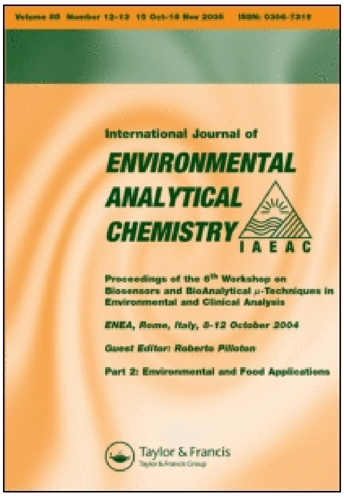

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Carbonate Equilibria and Groundwater Sample Collection: Implications for Estimated Average Subsurface Properties in Continental North America

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CARBONATE EQUILIBRIA AND GROUNDWATER SAMPLE COLLECTION: IMPLICATIONS FOR ESTIMATED AVERAGE SUBSURFACE PROPERTIES IN CONTINENTAL NORTH AMERICA

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The geochemistry of carbon dioxide in oxygenated groundwater may have a profound impact on analytical results obtained from efforts to measure *in situ* groundwater pH conditions and on the speciation, partitioning behavior and potential transport of inorganic contaminants in aquifers. Based on the observation that an estimate of the mean, national-average groundwater pH changes from 6.65 to 6.83, depending on the delay time before analysis, a mechanism of pH alteration resulting from CO_2 degassing is examined to provide an estimate of the ratio between groundwater and atmospheric partial pressures of CO_2 ($P_{CO_2,GW}/P_{CO_2,atm.} = 1.5$).

The groundwater-degassing P_{CO2} estimate is considerably less than literature values of groundwater P_{CO_2} and estimates of P_{CO_2} derived from the same data assuming other mechanisms. An examination of the potential sources of error in the degassing P_{CO_2} estimate suggests significant sample degassing may have occurred prior to measurement in previous field groundwater sample pH determinations. The instability in groundwater sample pH after exposure to the atmosphere may be useful for characterizing the source environments. An estimate of groundwater P_{CO_2} (4.67E-2 atm.) derived from an average groundwater bicarbonate concentration is within the range of values reported in the literature.

KEY WORDS: Groundwater, carbon dioxide, sample collection, pH instability.

INTRODUCTION

The speciation, partitioning behavior, and potential transport of inorganic contaminants in subsurface environments can be sensitive to the carbonate geochemistry

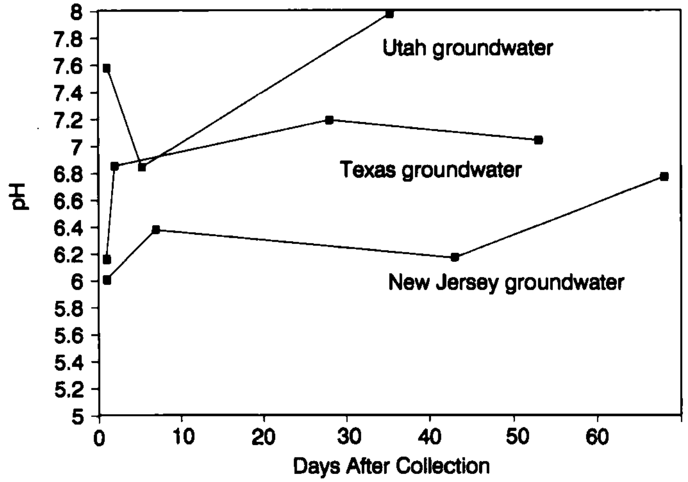

Figure 1 Comparison of measured groundwater pH values as a function of time for three groundwater samples. Initial pH values were determined in the field using in-line monitoring equipment.

