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Use of diffusion samplers in oligotrophic lake sediments: Effects of free oxygen in sampler material

Abstract—In the anoxic sediments of an oligotrophic lake, acrylic pore-water diffusion samplers conditioned by a 30-d exposure to N_2 before use gave pore-water concentration profiles of total Fe, Fe^{2+}, dissolved reactive P, and SO_4^{2-} that were significantly different from those obtained with samplers in which only the aqueous dissolved O_2 had been removed by bubbling for 18 h with N_2. The differences in concentrations are attributable to the loss of substantial amounts of O_2 by the plastic material and reaction of the liberated O_2 with reduced pore-water constituents. Laboratory tests show that acrylic in equilibrium with atmospheric O_2 can store up to 1.6% (vol/vol) of O_2 that will be slowly lost (half-time, ~5.7 d) once exposed to an anoxic environment. Oxygen solubility at 23°C is highest in polycarbonate (3.7%) and Teflon (2.8%) and lowest in high-density polyethylene (0.6%) and polyvinylidene fluoride (0.8%). Samplers made of such materials should not be exposed to atmospheric O_2 for more than a few hours.

Diffusion samplers have become widely used to sample sediment pore waters since their introduction by Hesslein (1976). The samplers usually consist of plastic sheets bored with arrays of compartments that are filled with distilled water and covered with a porous membrane. Samplers are inserted into sediments for days to weeks, until chemical equilibrium between the compartments and the outside interstitial water is approached. Such samplers owe their popularity to their simplicity compared to other methods in which pore waters must be extracted by centrifugation or pressure filtration. These samplers are, however, prone to several artifacts (e.g. Carignan 1984; Carignan et al. 1985; Brandl and Hanselmann 1991). In particular, equilibration time and type of membrane are critical. When they are used to sample anoxic pore waters, dissolved oxygen must be removed from the compartments, usually by bubbling the samplers with N_2 in distilled water for 12–24 h, depending on sampler configuration.

During our work in the anoxic sediments of oligotrophic lakes on the Canadian Shield, we have observed in several instances a light yellow-orange coloration of anoxic pore waters sampled with diffusion samplers made of acrylic (Plexiglas), even when care was taken to remove dissolved oxygen from the samplers by initially bubbling them for 12–24 h with N_2 and to insert them into the sediments rapidly. In some cases, faint orange membrane stains were observed on the entire length of the samplers. We initially attributed these observations to high DOC concentrations in pore waters or to the possible persistence of Fe(III) compounds in anoxic sediments (Lovley and Phillips 1986; Giblin et al. 1990). Another possible explanation for these observations is the diffusion of molecular oxygen out of the plastic in quantities large enough to cause the oxidation and precipitation of some pore-water Fe^{2+} that diffuses into the compartments.

We tested the latter possibility in August 1991 in Lake Tantaré, a small (1.1 km^2) oligotrophic lake (Chl *a*, ~0.2–0.5 μg liter^{-1}; total P, ~0.15 μmol liter^{-1}) 40 km north of Québec City (47°04'N, 71°32'W). Our samplers were 17 × 40 cm and made of acrylic plates (12 mm thick); they contained two vertical rows of horizontal compartments (70 × 6 × 10 mm deep, 4-mm spacing) covered with a Gelman HT-200 membrane (0.2-μm nominal pore size). Six samplers were initially cleaned with a P-free detergent, soaked for 2 weeks in 0.5 N H_2SO_4, and rinsed with distilled water. Three of these samplers were then placed (unassembled) in N_2 for 30 d to allow O_2 to diffuse out of the plastic (anoxic samplers); the others (oxic samplers) were exposed to a normal atmosphere. The six samplers were then processed as usual. They were rinsed again and filled with deionized water, assembled in air, and bubbled with N_2 for 18 h in distilled water in a single acrylic container (wall thickness, 5 mm) that

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was sealed and taken to the field within 4 h. The use of a single deaeration bath ensured that all six samplers had the same residual dissolved O_2 concentration in the compartments. At the field site, the samplers were removed from their O_2-free bath and inserted within 2 min into the sediments in a 5- × 5-m area.

