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Introduction

Hazardous waste sites that are located in nearshore areas may be hydraulically connected to coastal and estuarine waters. For these sites, a major concern is the influence of seawater on the partitioning and potential migration of contaminants that are present in the soils and groundwater located at the site. Due to the interactions among seawater, groundwater, soils, sediments, and the chemical contaminants, complex physical and geochemical processes will affect the transport and mobility of chemicals from the waste site. The purpose of this article is to review the influence of seawater on important processes that may affect the solubility, partitioning, and transport of chemicals from nearshore landfills and disposal sites.

The potential influence of seawater on the migration of contaminants from nearshore soils and groundwater is a function of transport from density and tidal mixing and the physiochemical properties of seawater that will affect the solubility and binding capacity of chemicals which come into contact with the salt water. Because seawater is physically and chemically different than fresh groundwater, chemicals will behave differently in seawater than in fresh groundwater. Relative to a chemical's behavior in fresh groundwater, the properties of seawater that are most likely to affect chemical behavior are the presence of dissolved salts, higher concentrations of dissolved organic matter and colloidal material, a higher reduction-oxidation (Redox) potential, greater buffering of pH, and changes in the kinetic rates of reactions over time.

Since the behavior of contaminants will be a result of the interaction between the seawater, groundwater, soils, sediments, and the concentration of the contaminants, the behavior of each chemical will be dependent on the characteristics of the site. However, a general description of the important processes will aide in identifying critical parameters needed for more detailed site assessments and evaluations. The critical processes are reviewed and the theoretical basis of the interactions that will be affected by the presence of seawater are presented. As appropriate, the governing equations are provided for easy reference and the bibliography provides references for further reading.

Physical Transport and Mixing

A typical nearshore disposal area may be visualized as consisting of the source of contamination, a contaminant plume, groundwater which may be confined or unconfined, and seawater intrusion areas (Figure 1). Aquifers located in coastal areas are generally recharged inland and the seaward slope of the strata causes the freshwater to flow seaward (Fetter 1994). Water is discharged from unconfined aquifers primarily by evapotranspiration and by direct discharge into springs, streams, tidal waters, and the sea bottom (Fetter 1994). Confined aquifers can only discharge by diffusive flow or flow generated by hydraulic or osmotic pressure gradients (Fetter 1994). In many coastal areas, passive or active seawater encroachment is present. Caused by the diversion of freshwater, passive seawater intrusion occurs as the boundary between fresh and saline groundwater moves landward. In cases where freshwater diversion has reversed the hydraulic gradient, saltwater will actively intrude until it reaches the low point in the hydraulic gradient (e.g. the cone of depression in the center of groundwater withdrawal) (Fetter 1994).

Because seawater has a higher density than the fresh groundwater, a density-dependent mixing zone will form at the boundary between the fresh and saline groundwater (Figure 1). In this zone, there will be a constant change in the composition of the fresh groundwater as it mixes with the saline groundwater. In unconfined aquifers, the density gradient will cause the fresh groundwater to flow upward and discharge near the shore while the saline groundwater will form discharge and recharge cycles on the salty side of the boundary (Fetter 1994). The width of the mixing zone (zone of diffusion) is usually narrow but tidal fluctuations in the hydraulic head will increase its size. The depth to which fresh groundwater extends below sea level and the extent of density driven seawater intrusion can be estimated by the height of the water table above sea level and the difference between the density of fresh groundwater (ρ_w) and seawater (ρ_s) (the Ghyben-Herzberg Principle, Fetter 1994):

$$z(x,y) = \frac{\rho_w}{\rho_s - \rho_w} h(x,y) \quad [1]$$

where $z(x,y)$ = the depth to the seawater interface at point (x,y), and

$h(x,y)$ = the height of the water table above sea level at point (x,y).

By assuming steady-state flow conditions and that there is a sharp interface between fresh and saline groundwater, the cross-sectional flow is dependent on the difference in density between the fresh and saline groundwater ($G = \rho_w/(\rho_s - \rho_w)$), the aquifer recharge rate (w m/day), and the hydraulic conductivity of the soils and sediments (K_H m/day) (Fetter 1994). The steady state cross-sectional flow is estimated by the partial second-derivative of the change in the water table height across the x-y plane (Fetter 1994):

$$\text{steady state cross-sectional flow} = \frac{\partial^2 h^2}{\partial x^2} + \frac{\partial^2 h^2}{\partial y^2} = \frac{-2w}{K_H(1+G)} \quad [2]$$

In coastal areas with strong tides, tidal mixing zones may form from the movement of seawater into the aquifer. Evidence of tidal influence on the potentiometric surface of the groundwater table can be obtained from water levels in monitoring wells that fluctuate with the rise and fall of the tides. The degree of tidal mixing is dependent on the amplitude of the tidal

height (H_0 m), the tidal period (t_0 hr), and the storativity (S_A dimensionless) and transmissivity (T_A m²/hr) of the aquifer. The storativity and transmissivity can be estimated from direct measurements at the site (e.g. pumping tests, Fetter 1994). Storativity is the rate the aquifer exchanges water per unit surface area per unit change in head. Transmissivity is the rate water flows through a unit width of the aquifer. Transmissivity is a function of the properties of the fluid and the porosity and thickness of the media through which the fluid flows. The amplitude of the tidal mixing zone can be estimated for a given distance (x) from the coast by (Fetter 1994):

$$H_x = H_0 e^{-x \sqrt{\frac{\pi S_A}{t_0 T_A}}} \quad [3]$$

where H_x = the amplitude of the tidal mixing zone at x distance from the coast

π = the constant Pi which is approximately equal to 3.141593...