found in groundwater. For example, at elevated pH and dissolved CO_3^{2-} conditions, many cationic contaminants may potentially display enhanced solubilization via formation of soluble dicarbonato metal complexes (e.g., Cd, Cu and Ni).[1] In contrast, the formation of carbonate minerals (sensitive to dissolved CO_3^{2-}) can immobilize inorganic contaminants either directly through mineral phase precipitation ($BaCO_3$ [ref. 2], $CdCO_3$ [refs. 3, 4], $FeCO_3$, $PbCO_3$ and $ZnCO_3$ [ref. 5]) or indirectly by adsorption/co-precipitation/solid-solution formation with primary or secondary carbonates (Cd [refs. 6,7], Zn [refs. 8,9]). An estimate of a national-average, oxidic-environment CO_2 partial pressure in groundwater—one aspect of the present study—may be a useful input parameter in developing geochemical speciation-based risk assessments for the potential migration of many inorganic contaminants in groundwater systems.

Recent recommendations[10,11] for the collection of groundwater samples include the suggestion that low-velocity, sample collection methodologies be used that minimize exchange with atmospheric gases. This may include isolating the screened interval in the well casing from overlying water exposed to atmospheric gases. In-line sample collection and filtration also is recommended. These procedures are designed to minimize the well-known phenomenon of groundwater sample pH and Eh instability due to either sample degassing (accentuated by vacuum collection procedures or extensive exposure to atmospheric gases) or oxidation of dissolved, reduced species in the sample by intrusion of atmospheric oxygen into the sample from either aeration or diffusion of molecular oxygen through the sample tubing of an in-line sample collection system.[12]

An illustration of these effects is given in Figure 1. This figure depicts field and laboratory measurements of groundwater pH as a function of time from the period of collection (reference 13 and unpublished data). Using an in-line monitoring system, pH values were determined in the field at sampling locations in Texas, New Jersey and Utah. pH values also were determined in the laboratory on samples stored at 4 °C following collection. The pH versus time profiles for the Texas and New Jersey samples are typical of the pH instability observed in samples from aerobic environments, showing a significant pH increase during the first few days. The profile for the Utah sample, an anaerobic groundwater presumably in contact with the Great Salt Lake, displays a dramatic drop in pH.

METHODS AND RESULTS

For the purposes of clarification, the methods and results sections of the present document will be presented together. Specifically, in the present study, groundwater analytical data are interpreted using the MINTEQA2[14,15] geochemical speciation model. Because this interpretation uses MINTEQA2 simultaneous equilibrium speciation descriptions of the analytical data to justify subsequent steps in the investigation, for both clarification and brevity, the methods and results sections are intertwined.

Speciation of Carbon Dioxide Natural Waters

Exposing a water sample from an environment of one gaseous composition to an environment with a different composition will lead to volatilization of those gases with a (new) lesser partial pressure and an increased dissolved concentration of those gases with an increased partial pressure. The significance of these gas exchange processes for CO_2 is given below.

According to conventional geochemistry, carbon dioxide can be speciated in the aqueous environment among several gaseous and soluble components:

$$CO_2(g) \overset{K_1}{\rightleftharpoons} CO_{2(aq)} \overset{K_2}{\rightleftharpoons} H_2CO_3 \overset{K_3}{\rightleftharpoons} HCO_3^- + H^+ \overset{K_4}{\rightleftharpoons} CO_3^{2-} + H^+. \qquad (1)$$

From an inspection of expression 1, increasing the partial pressure of CO_2 will result in shifting these equilibria to the right. Specifically, increasing the partial pressure of CO_2 will increase the concentration of all of the species in expression 1, and, increasing the carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) concentrations will result in a net release of hydronium ions to solution (leading to a net decrease in the pH of the water). In contrast, decreasing the partial pressure of CO_2 (as may occur when a groundwater sample is exposed to atmospheric conditions) can result in a net release (evolution) of CO_2 gas with a net consumption of hydronium ions resulting in an increase in sample pH.