The site selected for this study is a 15.5-m-deep hypolimnetic station located below the photosynthetic compensation depth in the westernmost basin of the lake. Recent sediment accumulation rate (^{210}Pb) is 4.1 mg cm^{-2} yr^{-1}, or 0.8 mm yr^{-1} (Carignan and Tessier 1985). The sediments have a 60% organic matter content and a surficial 0.2–1.0-cm-thick oxic layer underlain by anoxic sediments containing 0.1% reduced inorganic S (FeS_{am} + FeS_2, Carignan 1988). Pore-water pH varies from 5.4 at the sediment–water interface to 6.3 at 20 cm below the interface. Sediment is irrigated by chironomids (500–1,000 m^{-2}) to a depth of 3–4 cm. Sediment oxygen consumption measured with benthic chambers during the ice-free period is 2.0 mmol m^{-2} d^{-1} (Carignan unpubl.).

After an equilibration period of 16 d, each sampler was retrieved and completely sampled within 2 min. The samples (3 ml) were injected into clean polystyrene containers to which 30 µliter of 1 N Ultrex HCl had been added as a preservative. When we retrieved the samplers we noted that those submitted to the 30-d N_2 pretreatment had colorless pore waters and unstained membranes (except for a ~5-mm-wide orange band at the interface), whereas pore waters in those which were treated normally had a distinct orange tint and their membranes were stained. Samples were stored for 1–6 weeks at 4°C until analyzed for dissolved reactive P (DRP), dissolved reactive FE(II) (henceforth Fe^{2+}), total Fe (TFe), and SO_4^{2-}. For each treatment, six profiles of TFe and DRP were analyzed (the two rows of each sampler were analyzed), whereas only three profiles of Fe^{2+}, NH_4^+, NO_3^-, and SO_4^{2-} were obtained. DRP (molybdenum blue), NH_4^+ (indophenol blue), NO_3^- (cadmium reduction), and Fe^{2+} (TPTZ) were measured with a Technicon AutoAnalyzer (Technicon methods 154-71W, 100-700 W/B, 155-71W, 109-71W/B+, respectively) using 2- or 5-cm flow cells. TFe was measured by flame atomic absorption and SO_4^{2-} by ion chromatography (Dionex DX-300; detection limit, 0.2 µmol $liter^{-1}$).

Since each sampler had two vertical rows of compartments, we had a possibility of six profiles for each treatment. We maximized replication for certain constituents (DRP, TFe) by verifying whether two horizontally adjacent compartments on a sampler could be considered independent samples by generating, for each treatment, two populations of concentration differences between adjacent or nonadjacent compartments. Model 1 ANOVA showed that adjacent or nonadjacent concentration differences were not significantly different ($P < 0.05$). In other words, horizontal variability of concentrations was comparable at the scale of centimeters to meters. All other tests of significance ($P < 0.05$) on the effect of treatment (oxic vs. anoxic) on concentration differences reported here are based on ANOVA performed on population sizes of six or twelve compartments (3 or 6 profiles × 2 vertically adjacent compartments) for each treatment.