Based on measurements made at wells placed shoreward of the coast, the time lag (t_τ hr) from high tide to the highest observed point in the well is also related to the period of the tide and the Storativity and Transmissivity of the aquifer (Fetter 1994):

$$t_\tau = x \sqrt{\frac{t_0 S_A}{4\pi T_A}} \quad [4]$$

Equations 3 and 4 can be used to estimate the degree of tidal influence on the potentiometric surface of the groundwater. The tidally mixed zone may be important in estimating the amount of groundwater extracted due to tidal pumping (Moore 1996). Tidal pumping is used to describe the process where higher density tidal waters mix with groundwater at high tide, and then as the tide recedes, the mixture of seawater and fresh groundwater is drawn out into the coastal waters. Because this process repeats every tidal cycle, appreciable volumes of groundwater can be extracted by tidal pumping (Moore 1996).

The degree of seawater intrusion will depend on the elevation of the waste and plume with respect to sea level, the tidal range of coastal waters, the groundwater recharge rate, and the porosity and composition of the soils and sediments in the intertidal area. The rate of movement of the chemicals from the source of the contamination will be dependent on the chemical properties of the contaminants, the nature and type of soils present, and the route of groundwater movement through the contaminated area. When permeable soils lie above the source of contamination, rain water may percolate through the contaminated material transporting the wastes into the groundwater. In other cases, regional groundwater flow may raise the water table to come into contact with the wastes. When a layer of soil with low permeability (e.g. clays from glacial outwash) are present above the regional groundwater table, a lens of perched water may form above the regional water table. Usually not very large, perched water tables are recharged by local rainfall (Fetter 1994).

Evidence of seawater intrusion can be obtained from groundwater monitoring wells that rise and fall in conjunction with tidal fluctuations and saline or brackish concentrations of seawater salts measured in groundwater or inland surface water samples. In some cases, water

can be observed seeping from the site into the coastal/estuarine water. These seeps may be fresh or a mixture of fresh and saltwater that is being discharged from surface runoff, the regional or perched groundwater water tables, tidal waters, and/or saline groundwater. It is in the seawater intrusion zones where the seawater mixes with the fresh groundwater that the physiochemical properties of seawater will influence the behavior of the contaminants. It is within these zones that the seawater will either come into direct contact with the wastes or mix with groundwater that has already been contaminated.

Dissolved Salts

The most striking difference between seawater and fresh water is the content of dissolved salts in seawater. Giving the sea water its salty flavor, the dissolved salts or salinity content increases the water's density (Table 1) and changes the ionic strength of the solution (Table 2). In addition to increasing density, dissolved salts will lower the freezing point, depress the vapor pressure, raise the boiling point, and elevate the osmotic pressure of the solution (Pilson 1998). The dissolved salts also have a profound effect on chemical activities and equilibrium concentrations of chemical reactions occurring within the solution (Horne 1969, Stumm and Morgan 1981, Pilson 1998). In general, ionic compounds will be more soluble in solutions with higher salinity while nonionic compounds will be less soluble. However, because of the competing electrostatic interactions among individual ions and their interactions with the surrounding ions in solution, it is very difficult to predict chemical behavior based on theoretical principles alone (Horne 1969, Stumm and Morgan 1981, Pilson 1998).

The amount of an ionic compound that will dissolve in a solution depends on the ionic strength of the solution and the concentrations of ions involved in the reaction. The ionic strength of a solution is dependent on the molal (moles/Kg) concentration and charge of the individual ions present (Pilson 1998)

$$I = \frac{1}{2} \sum m_i z_i^2 \quad [5]$$

where

m_i = the molal¹ concentration of the *i*th ion, and

z_i = the charge of the *i*th ion.

In seawater there is a constant proportion of the major salts relative to each other. Therefore, for a given salinity the relative abundance of cations and anions will be constant

¹ A mole is the amount of atoms, molecules, ions, electrons, or particles that is equal to the number of atoms in 0.012 Kg of ¹²Carbon (e.g. the number of atoms in one mole of C is 6.022 x 10²³ - Avogadro's Number). The concentration of moles can be expressed by volume (molar = moles/Liter) or by weight (molal = moles/Kg). Because the density of solutions change with high concentrations of dissolved salts, it is more accurate to use the molal concentration.

(Brown et al. 1989). Because changes in salinity will have no effect on the relative proportions of the major salts, the ionic ratios in the solution will remain constant as seawater mixes with (is diluted by) fresh groundwater and the ionic strength will be directly proportional to changes in the salinity (Table 2). In other words, as fresh groundwater becomes more saline, it will behave more like seawater.

Under ideal conditions, the law of mass action can be used to describe the equilibrium between chemical reactants (Fetter 1994):



where $A + B$ are the reactants and

$X + Y$ are the products and

\rightleftharpoons indicates that the reaction is reversible and an equilibrium state is possible

At equilibrium the forward and backward reactions will be equal and an equilibrium constant (K) can be used to describe the ratio between the products and reactants:

$$K = \frac{[X]^x [Y]^y}{[A]^a [B]^b} \quad [7]$$

where the brackets [] represent the molal concentration of each ion and the exponents are the number of molecules of the ion involved in the reaction.

