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Stable Isotope Composition of Dissolved O_2 Undergoing Respiration in a Ground-Water Contamination Gradient

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ABSTRACT

Dissolved oxygen is a key ground-water constituent, controlling both the geochemistry and microbiology of an aquifer. Two methods were developed to analyze isotopes of dissolved O_2: a traditional method, that uses dual inlet mass spectrometry for analyzing CO_2 previously converted from O_2, and a newly developed method, that uses continuous flow isotope-ratio mass spectrometry for analyzing directly the isotopes of dissolved O_2. The major differences between the two methods are in the sample size and sample handling in the field and laboratory. Isotope analyses of dissolved O_2 were used to document the occurrence of microbial respiration near the boundary of an anoxic ground-water plume consisting of treated wastewater at the Massachusetts Military Reservation on Cape Cod. The upper boundary of the plume was a mixing zone between contaminated, anoxic plume water and uncontaminated, oxic local recharge water. Concentrations of dissolved oxygen decreased downward near the top of the plume and were inversely correlated with $\delta^{18}O$. Apparent oxygen isotope fractionation factors (ε) were -1 to -10 per mil (‰) in the absence of a dilution correction, whereas values as low as -20 ‰ were obtained by adjusting for the effects of dilution.

INTRODUCTION

Microorganisms are important factors in controlling the geochemistry of ground water. One of the most significant microbial processes is oxygen respiration, which controls ground-water redox conditions by altering concentrations of dissolved oxygen. In contaminated environments, oxygen demand and aerobic versus anaerobic pathways of degradation largely determine whether remediation of a particular set of contaminants occurs and what kind of additional *in situ* reclamation approaches might be possible.

Because molecular oxygen is a terminal electron acceptor, it is indicative of total microbial community metabolism. Because microbial processes fractionate low molecular weight molecules owing to the tendency of lighter isotopes to react faster than heavier isotopes, the fractionation of oxygen isotopes can be used to identify oxygen respiration in aquatic systems. The importance of oxygen as a ground-water constituent is widely recognized. But despite the reported fact that aerobic respiration results in fractionation of oxygen isotopes in the ocean (Bender, 1990; Quay, and others, 1993), the fractionation of oxygen isotopes in ground-water environments has not been widely investigated.

For the study of isotopic variation by oxygen respiration upon the residual oxygen pool, we developed two methods to analyze the $\delta^{18}O$ of dissolved oxygen. The major differences between the two methods are the requirements for amount of dissolved O_2, and procedures for handling samples in the field and laboratory. The traditional method requires a dual inlet isotope ratio mass spectrometry (DI-MS) to measure the isotope ratio of oxygen in CO_2 obtained by quantitative conversion of O_2 to CO_2. Sample size requirements are such that 500 mL of water with at least 1 mg/L dissolved oxygen is required for the off-line separation and conversion of oxygen to CO_2 The newly developed method uses continuous flow isotope

ratio mass spectrometry (CF-IRMS) with on-line separation and direct isotope-ratio measurement of dissolved gas constituents (i.e. O_2 and N_2). This allows a smaller sample size, about 125-mL, with a minimum concentration of 0.2 mg/L of dissolved O_2 . This paper describes the 2 methods and gives an application at a USGS test site.

STUDY SITE

The study site is a freshwater, unconfined aquifer located on western Cape Cod, Massachusetts (figure 1)