Pore-water profiles (Fig. 1) obtained with both treatments show the classical vertical reduction sequence [NO_3^-, Fe(III), SO_4^{2-}] expected on thermodynamic grounds. Exposure time to N_2 had no detectable effect on NH_4^+ and NO_3^- profiles. The virtually identical NH_4^+ profiles show that sediment metabolism was horizontally homogeneous within the 25-m^2 site. However, profiles of TFe, Fe^{2+}, DRP, and SO_4^{2-} showed significant differences that are consistent with the release of substantial quantities of O_2 by the plastic material of the oxic samplers. TFe was systematically higher and more variable in the oxic than in the anoxic samplers. TFe profiles obtained with oxic samplers also showed a pronounced TFe peak just below the interface that was not significant in profiles obtained with anoxic samplers. As a result, concentration gradients of TFe observed below the interface with oxic samplers were twice as high as those observed with anoxic samplers. Prolonged treatment with N_2 also influenced Fe speciation. In the 5–25-cm zone, TFe was essentially equivalent to Fe^{2+} for the anoxic samplers but significantly higher than Fe^{2+} for the oxic samplers. In the oxic samplers, the ~30% difference between TFe and Fe^{2+} is probably attributable to the reaction of O_2 with Fe^{2+} to form hydrous oxides.