The thermodynamic equilibrium constants used to describe the gas/liquid and acid/base reactions in expression 1 are listed in Table 1. These temperature-corrected formation constants (at 14.4 °C) are present in the thermodynamic constant database of the MINTEQA2 geochemical speciation model and will be

Table 1 Equilibrium formation constants for carbon dioxide, bicarbonate, carbonate and hydroxyl ions in natural water at 25 °C and 14.4 °C (MINTEQA2[14,15]).

log(K) *25 °C*	*log(K)* *14.4 °C*	*Formulation*	*Equilibrium reaction*[a]
18.147	18.174[b]	$\frac{P_{CO_2}}{a_{H^+}{}^2 a_{CO_3^=}}$	$CO_3{}^{2-} + 2H^+ \Leftrightarrow CO_2(g)$
10.330	10.436[c]	$\frac{a_{HCO_3^-}}{a_{H^+} a_{CO_3^=}}$	$CO_3{}^{2-} + H^+ \Leftrightarrow HCO_3{}^-$
16.681	16.859[d,e]	$\frac{a_{H^2CO_3}}{a_{H^+}{}^2 a_{CO_3^=}}$	$CO_3{}^{2-} + 2H^+ \Leftrightarrow HCO_3$
−13.990	−14.359[b]	$a_{OH^-} a_{H^+}$	$H_2O \Leftrightarrow OH^- + H^+$

Ionized species activity coefficient (Davies extension):

$$\log(\gamma_i) = -AZ_i{}^2[\mathrm{SQR(IS)}/(1+\mathrm{SQR(IS)}) - 0.24*\mathrm{IS})]$$

where A = a constant for water at 25 °C

Z = valence of ion *i*

IS = ionic strength (*M*)

Neutral species activity coefficient (Helgeson 1969[16]):

$$\log(\gamma_i) = 0.1 * \mathrm{IS}$$

[a] Subscripted a's designate activities; P_{CO_2} is the partial pressure of carbon dioxide.

[b] Temperature corrections obtained using the Van't Hoff relationship between enthalpy of reaction and temperature; reference $T = 25$ °C.

[c] $\log(K_{HCO_3^-}) = -6.498 + 0.02379 * T + 2902.39/T$.

[d] $\log(K_{H_2CO_3}) = -21.3415 + 0.05657 \bullet T + 6307.1/T$.

[e] As with previous convention, this equilibrium constant is formulated based on the fiction that all dissolved CO_2 exists as H_2CO_3.

used in subsequent simulations designed to interpret groundwater-sample pH instability in terms of carbonate ion speciation and CO_2 degassing.

Estimation of Groundwater P_{CO_2} from Groundwater pH Instability

As exhibited in Table 1, the carbonate equilibria (and concentrations) in groundwater will depend in large part on the groundwater pH and the (unknown) partial pressure of carbon dioxide in the groundwater environment. A principal objective of this study was to investigate sample pH instability as a means of estimating the *in situ* groundwater P_{CO_2}; hence, the major information required for the present study includes average changes in groundwater composition and pH after exposure to the atmosphere and an estimate of atmospheric P_{CO_2}.

The partial pressure of atmospheric carbon dioxide may vary on a seasonal basis. Due to the increased combustion of fossil fuels and other human-generated activities, it is known that the CO_2 partial pressure in the atmosphere has increased since the period circa 1900 from approximately 3.15E-4 atm to the present value of approximately 3.50E-4 atm (as measured at Mauna Loa[17]). An estimated atmospheric value of 3.50E-4 atm for the P_{CO_2} will be used in subsequent simulations.

Table 2 Summary of mean total major element groundwater concentrations obtained from the STORET database[18] and subsequent MINTEQA2 predicted speciation compositions at pH values of 6.65 and 6.83 at an assumed atmospheric CO_2 partial pressure of 3.50E-4 atm. and a temperature of 14.4 °C.

