

CHAPTER 2

APPLICATIONS OF A TOTAL DISSOLVED GAS PRESSURE PROBE IN GROUNDWATER STUDIES

Introduction

The measurement of dissolved gas concentrations has become widespread in ground water hydrology. Dissolved gases are utilized as environmental tracers in several ground water dating techniques ($^3\text{H}/^3\text{He}$, chlorofluorocarbons, noble gas radioisotopes, etc.), and in the determination of recharge temperature (Mazor, 1991). They are also now used as applied tracers (e.g., Sanford et al., 1996). Because dissolved gases can act as electron acceptors, electron donors, or reaction products in microbial reactions, their concentrations are regularly measured at contaminant sites where bioremediation either is or may be employed. The field measurement of total dissolved gas pressure has many potential applications in ground water studies that employ dissolved gases, including: (a) enabling the use of gas-filled passive diffusion samplers for determining accurate dissolved gas concentrations; (b) determining approximate levels of excess air, which may provide information about the time and location of recharge; (c) screening wells for air contamination, which can compromise the accuracy of dissolved gas tracer techniques; (d) detection of a trapped gas phase (bubbles), which can reduce hydraulic conductivity (Ronen et al., 1989) and impede the transport of dissolved solutes and gases

(Donaldson et al., 1998); and (e) determining relative concentrations of CH₄ and CO₂ when they are known to be highly abundant.

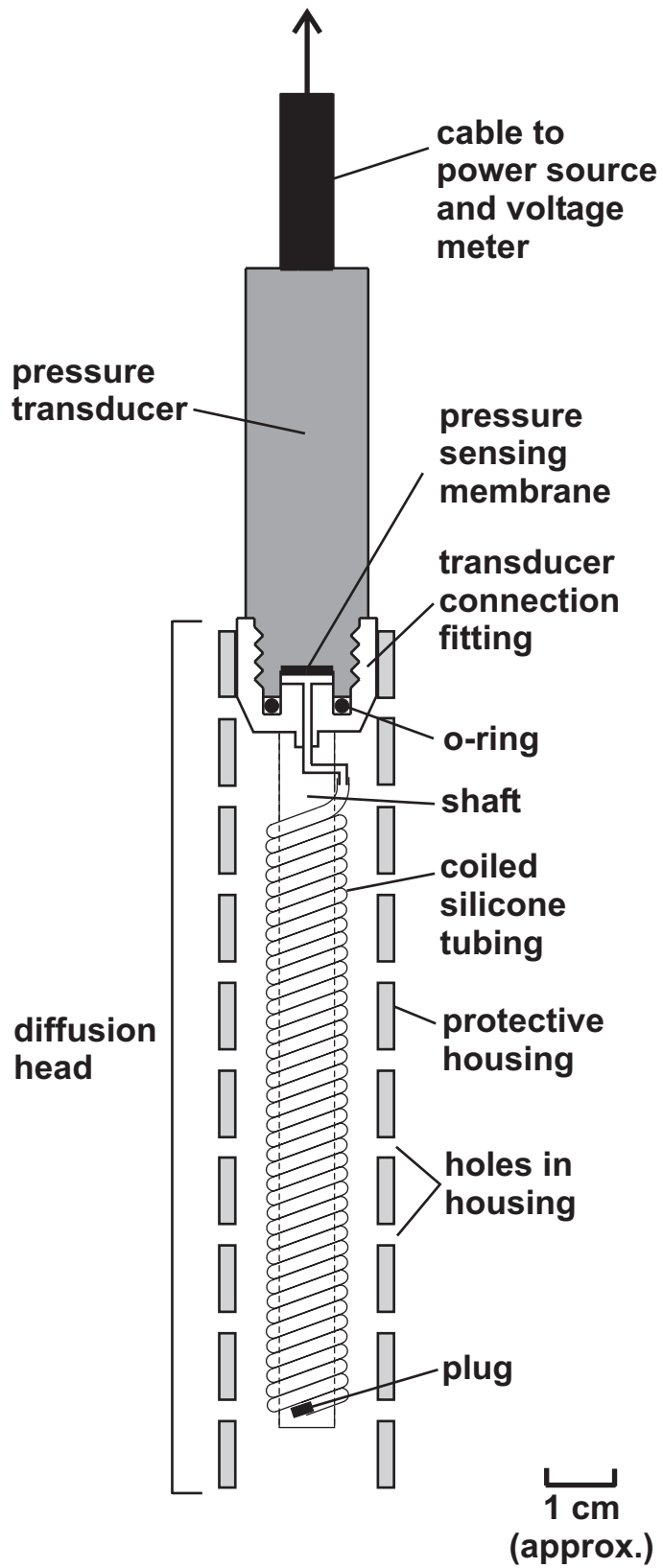
Total dissolved gas pressure (TGP) probes of various designs have been used in fisheries management, oceanography, and limnology for several years (e.g., D'Aoust and Clark, 1980; Anderson and Johnson, 1992; Watten et al., 1997). Recently, TGP probes suitable for use in standard-sized ground water monitoring wells have become commercially available (we are aware of the following manufacturers: Common Sensing, Alpha Designs, Hydrolab, and Dryden Aqua). Yet, a thorough search of the ground water literature reveals no reported field measurements of total dissolved gas pressure in ground water. In this paper we present what are, to our knowledge, the first reported ground water dissolved gas data collected using a TGP probe. We also explain the basic operating principles of TGP probes, emphasizing issues unique to ground water applications. Finally, we discuss some potential applications of TGP probes in ground water studies.

Prior to the commercial availability of TGP probes that fit in 5.1-cm (2-inch) diameter and smaller monitoring wells, we developed a 2.5-cm diameter TGP probe for our own use. The following discussion of probe operating principles, equilibration speed, and accuracy specifically refers to our own probe. However, our probe is similar enough in design to the commercially available TGP probes for it to be considered generally representative of these other probes.

