Practical Considerations for Measuring Hydrogen Concentrations in Groundwater

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Several practical considerations for measuring concentrations of dissolved molecular hydrogen (H₂) in groundwater, including (1) sampling methods, (2) pumping methods, and (3) effects of well casing materials were evaluated. Three different sampling methodologies (a downhole sampler, a gas-stripping method, and a diffusion sampler) were compared. The downhole sampler and gas-stripping methods gave similar results when applied to the same wells. The diffusion sampler, on the other hand, appeared to overestimate H₂ concentrations relative to the downhole sampler. Of these methods, the gas-stripping method is better suited to field conditions because it is faster (~30 min for a single analysis as opposed to 2 h for the downhole sampler or 8 h for the diffusion sampler), the analysis is easier (less sample manipulation is required), and the data computations are more straightforward (H₂ concentrations need not be corrected for water sample volume). Measurement of H₂ using the gas-stripping method can be affected by different pumping equipment. Peristaltic piston, and bladder pumps all gave similar results when applied to water produced from the same well. It was observed, however, that peristaltic-pumped water (which draws water under a negative pressure) enhanced the gas-stripping process and equilibrated slightly faster than water produced from the same well. The second method is referred to as a "downhole sampler" (Figure 1a). This sampler is designed to obtain a groundwater sample at in situ pressure that is not in contact with metal or plastics that might absorb or produce H₂. It consists of a glass chamber (35 mL) with glass valves at either end. The glass components of the downhole sampler were hand-blown and sized so that they could fit into a 5.08 cm (2 in.) well. The sampler is lowered down a well, the valves at each end are opened, and water is drawn through the bottom inlet and out the outlet at the top with a peristaltic pump at land surface. After water has flushed the sampler for several minutes, the pneumatic valves are activated with a separate peristaltic pump, trapping a water sample in the glass sampler. The sampler is then brought to land surface. At land surface, two glass syringes continuously produced by fermentative microorganisms metabolizing natural or anthropogenic organic matter. This H₂ is then utilized by respirative microorganisms that most commonly use Fe(III), sulfate, or carbon dioxide (CO₂) as terminal electron acceptors. Significantly, each of these terminal electron-accepting processes (TEAPs) has a different affinity for H₂ uptake (1). CO₂ reduction (methanogenesis) has the lowest H₂ affinity, and observed steady-state H₂ concentrations in methanogenic aquifers are relatively high (5–30 nmol/L (nM)). Sulfate reduction has a slightly greater affinity for H₂ than methanogenesis and is observed to have lower characteristic H₂ concentrations (1–4 nM). Fe(III) reduction (0.2–0.8 nM) and nitrate reduction (~0.1 nM) have even greater affinities for H₂ and are observed to have progressively lower steady-state H₂ concentrations (1). Thus, concentrations of H₂ are a useful indicator of TEAPs in groundwater systems (~3), particularly when interpreted in the context of electron acceptor (nitrile, Fe(III), and sulfate) availability and the presence of final products (Fe(II), sulfide, and methane) of microbial metabolism (4).

Because the biodegradation of many groundwater contaminants is affected by TEAP conditions, H₂ concentrations are increasingly being used to characterize contaminated groundwater systems (5, 6). Like many trace constituents of ground water, however, measured H₂ concentrations can be affected by sampling methods, by different pumping systems, and by materials used to construct wells. The purpose of this paper is to document some of these sampling-induced effects and to illustrate how they can affect the measurement and interpretation of H₂ concentrations in groundwater.

Study Sites

Each of the sites used in this study has been previously described. The comparison of sampling methods was performed at the Rimini site in South Carolina (3), the effects of different pumping methods were investigated at the Hanahan site in South Carolina (7), and the effects of steel casings were investigated at Wurtsmith AFB in Michigan (5) and Fort Wainwright in Alaska (8). On the other hand, the diffusion sampler was observed to produce H₂ and was not suitable for measuring H₂ in groundwater. Measurements from two field sites indicate that iron or steel well casings produce H₂, which masks H₂ concentrations in groundwater. PVC-cased wells or wells cased with other materials that do not produce H₂ are necessary for measuring H₂ concentrations in groundwater.

Introduction

Understanding the distribution of microbial terminal electron-accepting processes is fundamental to characterizing the microbiology and geochemistry of groundwater systems. Under anaerobic conditions, molecular hydrogen (H₂) is

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FIGURE 1. Construction and operation details of (a) downhole sampler, (b) gas stripper, and (c) the diffusion probe sampling devices used to measure H₂ concentrations in groundwater.