Specie	*Total (Molal)*	*Predicted conc. at ph = 6.65*	*Predicted conc. at pH = 6.83*	*Anion/cation balance; activity coefficients*
Ca^{2+}	1.810E-03	1.522E-03	1.522E-03	
Mg^{2+}	1.390E-03	1.192E-03	1.192E-03	at pH = 6.65
Na^+	2.320E-03	2.303E-03	2.303E-03	
K^+	1.250E-04	1.238E-04	1.238E-04	SUM (anions) = 6.753E-3
Cl^-	1.670E-03	1.670E-03	1.670E-03	SUM (cations) = 7.856E-3
$SO_4{}^{2-}$	3.020E-03	2.516E-03	2.516E-03	% diff. = 7.548
SiO_4H_4	3.600E-04	1.832E-04	1.832E-04	Calculated IS = 0.01254
H^+		2.507E-07	1.656E-07	
Derived species (complexes and ion pairs)				
H_2CO_3 (aq)		1.688E-05	1.688E-05	
$CO_3{}^=$		7.344E-09	1.683E-08	at pH = 6.83
$HSO_4{}^-$		2.918E-08	1.928E-08	
OH^-		2.190E-08	3.314E-08	SUM (anions) = 6.770E-3
$H_3SiO_4{}^-$		6.119E-08	9.262E-08	SUM (cations) = 7.855E-3
$H_2SiO_4{}^=$		2.066E-13	4.734E-13	% diff. = 7.424
$MgOH^+$		2.399E-09	3.630E-09	Calculated IS = 0.01254
$MgCO_3$ (aq)		2.868E-09	6.569E-09	
$MgHCO_3{}^+$		2.662E-07	4.028E-07	
$MgSO_4$ (aq)		1.975E-04	1.975E-04	
$CaOH^+$		4.948E-10	7.489E-10	Activity coefficients
$CaHCO_3{}^+$		2.321E-07	3.513E-07	
$CaCO_3$ (aq)		5.254E-09	1.203E-08	(Davies extension)
$CaSO_4$ (aq)		2.876E-04	2.875E-04	
$NaCO_3{}^-$		1.146E-10	2.625-10	Neutral = 1.003
$NaHCO_3$ (aq)		2.580E-08	3.905E-08	Monovalent = 0.8932
$NaSO_4{}^-$		1.724E-05	1.724E-05	Divalent = 0.6365
$KSO_4{}^-$		1.151E-06	1.151E-06	
$HCO_3{}^-$		3.199E-05	4.842E-05	

Table 2 lists national-average analytical data for the groundwater samples and the results from MINTEQA2 simulations with these data. The second column in Table 2 lists the arithmetic mean values for analytical total "major element" concentrations derived from a statistical analysis[18] of the STORET database (STORET is the USEPA database of national water quality measurements) of groundwater samples collected in the United States. The mean groundwater temperature was estimated to be 14.4 °C. In addition, two mean pH values (6.65 and 6.83) were derived from a statistical analysis of both "field" (i.e. immediate and/or preferably, in-line) and "laboratory" (i.e., delayed) measurements. These measurements may or may not have been determined on the same samples; however, this pH discrepancy between field and laboratory measurements (0.18 pH units) is generally consistent with the results obtained in a field sample collection effort conducted by the Athens Laboratory during 1987 and 1988 (average "field" value = 6.84; average "laboratory" value = 7.04; $n = 6$ sites[13]). The third and fourth columns in Table 2 depict the MINTEQA2 predicted speciation of these major elements at pH values of 6.65 and 6.83 assuming a CO_2 partial pressure of 3.50E-4 atm. The third, fourth and fifth columns in Table 2 illustrate two points: 1) the average ionic strength at both pH values was estimated to be 0.0125 *M*, and 2) the anion and cation balances were typically within 8%. These findings suggest that the quality of the data is perhaps better than might be expected from a "national-average" value approach. In addition, although not shown here, Si was the only element predicted to be supersaturated under the conditions of the simulations (as either quartz or cristobalite, a polymorph of SiO_2).