General Design and Operating Principles

The TGP probe consists of a pressure transducer connected to a diffusion head (Figure 2.1). Our probe's transducer is a Druck PDCR 830 Series on the end of a cable

Figure 2.1. Generalized design of our total dissolved gas pressure probe. The design is similar to that of commercially available total dissolved gas pressure probes suitable for ground water applications.



ranging in length from 15 to 120 m. The transducer measures gauge pressure to ± 10 psi and must be used in conjunction with a barometer to determine absolute pressure. It is powered by a 10-volt source and has a rated accuracy of $\pm 0.1\%$. The diffusion head screws on to the transducer creating a void volume in which the dissolved gas pressure can be measured with the transducer. The diffusion head consists of a transducer connection fitting and a 2-m length of small-diameter (0.64 mm), thin-walled (0.17 mm) silicone tubing coiled around a shaft. The silicone tubing is permeable to gases, but not water. The fitting provides a connection between the tubing, which is plugged at the opposite end, and the transducer's pressure-sensing membrane. The void volume thus consists of the space between the connection fitting and the pressure sensing membrane, the space inside the connection fitting, and the space inside the tubing.

Dissolved gases are exchanged between the water and the probe's void volume via diffusion through the wall of the silicone tubing. The void volume simply contains air prior to submersion in water. When the probe is submerged, gas exchange across the tubing wall will proceed until equilibrium is achieved between the dissolved gases and the gases filling the void volume. The partial pressure of gas i in the void volume at equilibrium (p_i) is controlled by Henry's law:

$$p_i = \frac{C_i}{H_i(T, S)} \quad (2.1)$$

where C_i is the dissolved concentration of gas i and H_i is the Henry's law proportionality constant for gas i , a function of temperature, T , and salinity, S . Equation (1) does not apply to p_{H_2O} because the water vapor pressure depends on temperature only. As dictated by Dalton's law, the total pressure in the void volume is the sum of the partial pressures

of each gas in the void volume. After equilibration is achieved, the probe therefore measures the equilibrium total dissolved gas pressure, $P_T = \sum p_i$.

The Henry's law proportionality constant is independent of the hydrostatic pressure, P_h (although we should note that we are unaware of any literature that specifically supports this independence). This means that both p_i and P_T are independent of P_h in the water column outside the void volume, because the compressibility of the void volume is limited. This also means P_T should be constant with depth if temperature and dissolved gas concentrations remain constant.

Nitrogen and O₂ compose approximately 99% of the atmosphere (dry), the remaining 1% being mostly Ar (Table 2.1). Because ground water equilibrates with the atmosphere prior to recharge, N₂, O₂, and water vapor will compose approximately 99% of the gas in the probe's void volume at equilibrium for most waters. Therefore, when the probe is used with a dissolved oxygen (DO) meter and a thermometer, p_{O_2} and p_{H_2O} can be determined and subtracted from P_T to yield a close approximation of p_{N_2} . Some waters may also have significant p_{CO_2} due to calcite dissolution or high CO₂ production in the unsaturated zone. Elevated p_{CH_4} is also possible due to anaerobic microbial reactions. The TGP probe should not be used to estimate p_{N_2} when concentrations of these other gases are suspected to be high.

Equilibration Speed and Accuracy

A gas diffusing between the water and the void volume must do so through both a boundary layer in the water and the silicone tubing wall. If the boundary layer is kept thin by stirring, the probe's equilibration time will approximately equal the time required for O₂ and N₂ to diffuse through the tubing wall (Anderson and Johnson, 1992). The

Table 2.1. Major Atmospheric Gases and Their Dissolved Concentrations in Air-Equilibrated Fresh Water

Gas	Atmospheric concentration ^a (mole fraction)	Henry's law constant ^b (cm ³ STP Kg ⁻¹ atm ⁻¹)		Dissolved concentration ^c (cm ³ STP Kg ⁻¹)	
		0 °C	15 °C	0 °C	15 °C
N ₂	0.781	23.66	17.06	18.37	13.10
O ₂	0.209	49.22	34.22	10.22	7.03
Ar	9.34 x 10 ⁻³	53.54	37.48	0.50	0.34

^a In dry air

^b From Benson and Krause (1976)

^c Assumes 100% humidity and equilibration pressure = 1 atm

transient equilibration time, t_E , for a gas is given by the following expression derived from Fick's first law of diffusion:

$$t_E = -\frac{V_v \delta}{AD_i} \ln\left(1 - \frac{E}{100}\right) \quad (2.2)$$

where

V_v = void volume

δ = tubing wall thickness

A = tubing surface area

D_i = diffusion constant for gas i in silicone

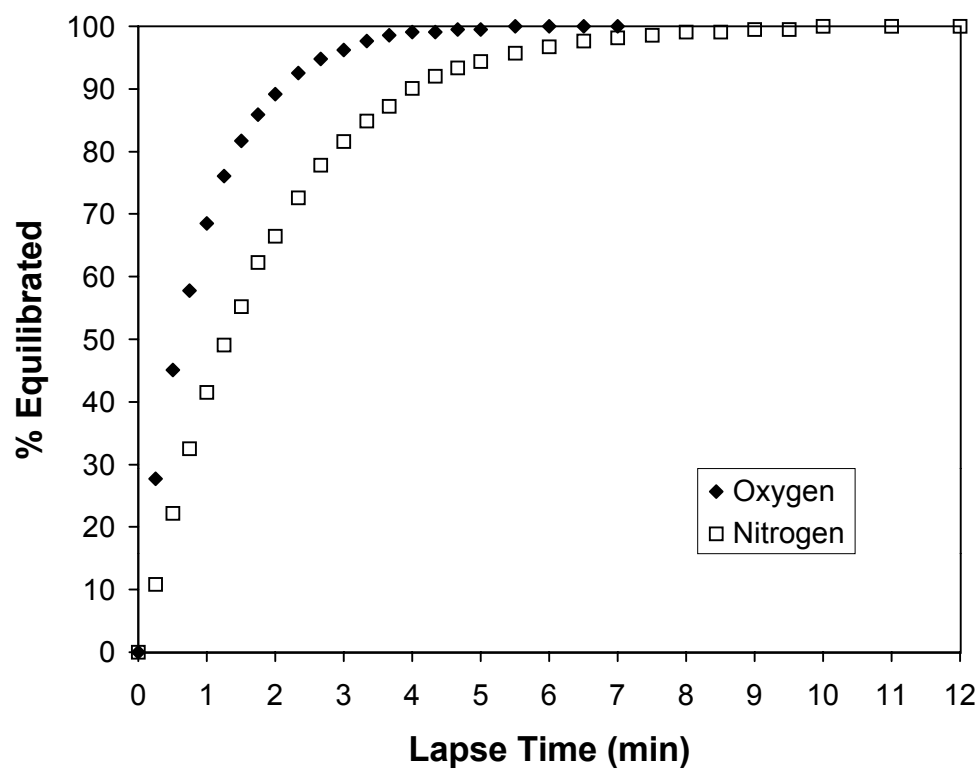
E = percent equilibrated, defined as:

