements in seawater including Mn, Fe, and Si by ICP-OES; SO_4 by ion chromatography; Ca, Mg, and chlorinity by titration; and Si by colorimetry.

Analyzing samples selectively to obtain an overview, followed by further analyses during times of interest, can significantly reduce the analytical effort. Sequential samples can also be combined for further analyses requiring larger volumes, albeit at a lower temporal resolution.

If samples have the potential to be supersaturated with gas at 1 atm, a four-way valve can be used to isolate the sample coil before recovery. This prevents degassing within the sample tube during depressurization and warming, and avoids sample loss out the intake during recovery. Regular hemostats can be used to temporarily pinch Teflon sample tube during sectioning.

Assessment

Osmotic pumps—Osmotic pumps, made with both Alza and RO membranes, have been used in numerous laboratory and field experiments (Jannasch et al. 1994; Dickey et al. 1997; Wheat et al. 2000). Pumps made with Alza membranes tested in the lab and field, work well at temperatures ranging from 4°C to 70°C (Fig. 2). As expected, rates of flow are mainly affected by temperature, highlighting the importance of diffusion of water across the membrane as the most significant element in controlling the flow rate into the sample tubing.

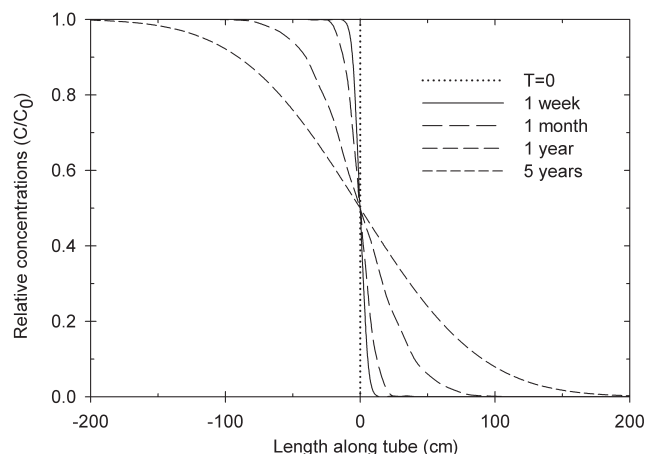


Fig. 3. Gradient dispersion due to diffusion. Each line represents the spreading distance of a step concentration change for a given time within the OsmoSampler tubing due to diffusion alone (Eq. 1).

Sample dispersion within the sample tubing—One concern with a continuous water sampler is the ability of the sampler to retain temporal variations in the chemical composition of the sample. Temporal changes in the chemical composition of samples that are pulled through the sample tubing are prone to broadening by molecular diffusion, gradient dispersion due to shear in the flow stream, and chemical interactions with the tubing walls, resulting in decreased temporal resolution.

If we consider the simplest case, that of molecular diffusion, then we can calculate the effective diffusion within a concentration gradient from an analytical solution derived from Fick's second law (Crank 1975). A step concentration change at a plane in solution diffuses outward and is described by,

$$C(x,t) = \frac{C_0}{2} \operatorname{erf} \frac{x}{2\sqrt{Dt}} \quad (1)$$

where $C(x,t)$ is the concentration at distance x from the initial boundary at time t , C_0 is the initial concentration at $x < 0$ ($C = 0$ for $x > 0$ at $t = 0$), and D is the bulk diffusion coefficient for ions in solution. The spreading of a concentration gradient is shown as a function of time in Fig. 3, with a typical molecular diffusion coefficient of $1.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (Li and Gregory 1974). These calculations show that, due to molecular diffusion alone, >99.9% of a step change in concentration will remain within a 2-m section of tubing for a full year, and within a 4-m section for a 5-yr period. These calculations imply that a 360-m sample tube filled during a 1-yr deployment will exhibit concentration changes with a temporal resolution of about 2 d. Similarly, a 1000-m tube deployed for 5 yr retains a temporal resolution of about 1 week.

Flow-induced dispersion of chemical gradients during flow-through small-bore tubing has been described in studies of flow-injection analysis (e.g., Tijssen 1980; van den Berg 1980).

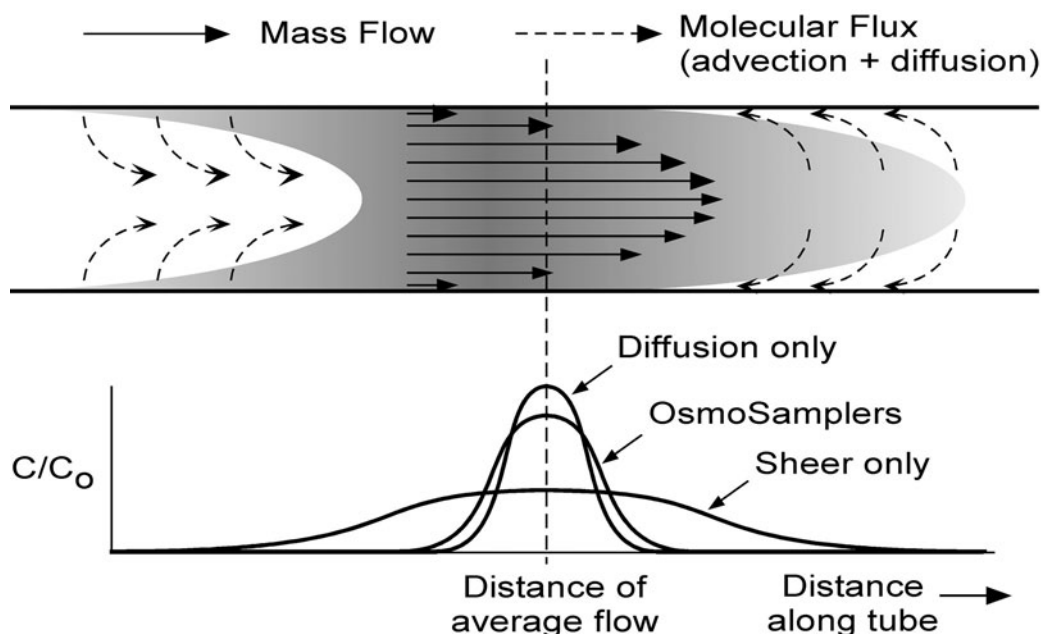


Fig. 4. Schematic representation of sample dispersion within a tube. The along-tube dispersion is due to advection and diffusion (Eqs. 2 and 3). Radial diffusion significantly improves plug-flow in small-bore tubing with low flow velocities.