When the reaction under question is dissolution, the equilibrium constant is called the solubility product (K_{sp}) and it represents the equilibrium ratio between the dissolved and solid species (the concentration of the solid is defined as 1) under ideal conditions. For example, in pure water lead chloride ($PbCl_2$) disassociates into lead and chlorine ions:



$$K_{sp} = \frac{[Pb^{2+}][Cl^-]^2}{[PbCl_2]} = 10^{-4.8} \text{ (Stumm and Morgan 1981)} \quad [9]$$

Because 1 mole of $PbCl_2$ produces 1 mole of Pb^{2+} and 2 moles of Cl^- , the solubility of $PbCl_2$ can be calculated as:

$$10^{-4.8} = \frac{[Pb^{2+}][Cl^-]^2}{1} = [X][2X]^2 = 4X^3 \quad [10]$$

and the amount of

$$[PbCl_2]_{dissolved} = \sqrt[3]{10^{-4.8}/4} = 0.0158 \text{ mol/Kg} \quad [11]$$

The thermodynamic solubility products for most ions are listed in chemical handbooks but because the behavior of ionic species in seawater is nonideal, the apparent solubility products (K_{sp}') observed for many ionic compounds in seawater solutions are much different. When other ions are present in the solution they may inhibit or enhance the solubility of solid species. For example, the concentration of chlorine in seawater is about 0.5 mol/Kg (Table 1) so there will be additional chlorine ions already in the solution to react with the $PbCl_2$ (common-ion effect, Fetter 1994, Stumm and Morgan 1981):

$$K_{sp} = 10^{-4.8} = \frac{[Pb^{2+}][Cl^-]^2}{1} = [X][2X + 0.5]^2 = 4X^3 + 2X^2 + .25X \quad [12]$$

Because X is small ($4X^3 + 2X^2$) will be even smaller so it can be ignored, therefore

$$X = 10^{-4.8}/.25 = 0.000063 \text{ mol/Kg} \quad [13]$$

The results obtained for equations [11] and [13] suggest that lead chloride is about 250 times less soluble in seawater than in pure water. However, the calculation is oversimplified because it neglected the fact that there are many other cations and anions, besides chlorine (Table 2), that will affect chemical interactions in the seawater solution.

In order to account for competing electrostatic interactions among individual ions and their interactions with the surrounding ions in solution, the chemical activity of the ion must be determined (Horne 1969, Stumm and Morgan 1981, Pilson 1998). In complex saline solutions like seawater, activity coefficients are used to relate the chemical's concentration to its chemical activity (Horne 1969, Fetter 1994, Pilson 1998):

$$\alpha = \gamma m \quad [14]$$

where

α = the chemical's activity

γ = the activity coefficient for the reaction and solution under consideration

m = the molal concentration of the chemical

By incorporating activity coefficients, thermodynamic equilibrium constants can be used to evaluate chemical behavior from a theoretical basis (Pilson 1998).

$$K_{sp} = (a_{M^+})^{V^+} (a_{A^-})^{V^-} \quad [15]$$

$$= (\gamma_+ m^+)^{V^+} (\gamma_- m^-)^{V^-} \quad [16]$$

where a_{M^+}, a_{A^-} = the activities of the cation and anion, respectively

m^+, m^- = the molal concentration of the cation and anion, respectively

- γ_+, γ_- = the activity coefficients of the cation and anion, respectively
- V_+, V_- = the moles of cations and anions, respectively, involved in the reaction.

However, the activity coefficients of individual ions can not be measured directly. Only the mean activity of both cation and anion can be measured (Horne 1969, Pilson 1998). Hence, the activity coefficients can be considered "fudge factors" that are used to account for the electrolytic interactions in the solution (Horne 1969). The activity coefficients are a function of the ionic strength, pressure, and temperature of the solution. At infinite dilution, and standard pressure (1 atm) and temperature (25°C) the activity coefficients are equal to 1. For estimating the activity coefficients of ions in solutions up to about 0.1 molal, the Debye-Huckel equation can be used. The Debye-Huckel equation takes into account the deviation from ideal behavior that is contributed by the electrical charge of the individual ions and the charge from the surrounding ionic mixture (Fetter 1994):

$$\log(\gamma_i) = -\frac{[Az_i^2\sqrt{I}]}{1 + (a_iB\sqrt{I})} \quad [17]$$

where

- γ_i = the activity of the ion
- I = ionic strength of the solution, see equation [5]
- z_i = the charge of ion
- A = a temperature-dependent constant (0.5085 at 25°C)
- B = a temperature-dependent constant (0.3281 at 25°C)
- a_i = the effective width of the ion

Equation [17] can be used to calculate activity coefficients in mixtures of seawater and fresh groundwater where the groundwater constitutes at least 90% of the mixture (e.g. salinity (S) is below 3.5 psu², Table 2). In mixtures with higher concentrations of seawater, the activity coefficients for most ions will be less than one meaning that more of the ion will dissolve into seawater that would dissolve in freshwater. Activity coefficients of the major ions in seawater can be found in a variety of sources (Horne 1969, Riley and Chester 1971) but very few data are available for ions of trace elements. For seawater solutions, some authors recommend using activity coefficients of 0.7 for monovalent cations, 0.12 for divalent cations, and 1.13 for uncharged species and organic compounds (Riley and Chester 1971).

² psu = Practical salinity units which is defined from the Practical Salinity Scale. Salinity is now defined as a ratio of the conductivity between seawater and a standard KCl solution (32.4356 g KCl dissolved in enough pure water to create 1 kg of water). Therefore, S is a dimensionless ratio and the symbol ‰ (for parts-per-thousand) is traditional (Pilson 1998).

More importantly, other factors will have a much greater effect on speciation than deviations from ideal behavior due to electrolyte interactions. For example, additional side reactions with other inorganic and organic complexing agents (ligands³) present in seawater also occur simultaneously with the electrolytic reactions (Stumm and Morgan 1981) making it almost impossible to predict the outcome. Because there is considerable uncertainty in the solubility constants reported by various authors (Stumm and Morgan 1981), the theoretical calculations can lead to erroneous conclusions. In addition, effects on ion concentrations caused by the removal of ionic species by coprecipitation with more abundant minerals (iron, manganese) (Brown et al. 1991), adsorption of ions on surfaces of organic (detritus) and inorganic (clays and hydroxides) particles (Brown et al. 1991), and changes in the valence of the ions in response to oxidation-reduction equilibria (Brown et al. 1991) will also be more important than electrolyte interactions in determining the concentrations and species of ions present in the solution.