$$E = \left[\frac{(p_i^t - p_i^o)}{(p_i - p_i^o)} \right] \times 100 \quad (2.3)$$

where p_i^o is the initial partial pressure of gas i in the void volume, and p_i^t is the partial pressure of gas i in the void volume at time t (Sanford et al., 1996; Anderson and Johnson, 1992). Recall that p_i is the partial pressure of gas i in the void volume at equilibrium, after equilibration is complete. Equilibration time is therefore a function of the time constant $V_v \delta / AD$. At 25°C, the diffusion constant for N₂ in silicone is half that of O₂ (Galletti et al., 1966). Therefore, equilibration of N₂ should usually control the probe's equilibration time.

Equilibration times for the commercially available TGP probes we are aware of range from 3 to 15 minutes. For our probe, equilibration time for O₂ is about 5 minutes and for N₂ is about 10 minutes at 22°C (Figure 2.2). Equilibration times in water near

Figure 2.2. Plot of lapse time versus % equilibrated for our total dissolved gas pressure probe. Equilibration times are about 5 minutes for O₂ and about 10 minutes for N₂. Reported complete equilibration times for commercially available probes range from 3 to 15 minutes.



0°C should be 20% to 30% greater (Carignan, 1998). Note that ground water is often oversaturated with N₂ and undersaturated with O₂ relative to atmospheric pressures, so that the transient total dissolved gas pressure is the net sum of the N₂ partial pressure increasing with time and the O₂ partial pressure decreasing with time. Extrapolating P_T from a transient total dissolved gas pressure should thus be performed with caution. The equilibration speed for some probes begins to decrease at some submersion depth. For example, equilibration slows down for our probe at depths greater than about 10 m. Although the cause is not certain, we suspect that it is due to either partial collapse of the diffusion tubing or minor leakage of water into the tubing (both effectively decrease the length of the tubing, increasing V_v/A). Note that very small amounts of water (not visible) leaking into the tubing may only compromise the equilibration speed (because a water drop will clog the capillary inside the tubing), but significant leakage will result in erroneous P_T measurements. Reported submersion depth limits of commercially available probes range from 2 m to 30 m, but at least one manufacturer claims consistent equilibration speeds to considerably greater depths. Equilibration speed will also decrease markedly if the probe is not stirred. One of the probes we are aware of has a built-in stirrer, but the rest must be stirred manually (gently moved up and down about 0.3 m in the water column).

The above equilibration speeds assume that the net amount of gas diffusing into or out of the void volume is negligible in comparison to the total amount of gas dissolved in the water in the sampled interval of the well. If such is not the case, then dissolved gases must migrate into or out of the aquifer in order for complete equilibration to occur. This migration can take several days, particularly if the well is screened in low-

permeability material and solute transport is diffusion-dominated (Harrington et al., 2000). The void volume of our probe and the others we are aware of is $< 0.3 \text{ cm}^3$. For a 5-cm diameter well, the net amount of gas gained or lost through equilibration of a probe with $V_v < 0.3 \text{ cm}^3$ is $\leq 1.5\%$ of the total amount of gas dissolved in the sampled interval (0.3 m) of the well. This assumes normal recharge and sampling conditions in which excess air is $\leq 6 \text{ cm}^3\text{STP/Kg}$ and the well temperature is $\leq 25^\circ\text{C}$. The assumption that complete probe equilibration does not require transport of dissolved gases into or out of the well casing thus appears valid for wells with a diameter of $\geq 5 \text{ cm}$. However, in a 2.5-cm diameter well, probe equilibration can result in up to a 6% change in the total amount of gas dissolved in the sampled interval, and for a 1-cm diameter well this number rises to 38%. We should note that another possible problem resulting from these large percentages of gas exchanging during probe equilibration is contamination of the well by atmospheric gases diffusing out of the void volume. Clearly, if TGP probes are developed in the future for use in smaller diameter wells, the void volume size must be reduced.

We performed two accuracy tests on our probe mainly to confirm the absence of unforeseen sources of error (Table 2.2). Additional concerns included possible air bubble entrapment and measurable variation of P_T with water depth resulting from non-negligible variation of p_{H_2O} with P_h . Air bubbles trapped on the probe and transported to depth would equilibrate with the water surrounding the probe at high pressure ($P_a + P_h$, where P_a is the atmospheric pressure at the top of the water column), possibly leading to erroneously high P_T measurements. In previous studies involving TGP probes (e.g., D'Aoust and Clark, 1980; Anderson and Johnson, 1992; Carignan, 1998), the dependence

Table 2.2. TGP Probe Accuracy Test Results

Depth (m)	Expected P_T (atm)	Measured P_T (atm)	P_T Difference (atm)
Test 1			
1	0.793	0.797	0.004
3	0.794	0.795	0.001
6	0.791	0.794	0.003
9	0.776	0.776	0.000
Test 2			
1	0.668	0.664	-0.004
3	0.670	0.666	-0.004
6.5	0.635	0.633	-0.002
9	0.624	0.625	0.001

of p_{H_2O} on P_h has been either ignored or assumed to be negligible. In the case of an air headspace in equilibrium with water, and the water pressure ($P_a + P_h$) and the headspace pressure being equal, the following equation describes the dependence of p_{H_2O} in the headspace on $P_a + P_h$, assuming water vapor to be an ideal gas:

$$p_{H_2O} = p_o \left(\exp \left[\frac{\bar{V}_{H_2O}}{RT} (P_a + P_h - p_o) \right] \right) \quad (2.4)$$

where p_o is the orthobaric pressure (p_{H_2O} when p_{H_2O} and the water pressure are the same), \bar{V}_{H_2O} is the molar volume of liquid water, and R is the universal gas constant (Castellan, 1971). This equation describes p_{H_2O} in the probe's void volume only for the case where the water is completely saturated with gas at all depths ($P_T = P_a + P_h$). In this special case, the increase in p_{H_2O} with P_h is indeed very small (<1% for waters 0° to 25°C) to a depth of about 140 m. However, ground water is usually undersaturated at depths greater than a few meters because P_T seldom exceeds 1.5 atm. If $\Delta P = P_a + P_h - P_T$, ΔP values can reach 10+ atm at typical ground water sampling depths. The accuracy tests were thus performed in part to determine if P_T increases measurably with water depth as a result of p_{H_2O} increasing with ΔP .