These studies show that concentration gradients, which are pumped through sub-millimeter tubing, have less dispersion than expected from the parabolic velocity profiles that occur across the tubing. Dispersion is significantly reduced by radial diffusion in these smaller tubes. Because the rate of pumping in the OsmoSamplers is reduced even further than in flow-injection analysis applications, the importance of radial diffusion is increased, thus counteracting the effect of peak spreading due to parabolic flow. This was first modeled by Taylor (1953), who showed that gradients flowing through a small-bore tube dispersed evenly around a center plane that moves at the rate of the average fluid flow. He derived an effective diffusion coefficient, k ,

$$k = \frac{r^2 v^2}{48D} \tag{2}$$

where r is the inner radius of the tubing, v the average velocity, and D the diffusion coefficient of the solute. This effect is graphically shown in Fig. 4. It is interesting to note that larger diffusion coefficients, such as those found for gases, result in lower k 's, and thus, decreased gradient smearing. The equation incorrectly predicts that k tends toward zero as velocities approach zero. Because Eq. 2 was derived assuming only radial diffusion and along-axis flow, we can approximate peak smearing at the slow-flow rates observed in the OsmoSamplers by summing the effects of fluid flow and along-axis diffusion as,

$$k' = k + D. \tag{3}$$

Calculated values of k' for various tube diameters and flow rates

are shown in Table 1. These calculations show that peak smearing due to fluid flow does not affect along-axis molecular diffusion (i.e., $k \ll D$) at flow rates $< 1 \text{ mL d}^{-1}$ and tube IDs $> 0.5 \text{ mm}$. Increased dispersion does occur in faster pumping OsmoSamplers.

An additional potential cause of peak spreading may occur by chromatographic separation (i.e., surface binding). Because these potential dispersive effects are more difficult to model, we developed a series of laboratory experiments to determine the signal resolution that could be maintained within an OsmoSampler.

Laboratory experiments—Two osmotic pumps with 7 membranes (Alza 2ML1), each pumping about $28 \mu\text{L h}^{-1}$, were connected to 100 m of 0.8-mm-ID Teflon tubing filled with degassed distilled water. The samplers were fully submerged in a 40-L tank at room temperature ($\sim 20^\circ\text{C}$) to maintain ther-

Table 1. Approximations of dispersion as calculated by effective diffusion coefficients (k') within a tube due to fluid flow (k) and molecular diffusion (D) using $D = 1.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (from Eq. 3)

Tubing ID (mm)	Osmotic membranes			
	1 Alza	4 Alza	12 Alza	RO ^a
	Flow rates (mL d ⁻¹ at 20°C)			
	0.08	0.33	1	12
	$k' (10^{-5} \text{ cm}^2 \text{ s}^{-1})$			
1.2	1.50	1.56	2.0	77
0.8	1.51	1.63	2.7	170
0.5	1.52	1.84	4.5	440

^aReverse osmosis (RO) membrane is 7 cm diameter.

Table 2. Ionic concentrations (M) used for laboratory OsmoSampler experiments

	Seawater	Altered seawater
Cations		
Na ⁺	0.4725	0.4410
Mg ⁺⁺	0.0500	0.0050
Ca ⁺⁺	0.0100	0.0550
K ⁺	0.0100	0.0070
Sr ⁺⁺	0.0001	0.0001
H ₄ SiO ₄	0.00015	0.00065
Anions		
Cl ⁻	0.5402	0.5672
SO ₄ ⁼	0.0300	0.0160
CO ₃ ⁼	0.0013	0.0005

mal equilibrium. The input to the sample tube was inserted in bottles of either artificial seawater, distilled water, or altered seawater (similar to that from a low-temperature hydrothermal system, Wheat et al. 1997; Mottl et al. 1998). Concentrations of Na, Cl, Ca, Mg, K, Si, and SO₄ are shown in Table 2. One experiment alternated between seawater and distilled water to emphasize differences in ionic and physical characteristics. The other experiment alternated between seawater and altered seawater, each with about the same salinity. After a period of 3 months, the sample tubing was cut into 1-m sections and the samples were discharged into 1-mL microcentrifuge tubes.

The distinct oscillations in concentrations of the major ions accurately result from the changing fluid input to the OsmoSamplers (Fig. 5) and demonstrate the measurable separation between samples. The initial distilled water-sea water interface was pulled 62 and 65 m into the sample tubing for the two experiments. This interface was used to locate the start of the experiment. The difference in the lengths of tubing filled is due to variations in membrane potting, resulting in slightly different areas of the membrane that are exposed. Calculations of static diffusion predict that the concentration changes would be contained within an 80-cm section of tubing. This calculated result is in agreement with the experimental results, which show that almost all concentration gradients, which started as step-changes when the intake tube was moved from one bottle to another, were still fully contained within a single 1-m section of tubing after 3 months. These experimental results confirm that peak smearing caused by the sample flow through the tubing is not significantly greater than that from molecular diffusion alone.

The dissolved chemical species (Cl, Ca, Mg, K, Si and SO₄; Fig. 4) used in these experiments acted as conservative elements. Other elements such as Fe and Mn are sensitive to redox conditions. Consider, for example, a reducing hydrothermal fluid that is sampled by an OsmoSampler, where the intake is in the hydrothermal vent, but the sampler is located in nearby

cool, oxic bottom seawater to maintain a uniform rate of pumping. As the reduced fluid is drawn into the sampler, dissolved oxygen will diffuse across the Teflon tubing thus potentially oxidizing the reduced Fe and Mn. The oxidized forms of these metals are surface active and less soluble. Under these conditions, Fe and Mn may exhibit more peak smearing due to oxidation and temporary binding with the inside surface of the Teflon tubing as the sample passes through the tubing. Furthermore, other surface-active compounds (e.g., organics) may tend to partially adsorb onto the walls of the Teflon tubing. If this binding is reversible, one could expect a chromatographic type separation of that element from the bulk sample. To address this issue, we conducted two similar experiments in which samplers drew from an anoxic solution of Fe⁺² and Mn⁺² that was bubbled continuously with nitrogen. This solution was sampled directly by one OsmoSampler. The other OsmoSampler included a second osmotic pump which added 10% HCl with an acid/sample ratio of 1:28. This additional pump reduced the pH of the sample stream from about 5.6 to 3.5. Results from these experiments show that similar increases in Mn and Fe concentrations (due to evaporation by nitrogen bubbling) were observed in both OsmoSamplers as well as in discrete samples that were collected periodically from the sample reservoir (Fig. 6). The difference between the acidified and unacidified OsmoSamplers indicates that some Fe retention occurred within the unacidified sample tube, and that acidification is necessary for sampling redox-sensitive and surface active elements. We therefore refer to these modified samplers as acid-addition OsmoSamplers.