(2.5 mL) with needles are flushed with H₂-free N₂, and one (syringe A) is filled with 2 mL of N₂. The needles on the syringes are then pushed through a butyl rubber septum in the side of the sampler (Figure 1a). The N₂ from syringe A is injected into the sampler while 2 mL of displaced water is collected in syringe B. The sampler is then shaken for 1 min to equilibrate the dissolved H₂ with the gas phase. The 2 mL of water is pushed back into the sampler, and 2 mL of water was collected in syringe A. After another minute of shaking, the gas bubble is drawn into syringe B and analyzed for H₂ using gas chromatography with reduction gas detection (Trace Analytical, Menlo Park, CA).
The second method used for measuring H₂ in groundwater is a gas-stripping procedure that has previously been referred to as the "bubble strip" method (4-7). In this method, a standard 250-ml gas-sampling bulb (Supelco) is continuously purged with groundwater at a rate of about 500 ml/min (Figure 1b). A 20-ml bubble of H₂-free N₂ gas is introduced into the sampling bulb through the septum. As the bubble is vigorously agitated by the stream of inflowing water, slightly soluble gases such as H₂ are stripped from the water to the gas phase over time and asymptotically come into equilibrium with the water flowing through the bulb. After equilibrium is achieved (~20-30 min), a gas sample is withdrawn from the bulb and analyzed for H₂.

The third method used to measure H₂ in groundwater was a diffusion probe. In this method, a length of Teflon tubing fitted with a three-way valve on either end is wound around a PVC cylinder that is weighted with sand (Figure 1c). The Teflon tubing is filled with H₂-free N₂, and the diffusion probe is lowered into the well and suspended in the interval of interest. H₂ in the aqueous phase diffuses through the Teflon tubing and accumulates in the artificially created headspace. Once equilibrium between the aqueous and gas phases is achieved (approximately 8 h), the probe is removed from the well and H₂ in the gas phase is quantified.

**H₂ Concentration Computations.** The downhole sampler procedure yields a concentration of H₂ in the gas phase (μL/L) that may be converted to molar units (nm/L) using a conversion factor derived from the ideal gas law (25 °C):

$$1 \, \mu L/H/1 = 40.9 \, nm/H/1$$

The concentration of H₂ in the aqueous phase (Cₐ, nm/L) may then be calculated from the concentration of H₂ in the gas phase (C₉; nm/L) using Henry's law:

$$C_9 = C_a / 50.4 \quad (2)$$

The concentration of H₂ in the original water sample (C₉ₜ, nm/L) may then be calculated with the mass balance equation:

$$C_9_{t} = \left\{ (C_9 V_T) + (C_a V_w) \right\} / V_w$$

where Vₜ is the volume of gas and Vₜ is the volume of water. For downhole sampler method, if the measured concentration of H₂ in the 2.0-ml gas phase is 1.0 μL/L, the calculated H₂ concentration in the 35-ml water sample is 3.15 nM.

For the gas-stripping procedure and the diffusion sampler, the concentrations of H₂ in the aqueous phase are assumed to be in equilibrium with the gas phase. The concentration of H₂ in the aqueous phase can then be calculated directly from the measured gas-phase concentration using eqs 1 and 2. For example, if the measured concentration of H₂ in the gas phase is 1.0 μL/L, the concentration of H₂ in the groundwater is 1.0 × (40.9/50.4) = 0.812 nM.

**Pumping Methods.** Four different methods for pumping groundwater were evaluated. These were (1) a peristaltic pump (Geotech Environmental Equipment, Inc., Denver, CO), (2) a stainless steel piston pump (Bennett Sample Pumps, Inc., Amarillo, TX), (3) a bladder pump (Well Wizard Bladder Pump, QED Environmental Systems, Ann Arbor, MI), and (4) a stainless steel submersible pump (Fultz Pumps, Inc., Lewistown, PA). The peristaltic pump draws water under negative pressure, the piston and bladder pumps push water under positive pressure, and the Fultz pump pushes water under positive pressure by impellers driven by a direct current (dc) electrical motor.

**Well Casing Materials.** The effects of well casing materials on H₂ concentrations were evaluated at the Wurtsmith and Fort Wainwright sites. The Wurtsmith site is instrumented with galvanized steel-cased and PVC-cased wells. The Fort Wainwright site is instrumented with iron-cased and PVC cased wells.

**Results and Discussion**

**Sampling Method Comparison.** The downhole sampler method has been described previously (3) and has been shown to accurately reflect H₂ concentrations in groundwater. In practice, however, this method is problematic. The downhole sampler is cumbersome to use, is extremely delicate, and several hours of sampling time are often required to obtain a single measurement. For these reasons, the gas-stripping and diffusion probe methods, which are much easier to use, were developed. These three sampling methods, however, have not previously been systematically compared.