The general procedure for both tests involved filling a test well with water having a known P_T and measuring P_T at various depths. The test well was 10 m deep, constructed in a building stairwell out of transparent 5.1-cm diameter PVC pipe. For test 1, the well was filled with water equilibrated with air in the laboratory at known temperature and pressure. Water in the well was allowed to reach thermal stability because air in the stairwell was 2° to 5°C cooler than the equilibration temperature. A

vertical temperature gradient existed in the stairwell with the coolest air at the bottom.

Temperature and P_T were then measured at depths of 1 m, 3 m, 6 m, and 9 m.

Temperature measurements were necessary to calculate the expected P_T . The procedure for test 2 was the same as test 1, but the water was de-oxygenated (by adding sodium sulfite) between air equilibration and filling the well in order to maximize ΔP .

The tests indicate that our probe has an accuracy of ± 0.005 atm (Table 2.2). The probe's accuracy may actually be closer to ± 0.003 atm because uncertainty in the temperature ($\pm 0.2^\circ\text{C}$) and pressure (± 0.003 atm) at which the well water was air-equilibrated (i.e., uncertainty in expected P_T) could account for about half of the observed error. This is still slightly poorer than the rated accuracy of our probe's strain gauge (± 0.0012 atm), suggesting that other sources of error do exist. An accuracy of ± 0.003 to 0.005 atm is also slightly poorer than the reported accuracy of other TGP probes (0.0012 to 0.0026 atm), and should probably be considered an approximate minimum accuracy for TGP probes. This accuracy is adequate for most dissolved gas applications. In the use of passive diffusion samplers (Sanford et al., 1996), for example, an uncertainty of ± 0.005 atm results in an uncertainty of $\leq 1\%$ in dissolved gas concentrations, assuming typical P_T values (> 0.5 atm). Such an uncertainty is comparable to laboratory analytical error for dissolved gas measurements. Small bubbles were often observed on the diffusion head upon submersion. However, these consistently could be removed by vigorously shaking the probe. We therefore recommend shaking TGP probes immediately after submersion as a standard procedure to remove bubbles. Differences between measured and expected P_T show no significant correlation with depth, so any increase in p_{H_2O} caused by increasing ΔP appears to be smaller than other sources of

error. Although this may not be the case at greater measurement depths and water temperatures (higher ΔP values), the test results suggest that any such variations in p_{H_2O} are probably very small.

Potential Applications

Supporting Passive Diffusion Samplers

Passive gas-filled diffusion samplers have been recently developed for sampling dissolved gases (Sanford et al., 1996). These in-situ sampling devices consist of a length of copper tubing sealed at one end and connected to a sealed length of silicone tubing at the other. The samplers are placed in a well and left for an adequate period to allow dissolved gases in the water to equilibrate with the sampler headspace via diffusion through the silicone tubing. The samplers are then removed from the well and the copper tubing is immediately sealed, either with a valve or by crimping (cold weld). Gases in the sampler are then let directly into a mass spectrometer for analysis.

The standard method of sampling dissolved gases involves collecting a water sample in a length of copper tubing sealed at each end with clamps. Using passive diffusion samplers has several advantages over this standard technique, include the following: (a) it is less cumbersome and time consuming; (b) it eliminates concerns about incorporating bubbles into the sample during the sampling process, so excess air in the sample is known to be natural (Manning and Solomon, 2000); (c) gases need not be extracted from the samples in the laboratory; (d) no extraction of water from the well is required, minimizing both investigation-derived waste and disturbance to the natural ground water flow system; and (e) vertical profiles are possible in long well screens. However, attempts to create passive diffusion samplers that maintain constant volume

during sealing have been unsuccessful. Prior to sealing, the sampler's internal pressure equals P_T , but the slight volume change upon sealing means that the pressure in the sealed sampler is slightly different from P_T . As a result, the gas partial pressures measured in the sampler are not equal to the equilibrium partial pressures, which are required to calculate dissolved gas concentrations in the sampled water. The TGP probe measures P_T directly, so mole fractions obtained from sample analysis can be multiplied by P_T (instead of sampler total pressure) to derive more accurate dissolved concentrations.

Field Excess Air Probe

Most natural ground waters have dissolved gas concentrations in excess of those expected for water equilibrated with the atmosphere. The excess component typically has a composition very similar to air, and is thus termed 'excess air' (Herzberg and Mazor, 1979; Heaton and Vogel, 1981). Though the origin of natural excess air is not fully understood, it is typically attributed to the complete or partial dissolution of air bubbles trapped during water table fluctuations in the recharge zone (Stute and Schlosser, 2000). The amount of excess air should therefore be related to two main characteristics of the recharge zone: the aquifer material and the degree of water table fluctuation. This inferred relationship is supported by reported correlations between excess air and both lithology and precipitation amounts in the recharge area (Wilson and McNeill, 1997). Because these physical aspects of recharge could in turn be correlated with other important aspects of the ground water flow system, such as recharge location or ground water age, the ability to measure approximate excess air amounts in the field could be valuable.

If recharge temperature and elevation are moderately well constrained, the TGP probe can function as an excess air probe. When the probe is used with a DO meter, p_{N_2} can be closely approximated with $p_{N_2} \approx P_T - p_{O_2} - p_{H_2O}$, and C_{N_2} can be estimated. If DO is not highly depleted, denitrification is unlikely, so changes in C_{N_2} after recharge are also unlikely. An excess air concentration can then be calculated from C_{N_2} using an assumed recharge temperature and elevation. If recharge temperature is known to $\pm 2^\circ\text{C}$ and recharge elevation is known to ± 250 m, excess air concentrations derived from C_{N_2} will have an accuracy of about ± 1 cm³STP/Kg. Excess air concentrations typically range from 0 to 6 cm³STP/Kg (Wilson and McNeill, 1997), so this accuracy would be sufficient for determining approximate excess air concentrations.