Marine applications—OsmoSamplers have also been deployed in various remote marine environments for time frames from weeks to more than 3 yr. OsmoSampler configurations and initial data from three deployments are presented as a further assessment under real conditions. An in-depth scientific analysis of these field experiments will be presented in subsequent papers.

Axial Seamount. After a major eruption reshaped the summit of Axial Seamount off the coast of Oregon in January 1998, several research cruises were launched to study the post-eruption evolution of the undersea volcano (Chadwick et al. 1999; Embley et al. 1999). Among the experiments that were carried out, a series of OsmoSamplers were deployed to monitor the effluents from some of the newly formed hot water vents. One of the most actively venting hydrothermal sites was located near the southeast edge of the caldera, referred to as "Marker 33," located at about 46°N, 130°W, in 1500 m of water. The vent consisted of a crack about 7 cm wide, 15 cm deep, and 10 m long, from which hydrothermal fluids were venting. The OsmoSamplers were deployed several meters away from the vent to avoid the temperature variations of the venting waters. They were connected to the sample intakes, deployed inside the vent, with 2-m-long by 1-cm-diameter PVC tubing. The intake end of the Teflon sample tube was threaded through the PVC tube. The intakes of the OsmoSamplers were attached

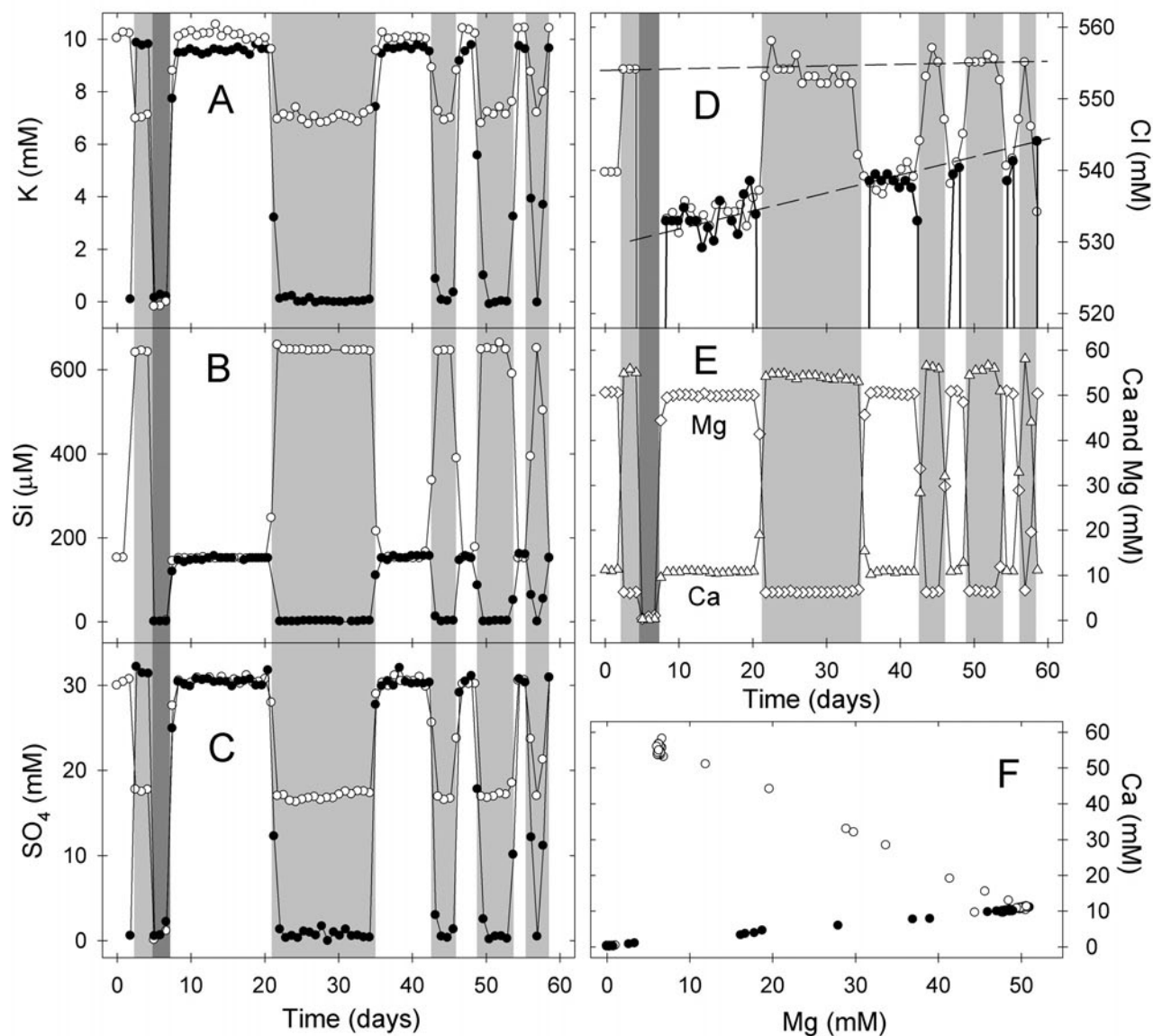


Fig. 5. Laboratory results showing sample separation within an OsmoSampler over a 2-month period. Concentrations were measured from samples within 65 sections of 1-m (0.5 mL) OsmoSampler tubing. The data are from two experiments, where the sample intakes were switched between bottles of seawater and either distilled water (solid symbols) or altered seawater (hollow symbols). The panels show the sample resolution of K (A), Si (B), SO_4 (C), Cl (D), and Ca and Mg (E). All concentration boundaries are within a single subsample, each integrating about 1.5 d. The increase in Cl concentration over time is due to the evaporation from the sample bottles during the experiment. The background shades show the timeframes where the sample intakes were in seawater (white) and altered seawater or distilled water (gray). All sample intakes were in distilled water from day 5 to 7 (dark gray). The linear correlation between Ca and Mg shows no differential behavior within the OsmoSampler tubing (F).

to T-handles and temperature loggers easily manipulated by the submersibles, and placed within the crack near the site with the most intense venting. Sample was collected at the intake directly into the Teflon sample tubing protected with a 30- μm Nytex mesh.