A comparison of H₂ measurements made by the downhole sampler and gas strip methods in the wells of the Rimini site are shown in Figure 2a. In this comparison, the H₂ concentrations obtained with the two methods plot closely to the 1:1 line, indicating good correspondence. H₂ concentrations measured with the downhole sampler and the diffusion probe (Figure 2b) do not correspond as well, with the diffusion probe indicating H₂ concentrations that are about 2 nM higher than those indicated by the downhole sampler in the higher concentration range. In addition to not comparing well to the downhole sampler, the diffusion probe method had other drawbacks. The long equilibration time (overnight) involved makes it difficult to sample a large number of wells rapidly. Also, the fact that water standing in a wellbore may exhibit different H₂ concentrations than water in the aquifer is a possible problem. Because the wells at Rimini flowed continuously under artesian pressure (3), the problem was minimized in this study. Nevertheless, this may be a problem.
at other sites. Finally, it was found that the Teflon tubing of the diffusion probe itself stores considerable amounts of H₂.

In one instance, a particular diffusion probe was used to sample a well tapping a methanogenic zone where groundwater exhibited relatively high concentrations (~10 nM) of H₂. When this same probe was then refilled with N₂ and placed in a well with much lower H₂ concentrations characteristic of Fe(III) reduction (~0.2 nM), H₂ stored in the Teflon continuously leaked into the sampler for as long as 1 week before equilibration with the lower H₂ concentration was achieved. Thus, the equilibration time required for the diffusion probe can vary significantly. This, in turn, can easily lead to erroneous H₂ measurements under time-limited field conditions. For these reasons, the diffusion probe is not well-suited for routine field investigations.

Of the three methods used in this study, the gas-stripping method was by far the most practical to perform under field conditions. The equilibration time was relatively short (~20–30 min), and moving between wells with widely different H₂ concentrations did not cause any apparent variations in measured H₂ concentrations. With this method, it was possible to obtain about one H₂ measurement per hour under field conditions. Furthermore, because H₂ measurements obtained with the gas-stripping method corresponded well with measurements made with the downhole sampler and because previous studies have shown that gas-stripping H₂ measurements correspond with measured microbial processes (3), this is an appropriate methodology for measuring H₂ concentrations in groundwater.

Pumping Method Comparison. The effects of pumping methods on measured H₂ concentrations using the gas-stripping procedure was evaluated at the Hanahan, SC, site (3, 7). Each pumping method was applied to the same well on the same day. Three of the pumping methods (the bladder pump, the piston pump, and the peristaltic pump) gave virtually the same results (mean of three measurements plus or minus one standard deviation) when applied to a well screened in a methanogenic zone (well MW-USGS-31B) (Figure 3). In contrast, the direct current-driven submersible pump gave much higher H₂ concentrations. Because H₂ can be electrolytically produced by dc, it is probable that the high H₂ concentrations observed using this submersible pump reflect the interaction of dc with water. This behavior has been noted by other investigators using dc submersible pumps as well (D. Kamphill, U.S. EPA, verbal communication, 1996). For this reason, dc submersible pumps are not considered suitable for measuring H₂ concentrations in groundwater.

Alternating current-driven pumps were not systematically tested in this study. However, previous studies have used alternating current-driven pumps without apparent interference from electrolytically produced H₂ (9). Further studies on the efficacy of alternating current-driven pumps for sampling H₂ are warranted.

There were slight apparent differences observed between the equilibration times required for each pumping method (Figure 4a). When the peristaltic pump was used, H₂ concentrations in the bubble took about 20 min to reach equilibrium. The piston pump appeared to take slightly longer to equilibrate (~25 min), and the bladder pump appeared to take even longer (~30 min) to reach equilibrium. However, because these were single measurements done in time series (i.e., without duplicate analyses), it cannot be concluded with certainty that these apparent differences are statistically significant. Nevertheless, because suction (peristaltic) pumping places a negative pressure on the water column, it may facilitate degassing, resulting in shorter equilibration times (Figure 4a). When the peristaltic pumping rate was increased from 500 to 1000 mL/min, equilibration was achieved in proportionally less time (Figure 4b) as would be expected. These observations indicate that equilibration times and thus the accuracy and reproducibility of the gas-stripping method can vary depending on pumping methods and rates. These
TABLE 1. Measured Concentrations of Dissolved Hydrogen in Fe(III)-Reducing Groundwaters (H₂ Concentrations Expected To Range from 0.2 to 0.8 nM) from Wurtsmith AFB (WS) and Fort Wainwright (FW) Produced from PVC, Galvanized Steel, and Iron Well Casings