Dissolved Organic Matter

Most groundwaters have very low concentrations of dissolved and particulate organic matter. This is because the organic matter in groundwater is produced in surface water or soil and most groundwaters have long residence times (hundreds to thousands of years) so there is plenty of time for the organic matter to be broken down and mineralized by microbes (Thurman 1985). Organic matter also readily adsorbs onto the surfaces of the solids present in the aquifer (sandstone, limestone, igneous rock, sand, and gravel) and the aquifer materials themselves have very little organic carbon that is water soluble (unless there are coal or oil/shale deposits in the aquifer) (Thurman 1985). Concentrations of dissolved organic carbon (DOC) in groundwater normally range from about 0.2 to 1.0 mg/L (Thurman 1985).

Due to the large amount of organic matter being carried to the sea, rivers usually have high concentrations of dissolved organic carbon (DOC 1 - 15 mg/L) (Thurman 1985). Oceanic seawater has relatively low DOC (0.3 - 2.0 mg/L), while coastal and estuarine waters have highly variable DOC concentrations, ranging from riverine levels (15 mg/L) at the high end to oceanic levels (1 mg/L) on the low end. On average, coastal and estuarine waters have from two to ten times more DOC than groundwaters. The interstitial waters of marine sediments have very high concentrations of DOC ranging from 4 - 20 mg/L in aerobic sediments to greater than 80 mg/L in anaerobic interstitial waters where O₂ has been depleted by microbial activity (Thurman 1985).

Although organic matter in natural waters is thermodynamically unstable, it can play a very important role in the fate and transport of contaminants in coastal and estuarine ecosystems. In seawater, humic substances constitute the largest fraction of DOC. Humic substances are composed of polymers containing phenolic (single aromatic rings e.g. C₆H₅OH) and aliphatic (straight and branched chains and acyclic compounds e.g. C₆H₈) alcohols (compounds with one or more hydroxyl groups -OH), and carboxylic groups (ionizable functional groups -COOH).

³ Molecules that are available to bind with a cation (form a coordination compound) are referred to as ligands (Stumm and Morgan 1981). The most important ligands in seawater are H₂O, OH⁻, Cl⁻, SO₄²⁻, CO₃²⁻, (Horne 1969) and organic complexes (Stumm and Morgan 1981).

Dissolved humic substances are often separated into two operationally-defined components: humic acids (which precipitate at pH=1) and fulvic acids (which do not precipitate at pH=1). Fulvic acids are highly soluble, low molecular weight (800 - 2000 MW) organic molecules with many functional groups. Humic acids are more colloidal⁴ in nature, have a higher molecular weight (2000 - 3000 MW), and less functional groups than fulvic acid. Humic acids are usually associated with amorphous iron and aluminum oxide particles. The humic (10%) + fulvic acid (40%) fractions usually account for about 50% of the organic carbon in DOC. Comprising about 30% of the DOC are hydrophilic acids that are composed of a mixture of water soluble organic acids, fatty acids, hydroxy acids with many hydroxyl and carboxyl groups (Thurmond 1985). The remainder of the DOC is made up of simple biological compounds including carbohydrates (e.g. sugar C₆(H₂O)₆), carboxylic acids (-COOH), amino acids (e.g. glycine NH₂CH₂COOH), and hydrocarbons (e.g. ethane C₂H₆) (Thurman 1985).

With respect to interacting with contaminants, DOC has three main properties (Stumm and Morgan 1981):

1. *Binding with contaminants and attaching to surfaces.* Humic and fulvic acids are especially adept at adsorbing or trapping a wide variety of organic substances including toxic chemicals. Humic substances as a whole have a strong tendency to adsorb to solid surfaces (e.g. hydrous oxides, clays, etc.) and can participate in ligand exchange reactions with the solid surfaces.

2. *The tendency to complex with metal ions.* Humic and fulvic acids are weak acids that readily complex with metal ions to form humic ligands and chelation compounds. Usually, each mg of DOC has enough metal-binding capacity to bind with about 10⁻⁶ moles of metal (i.e. 1 μEq of metal binding capacity) (Thurman 1985). Depending on the situation, these complexed compounds can be transported as part of the DOC or they will be transferred to the solid phase. In either case, the complexed metal will be less toxic than the free metal ion.

3. *Precipitation and colloidal behavior*⁵. A large percentage of humic materials are present as negatively-charged colloids. In the presence of Ca²⁺ and Mg²⁺, these colloids coagulate and will precipitate out of solution (sometimes referred to as the "salting out effect"). Because many of the humic colloids also have functional groups that are capable of binding with organic and inorganic contaminants, the fate of the contaminants will be determined by the behavior of the colloids in the water column and the pore spaces of the sediment.

As seawater and groundwater mix, the DOC contributed from the seawater could have a profound effect on contaminant availability and mobility. The organic matter would coat any particles present changing the equilibrium between the solid and dissolved species. The equilibrium between the sorbed and dissolved species will be affected by the large cation exchange capacity of the organic matter. Cation exchange is the capacity to cause ions bound to solid surfaces to exchange with other ions in solution (Thurman 1985, Fetter 1995). Cation

⁴ Colloids are very small solid particles that can pass through a .45 μm filter so they are classified as "dissolved".

⁵ Because of their very small size, colloids have very slow settling rates and may remain in suspension indefinitely.

exchange reactions preferentially bind with specific ions by releasing other ions. In cation exchange reactions, divalent ions (Mg^{2+} , Ca^{2+} , and heavy metals) will tend to replace monovalent ions (Na^+ , K^+ , etc.) on the surfaces of charged particles. Most marine clays and silts have high cation exchange capacities while alumina and silica aquifer materials have low cation exchange capacities. When these latter surfaces are coated with organic matter, the cation exchange capacity can be increased by as much as 20-fold (Thurman 1985). A study that evaluated the influence of decreasing salinity on the partitioning of the polycyclic aromatic hydrocarbons (PAHs) benzo[a]pyrene and phenanthrene showed that there was only slightly more PAHs sorbed to suspended sediment in seawater ($S=35$) than in freshwater ($S=0$) (Hegeman et al. 1995). This suggests other factors, including DOC content, temperature, and estuarine mixing are probably more important than salinity in determining partition coefficients of hydrophobic organic compounds (Hegeman et al. 1995).