Both long-term (1-yr deployments with Alza membranes) and high-resolution (2-week deployments with RO membranes) OsmoSamplers were deployed and recovered by submersibles. Long-term OsmoSamplers were constructed with

sample pumps fitted with 5 Alza 2ML1 membranes and a 300-m by 0.8-mm-ID Teflon sample coil. Flow rates were about $\sim 0.5 \text{ mL d}^{-1}$ at 20°C . They pumped $\sim 0.25 \text{ mL d}^{-1}$ at in situ temperatures of $\sim 4^\circ\text{C}$ and were capable of collecting sample for up to 18 months. These samplers were also configured as acid-addition OsmoSamplers with a second smaller osmotic pump with a single Alza 2ML4 membrane connected to a 10-m-long 1.2-mm-ID Teflon acid-filled coil for preserving the sample (Fig. 7). Experiments used either concentrated HCl or HNO_3

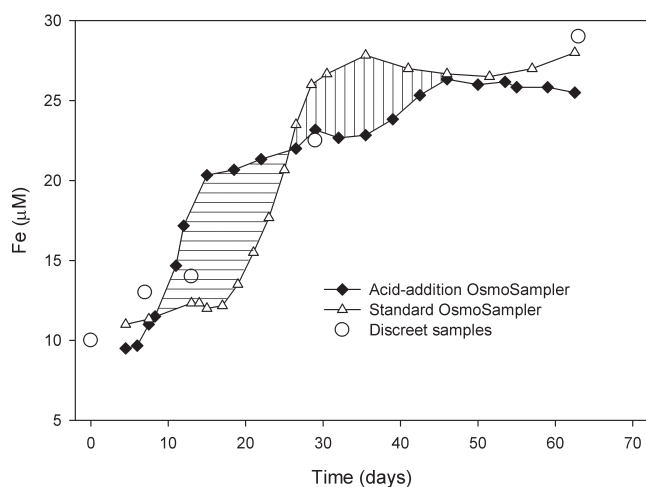


Fig. 6. Reduced Fe^{2+} concentrations (3-pt averaged) in anoxic fluids as measured by OsmoSamplers located within an oxic environment with and without acid-addition. The difference between the two samplers shows that a portion of the Fe in the unacidified OsmoSampler was held back in the sample tubing due to its surface activity (from horizontal to vertical hatch). The overall increase from the initial $10 \mu\text{M}$ Fe^{2+} concentration was due to evaporation caused by nitrogen bubbling maintaining anoxia in the sampling bottle.

solutions and were spiked with KBr to monitor the rate of acid addition. The acid delivery line was also run through the PVC tube out to the T-handle. The acid was added ~ 1 cm behind the intake to prevent metal precipitation and loss of acid. The ratio of acid to sample was $\sim 1:20$.

The high-resolution OsmoSamplers capable of resolving tidal variability were constructed with $\sim 40 \text{ cm}^2$ reverse-osmosis (RO) membrane with no acid-addition, but were otherwise similar to the long-term OsmoSamplers. These samplers pumped about $\sim 12 \text{ mL d}^{-1}$ at 1 atm at $\sim 20^\circ\text{C}$ and were expected to pump $\sim 6 \text{ mL d}^{-1}$ at $\sim 4^\circ\text{C}$, capable of collecting sample for up to 3 weeks.

After recovery, the outside of the sample coil was immediately rinsed with distilled water and sub-sampled, using plastic gloves and a nonmetallic cutting blade. Beginning with the intake end, the sample tubing was cut into 1-m subsections, and the 0.5-mL sample aliquots were expelled into acid-cleaned 1-mL microcentrifuge tubes. An aquarium-style air pump with $0.45 \mu\text{m}$ in-line filter was used to flush out the tubing sections.

The analytical results from the long-term OsmoSampler and the temperature measured at the sample intake are shown for the 1999-2000 deployment in Fig. 8. The location of the distilled water/sample interface indicated that the in situ flow rate of the osmotic pump was very close to the predicted value. The elevated temperatures that were observed during November 1999 appear to be followed by significant increases in the concentrations of Si, Mn, and Fe, delayed by about 1 to 4 weeks. Similar behavior was not observed for Ba and Sr, indicating that the processes that govern these elements are

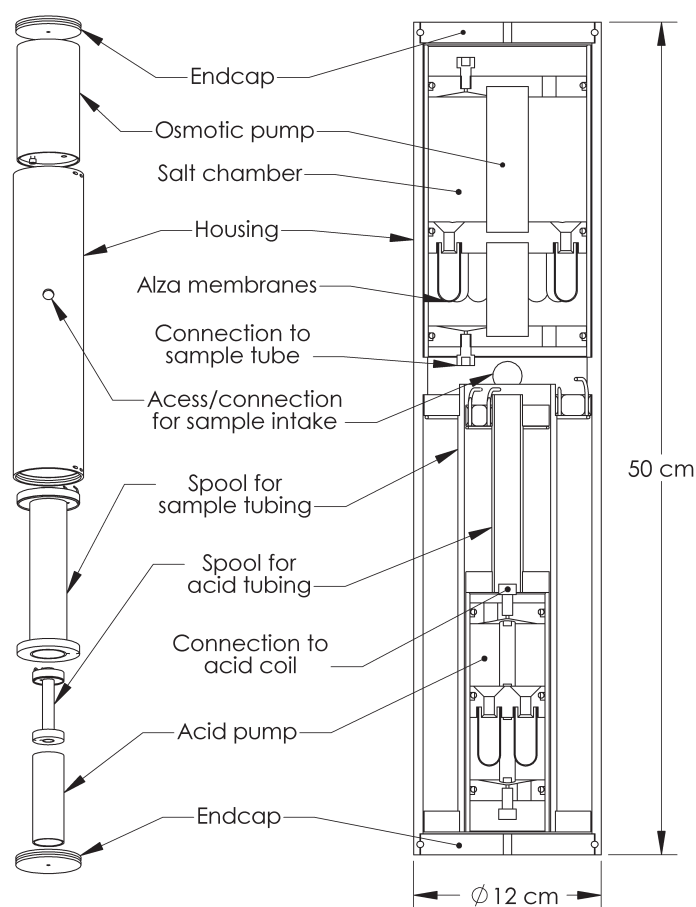


Fig. 7. Acid-addition OsmoSamplers as deployed in several field experiments. The major parts of the sampler are shown individually (left) and assembled in cross-section (right). The sample and acid tubing, and sample intake, is not shown for clarity.

decoupled from those that govern Si, Mn, and Fe. Such year-long time series provide a measure of chemical change that allows us to address questions related to the response of hydrothermal systems to volcanic and tectonic perturbations, evolution of hydrothermal systems, and the extent of chemical variability associated with hydrothermal communities. Each 1-m segment of tubing integrated about 1.6 d, however, only every sixth sample was analyzed for the overview shown in Fig. 8. Further analysis of the remaining samples would thus yield a much finer temporal resolution.