<table>
<thead>
<tr>
<th>well number and casing material</th>
<th>measured hydrogen concn (nM)</th>
<th>apparent TEAP*</th>
</tr>
</thead>
<tbody>
<tr>
<td>WS FT9 (Steel)</td>
<td>16.0</td>
<td>methanogenesis</td>
</tr>
<tr>
<td>WS FT9 (PVC)</td>
<td>0.57</td>
<td>Fe(III) reduction</td>
</tr>
<tr>
<td>FWM-6884 (PVC)</td>
<td>0.20</td>
<td>Fe(III) reduction</td>
</tr>
<tr>
<td>FWM-6390 (PVC)</td>
<td>0.22</td>
<td>Fe(III) reduction</td>
</tr>
<tr>
<td>FWM-7073 (PVC)</td>
<td>0.19</td>
<td>Fe(III) reduction</td>
</tr>
<tr>
<td>FWM-7072 (PVC)</td>
<td>0.75</td>
<td>Fe(III) reduction</td>
</tr>
<tr>
<td>FWM-6894 (PVC)</td>
<td>0.53</td>
<td>Fe(III) reduction</td>
</tr>
<tr>
<td>FWM-7075 (PVC)</td>
<td>0.21</td>
<td>Fe(III) reduction</td>
</tr>
<tr>
<td>FWD-294 (iron)</td>
<td>&gt;400</td>
<td>undetermined</td>
</tr>
</tbody>
</table>

*Terminal electron accepting process.

results indicate that specific combinations of pumping systems and rates should be individually tested to evaluate the length of time needed for gas-aqueous phase equilibration.

Effects of Iron Well Casings. Under anoxic conditions, metallic iron can reduce water leading to the generation of free H₂ according to (10)

Fe₀(s) + 2H₂O(l) → Fe²⁺(aq) + 2OH⁻(aq) + H₂(aq) (4)

It is possible, therefore, that well casings containing metallic iron can generate H₂ and this may interfere with the measurement of H₂ in groundwater. Field observations made at several sites confirm that iron casings can interfere with measuring H₂ concentrations in groundwater. Table 1 shows data gathered from two sites, Wurtsmith AFB in Michigan, and Fort Wainwright in Alaska. The Wurtsmith site has been previously described (5, 11) and is characterized by petroleum-hydrocarbon-contaminated groundwater. Much of the plume is Fe(III) reducing, and groundwater contains between 0.2 and 0.8 nM H₂. At one location in the Fe(III)-reducing part of the plume, the same portion of the aquifer is screened by a galvanized steel well and by a PVC well. The wells are approximately 3 m apart. The measured H₂ concentration in the PVC well was 0.57 nM, consistent with Fe(III) reduction (Table 1). However, the measured H₂ concentration in the galvanized steel well was 16 nM, which would indicate methanogenic conditions (Table 1). Other geochemical evidence from this site (5, 11) indicates that this portion of the plume is in fact Fe(III) reducing, suggesting that the H₂ measurement in the galvanized steel well was not representative of actual redox conditions in the aquifer but reflected H₂ generation by the steel casing.

Even more extreme differences in H₂ concentrations measured in metal versus PVC wells were observed at the Fort Wainwright site. Hydrogen concentrations measured in groundwater produced from PVC wells indicated uniformly Fe(III)-reducing conditions at the site (Table 1), and other geochemical evidence suggests that Fe(III) reduction predominates at this site (8). In contrast, an iron-cased well located 5.6 m from the nearest PVC well (well FWM-7070) showed H₂ concentrations of greater than 400 nM H₂. This H₂ concentration is much higher than is characteristic of microbially controlled aquatic sediments (1) and does not appear to be indicative of microbial conditions in the aquifer itself. These observations at the Wurtsmith and Fort Wainwright sites suggest that steel or iron well casings may artificially increase measured H₂ concentrations in groundwater. This, in turn, suggests that H₂ concentrations measured in steel or iron-cased wells are not reliable indicators of aquifer redox conditions.

In conclusion, H₂ concentrations in groundwater can be measured in the field using a downhole sampler, a gas-stripping procedure, or a downhole diffusion sampler. Of these methods, the gas-stripping procedure is more suited for routine groundwater investigations. The equilibration time of the gas-stripping procedure can be affected by (1) the use of positive-pressure (piston or bladder pump) or negative-pressure (peristaltic) pumping systems and by (2) the flow rate of water to the gas-sampling bulb. It was also found that dc electrically-driven submersible pumps produce H₂ by electrolysis and interfere with H₂ measurements in groundwater. Finally, there is evidence that iron or steel well casings can produce H₂ under anaerobic conditions that can interfere with the measurement of H₂ concentrations in groundwater.

Acknowledgments

This research was funded by the Toxics Substances Hydrology Program of the U.S. Geological Survey. The use of trade names in this paper does not constitute endorsement by the U.S. Geological Survey.

Literature Cited


Received for review January 31, 1997. Revised manuscript received June 4, 1997. Accepted June 14, 1997.*

ES970065C

*Abstract published in Advance ACS Abstracts, August 15, 1997