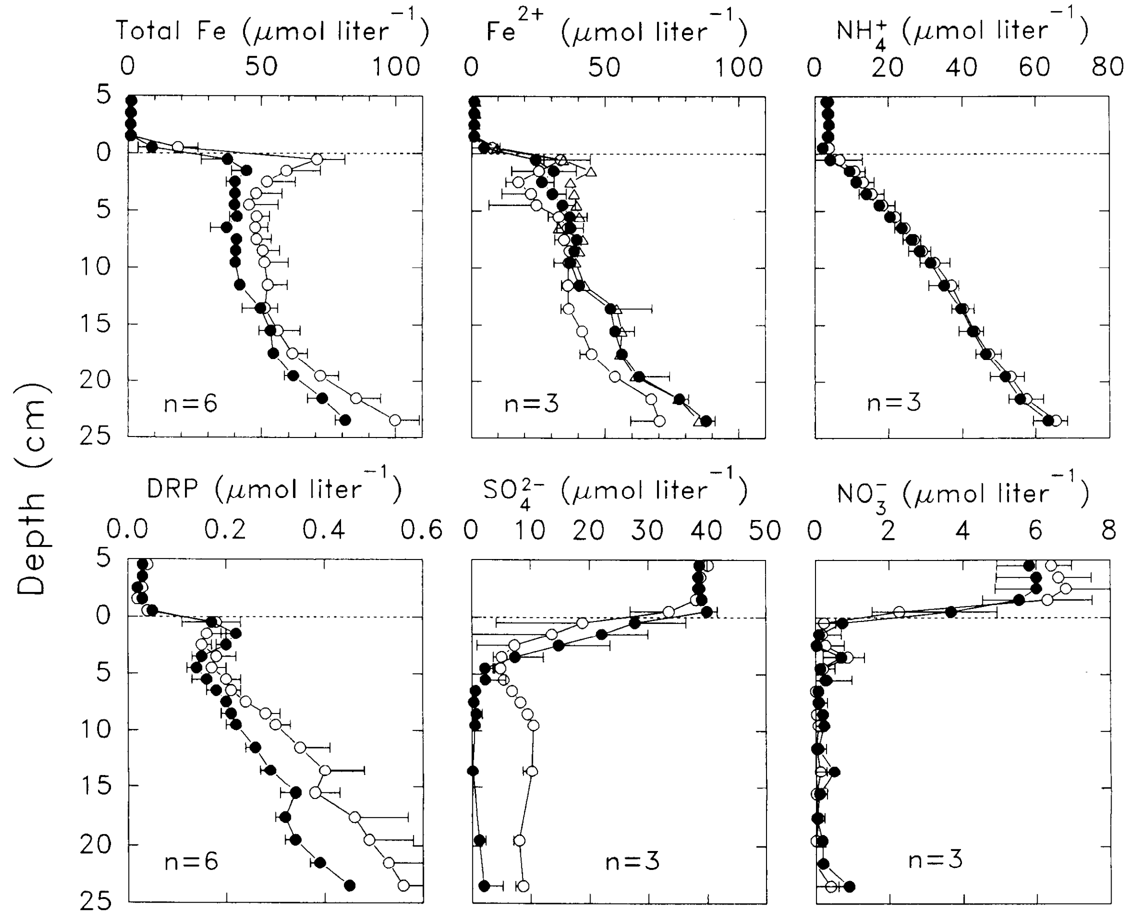

Fig. 1. Pore-water profiles obtained with diffusion samplers bubbled for 18 h with N_2 before insertion into sediments (○) and samplers exposed for 30 d to N_2 before use (●). The Fe^{2+} panel also shows TFe (△) for the three profiles for which Fe^{2+} was measured. Error bars show ± 1 SE of six (TFe, DRP) or three replicate profiles (*see text*).

This interpretation is further supported by significantly lower Fe^{2+} concentrations in the oxic samplers.

During previous tests carried out in September 1986 at the same site, we deployed six identically treated samplers (18 h of initial bubbling). One vertical row of compartments was sampled as above, whereas on-line N_2-purged 25-mm holders with 0.45-μm Nuclepore filters were used to sample the adjacent row. Even if the samples had the characteristic yellow-orange color, no significant difference in TFe concentration was observed between the filtered and unfiltered samples. These results suggest that much of the precipitated hydrous oxides could be of colloidal size. The formation of hydrous Fe oxides is likely to influence the distribution of other pore-water constituents that are either unstable in their presence (H_2S) or that can be strongly adsorbed (orthophosphate, trace metals).

DRP concentrations were significantly higher in the 8–25-cm interval of the oxic profiles (Fig. 1). A diffuse-layer surface complexation model (Dzombak and Morel 1990) was used to test the hypothesis that the higher analytical DRP concentrations obtained with oxic samplers were due to the adsorption of reactive phosphate onto the hydrous Fe oxides that presumably form in these samplers. We assumed that the difference between TFe and Fe^{2+} (1.5–10 μmol liter^{-1}) corresponds to hydrous FE oxides and that the anoxic DRP corresponds to the DRP concentrations in the oxic sam-

Table 1. Calculated phosphate adsorption (Fe-ox-P) onto hypothetical colloidal hydrous Fe oxides ({Fe-ox}) forming in oxic samplers, and observed analytical DRP excess in oxic vs. anoxic samplers. Fe oxide surface area and site concentrations were calculated from {Fe-ox} and specific values reported by Dzombak and Morel (1990).

Depth (cm)	pH	{Fe-ox} (μmol liter^{-1})	Surface (m^2 liter^{-1})	[Sites]	DRP	Fe-ox-P	DRP excess
				(μmol liter^{-1})			
4.5	6.20	5.5	0.29	1.1	0.14	0.36	0.03
8.5	6.15	10.0	0.53	2.0	0.21	0.72	0.07
13.5	6.20	1.5	0.08	0.3	0.29	0.13	0.11
19.5	6.24	10.0	0.53	2.0	0.34	0.76	0.15

plers. pH data previously collected at the same site were used in the calculations. We further assumed a specific surface area of 600 m^2 g^{-1} and a site density of 0.2 mol mol^{-1} for hydrous Fe oxides and used the intrinsic complexation constants determined by Dzombak and Morel (1990). These values are averages reported by Dzombak and Morel. The results (Table 1) give Fe-bound P concentrations that are higher than but within the same order of magnitude as the excess DRP observed in oxic profiles. Thus, phosphate adsorption appears, in theory, to be more than sufficient to account for higher DRP concentrations in oxic profiles. The higher concentrations predicted for adsorbed P may be due to a number of factors, including the presence of Mo-reactive organic P in the pore water and uncertainty in adsorption equilibrium constants and specific surface and site density values assumed by hydrous Fe oxides.