High-resolution OsmoSamplers with RO membranes were deployed in September 1998 for 15 d. Upon recovery, the distilled water-sample interfaces in all three samplers had moved completely through the sample tube. Flow rates, from 26 to 28 mL d^{-1} or about four times the expected value, were estimated from the amount of Cl and Br that had collected in the fresh-water chamber of the osmotic pump. We suspect that these membranes suffered a significant pressure effect. For these high resolution OsmoSamplers, each 1-m tubing segment integrated about 30 min. Again, every sixth sample has been

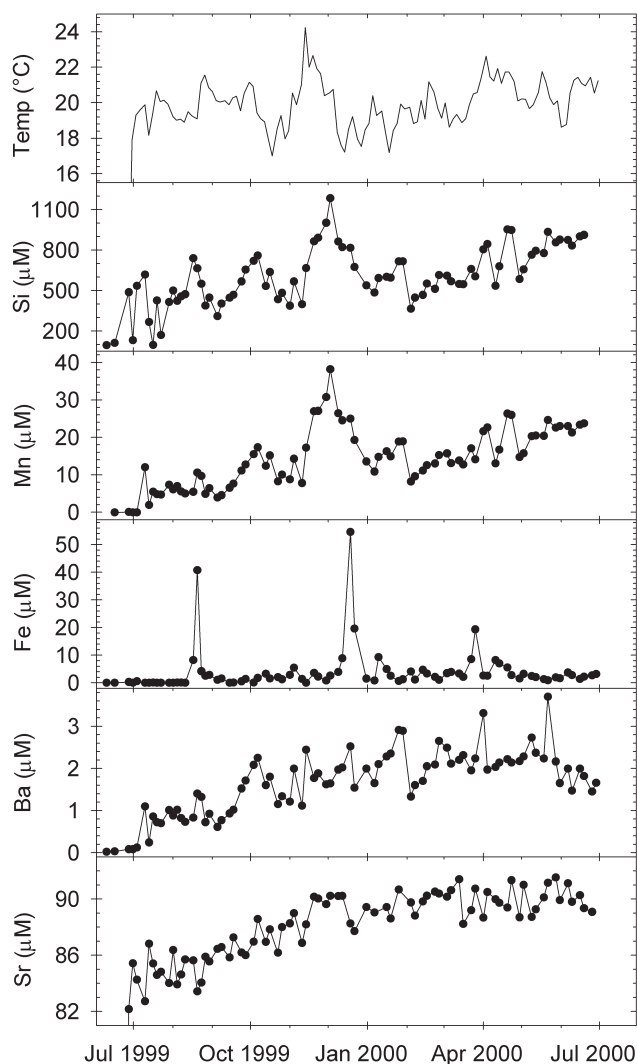


Fig. 8. A year-long record of OsmoSampler analyses from the "Marker 33" vent on Axial Seamount. The elevated temperatures observed during November 1999 had significant effects on the chemical composition of the venting water. Si, Mn, and Fe concentrations increased within one to 4 weeks after the temperature event, whereas Ba and Sr concentrations appear unaffected. The chemical data shown here integrate about 1.6 d, but only every sixth sample was analyzed.

analyzed, and the data for a continuous 5-d record of Cl, Mn, and Fe from the "Marker 33" vent, along with tide height and temperature, are shown in Fig. 9. These data provide evidence for the upwelling of a vapor-rich hydrothermal fluid that cools conductively during ascent, reacts with wall rock, mixes with seawater at depth, and continues to ascend without further reaction. The rate of mixing between seawater and hydrothermal fluids cycles between 24% to 10% hydrothermal fluid with a periodicity of 1 d. Periodically iron is released to the system, probably in the form of colloid-sized particles that are captured by the sampler. Deployments such as this one provide a measure of short-term change that can be used to

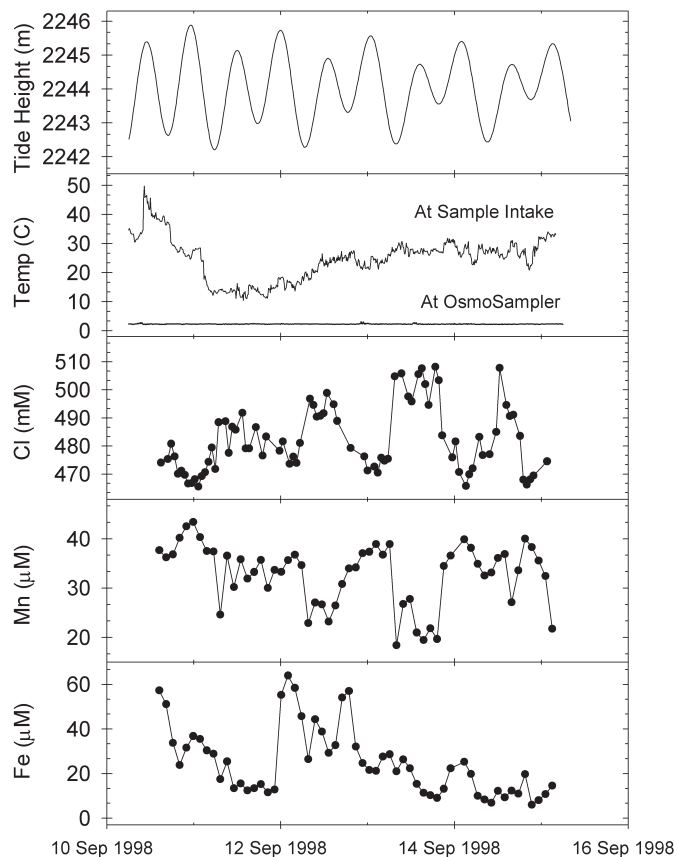


Fig. 9. A 5-d record of the tidal cycle, thermal signature, and chemical composition of hydrothermal fluids from the "Marker 33" vent. This OsmoSampler was fitted with faster pumping reverse-osmosis (RO) membrane, and is therefore capable of resolving tidal variability. A 0.5 mL sample yields 30 min resolution, with every sixth sample shown.

address problems associated physical and biological forcing on tidal scales.