Perhaps one of the most valuable uses for the TGP probe is determining relative excess air concentrations within a single ground water system in the field. Dissolved gas data from two areas in northern Utah demonstrate this capability of the probe (Figures 2.3 and 2.4). Total dissolved gas pressure measurements were made in production wells in the eastern Salt Lake Valley and in springs in the central Wasatch Mountains. Noble gas samples were also collected, allowing for the derivation of accurate excess air concentrations. In the eastern Salt Lake Valley, a clear correlation is observed between field-measured p_{N_2} and excess air (Figure 2.3). Because DO varies significantly throughout the study area, p_{N_2} (determined using the TGP probe and a DO meter together) is a better indicator of relative excess air levels than P_T .

In the central Wasatch Mountains, gauge total dissolved gas pressure (P_g) correlates well with excess air (Figure 2.4a). The gauge total dissolved gas pressure is simply the difference between P_T and P_a at the measurement location ($P_g = P_T - P_a$). The

Figure 2.3. Field-measured dissolved N₂ pressure (p_{N_2}) versus excess air for production wells in the eastern Salt Lake Valley, northern Utah. p_{N_2} was determined using a total dissolved gas pressure probe and a dissolved oxygen meter in combination (dissolved oxygen varies widely throughout the study area). Excess air was determined from dissolved noble gas data. A linear regression line is also shown. The observed correlation suggests that the probe can be used to approximate relative excess air concentrations in the field in the eastern Salt Lake Valley.

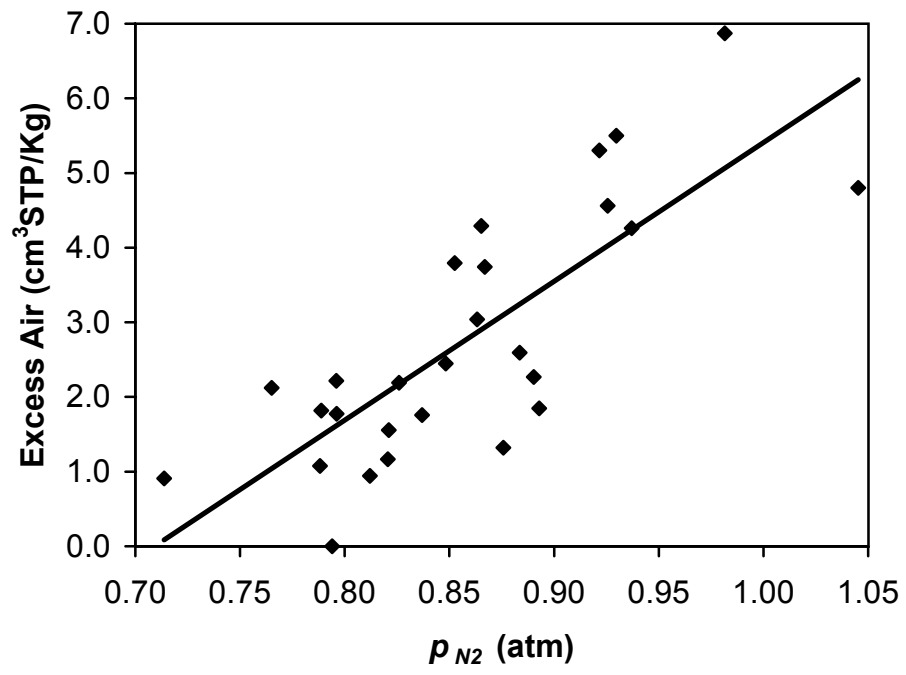
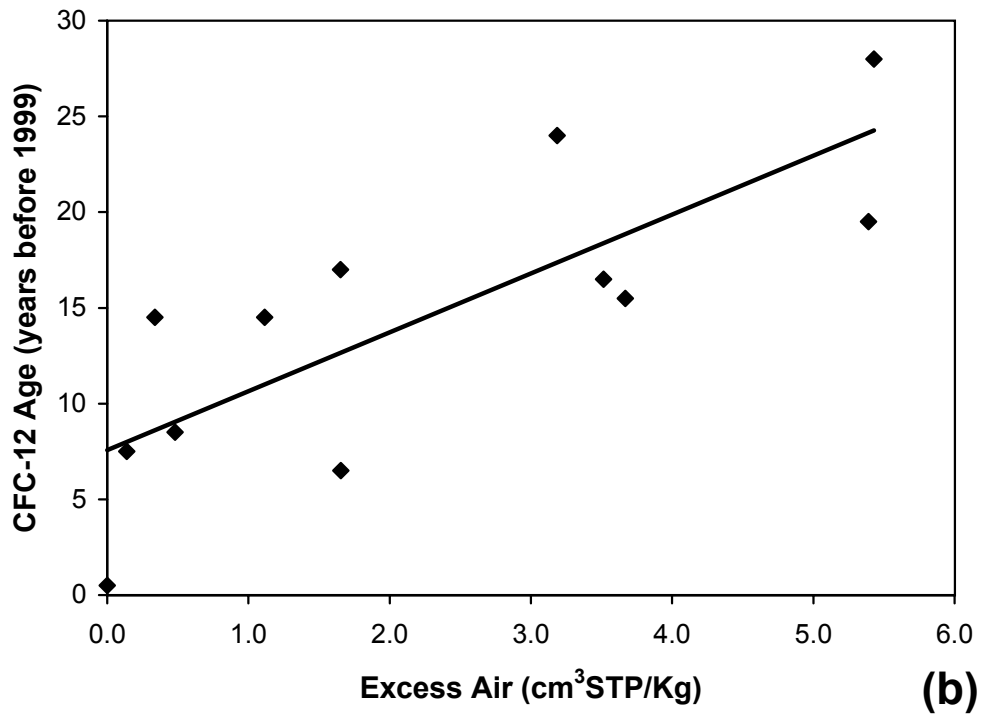
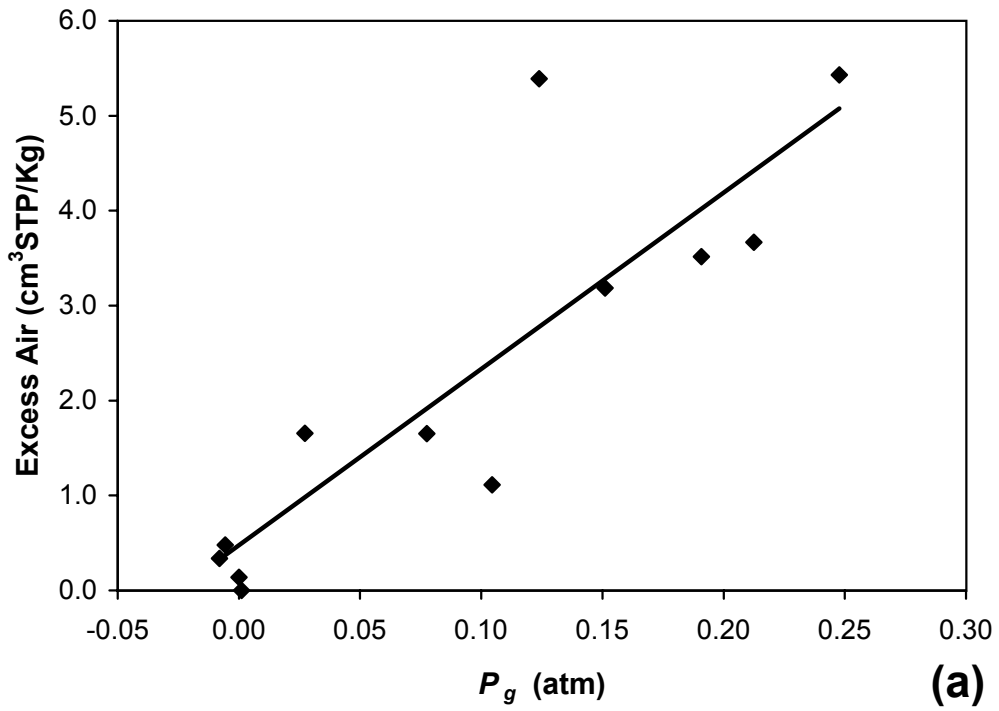