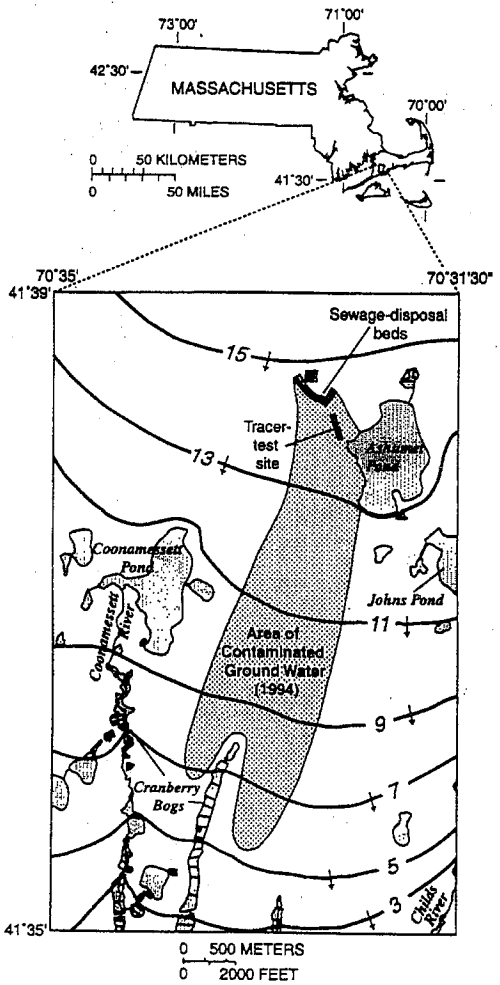

Figure 1. Study area location.

A plume of contaminated ground water was formed by continuous discharge of dilute, treated sewage to the land surface between 1936 and 1995 (LeBlanc, 1984). The plume is roughly 5 km long, 1.5 km wide, and 25 m thick. There are vertical and horizontal gradients of various properties in and around the plume, such as specific conductance (50 to 400 µS), dissolved oxygen (0 to 8 mg/L), dissolved organic carbon (1 to 4 mg/L), chloride (0 to 28 mg/L), sulfate (4 to 30 mg/L), and nitrate (0 to 16 mg of N /L) (Smith and others, 1991). The test site is equipped with an array of multi-level samplers (MLS). The MLS allow sampling of the ground water at closely spaced intervals in vertical and horizontal directions (LeBlanc and others, 1991). Each MLS consists of 15 color-coded polyethylene tubes (0.47 cm inside diameter, 0.64 cm outside diameter). The tubes run from the land surface down the inside of a 3.17-cm diameter PVC casing exiting through holes drilled through the PVC at various depths. This sand and gravel aquifer, characterized by both vertical and horizontal gradients of dissolved oxygen, shows a wide range of electron acceptor demand from pristine to moderately contaminated conditions.

SAMPLING

Based on preliminary oxygen concentration measurements, water samples were collected at the depth range that showed the steep oxygen gradient. Samples were collected by a peristaltic pump after stabilization of the chemistry of the well water. The concentrations of dissolved oxygen (O_2) were remeasured in the field by colorimeter (Chemetrics, Inc.), and water samples for $\delta^{18}O$ measurement of O_2 were collected promptly.

Samples for the traditional method were collected in approximately 500-mL"side arm"(2-chamber) evacuated vessels as described by Pearson and others (1978). Samples for the new method were collected in 125-mL serum bottles without headspace (Busenberg and others, USGS, unpublished data). Immediately before closing the bottle with a thick blue butyl rubber stopper, one KOH pellet (~100 mg) was dropped into each sample as a preservative. Samples were stored at 4 °C.

Samples for anions were filtered in the field (0.45 μm) and were analyzed by ion chromatography at the USGS, in Reston,VA., except for nitrate which was analyzed using a flow-injection autoanalyzer at the USGS laboratory in Boulder CO.

Water samples, which were saturated with air at 24 °C, and air samples were collected as control samples for both methods.

METHODS

For the traditional method, low pressure dissolved gases containing O_2 were extracted from the headspace under vacuum by a Toepler pump through a capillary to minimize water vapor in the gas phase. The oxygen gas was separated by gas chromatography (Révész and others, 1995) and converted to CO_2 by reaction with graphite at sufficiently low temperature (550-600 °C) to prevent CO formation. CO_2 was continuously frozen out in a liquid nitrogen-cooled trap to prevent its decomposition to CO in the presence of hot carbon. Yields of CO_2 were determined manometrically and isotope analysis was performed on a DuPont double collecting dual inlet mass spectrometer. The precision of this method was better than 0.2 per mil (1 σ), but it required large samples (500 mL with a minimum of 1 mg/L of dissolved O_2). In addition, it required relatively complex procedures in the field and laboratory.