Juan de Fuca boreholes. Long-term OsmoSamplers were deployed to study the evolution and temporal variability of fluids within boreholes drilled by the Ocean Drilling Program (ODP). In June to August 1996, ODP drilled and capped four new holes on the eastern flank of the Juan de Fuca Ridge (sites 1024 to 1027). Each hole was fitted with a re-entry cone, temperature, and pressure logger, thermistor string, and a 125-kg sinker bar, with the sensors and samplers hanging within the hole below a hydraulic seal (Davis et al. 1997).

Samplers were designed to fit within the 12-cm-diameter casing and collect ~ 400 mL y^{-1} over a 5-yr period, at in situ temperatures ranging from 20°C to 80°C. The OsmoSamplers had an outside diameter of ~ 8 cm, a 2.5 cm inside diameter for the thermistor cable to pass through, and an overall length up to 3.8 m (Fig. 10). The polycarbonate housing contained a single osmotic pump with 3 to 8 Alza membranes, depending on the expected in situ temperature, and up to seven spools with ~ 300 m of 1.2-mm-ID Teflon tubing each. The intake was located near the bottom of the sampler. The thermistor strings

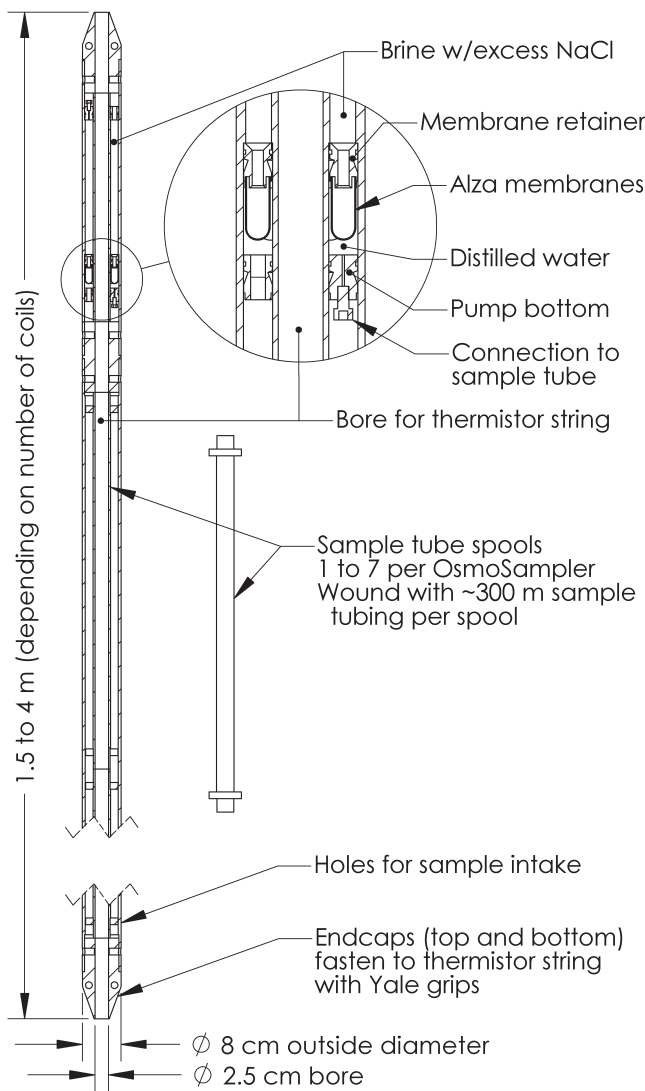


Fig. 10. Cross-section of a borehole OsmoSampler. These OsmoSamplers were designed to hang on the thermistor string of a sealed borehole up to 800 m below the sea floor and 80°C, and sample 400 mL yr⁻¹ for 5 y.

were passed through the OsmoSamplers, which were attached with Yale grips on each end. The OsmoSamplers were located from 165 to more than 700 m below the sea floor.

Three years later, in September 1999, two of the four samplers were recovered. Both OsmoSamplers had collected about 1300 mL of sample in approximately 1.6 km of tubing. Throughout the experiment, the distilled-to-seawater transition had spread less than 3.5 m, further verifying the basic principle in Eq. 3.

A portion of the analytical results from ODP Site 1027 is illustrated in Fig. 11. Initial concentrations are similar to that of surface seawater (Ca ~10.4 mM; Mg ~54 mM), which is used during drilling to flush cuttings from the hole. Similar to the thermal data (Davis and Becker 2002), this seawater composi-

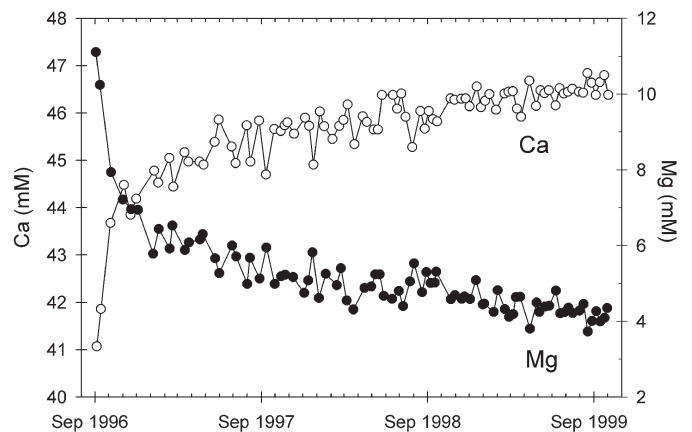


Fig. 11. Ca and Mg data from the OsmoSampler deployment in ODP borehole 1027 on the eastern flank of the Juan de Fuca Ridge over 3-y period. Ca and Mg were initially about 10 and 50 mM, respectively.

tion changes rapidly within the first 20 to 40 d after the borehole is sealed at the seafloor to an altered fluid with a Ca concentration of about 44 mM and a Mg concentration of about 7 mM. This rapid change in composition requires a flow of ~1500 kg of formation fluid into and out of the borehole per day (Wheat et al. 2003). After this initial change, we observed a more gradual change requiring a flow rate of ~17.5 kg/day at ODP Site 1027 (Fig. 11) (Wheat et al. 2003). In addition to these and other potential hydrogeologic results, OsmoSampler data from this setting also provide a measure to address the extent of crustal alteration, the magnitude of ridge flank chemical fluxes in relation to global geochemical budgets, and the size and structure of microbial communities that comprise the subsurface biosphere.