Figure 2.4. Results of dissolved gas sampling and total dissolved gas pressure measurements for springs in the central Wasatch Mountains, northern Utah. A linear regression line is shown on each plot. (a) Gauge total dissolved gas pressure (P_g) versus excess air. P_g is the difference between the total dissolved gas pressure and the atmospheric pressure at the measurement location (spring elevations vary widely). Excess air was determined from dissolved noble gas data. (b) Excess air versus age determined from chlorofluorocarbon-12 concentrations (CFC-12 age). The observed correlations suggests that the probe can be used to approximate both relative excess air concentrations and relative ground water age in the field in the central Wasatch Mountains.



spring waters are generally well oxygenated, but P_a varies considerably between measurement locations due to the variation in spring elevation. As a result, P_g is a more accurate indicator of relative excess air levels than P_T in this case. Ages were also determined for the spring samples using chlorofluorocarbon (CFC-12) concentrations. The CFC-12 data indicate that age is positively correlated with excess air (Figure 2.4b). Note that an excess air correction was applied to the CFC-12 ages prior to plotting the ages against excess air concentrations (and failing to do so would result in a negative instead of a positive correlation). The correlation between age and excess air further supports the hypothesis that excess air is related to important physical characteristics of the ground water flow system. A possible explanation for the correlation is that water table fluctuations increase significantly with distance from the discharge point in mountainous terrain, meaning that older waters that have followed longer flow pathways recharged where water table fluctuations are greater. Regardless of why age and excess air are correlated, the relationship begets a correlation between age and P_g . The TGP probe can thus be used in the central Wasatch Mountains to approximate relative ground water age quickly and conveniently in the field.

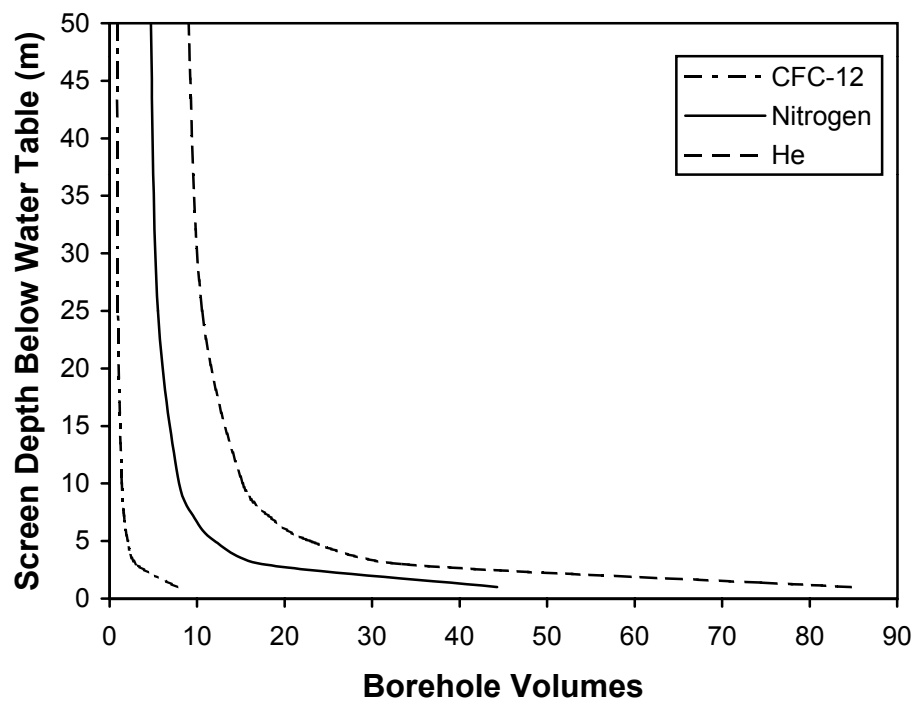
Field Screening for Air-Contaminated Wells

Certain well drilling techniques, such as air rotary, and well development by air-lifting involve forcing air into the water column. This air can become trapped as bubbles in the well, filter pack, and possibly the formation near the well. The subsequent dissolution of these bubbles will lead to 'air contamination' in and near the well, which complicates dissolved gas tracer methods. The magnitude of possible error resulting from air contamination depends on not only the amount, but also the type of air

contamination. Two types of air contamination are possible: 'artificial excess air' and 'reequilibration air'. If the volume of trapped air is less than that required to completely saturate the water in and near the well at the screen depth ('air saturation volume'), then all of the trapped air will dissolve relatively soon after injection resulting in artificial excess air. If, however, the volume of trapped air is greater than the air saturation volume, the trapped air can persist long after injection (see below). Water in and near the well will reequilibrate with this air at the temperature and pressure ($P_a + P_h$) within the screened interval, resulting in reequilibration air. The completeness of reequilibration will depend on the velocity of ground water flow through the well and the distribution of the bubbles. A low flow velocity and even bubble distribution will result in nearly complete reequilibration. If, however, the flow velocity is sufficiently high and/or the bubble distribution very nonuniform, gas exchange between the bubbles and the water will be limited, allowing only partial reequilibration.