Depending on the composition of the DOC, a variety of processes including ligand-exchange reactions, cation exchange, metal-ion complexation, and adsorption of organic compounds, will influence the equilibrium of the solution. Within the interstitial waters of the sediments, especially under anaerobic reducing conditions, contaminants would not be very mobile and would most likely become associated with the solid phase of the sediments. The increased organic matter contributed from the seawater could also change the redox potential and alter the pH within the mixing zones.

Overall the net effect on contaminant migration from the interaction with DOC would be dependent on the specific conditions at the site. Given the length of time that most hazardous waste sites have been present, steady state conditions probably predominate. Therefore data on the actual distribution coefficients between the dissolved and solid phases measured at the site would be very useful in evaluating the importance of various sorption mechanisms. If one assumes that the concentration of the chemical in the sediment (solid phase - C_s) is proportional to its concentration in the water (aqueous phase - C_w) then a distribution coefficient (K_D) can be defined where:

$$C_s = K_D C_w \quad [18]$$

The distribution coefficient can be empirically calculated from the ratio of the chemical concentrations measured in the sediment and in the water.

$$K_D = \frac{C_s}{C_w} \quad [19]$$

Where

K_D = the distribution coefficient ($\mu\text{g/g}$ solid)/($\mu\text{g/L}$ water)

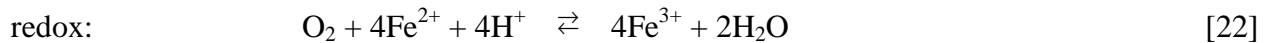
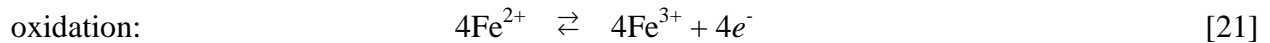
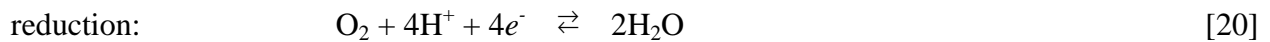
C_w = concentrations of chemical in the aqueous phase ($\mu\text{g/L}$)

C_s = concentration of chemical in the solid phase (soil or sediment) ($\mu\text{g/g}$)

Redox Potential

Used to describe the potential for electrons to be transferred between ions, the oxidation-reduction potential (redox potential) represents the "oxidizing power of the system at equilibrium" (Riley and Chester 1971, p76). In redox reactions, oxidation refers to the loss of an electron (e^-), reduction refers to gaining an electron, and the redox potential, which can be measured with an ion specific electrode, is positive if conditions favor oxidation and negative if conditions favor reduction.

In natural systems there are no free electrons so every redox reaction has both a reduction and oxidation component (Stumm and Morgan 1981):



Theoretically, the redox potential of a system is dependent on the activity of the electrons at equilibrium. The parameter, pE, is used to estimate the tendency of a solution to accept or donate electrons:

$$\begin{aligned} \text{pE} &= -\log[e^-] \quad [23] \\ &= E_H / \frac{2.3RT}{F} \\ &= E_H / 0.5915 \text{ at } 25^\circ\text{C} \text{ (Riley and Chester 1997)} \end{aligned}$$

where E_H = the equilibrium redox potential in volts (hydrogen scale)

R = the gas constant 0.001987 kcal/mol·Kelvin

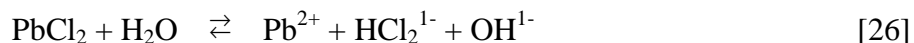
T = temperature (Kelvin)

F = the Faraday constant 23.06 kcal/V

Under reducing conditions heavy metals would have a tendency to gain electrons resulting in reactions that will lower the valence state, mobility, and toxicity of the metal. For example:



Whereas, under oxidizing conditions metal ions will have a tendency to under go reactions that will cause the loss of electrons resulting in a increase in the valence state, mobility, and toxicity of the metal. For example:



In natural waters, redox reactions are usually quite different from what would be predicted based on thermodynamics (Horne 1965, Stumm and Morgan 1981). This is because many redox reactions are slow and the redox potential is controlled by the presence of dissolved oxygen (O₂) which is biologically mediated and can be highly variable (Stumm and Morgan 1981). A strong oxidizing agent, the oxygen content in natural waters is controlled by the contact with the atmosphere, primary production which produces O₂, and microbial breakdown of organic matter which consumes O₂. Due to varying rates of diffusion, dispersion, microbial activity, and different constituents in the sediments and groundwaters, local redox reactions can result in very different redox potentials within microenvironments of surface water, groundwater, soils, and sediments.

Seawater, which usually has high concentrations of O₂ from contact with the atmosphere and primary production, is an oxidizing environment and sediment, because of high microbial activity and isolation from the atmosphere, is usually a reducing environment. The redox of groundwater can vary greatly. Groundwaters can be classified into four general redox domains (Allard 1995):

1. *Oxidized groundwaters.* Groundwaters with oxygen levels near saturation because the groundwater has short residence time (atmospheric equilibrium is maintained) and/or there is very little organic matter for microbial decomposition.

2. *Moderately reduced groundwaters.* Groundwaters with concentrations of Fe²⁺ and Mn²⁺ where the redox potential is controlled by the solid phase iron (Fe(OH)₃) or Fe₂O₃) and manganese (MnO₂) minerals.