If it is assumed that the increase in pH results from a loss of CO_2 from the groundwater samples, then an estimate of the groundwater CO_2 partial pressure can be derived from the data in Table 2 and the equilibrium constants in Table 1 using the following procedure:

1) An estimate is made of the molar quantity of protons consumed in raising the pH from 6.65 to 6.83 when both systems contain a head space that has a carbon dioxide partial pressure of 3.50E-4 atmospheres. Mathematically, this is equivalent to "titrating" all of the weak acids and is expressed by:

$$\begin{aligned}\Delta[H^+]_{consumed} = {} & \Delta[H^+] + \Delta[HSO_4^-] - \Delta[OH^-] - \Delta[HCO_3^-] - 2\Delta[CO_3^=] \\ & - \Delta[H_3SiO_4^-] - \mathrm{SUM}\{[\Delta X^zOH^{z-1}] + \Delta[X^zHCO_3^{z-1}] \\ & + 2\Delta[X^zCO_3^{z-2}]\}\end{aligned} \qquad (2)$$

SUM = summation function

$\Delta[\ ] = [\ ]_{pH=6.65} - [\ ]_{pH=6.83}$

X^z = cation of valence z.

Expression 2 is based on five assumptions: (1) the excess OH^- generated in raising the pH occurred by a commensurate release of H^+ through the dissociation of water, (2) increases in bicarbonate and carbonate ion concentrations result from the hydrolysis of carbon dioxide, (3) differences in sulfate complex concentrations (e.g., KSO_4^- and $NaSO_4^-$, etc.) are not directly involved in altering the pH, (4) differences in HSO_4^- and $H_3SiO_4^-$ concentrations result from deprotonation of neutral species, and (5) differences in pH-dependent ionic species concentrations of less than 1E-10 *M* can be ignored. From expression 2 and the data in columns 3 and 4 of Table 2, the quantity of protons consumed in raising the pH is then estimated to be 1.688E-5 *M*. It should be noted that the difference in HCO_3^- accounts for

97.3 percent of the estimated molar concentration of protons consumed in raising the pH from 6.65 to 6.83.

2) The second step in the present investigation is to assume that the molar quantity of protons consumed (1.688E-5 *M*) results solely from the loss of protons that occurs when aqueous bicarbonate and carbonate ions are protonated from the equilibrium shift due to the degassing of aqueous CO_2 from the system. Specifically:

$$\Delta[H^+]_{\text{consumed}} = -(\Delta[HCO_3^-] + 2\Delta[CO_3^{2-}]) \tag{3}$$

From an inspection of column 3 in Table 2, the molar ratio of carbonate to bicarbonate is estimated to be 2.3E-4 (at pH = 6.65), hence, expression 3 can be further simplified to:

$$\Delta[H^+]_{\text{consumed}} \cong -[HCO_3^-] \tag{4}$$

3) Within the context of these assumptions, a potential bicarbonate ion concentration (at pH = 6.65) required for degassing that leads to a net consumption of 1.688E-5 *M* of protons can be estimated as:

$$[HCO_3^-]_{\text{potential, pH}=6.65} = (1.688\text{E-}5 + 3.199\text{E-}5) = 4.887\text{E-}5\ M \tag{5}$$

4) The final step in the present analysis is to estimate the required partial pressure of CO_2 that leads to an equilibrium bicarbonate concentration at pH 6.65 of 4.887E-5 *M*. From Tables 1 and 2, an expression relating bicarbonate ion concentrations to the partial pressure of CO_2 can be obtained by rearranging activity coefficients and the first two equilibrium constants in Table 1:

$$P_{CO_2} = [H^+][HCO_3^-]K^* \qquad \{\log(K^*) = 7.640\} \tag{6}$$

The log(K*) value in expression 6 is a conditional value incorporating activity coefficient corrections at an assumed constant ionic strength of 0.01254 *M*.

At a pH of 6.65 and a bicarbonate ion concentration of 4.88E-5 *M*, the estimated P_{CO_2} is then 535E-6 atm. or approximately 1.5 times the atmospheric value.