All air trapped during well installation and development will eventually dissolve. However complete dissolution can take a considerable period of time under natural flow conditions (Figure 2.5). Consider the case of a 5.1-cm (2-inch) diameter well installed in a 15.2-cm (6-inch) diameter boring, with a screen length of 3 m and with 10% of the sand pack pore volume filled with trapped air. Figure 2.5 shows the number of saturated borehole volumes required to completely dissolve different gases within the trapped air assuming: (a) each borehole volume completely reequilibrates with the trapped air; (b) the well temperature is 15°C; (c) the sand pack has a porosity of 0.3; (d) $P_a = 1$ atm; and (e) the well water recharged in the year 2000 (for CFC-12 calculations) at 15°C, 1 atm, and has no excess air. The number of saturated borehole volumes is strongly dependent

Figure 2.5. Well screen depth versus the number of saturated borehole volumes required to completely dissolve different components of air trapped in the well's sand pack (see text for assumptions used). Air-rotary drilling and/or development by air-lifting may cause air entrapment in the well ('air contamination'). The number of saturated borehole volumes required to remove the air contamination is strongly dependent upon the gas of concern and the depth of the well screen. Under typical natural flow conditions, air contamination can persist for months to years in wells screened near the water table.



upon the gas of concern and the average depth of the well screen below the water table. Complete dissolution of He, one of the least soluble atmospheric gases, requires about 10 times more borehole volumes than CFC-12, one of the more soluble atmospheric gases. It will thus take 10 times longer for the well to become suitable for tracer methods employing He than for those employing CFC's. For each gas, the number of borehole volumes required at an average screen depth of 1.5 m below the water table is about 8 times the number required at 50 m because the higher P_h at 50 m allows more air dissolution per borehole volume.

Assuming a hydraulic conductivity of 10^{-4} m/s (medium-grained clean sand), all horizontal flow, and a typical horizontal hydraulic gradient (0.001), the time required for 1 saturated borehole volume to flow through the borehole is about 5 days. This calculation along with Figure 2.5 demonstrates that trapped air can persist in a well for months to years under natural flow conditions, particularly in wells screened just below the water table in fine-grained materials. Note that an order of magnitude decrease in hydraulic conductivity leads to an order of magnitude increase in the time required to dissolve the trapped air. This means that even considerably smaller amounts of trapped air (<1% of the pore volume) could be problematic in aquifers with low flow velocities. While pumping the well will enhance the rate of trapped air removal, more borehole volumes will be required than indicated on Figure 2.5 because water flowing rapidly into the well will only partially reequilibrate with the trapped air.

In air contaminated wells, P_T is elevated above the values expected based on reasonable assumptions about the recharge conditions. Identifying a well contaminated with reequilibration air is straightforward in the case of complete reequilibration ($P_T \approx P_a$

+ P_h). In contrast, distinguishing a well contaminated with artificial excess air from one contaminated with reequilibration air introduced by partial reequilibration is impossible based on P_T alone; in both cases, P_T is greater than expected, but less than $P_a + P_h$.

The process of identifying air contamination with the TGP probe and the potential effect of air contamination on dissolved gas tracer techniques are best illustrated by considering an actual air-contaminated monitoring well. The well is located at a site in the Salt Lake Valley, northern Utah, and was drilled using air rotary and developed by air-lifting. It has a P_T of 1.656 atm, measured with the TGP probe. The well head is approximately 1400 m above sea level ($P_a = 0.84$ atm), and the measurement was taken 18 m below the water table ($P_h = 1.77$ atm). Other wells in the general vicinity of the site drilled several years ago do not have unusually high excess air levels (all < 5 $\text{cm}^3\text{STP/Kg}$). Assuming a maximum natural excess air concentration of 6 $\text{cm}^3\text{STP/Kg}$ (Wilson and McNeill, 1997) and a reasonable range of possible recharge temperatures and elevations, the maximum possible P_T in the absence of contamination is about 1.3 atm. Given that the measured P_T exceeds the maximum expected P_T by about 0.36 atm, and that the possibility of unusually high concentrations CO_2 or CH_4 can be ruled out, the well is apparently air-contaminated. Other wells at the site drilled and developed using the same methods also appear to be air-contaminated. The fact that $P_T < P_a + P_h$ (2.61 atm) means that the contamination could be either artificial excess air or reequilibration air introduced by partial reequilibration.

If ground water age were determined for a sample from this well using the CFC method, the error would depend on the type of air contamination. In the case of artificial excess air, about 15 $\text{cm}^3\text{STP/Kg}$ would be required to account for the air contamination

in the well, assuming a probable recharge temperature and elevation. The CFC-12 excess resulting from the addition of 15 cm^3 of year 2000 air per kilogram of water would be 44 pg/Kg. If water in the well recharged between 1970 and 1985, computed ages would be about 5 years too young. For pre-1970 water, the young age bias would be larger still, and post-1990 water would be undatable because concentrations would exceed that of water recharged in the year 2000. In the case of partial reequilibration, the resulting young-age bias cannot be calculated because the amount of excess CFC-12 dissolved in the well would be unknown. However, the CFC-12 excess at complete reequilibration would be $>400 \text{ pg/Kg}$, meaning that even a modest amount of partial reequilibration would significantly alter computed ages.