3. *Reduced groundwaters.* Groundwaters that have concentrations of H₂S⁻ and HS where the redox potential is controlled by sulfate (SO₄²⁻) reduction.

4. *Very reduced groundwaters.* Groundwaters where the redox potential is determined by the decomposition of organic matter.

In cases where seawater mixes with groundwater from domains 1 and 2, there will only be minor changes in the redox potential and the presence of oxidized species would be favored. Because oxidized metals are more biologically available and more mobile, chemicals would be more likely transported from the site under these conditions. In cases where seawater mixes with groundwater from domains 3 and 4 the potential to change the oxidation state is greater but it is unclear whether the oxidizing reactions would result in mobilizing contaminants. The oxidation and mobilization of heavy metals would be dependent on the rate of oxidation, which can be very slow, and the interaction with the solid phases present in the sediment. The solid phases present in reducing environments of the sediments include acid volatile sulfides (Di Toro et al. 1990, Di Toro et al. 1992), iron and manganese minerals (Stumm and Morgan 1981), and complex organic matter (Thurmond 1980, Stumm and Morgan 1981). These solid phases will be more important

in controlling the availability and mobility of contaminants than changes in the redox potential caused by mixing with seawater.

pH

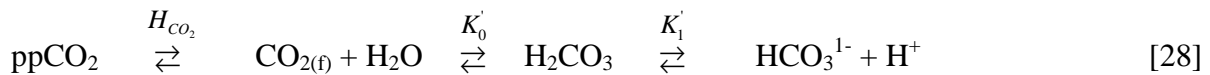
In natural waters the concentration of hydrogen is very important in determining chemical equilibrium. Commonly referred to as pH, the concentration (i.e. activity) of hydrogen can be measured with an ion specific electrode:

$$\text{pH} = -\log[\text{H}^+] \quad [27]$$

where $[\text{H}^+] =$ concentration of free hydrogen in the solution

In natural waters the concentration of free hydrogen is controlled primarily by the carbonate system. The carbonate system consists of dissolved (free) carbon dioxide ($\text{CO}_{2(\text{f})}$), carboxylic acid (H_2CO_3), bicarbonate (HCO_3^{1-}), and carbonate (CO_3^{2-}). The carbonate system can be defined as the equilibrium between CO_2 in the atmosphere, the dissolved species in seawater, and the solid species (e.g. calcium carbonate - CaCO_3) in the sediments and aquifer materials (Pilson 1998).

Surface waters in contact with the atmosphere will dissolve CO_2 in proportion to the partial pressure of the gas (ppCO_2) and the Henry's Law constant (H_{CO_2}) for the temperature and salinity of the water. The dissolved CO_2 will react with H_2O and disassociate until an equilibrium with the other carbon species⁶ is reached (Pilson 1998):



Where the K 's are the apparent disassociation constants and H^+ is the activity of hydrogen in solution. The disassociation constants are dependent on the temperature and salinity of the solution (Pilson 1998) and the concentration of CO_2 is affected by biological activity. Primary production consumes CO_2 and microbial decomposition releases CO_2 .

In addition to the carbonate species, boric acid (H_3BO_3) and borate ions (H_2BO_3^-) are present in seawater at high enough concentrations to affect the H^+ ion concentration⁷ (Pilson 1998). Boric acid will dissociate according to:

⁶ For simplicity, the disassociation of H_2O and interaction with the solid phase carbonates have been omitted from this analysis.

⁷ Other minor species present include OH^- , HPO_4^{2-} , MgOH^+ , $\text{H}_3\text{SiO}_4^{1-}$, NH_3^{1-} and organic matter. For simplicity these species were not included in this analysis.



where, K'_B is the temperature- and salinity-dependent disassociation constant. At equilibrium the concentrations of individual carbonate species can be calculated (Pilson 1998).

$$[\text{HCO}_3^{1-}] = \frac{K'_1 \times [\text{CO}_2]}{[\text{H}^+]} \quad [31]$$

$$[\text{CO}_3^{2-}] = \frac{K'_2 \times [\text{HCO}_3^{1-}]}{[\text{H}^+]} \quad [32]$$

The concentration of total borate [B] is directly proportional to the salinity (Pilson 1998):

$$[\text{B}] = 0.00001188 \times \text{S} \quad [33]$$

and the borate ion concentration can be calculated from its disassociation constant (Pilson 1998):

$$[\text{H}_2\text{BO}_3^{1-}] = \frac{K'_B \times [\text{B}]}{([\text{H}^+] + K'_B)} \quad [34]$$

Seawater is highly buffered and slightly alkaline. Highly buffered means that large changes in the hydrogen ion concentration will result in only small changes in the pH. The buffering occurs because the carbonate and borate species are present in high enough concentrations to bind with excess hydrogen ions. The buffering will continue until the carbonate and borate ions are exhausted and then a rapid change in pH will occur (Pilson 1998). The buffering capacity can be measured by titrating a sample of water with acid and is referred to as total alkalinity (TA mEq/Kg), where alkalinity refers to the ability of the solution to bind with acid $[\text{H}^+]$. The total alkalinity of the solution consists of the alkalinity contributed by the carbonate species (carbonate alkalinity - CA) and borate species (borate alkalinity - BA):

$$\text{TA} = \text{CA} + \text{BA} \quad [35]$$

Where

$$\text{BA} = [\text{H}_2\text{BO}_3^{1-}] \quad [36]$$

and

$$\text{CA} = [\text{HCO}_3^{1-}] + 2[\text{CO}_3^{2-}] \quad [37]$$

Given that a parcel of seawater of salinity 35 and temperature 25°C is in equilibrium with atmospheric CO_2 , the equilibrium pH is 8.2 and the concentration of each of the species can be calculated⁸ (Pilson 1998). Assuming that the ppCO_2 remains constant at 0.0003806 atm (e.g. no