Table 3 compares the degassing P_{CO_2} estimate (above) with estimates derived from bicarbonate alkalinities reported in the literature[18] and with a minimum estimated P_{CO_2} required to precipitate a carbonate mineral. The second and third entries in Table 3 are derived using Eq. 6 in conjunction with average pH and HCO_3^- values obtained from the STORET analysis and an analysis of data found in the literature.[18] Bicarbonate concentrations (mg/L as $CaCO_3$) were converted to molar concentrations by dividing by 50 g/equivalent. The fourth estimated P_{CO_2} value in Table 3 was obtained using the data in Table 2 to perform MINTEQA2

Table 3 Estimates of P_{CO_2} in North America based on CO_2 degassing, average bicarbonate alkalinity values, and estimated carbonate mineral saturation.

Estimated P_{CO_2} (atm)	*Method*	*Comments*
5.35E-4	pH instability	CO_2 degassing analysis of Storet data
4.67E-2	Storet average[a,b] bicarbonate	$[HCO_3^-] = 214$ mg/L $CaCO_3$, pH = 6.65
1.30E-2	Lit. average[a,b] bicarbonate	$[HCO_3^-] = 305$ mg/L $CaCO_3$, pH = 7.36
3.93E-1	Calcite solub.	pH = 6.65, $T = 14.4$ °C, IS = 0.03

[a] From Pope-Reid Associates (1985)[18].
[b] Equivalent weight for $CaCO_3 = 50$ g/equiv.

simulations to determine a minimum P_{CO_2} required to precipitate a carbonate mineral. Assuming a pH of 6.65 and a temperature of 14.4 °C, we predicted that calcite would precipitate at a P_{CO_2} value of approximately 0.4 atm. Aragonite and dolomite were both predicted to be unsaturated under these conditions; the computed ionic strength was estimated to be approximately 0.03 *M*.

DISCUSSION

The partial pressure of CO_2 in soils overlying groundwater has been estimated to range from 0.1 to 0.001 atmospheres;[19] a typical value in groundwater has been estimated to be 0.01 atmospheres.[20] The estimate obtained from our degassing calculations is 2 to 800 times less than both the literature estimates and estimates derived from the other mechanisms listed in Table 3. A detailed discussion of both the potential sources of error in the degassing methodology and their implications is given in the next section.

Sources of Error in the Degassing Estimate of P_{CO_2}

Five potential sources of error in the CO_2 degassing P_{CO2} estimate were examined; the significance of these potential sources of error will be addressed on an individual basis.

1) a significant number of "field" pH measurements were performed after an unknown quantity of degassing had occurred in the sample collection process; hence, the "field" pH value may be too high.
2) "laboratory" pH measurements are not representative of equilibrium CO_2 degassing; therefore, this pH value may be too low.
3) groundwater samples were not primarily aerobic; i.e., dissolved ferrous and sulfide ion concentrations were significant.

4) near isothermal and isobaric conditions were not maintained in either "field" or "laboratory" pH determinations.

5) the datasets used to establish the degassing estimate may differ from those used to derive previous estimates. The majority of subsurface CO_2 presumably results from microbial mineralization of soil organic matter. From a national perspective, soil organic matter content can vary greatly on an inter-regional basis.

The last possibility—non-representativeness in the dataset—is not likely because the degassing P_{CO_2} estimate is internally inconsistent with other estimates derived from the same data. Specifically, a consistency among estimates would be required to support the contention that the data used in the present effort are significantly different from previous efforts.

The effect of differences in total pressure also is not likely to be significant. From thermodynamic theory, an increase in total pressure will favor redistribution of the equilibrium to either reactants or products depending on which side of the equilibrium yields the lesser sum of molar volume(s). Because pressure effects are not commonly significant except at relatively large pressure differences (e.g., in excess of 100 atm. for significant perturbations in the solubility of several minerals)[21] differences in total pressure are not believed to be significant in the present study given that the groundwater samples usually were collected from relatively shallow aquifers.