If recharge temperature were computed from noble gas concentrations or ground water age were determined using either $^3\text{H}/^3\text{He}$ or ^4He , the potential error would depend again on the type of air contamination in the well. In the case of artificial excess air, none of these methods would be affected; all take excess air into account, and the origin of the excess air makes no difference. However, partial reequilibration would occur at the well temperature instead of the recharge temperature, so computed recharge temperatures would be erroneously warm. Partial reequilibration would also deplete both the tritiogenic component of ^3He and the terrigenous component of ^4He dissolved in the water (mole fractions of ^3He and ^4He in the trapped air are atmospheric) leading to erroneously young ages in both methods.

Field Screening for Trapped Gas

When $P_T = P_a + P_h$, the water is completely saturated and a trapped gas phase (bubbles) is likely present, or was present in the recent past. A measured P_T significantly

elevated above the expected P_T (based on background measurements or reasonable assumptions about recharge), but less than $P_a + P_h$, may also indicate the presence of trapped gas. Such is the case when the trapped gas is in the process of dissolving. Bubble dissolution occurs when the gas production rate is insufficient relative to the ground water flow velocity to maintain saturation of water near the bubbles. Note that $P_T = P_a + P_h$ in the case of a diffusion membrane leak, so this possibility must be eliminated first when $P_T = P_a + P_h$. The influence of trapped gas on P_T means that the TGP probe could be used to delineate portions of an aquifer that likely contain trapped gas.

Because trapped gas in a porous medium can reduce its hydraulic conductivity one to two orders of magnitude (Ronen et al., 1989; Fry et al., 1997; Brown and Overend, 1993), the ability to field screen for the presence of trapped gas could be valuable in many circumstances. For example, the formation of trapped gas in reactive barriers can cause flow to be diverted around the barriers, decreasing the effectiveness of the ground water remediation (Fryar and Schwartz, 1998). Nitrogen bubbles produced by denitrifying bacteria can cause significant clogging in waste-water injection wells (Oberdorfer and Peterson, 1985) and at sites employing in situ denitrification to remedy nitrate contamination (Soares, 2000). Bubbles can form around deep boreholes in fractured rock when the pressure drops in response to pumping (Jarsjo and Destouni, 2000). Although the probe could not be used to detect these bubbles directly, measurements of P_T in combination with an estimation of the induced pressure drop in the borehole (from the draw-down, for example) could be used to determine the likelihood that degassing has occurred.

Trapped gas can also significantly impede the transport of dissolved gases in ground water (Donaldson et al., 1998). This retardation is of particular concern when a dissolved gas such as He is being used as an applied ground water tracer (Gupta et al., 1994; Sanford et al., 1996). At contaminant sites employing in situ aerobic bioremediation, the transport of dissolved oxygen is usually of concern. In both of these cases, the TGP probe could be useful in identifying portions of an aquifer where trapped gas is likely present and dissolved gas transport velocities may be reduced. It should be noted that P_T can influence the effectiveness of introducing bubbles of oxygen or air to the ground water (either in the aquifer or in a direct gas transfer device) for the purpose of increasing DO and enhancing bioremediation (Bae et al., 1995). Because P_T cannot exceed $P_a + P_h$, an initially high P_T means that less O_2 can be dissolved into the water before saturation is achieved. The probe could thus aid in determining the potential effectiveness of this method of oxygen addition at a given site.

Determining Relative Concentrations of a Highly Abundant Gas

In areas where CO_2 and CH_4 are known to occur at concentrations far exceeding atmospheric-equilibrium values, P_T is a relative indicator of C_{CO_2} and C_{CH_4} . These exceptionally oversaturated (relative to the atmosphere) waters are the subject of many ground water studies. The distribution of C_{CO_2} anomalies has been used to identify deeply buried faults that are possible sources of geothermal water (Chiodini et al., 1995). Some waters that circulate deeply in sedimentary basins acquire p_{CH_4} values that greatly exceed normal P_T values (Andrews et al., 1991). Such waters have been investigated to determine the location and origin of natural gas deposits (Cramer et al., 1999). Many studies (e.g., Brown, 1998; Hackley et al., 1999) have focused on the significant CH_4

oversaturation that occurs in near-surface anoxic environments such as bogs and landfills. In the types of studies mentioned above, the probe could be useful as a field screening tool to determine relative levels of oversaturation. However, these oversaturated waters often exist at considerable depth, so modifications to present TGP probe designs would be necessary in order to measure many of these waters.

Summary

Total dissolved gas pressure probes suitable for ground water applications are now commercially available. Dissolved gas pressure is measured by submerging a void volume with a gas-permeable (silicone) membrane, allowing dissolved gases in the water equilibrate with gases in the void volume, then measuring the pressure in the void volume with a pressure transducer. The equilibration speed is directly proportional to the size of the void volume and the diffusion membrane thickness, while it is inversely proportional to the diffusion membrane surface area and the diffusion constant for nitrogen in silicone. The typical time required for complete equilibration is about 10 minutes. Accuracy tests indicate that TGP probes have an accuracy of ± 0.005 atm or better. Sources of error in addition to the uncertainty in strain gauge measurements apparently exist. The accuracy does not appear to decrease with increasing hydrostatic pressure. Bubbles usually are trapped on the probe upon submersion, but they can be consistently removed by shaking the probe.

Total dissolved gas pressure probes are a potentially valuable tool in ground water studies involving dissolved gases. We have identified several possible ground water applications for these probes, including: (a) conversion of mole fractions to accurate concentrations when using passive diffusion samplers; (b) field measurement of

approximate or relative excess air levels; (c) screening wells for air contamination; (d) detection of a trapped gas phase; and (e) determining relative concentrations of CO₂ and CH₄ when they are known to be highly abundant. This is not intended to be a comprehensive list, however, and other applications surely exist.

List of Terms

p_i = partial pressure of gas i

P_T = total dissolved gas pressure

P_h = hydrostatic pressure

P_a = atmospheric pressure

P_g = gauge total dissolved gas pressure

$\Delta P = (P_a + P_h) - P_T$

p_o = orthobaric pressure

C_i = dissolved concentration of gas i

H_i = Henry's law proportionality constant for gas i

T = temperature

S = salinity

t_E = transient equilibration time

V_v = void volume

δ = tubing wall thickness

A = tubing surface area

D_i = diffusion constant for gas i in silicone

E = percent equilibrated

\bar{V}_{H_2O} = molar volume of liquid water

R = universal gas constant

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