⁸ Because the concentration of H_2CO_3 is very small and directly proportional to $\text{CO}_{2(f)}$, the activity of dissolved $[\text{CO}_2]$ is defined as $[\text{CO}_2] = [\text{CO}_{2(f)}] + [\text{H}_2\text{CO}_3]$.

changes in CO₂ from biological activity) the concentration of dissolved CO₂ can be calculated by:

$$[\text{CO}_2] = \text{H}_{\text{CO}_2} \times \text{ppCO}_2 \quad [38]$$

and

$$\text{ppCO}_2 = [\text{CO}_2] / \text{H}_{\text{CO}_2} \quad [39]$$

Using the above relationships, the changes in pH as a function of ppCO₂ and TA can be estimated for mixing seawater (S=35, T=25°C) with groundwater (S=0, T=5°C) (Appendix A). The calculations were made for mixing with three types of groundwater, neutral groundwater with the same ppCO₂ as seawater (neutral groundwater), acidic groundwater with and the same ppCO₂ as seawater (acidic groundwater), and very acidic groundwater isolated from the atmosphere with a higher ppCO₂ than seawater (Figure 2). The first two cases simulate seawater and groundwater mixtures that are in contact with the atmosphere (constant ppCO₂), while the latter case simulates mixing when the waters can not exchange gases with the atmosphere. These calculations were checked by mixing a sample of Narragansett Bay water (S=30, pH=7.97) with deionized water from the laboratory. The pH measured in the mixtures showed good agreement with the calculations (Figure 2).

Neutral groundwaters (pH=7) commonly occur when the groundwater pH is controlled by equilibrium with calcium carbonate (Allard 1995). Acidic groundwaters (pH=3) can occur if the groundwater has large concentrations of metal hydroxides obtained from the dissolution of iron and aluminum oxides (as can occur from mine tailings, Allard 1995). Very acidic (pH=2.4) groundwaters could also occur if groundwater high in organic matter was isolated from the atmosphere and microbial activity consumed all the available oxygen. When isolated from the atmosphere, the buildup of CO₂ will result in a much higher ppCO₂ in the groundwater than in the atmospherically-stable seawater.

Assuming that groundwater (S=0, T=5°C) was saturated with oxygen when it was formed, the dissolved oxygen concentration would be 0.0003991 mole O/Kg or 0.000199 mole O₂/Kg (Pilson 1998). If all the oxygen were consumed by the microbial reduction of organic matter 0.000199 mole CO₂/Kg would be added to the groundwater. If the groundwater was in equilibrium with the atmosphere (ppCO₂ = 0.000354 atm) at the time of formation the initial [CO₂] would be 0.00002268 mol/Kg (Pilson 1998). Isolated from exchange with the atmosphere, the increase in CO₂ would raise the dissolved CO₂ (0.0002254 mole CO₂/Kg) and increase ppCO₂ (Equation [39]) to 0.003578 atm. The pH resulting from such a high increase in CO₂ was calculated to be 2.4 (Appendix A).

The mixing simulations show the high buffering capacity of seawater (Figure 2, Table 4). Initially, there are only small changes in pH. The pH of the solution remains near neutral until the solution is more than 90% groundwater (S=3.5), then a rapid change in pH occurs. These results indicate that as groundwaters mix with saline waters the pH would be neutralized. Therefore, contaminants that would be more toxic and mobile at lower pH levels in the groundwater would become less toxic and less mobile before exposure to marine and estuarine receptors would occur. The extreme changes in pH calculated in the mixing examples represent the "worst case" and ignore changes in pH from maintaining equilibrium with the solid phase carbonates (which would dissolve in response to low pH providing further buffering) and primary production (which would consume CO₂ raising the pH). Moreover, other reactions caused by the shift in pH

would determine the speciation of chemical present. For example, if iron rich groundwaters with low pH mix with more alkaline seawater, the resulting iron hydroxide precipitates will scavenge trace metals as coprecipitates reducing the trace metal concentrations to levels far below what would be predicted from their solubility product (Allard 1995). The actual conditions at the site will be very important in determining the factors that will control contaminant mobility and toxicity. Because pH can be easily altered by improper sample handling, care must be taken to assure that samples are representative of the hydrological conditions at the site (Allard 1995, Fetter 1994)

Kinetic Considerations

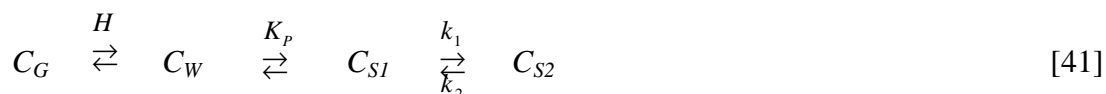
Given the fact that most hazardous waste sites have been in existence for considerable periods (decades), it is very likely that steady-state conditions have developed. Steady-state does not necessarily mean equilibrium in the thermodynamic sense, but rather that a balance between the competing, complimentary, and interacting processes has been established. This balance is a result of opposing forces and it follows that if the conditions change, then a new steady state will arise from the processes that will be favored under the new conditions. The rate of change from one steady state to another and the importance of some processes over others can be evaluated by considering the kinetics of the reactions.

If equilibrium conditions exist, then the adsorption rate, or uptake rate (k_1), of a chemical should be equal to the desorption rate, or release rate (k_2):

$$k_1 = k_2 \quad [40]$$

and there should be singularity, or identical curves obtained from measurements of adsorption and desorption. However, hysteresis (nonsingularity), or different curves of chemical adsorption and desorption have been observed in many studies (Pignatello 1991, Hutzinger and Alexander 1995, Alexander 1995) confirming that, in many cases, the uptake and desorption rates are not equal and reversible ($k_1 \neq k_2$). The hysteresis could be explained by, artifacts introduced by methods, chemical or biological transformations of the sorbing chemical, "competitive adsorption" or the creation of additional "sorptive sites" due to manipulation of the substrate during sorption experiments, the existence of a fraction of the sorbate that does not desorb because it is "resistant" or "irreversible," and the possibility that equilibrium was never reached (Pignatello 1989, Pignatello 1991).