The objectives of the new method were to (1) to simplify the procedures for sample collection and preparation, and (2) reduce the size of samples. In the laboratory, low-pressure headspace was created in each serum bottle by extracting about 10 percent of the water with a vacuum pump. The sample was re-equilibrated for 24 hours at room temperature. Then, constant-volume aliquots of the headspace were extracted through a syringe needle (23G1 gauge) into a He carrier gas equipped with a Nafion tube to remove water vapor. The He carrier gas was directed through a gas chromatograph for separation of its components (30-m long GS-Molesieve Plot GC Column) to the General-Purpose Interface inlet system of a Finnigan Delta Plus CF-IRMS. The CF-IRMS integrates masses 32 and 34 of the headspace aliquots, each containing about 1 μmol of O_2. The reproducibility of the method was better than 0.2 per mil (1σ). Because the isotopic compositions of air oxygen and nitrogen are constant (Dole, 1954), we used pressurized air, collected in an aluminum cylinder with an oil-free air compressor (Révész 1993), as a reference gas. In this manner, we could determine not only the isotopic composition of O_2, but also the isotopic composition of dissolved nitrogen relative to air.

Both methods were tested with air and air-saturated water samples for precision and accuracy.

RESULTS AND DISCUSSION

For the traditional method, the precision for $\delta^{18}O$ isotope measurement was better than 0.2 per mil (1σ). $\delta^{18}O$ values of the control air samples averaged 0.79 per mil more negative than those in air-saturated water (ASW), which is in good agreement with the theoretical value (Klots and Benson, 1961). With the CF-IRMS method, we monitored not only the $\delta^{18}O$ value of the O_2 component of the gas mixture, but the $\delta^{15}N$ of the N_2 component. The one-sigma standard deviation for n=3 of the isotope ratio measurements was 0.16 for $\delta^{18}O$ and 0.10 for $\delta^{15}N$. $\delta^{18}O$ and $\delta^{15}N$ of air samples were 0.75 per mil and 0.49 per mil more negative, respectively, than those in air-saturated water, in good agreement with the published values.

Samples from the Cape Cod test site were analyzed by the traditional method (DI-IRMS).

The concentrations of O_2 at all sites decreased from about 250 - 340 μM (80 - 90% of air-saturation) in the overlying wedge of local recharge water to less than 10 μM in the contaminated plume. High O_2 concentrations also occurred beneath the plume.

The $\delta^{18}O$ of O_2 ranged from about +24 per mil with respect to VSMOW reference water to +45 per mil, and the $\delta^{18}O$ of O_2 was correlated inversely with O_2 concentrations (figure 2).

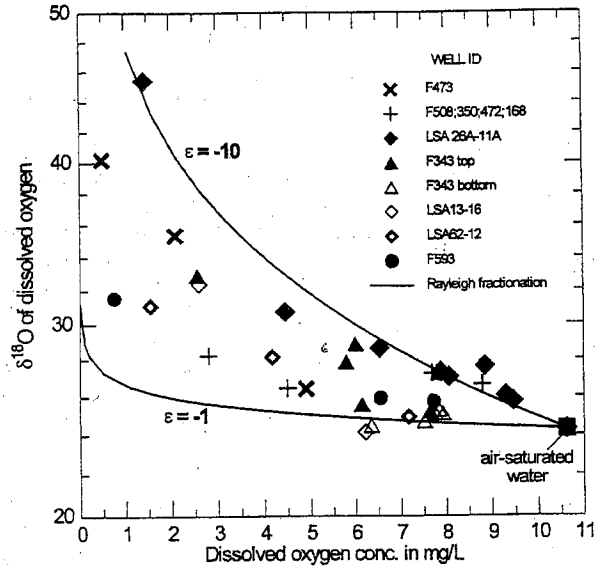

Figure 2. Isotopic composition of the diminishing oxygen reservoir as a function of the remaining fraction of dissolved oxygen reservoir.

The minimum $\delta^{18}O$ values of O_2 were near air-saturation, but sometimes higher than atmospheric equilibrium values. It is possible that the ground waters were recharged with 80-90 percent air saturation values, or that they lost 10-20 percent of their O_2 during transport through the unsaturated zone (Böhlke and others, 1999). The isotopic-ratio and concentration results of O_2 are qualitatively consistent with kinetic isotope fractionation by microbial O_2 reduction and indicate clearly that some O_2 reduction has occurred within the transition zone. The data were evaluated by using Rayleigh fractionation equation ($\ln(R/R_1)=\varepsilon\ln(C/C_1)$), where R and R_1 are the measured and initial $^{18}O/^{16}O$ ratios and C and C_1 are corresponding O_2 concentrations. Results indicate that the apparent oxygen isotopic fractionation factors (ε = -10 ‰) (figure 3) are somewhat smaller than most reported values derived from closed-system experiments or field studies (ε =-20 ±10‰) (Lane and Dole, 1956,Bender 1990, Quay and others, 1993).