Sulfate profiles obtained with the oxic samplers were strikingly different from those obtained with the anoxic samplers (Fig. 1). With both samplers, SO_4^{2-} concentrations initially decreased within the first 5 cm and were not significantly different within that interval. However, $[SO_4^{2-}]$ remained at 5–10 μmol liter^{-1} in the oxic samplers, although it reached much lower or undetectable values in the anoxic samplers. Substantial (5–20 μmol liter^{-1}) residual SO_4^{2-} has often been observed in anoxic pore waters sampled by diffusion (e.g. Rudd et al. 1986; Carignan and Nriagu 1985; Schwedhelm et al. 1988; Brandl and Hanselmann 1991). The present results suggest that some of the SO_4^{2-} may be produced by the reaction of residual O_2 with dissolved reduced sulfur compounds diffusing into the compartments or with solid phases (FeS, FeS_2) present in the anoxic sediments.

We measured the rate of O_2 loss by acrylic and by six other common polymers initially at equilibrium with atmospheric O_2 (Fig. 2) by placing 16.4 cm^3 of each material cut as 34.7 × 7.5 × 6.3-mm sticks into 60-ml glass serum bottles filled with He and capped with butyl rubber septa and Al crimps. The specific surface of the sticks (6.42 cm^2 cm^{-3}) is similar to that of our pore-water samplers (5.63 cm^2 cm^{-3}). Empty control bottles were also prepared. Free O_2 was initially flushed out of the bottles with 2 liters of He. The bottles were submerged into anoxic sediments (23°C) to prevent diffusion of atmospheric O_2 through the septa. Oxygen concentration inside the bottles was followed for 36 d by gas chromatography (TDC) with a Molecular Sieve 5A column and He as a carrier. The C.V. of triplicate bottles was <3%. The results (Fig. 2) show that the seven plastics can lose substantial amounts of O_2 for several days after their introduction into an O_2-free environment. Materials such as PVC, HDPE, PVDF, and Delrin released considerably less O_2 than Teflon, polycarbonate, and acrylic. Oxygen release $M(t)$ (μmol cm^{-2}) over time (t) follows a relationship of the form

$$M(t) = M_\infty[1 - \exp(-bt)]. \qquad (1)$$

M_∞ is the O_2 released at infinite time, and b is the O_2 loss rate constant. Nonlinear regression was used to estimate the characteristic M_∞ and b values of each polymer stick (Fig. 2). The half-times for O_2 diffusion out of the sticks varied from 0.6 d (Teflon) to 9.1 d (PVDF). These values are reported in Table 2 along with our experimental and published O_2 and H_2O solubilities (Raff 1971). Note that our $t_{1/2}$ values for O_2 release apply only to the particular size and shape of the experimental polymer sticks. The specific surface of the sticks (6.3 cm^2 cm^{-3}) is higher than that of our pore-water samplers (5.63 cm^2 cm^{-3}), so $t_{1/2}$ values may be slightly higher for our samplers.

In a second set of experiments, we compared the penetration of F^-, Cl^-, NO_3^-, and SO_4^{2-} ions into Teflon, HDPE, Delrin, and PVDF by soaking the sticks in a mixture (0.5 M each) of NaF, $NaNO_3$, NaCl, and H_2SO_4 for 10 d. The sticks were then washed and left for 7 d