Discussion

OsmoSamplers are extremely simple, yet working with such slow flow rate systems requires some care. All systems need to be carefully tested for micro-leaks after assembly. Pumps should be tested for several days pumping against a 10 to 50 cm head of water pressure, noting both the inflow and outflow volumes. Any salt crystals forming around fittings or glue joints are indications of leaks. Tubing spools should be observed for leakage while being filled with degassed distilled water and should be kept submerged after that to keep from absorbing gases that cause bubbles during temperature cycling. All connections should be zero-dead-volume fittings of laboratory quality (e.g., Upchurch or Alltech). Zero-dead-volume four-way valves should be pressure tested to in situ pressures to ensure proper sealing during deployment. Potting compounds should be degassed after mixing to avoid bubble formation during curing. Clear or opaque potting allows easier quality control. With proper precautions, OsmoSamplers are highly reliable, cost effective, and simple to use.

Limitations and additional applications—OsmoSamplers have several drawbacks, including difficulties in maintaining concentrations of labile compounds without some form of preservation. OsmoSamplers are also unable to deliver data in real time, nor can the rate of sampling change in response to events recorded by other means. In addition there are also a number of potential problems caused by microbial processes and biofouling. This was initially experienced in deployments on Loihi Seamount, where microbial Fe sheaths clogged the sample intake after several months (Wheat et al. 2000). Several solutions to overcome these drawbacks are possible, such as the acid addition system used at Axial Seamount, or maintaining the sample spool for reduced samples in a gas-impermeable housing with an oxygen stripper. OsmoSamplers with impermeable Cu sample tubing for gas analyses have also been successfully deployed (e.g., Lupton et al. 1998). In confined areas where brine would be a contamination concern, the outflow can be fitted with an impermeable bladder to collect the effluent.

The limited milliliter-sized volumes can cause difficulties when either specific analyses or low analyte concentrations require larger sample volumes. In these cases, sample volumes remaining after completing other analyses are combined, or larger samples are collected while sectioning the sample tubing. In either case, this will result in a decreased temporal resolution. It is recommended that analysis procedures and sample volumes required be planned in advance.

OsmoSamplers can also be used for studying processes that affect the chemical composition of porewaters while minimizing sampling artifacts. Typically, sediment cores are collected and squeezed or centrifuged to obtain pore fluids, but sampling artifacts using these methods can significantly alter the chemical composition of the pore fluids (de Lange et al. 1992). An alternative approach to collect pore fluids is to use a harpoon with several ports along a lance, or individual needles, that penetrate the sediment. Porewaters can then slowly be drawn into these ports and sample tubing over a period of weeks to years. By withdrawing porewaters at these slow rates, artifacts due to physical disturbance and mechanical separation are minimized.

OsmoSamplers have also been used to measure flow rates within or out of sediments. By using the outflow of the osmotic pump to inject a specific tracer solution upstream of the OsmoSampler intake, flow rates can be calculated by tracer dilution (e.g., Tyron et al. 1999; Weinstein et al. 2003).

Summary and conclusions

Tools for long-term monitoring of dissolved chemical species are needed to further understand non-steady state processes in the ocean, especially those that produce sporadic and rare events. The long-term samplers described herein offer several advantages over other systems. Because of their lack of dependence on electrical power and moving parts, they are inexpensive and robust. Osmotic pumps with Alza mem-

branes have worked reliably for periods of more than 3 yr. These pumps, operated at depths up to 4000 m, showed no significant effect on flow rate caused by ambient pressure, and can operate over a wide range of temperatures. OsmoSamplers can also be designed to fit into tight locations, such as in seafloor boreholes or terrestrial wells, and can contain up to 2.4 km of small-bore tubing for multi-year deployments in remote locations. A benefit of collecting sample fluids continuously is the provision for acquiring data with much higher temporal resolution than is possible with other available discrete samplers. This high resolution is in part due to recent advancement of ICP-OES analytical technologies that use extremely small sample sizes for multi-elemental analyses. In addition, the slow rate of sample inflow reduces effects on the local environment, thus minimizing concerns of a sampling artifact. Drawing sample fluid continuously ensures that significant sporadic or short-term events are included in the sample suite. Different materials can be used for the sample tubing, providing the capability to preserve concentrations of dissolved gases as well as trace metals. In addition, the system can add acid or a "fixing agent" to the sample stream to preserve the sample or prevent precipitation or adsorption.

In summary, OsmoSamplers can be designed to provide a range of flow rates and durations, allowing one to conduct a complete series of analytical measurements and to examine processes that occur at a variety of time scales. Thus, OsmoSamplers can easily be optimized to examine non-steady state behaviors of biogeochemical cycles in remote locations where traditional sampling is not possible. Their main advantage is their capability to collect sample with a high temporal resolution at a significantly reduced cost per sample. OsmoSamplers are relatively simple to fabricate, and can be deployed for up to several years in almost any limnological, marine, or groundwater environment, where temperature is reasonably stable.

References

- Abbott, M. R., K. H. Brink, C. R. Booth, D. Blasco, L. A. Codispoti, P. P. Niiler, and S. R. Ramp. 1990. Observations of phytoplankton and nutrients from a Lagrangian drifter off northern California. *J. Geophys. Res. Oceans* 95:9393-9409.
- Amundson, E. L., J. E. Pratt, and H. F. Hemond. 2000. Gastight sampler for sequential streamflow sampling. *Water Environ. Res.* 3:377-383.
- Bell, J., J. Betts, and E. Boyle. 2002. MITESS: a moored in situ trace element serial sampler for deep-sea moorings. *Deep-Sea Res.* 49:2103-2118.
- Boyle, E. A., R. A. Sherrell, G. T. Shen, M. P. Bacon. 1996. Temporal variability of lead in the western North Atlantic. *J. Geophys. Res.* 91:8573-8593.
- Chadwick, W. W., R. W. Embley, H. B. Milburn, C. Meinig, and M. Stapp. 1999. Evidence for deformation associated with the 1998 eruption of Axial Volcano, Juan de Fuca Ridge, from acoustic extensometer measurements. *Geophys. Res. Lett.* 26(23):3441-3444.