The effect of differences in temperature may be more significant. For example, from Table 1, the most temperature-sensitive equilibrium constant is that of the dissociation constant of water. From Table 1, the pH of pure (degassed) distilled water at a temperature of 25 °C would be 6.995. Decreasing the temperature to 14.4 °C would lead to a pH of 7.1795. Hence, a coincidental increase in groundwater temperature during the collection process also would tend to decrease the pH. Subjectively, from our sampling experiences, the pH of groundwater samples can be measured relatively quickly and this effect is probably not a major source of uncertainty in the present work.

Groundwater samples collected under anaerobic conditions may undergo several additional reactions that may alter either the magnitude or even the direction of the observed pH instability. The following reactions may potentially occur when anaerobic groundwater samples rich in sulfide and ferrous iron are exposed to atmospheric gases:

$$Fe^{2+} + 3H_2O \Leftrightarrow Fe(OH)_3(s) + 3H^+ + e^- \tag{7}$$

$$HS^- + 4H_2O \Leftrightarrow SO_4{}^{2-} + 9H^+ + 8e^- \tag{8}$$

$$HS^- + H^+ \Leftrightarrow H_2S(g) \tag{9}$$

Reactions 7 and 8—redox reactions potentially resulting from the intrusion of atmospheric oxygen into the sample—may occur in freshwater with Fe^{2+} and S^{2-}

at disappearance half lives significantly less than one day [refs. 12, 22, 23). The net result from these reactions, however, would be to decrease the pH of the sample. The degassing of hydrogen sulfide (reaction 9) is analogous to the degassing of carbon dioxide and, hence, would lead to an increase in sample pH.

From reactions 7 and 8, one can see that the oxidiation of anaerobic groundwater samples rich in ferrous iron and sulfides may have a profound impact on the pH instability of the sample. The pH profile for the Utah sample in Figure 1 may be indicative of oxidation processes. Indirectly, from the STORET database analysis (where an effort to exclude anoxic samples was conducted by ignoring samples with an iron content greater than 10 mg/L), the mean total iron content of the groundwater was estimated as 1.11 mg/L (2.0E-5 *M*). Assuming that this iron was dissolved as ferrous iron (Fe^{2+}), that near 100 percent oxidation of Fe^{2+} to Fe^{3+} occurred, and that near quantitative precipitation as amorphous iron hydroxide took place, we estimated the molar quantity of protons produced via reaction 8 to be 6.0E-5 *M* (3*2.0E-5). This quantity is of the same magnitude as that estimated to be consumed by CO_2 degassing. Similarly, the STORET mean sulfide concentration is given as 4.86 mg/L (1.52E-4 *M*). Consequently, oxidation of sulfide ions via reaction 8 would generate approximately 1.4E-3 *M* of protons and overwhelm any effects caused by carbon dioxide degassing. It is clear that some anaerobic groundwater samples were included in the STORET analysis; hence, oxidative phenomena may represent a significant source of error to the degassing P_{CO_2} estimate.

Quantifying the magnitude of these effects is more difficult. For example, in the STORET analysis, the maximum sulfide concentration was given as 290 mg/L ($n = 109$). The number of groundwater "field" pH values was gven as 24 500. Specifically, a few high concentrations of S^{2-} may have skewed the average value to a much higher level, particularly if concentrations less than the detection limit were omitted from the mean value calculations.

Implications for Field Pt Electrode Eh Measurements

Because the partitioning behavior and potential transport of ionized inorganic contaminants is directly or indirectly sensitive to the redox status of the subsurface environment, an effort is commonly made to measure the Eh of the groundwater sample using a platinum electrode. It is known that in oxygenated environments, the surface of a platinum electrode becomes coated with a pH-sensitive Pt-O layer [refs. 1, 24, 25]. The groundwater pH instability is not believed to be a significant source of error in these efforts to measure system Eh. For example, at 14.4 °C, the Nernstian relationship gives a value of −57.8 mV/pH unit for a monovalent ion. Hence a pH increase of 0.17 units due to CO_2 degassing in an oxygenated environment would lead to a corresponding decrease of about 10 mV with a platinum-electrode-based measuring system. Given the uncertainty in measuring (or interpreting) low-temperature environmental Eh conditions in general, and with the platinum-electrode in particular, a difference of 10 mV is not likely to be significant.