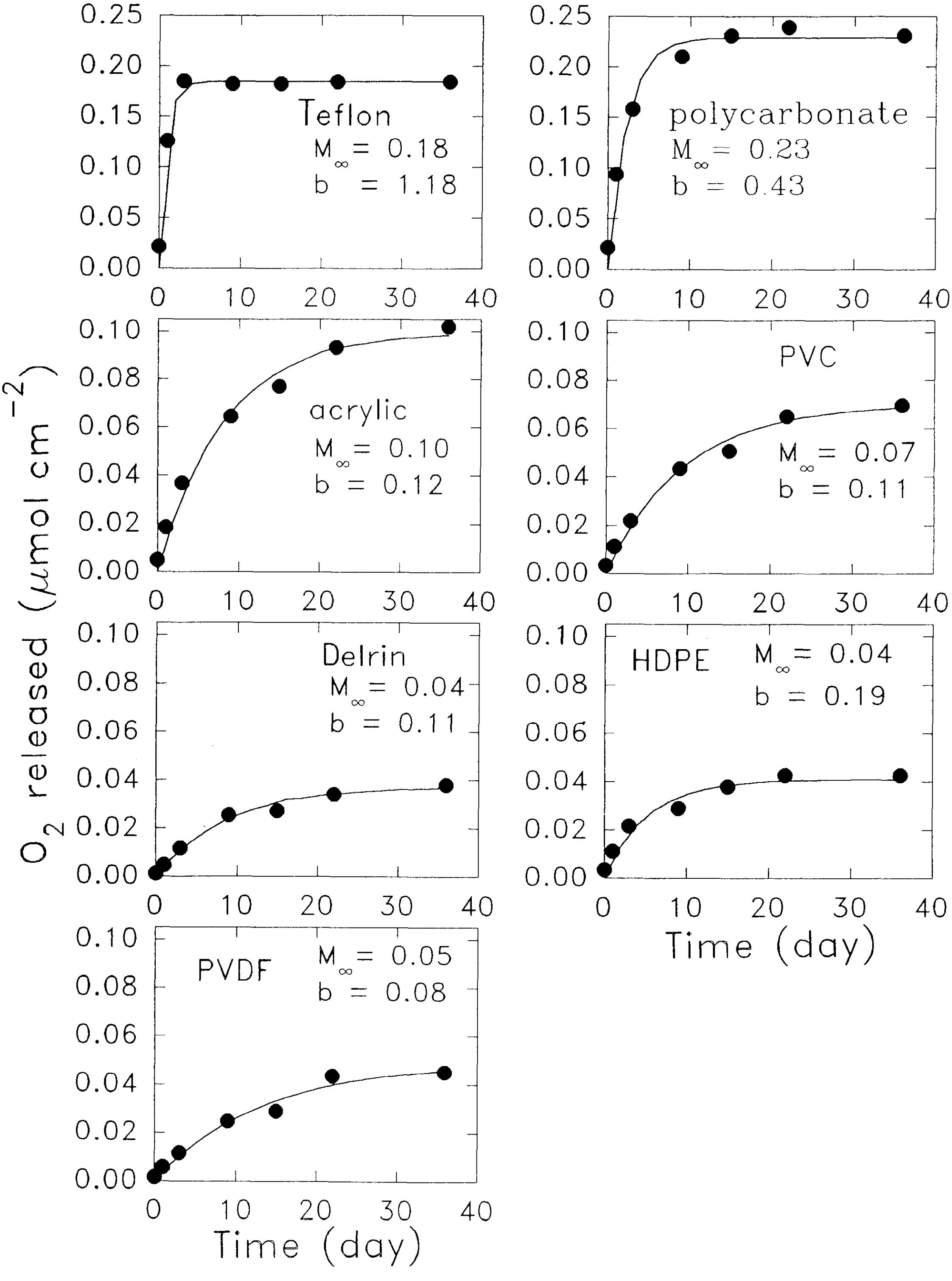

Fig. 2. Time-course of O_2 release by sticks (34.7 × 7.5 × 6.3 mm) of seven common polymers initially at equilibrium with atmospheric O_2 with curve-fit parameters to Eq. 1. Note that M_∞, b, and $t_{1/2}$ (Table 2) depend on the specific

in PTF tubes containing ultrapure deionized water. Anions were measured by ion chromatography. The four materials released large amounts of F^- (>0.05 μmol cm^{-2}) but no detectable Cl^- (<3 × 10^{-4} μmol cm^{-2}). NO_3^- release was below detection (<10^{-4} μmol cm^{-2}) for Teflon, HDPE, and PVDF but was 112 × 10^{-4} μmol cm^{-2} for Delrin. All four polymers released trace amounts of SO_4^{2-} (Teflon, 3.5 × 10^{-4} μmol cm^{-2}; HDPE, 3 × 10^{-4} μmol cm^{-2}; Delrin, 4.5 × 10^{-4} μmol cm^{-2}; PVDF, 1.5 × 10^{-4} μmol cm^{-2}).