- Chapin, T. P., H. W. Jannasch, and K. S. Johnson. 2002. In situ osmotic analyzer for the year-long continuous determination of Fe in hydrothermal systems. *Analytica Chimica Acta* 463:265-274.
- Chavez, F. P., H. W. Jannasch, K. S. Johnson, C. M. Sakamoto, G. E. Friederich, G. D. Thurmond, R. A. Herlien, and L. A. Codispoti. 1991. The MBARI program for obtaining real-time measurements in Monterey Bay. *Proceedings Oceans* 91:1:327-333.
- Crank, J. 1975. *The mathematics of diffusion*, 2nd ed. Oxford, pp 89-103.
- Davis, E. E., A. T. Fisher, J. V. Firth, et al. 1997. Proc. ODP Initial Reports 168, Ocean Drilling Program, College Station, TX.
- , and K. Becker. 2002. Observations of natural-state fluid pressures and temperatures in young oceanic crust and interferences regarding hydrothermal circulation. *Earth Planet. Sci. Lett.* 204:231-248.
- Dickey, T., D. Frye, H. W. Jannasch, E. Boyle, and A. H. Knap. 1997. Bermuda sensor system testbed. *Sea Technology* 38:81-86.
- Embley, R. W., W. W. Chadwick Jr., D. Clague, and D. Stakes. 1999. 1998 eruption of Axial Volcano: Multibeam anomalies and seafloor observations. *Geophys. Res. Lett.* 26(23):3425-3428.
- Jannasch, H. W., K. S. Johnson, and C. M. Sakamoto. 1994. Submersible, osmotically pumped analyzers for continuous determination of nitrate in situ. *Anal. Chem.* 66:3352-3361.
- , and M. Kastner. 1995. Long-term continuous monitoring of fluid composition with an osmotically pumped fluid sampler. *International Workshop on Dynamics of Lithosphere Convergence*, Miyagi, Japan.
- Johnson, K. S., C. L. Beehler, and C. M. Sakamoto-Arnold. 1986. A submersible flow analysis system. *Anal. Chim. Acta* 179:245-257.
- , and H.W. Jannasch. 1994. Analytical chemistry under the sea surface: Monitoring ocean chemistry in situ. *Naval Res. Rev.* 46:4-12
- , and L. J. Coletti. 2002. In situ ultraviolet spectrophotometry for high resolution and long-term monitoring of nitrate, bromide and bisulfide in the ocean. *Deep-Sea Res.* 49:1291-1305.
- Karl, D. M., and R. Lukas. 1996. The Hawaii Ocean Time-series (HOT) program: Background, rationale and field implementation. *Deep Sea Res.* 43:129-156.
- de Lange, G. J., R. E. Cranston, D. H. Hydes, and D. Boust. 1992. Extraction of pore water from marine sediments: a review of possible artifacts with pertinent examples from the North Atlantic. *Mar. Geol.* 109:53-76.
- Li, Y.-H., and S. Gregory. 1974. Diffusion of ions in sea water and in deep-sea sediments. *Geochim. Cosmochim. Acta* 38:703-714.
- Lupton, J. E., E. T. Baker, and R. R. Greene. 1998. Anomalous helium and heat signatures associated with the 1998 Axial Volcano event, Juan de Fuca Ridge. *Eos* 79:8135.
- Massoth, G. J., E. T. Baker, R. A. Feely, D. A. Butterfield, R. E. Embley, J. E. Lupton, R. E. Thomson, and G. A. Cannon. 1995. Observations of manganese and iron at the CoAxial seafloor eruption site, Juan de Fuca Ridge. *Geophys. Res. Lett.* 22:151-154.
- Michaels, A. F., and A. H. Knap. 1996. Overview of the U.S. JGOFS Bermuda Atlantic Time-series Study and the Hydrostation S program. *Deep Sea Res.* 43:157-198.
- Mottl, M. J., C. G. Wheat, E. Baker, K. Becker, E. Davis, R. Feely, A. Grehan, D. Kadko, M. Lilley, G. Massoth, C. Moyer, and F. Sansone. 1998. Warm springs discovered on 3.5 Ma-old oceanic crust, eastern flank of the Juan de Fuca Ridge. *Geology.* 26:51-54.
- Rebstock, GA 2002. An analysis of a zooplankton sampling-gear change in the CalCOFI long-term monitoring program, with implications for copepod population abundance trends. *Prog. Oceanogr.* 53:215-230.
- Taylor, G. 1953. Dispersion of soluble matter in solvent flowing slowly through a tube. *Proc. Royal Soc.* 219:186-203.
- Theeuwes, F., and S.I. Yum. 1976. Principles of the design and operation of generic osmotic pumps for the delivery of semisolid or liquid drug formulations. *Ann. Biomed. Eng.* 4:343-353.
- Tijssen R. 1980. Axial dispersion and flow phenomena in helically coiled tubular reactors for flow analysis and chromatography. *Anal. Chim. Acta* 114:71-89.
- Tyron, M. D., K. M. Brown, M. E. Torres, A. M. Trehu, J. McManus, and R.W. Collier. 1999. Measurements of transience and downward fluid flow near episodic methane gas vents, Hydrate Ridge, Cascadia. *Geology* 27:1075-1078.
- van den Berg, J. H. M., R. S. Deelder, and H. G. M. Egberink. 1980. Dispersion phenomena in reactors for flow analysis. *Anal. Chim. Acta.* 114:91-104.
- Weeks, D. A., and K. S. Johnson. 1996. Solenoid pumps for flow injection analysis. *Anal. Chem.* 68:2717-2719.
- Weinstein, Y., M. Kastner, and H. Jannasch. 2003. The Mosquito: a new sampler for monitoring fluid and solute fluxes between the sediment and the ocean. *Geophys. Res.* [abstract.] 5:13720.
- Wheat, C. G., M. J. Mottl, E. T. Baker, R. A. Feely, J. E. Lupton, F. J. Sansone, J. Resing, G. T. Alebon, and N. C. Becker. 1997. Chemical anomalies in the water column from low-temperature hydrothermal venting on the eastern flank of the Juan de Fuca Ridge. *J. Geophys. Res.* 102:15433-15446.
- Wheat, C. G., H. W. Jannasch, J. Plant, C. L. Moyer, F. J. Sansone, and G. M. McMurtry. 2000. Continuous sampling of hydrothermal fluids from Loihi Seamount after the 1996 event. *J. Geophys. Res.* 105:19353-19368.
- Wheat, C. G., H. W. Jannasch, M. Kastner, J. N. Plant, and E. H. DeCarlo. 2003. Seawater transport and reaction in the upper oceanic basaltic basement: Chemical data from continuous monitoring of sealed boreholes in a mid-ocean ridge flank environment. *Earth Planet. Sci. Lett.* 216:549-564.

Submitted 30 July 2003

Revised 6 October 2003

Accepted 9 January 2004