Comparison of Estimated P_{CO_2} Values

The P_{CO_2} estimates (Table 3) derived from the CO_2 degassing mechanism and the calcite solubility mechanism span the values reported in the literature and the estimate based on HCO_3^- concentrations. The calcite-saturation P_{CO_2} estimate is probably far too high. In soils, it has been suggested that calcium silicates and/or calcium alumino-silicates may be the dominant solubility control for calcium.[2] Specifically, an assumption of calcite saturation is erroneous based on these data.

For the reasons given in preceding sections, the P_{CO_2} estimate based on CO_2 degassing is probably too low. The P_{CO2} estimates based on average bicarbonate concentrations, although probably the more reasonable estimates, are not without ambiguity. For example, bicarbonate concentrations typically are determined from titrimetric alkalinity measurements where the bicarbonate alkanility is assumed to be one of (if not) the major component(s) of the total alkalinity.[25] The bicarbonate alkalinity estimate may be too high if corrections are not made for the buffering attributable to other weak acids present in the sample. Although other dissolved weak acids are not likely to represent a major component of the total alkalinity (from an inspection of Table 2). it is not unreasonable to assume that at least some of the alkalinity data may have been derived from samples containing significant "titrable" solids. Alternatively, the bicarbonate alkalinity may be too low if sufficient degassing occurs such that the "phenolphthalein" alkalinity portion of the total alkalinity is increased significantly. Given the relatively low pH values for groundwater, the error in the bicarbonate concentrations is probably in a positive direction. The national-average (STORET) P_{CO_2} estimate based on average bicarbonate concentrations is consistent with the literature and probably is the most accurate of the estimates.

The discrepancy between the P_{CO_2} estimates from the sample degassing mechanism and the average bicarbonate concentration has two probable explanations. First, significant CO_2 degassing occurred prior to "field" pH measurement in the majority of cases; specifically, the average "field" pH value is probably too high. Second, a significant number of anaerobic samples were included in the dataset used to obtain the national groundwater parameters.

In either case, the chemical properties of the groundwater samples in the STORET database were probably significantly altered due to exposure to atmospheric conditions. If the discrepancy between the degassing and bicarbonate P_{CO_2} estimates results from prior (field) degassing of CO_2, then the estimated pH values may be too high. Paradoxically, if the pH increase is not sufficiently large to generate an excess phenolphthalein component of the total alkalinity, then the bicarbonate P_{CO_2} estimate may be accurate. Given the importance of exchange with atmospheric gases, decreasing the uncertainty in estimates of national-average, groundwater chemical properties will require a dataset composed of analytical results obtained using monitoring systems isolated from the atmosphere.

The gas-exchange mechanisms presented in this document can easily be used to characterize the source environments from which groundwater samples are collected. For example, a comparison of in-line-collection-system pH measurements with field pH measurements obtained after exposure to the atmosphere could yield information in three areas: (1) the redox or P_{CO_2} status of the groundwater, (2) the potential for sample alteration in groundwater samples collected for laboratory studies, and (3) the potential effort required to inhibit sample alteration in storage.

SUMMARY

Carbonate equilibria may have a large impact on the potential subsurface migration of many inorganic contaminants. Various estimates of the subsurface P_{CO_2}—a key variable useful for quantifying these equilibria—display large discrepancies and, hence, indicate that current datasets of groundwater pH values are probably inaccurate due to sample alteration from exposure to the atmosphere. Groundwater-sample pH instability may be useful, however, for characterizing the source environment and for establishing a criterion for quality control of various chemical measurements. A national-average, groundwater P_{CO_2} value based on average bicarbonate concentrations (4.67E-2 atm.) in the STORET database is within the range of groundwater P_{CO_2} values reported in the literature.

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