After 15 d (a frequently used equilibration time for pore-water samplers), 0.083 μmol cm^{-2} of O_2 (=0.53 μmol cm^{-3}) had diffused out of the acrylic material (Fig. 2). Our samplers have 6.1 cm^3 of acrylic per chamber, with 57% of their total surface as internal chamber walls. Since chamber volume is 3.1 cm^3, the amount of O_2 lost to the compartments after 15 d is equivalent to ~600 μmol O_2 $liter^{-1}$ or more than twice the saturation concentration O_2 in water at 20°C. The actual rate of O_2 diffusion into the chambers and the amount of O_2 released may be slightly lower because the specific surface of the sticks (6.42 cm^2 cm^{-3}) used in the experiment was higher than that of the samplers (5.63 cm^2 cm^{-3}) and the field temperature was lower. In any case, the quantity of O_2 lost is more than enough to account for the observed chemical differences between pore waters collected with oxic and anoxic samplers. Although an initial 12–24 h of bubbling with N_2 does eliminate most of the dissolved O_2 present inside the compartments of such samplers, such bubbling is clearly insufficient to drive off the even larger amounts of O_2 present in the acrylic material ($t_{1/2}$ for release, 5.7 d) or in any of the other six polymers tested. We expect the resulting artifacts to be particularly important in oligotrophic lakes where pore waters and sediments have relatively low reductant concentrations.

Table 2. Oxygen and water absorption properties of the seven polymers tested. Oxygen solubilities and half-times of O_2 release are for 34.7 × 7.5 × 6.3-mm sticks (specific surface of 6.42 cm^2 cm^{-3}) initially in equilibrium with atmospheric O_2; values in parentheses are calculated from solubility coefficients reported by Brandrup and Immergut (1989) at unspecified temperatures in the 0–80°C range. Water absorption and specific gravity values are from Raff (1971).

Polymer	O_2 solubility (%vol/vol)	$t_{1/2}$ (d)	H_2O absorption (%wt/wt)	Sp gr (g cm^{-3})
Teflon	2.8(4.5)	0.6	0.00	2.1–2.3
Polycarbonate	3.7(11.2)	1.6	0.15	1.20
Acrylic	1.8(1.9)	5.7	0.4	1.18–1.19
PVC (clear)	1.1(0.6)	6.5	0.6	1.39
Delrin	0.6	5.0	0.25	1.42
HDPE	0.6(0.4)	3.7	0.15	0.94–0.97
PVDF	0.8	9.1	0.04	1.75

The ideal polymer for construction of diffusion samplers should have a very low O_2 solubility or a very long $t_{1/2}$ for O_2 release. Inspection of Fig. 2 and Table 2 shows that none of the materials tested has these qualities. All seven polymers can store and release O_2 in quantities large enough to potentially modify the chemical composition of anoxic pore waters. HDPE and PVDF appear to be more suitable than the other polymers we tested. The solubilities of O_2 and aqueous ions are relatively low in these two materials; they absorb little water and are unaffected by dilute mineral acids. Delrin is not recommended because of its susceptibility to dilute acids. Pore-water samplers made of these materials should be conditioned for at least 30 d in an O_2-free environment before assemblage and use, and exposure to O_2 should be kept to a minimum between uses.

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surface of the material. Values for actual diffusion samplers may differ by a factor of ~2, depending on design. Delrin—polyformaldehyde (–CH_2–O–); PVC—polyvinyl chloride; HDPE—high-density polyethylene (–CH_2–); PVDF—polyvinylidene fluoride (–CH_2–CF_2–).

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