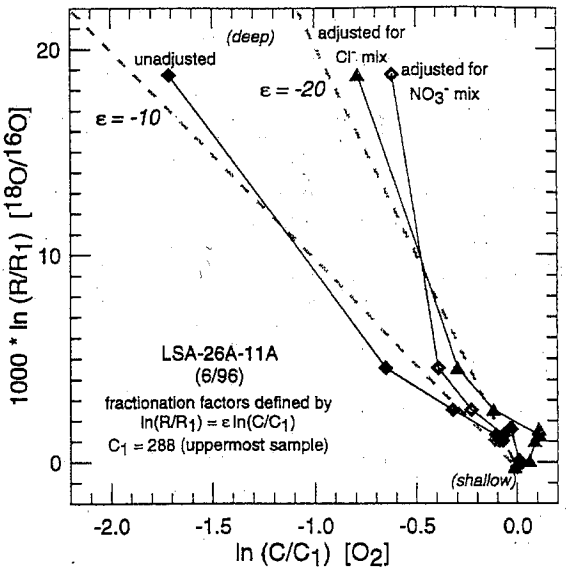

Figure 3. Isotope fractionation during O_2 reduction near the upper boundary of the contaminated plume at well LSA 26A-11A. The Rayleigh distillation equation yields linear arrays with slopes equal to apparent isotope fractionation factors (epsilon). The apparent epsilon value obtained by assuming a constant value for the un-reacted O_2 concentration (C_1) was around -10 per mil; larger epsilon values (around -20 per mil) were obtained by using C_1 values adjusted to account for conservative mixing between plume water and non-plume water, with mixing fractions determined from gradients in either NO_3^- or Cl^-(see figure 4).

At well LSA 26A-11A, the specific conductance and the concentrations of NO_3^-, Cl^-, and SO_4^{--} all increase from near background (uncontaminated) values to much higher values in the plume between about 10 and 13 m elevation (figure 4). By using those constituents as conservative indicators of the mixing fractions of anoxic plume water and oxic overlying groundwater, it is possible to adjust the values of $C[O_2]$ for individual samples to derive a more accurate relation between $\delta^{18}O$ of dissolved oxygen and the progress of the O_2 reduction reaction (figure 3). With that adjustment, the value of ε at well 26A-11A is around -20 per mil more like the closed-system values. A similar adjustment of data from Site F473-M011 altered the apparent value of ε from about -7 to -11 per mil.

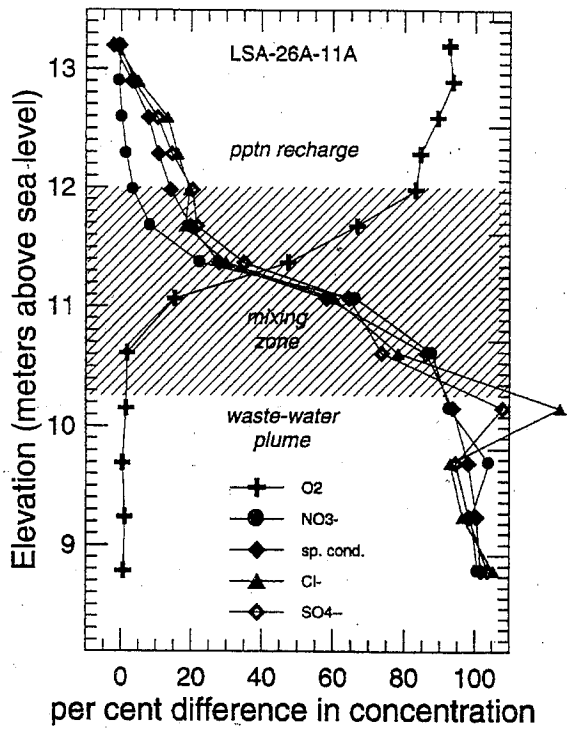

Figure 4. Concentration fraction of selected constituents, in well LSA-26A-11A. The per cent difference implicates the fraction of plume water (high NO_3^-, sp.cond., Cl^-, and SO_4^{--}) in mixtures of plume water and overlying precipitation recharge.

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