In its simplest formulation, a kinetic nonequilibrium model assumes that there are two zones (or two types of sites) where chemicals can sorb, a mobile (labile) zone and an immobile (nonlabile) zone (Figure 3). It is usually assumed that nonequilibrium is reversible and first order (Harmon et al. 1989), and can be conceptualized as a bicontinuum model:



where $C_G =$ concentration in gaseous phase

H = Henry's Law Constant

C_W = concentration in aqueous phase

K_P = partitioning coefficient

C_{S1} = concentration sorbed to the labile phase

C_{S2} = concentration sorbed to the nonlabile phase

and $C_S = C_{S1} + C_{S2}$ = total amount sorbed [42]

$C_{S1} = fK_P C_W$ [43]

$C_{S2} = (1 - f) K_P C_W$ [44]

where f is the fraction of sorption sites that equilibrates rapidly enough (instantaneously - TYPE I) to be described by equilibrium partitioning (Di Toro et al. 1991) and $(1 - f)$ is the fraction of sorption sites that are described by nonequilibrium sorption (TYPE II). The change in concentration with respect to time can be modeled for both types of sites:

TYPE I: $\frac{\partial C_{S1}}{\partial t} = fK_P \frac{\partial C_W}{\partial t}$ [45]

TYPE II: $\frac{\partial C_{S2}}{\partial t} = k_1 f K_P C_W - k_2 C_{S2}$ [46]

The bicontinuum model is based on modeling the mass transfer of chemical between the various phases, and thus avoids the necessity of elucidating the dynamics of all the chemical binding and adsorption processes that may be acting on the system. In addition, the mass transfer approach is not limited to specific processes so it is ideal for evaluating systems, such as aquatic sediments, where nonequilibrium sorption could be caused by a variety of factors including physical or transport interferences, chemical reactions between the sorbant and sorbate, and different sorption capacities between the labile and nonlabile fractions of the sorbent (Brusseau, Jessup and Rao 1990). By isolating specific processes in laboratory studies, the importance of various mechanisms in controlling sorption behavior can be evaluated and verified with field measurement (Brusseau, Jessup and Rao 1990). The applicability of using this approach to relate sorption processes to toxicity and bioaccumulation in marine and estuarine systems is part of a project to determine the assimilative capacity of sediments and other shoreline substrates (Johnston 1995, Johnston in prep).

It is important to consider the kinetics of the system because over time the factors controlling sorption and desorption can change. Recent studies have shown that the longer contaminants reside in soils and sediments the more tightly bound, resistant, and less toxic they become (Hutzinger and Alexander 1995, Alexander 1995). The toxicity and mobility of the contaminants decreases with duration because the compounds become sequestered in inaccessible microsites within the soil matrix. One theory hypothesizes that this occurs because organic compounds continually diffuse further and further into the nanopores of the organic

matter in the soil matrix greatly reducing their bioavailability, biodegradability, and transportability (Pignatello and Xing 1996).

Summary and Conclusions

The most important factor regarding the influence of seawater on the partitioning of contaminants in groundwater and soils is the situation at the site. Although every site is different, this review focused on factors and processes that are generally applicable to all sites. The complexity of the competing and interacting processes is apparent and the need to develop site-specific information is clear. The physical forces of tidal fluctuations and groundwater flow at the site will determine the degree to which tidal waters come into contact with contaminated material and the groundwater flow will determine the net discharge of groundwater into coastal and estuarine waters. Once the waters mix, the partitioning and sorption behavior of the contaminants will be governed by the physical and chemical properties of the resulting solutions (solvents) and substrates (sorbents) existing at the site.

Although the theoretical basis outlined above is very useful for providing a context for evaluating contaminant behavior, each site is essentially an experiment in progress and the outcome of the experiment can be best evaluated by direct observations made at the site. When the observations are conducted within a sound theoretical framework, the important factors that are controlling contaminant availability and transportability can be identified and explained. The information can then be used to develop practical remediation schemes. By developing remedial strategies that take advantage of the natural sorptive and detoxifying characteristics of the receiving material, it may be possible to cost-effectively remove contaminants from runoff and leachates, or to amend existing sediments and shoreline materials with highly sorptive substrates (such as, clays, peat, detrital material, etc.) to reduce or eliminate the exposure of toxic substances to aquatic organisms.

REFERENCES:

- Alexander, M. 1995. How toxic are chemicals in soil? *Environment Science and Technology*, 29:11, pp. 2713-2717.
- Allard, B., 1995. Groundwater. In Trace Elements In Natural Waters, Salbu, B. and E. Steinnes (eds.), CRC Press, Boca Raton, FL, pp. 151-176.
- Brown, J., A. Colling, D. Park, J. Phillips, D. Rothery, and J. Wright, 1989. Seawater: Its Composition, Properties And Behaviour. Pergammon Press, Oxford, 165 pp.
- Brusseau, M.L., R.E. Jessup and P.S.C. Rao, 1990. Sorption kinetics of organic chemicals: Evaluation of gas-purge and miscible-displacement techniques, *Environmental Science and Technology*, 24:5, pp. 727-735.
- Di Toro, D.M., J.D. Mahoney, D.J. Hansen, K.J. Scott, A.R. Carlson, and G.T. Ankley. 1992. Acid volatile sulfide predicts the acute toxicity of cadmium and nickel in sediments. *Environmental Science and Technology* 26: 96-101.
- Di Toro, D.M., J.D. Mahony, D.J. Hansen, K.J. Scott, M.B. Hicks, S.M. Mayr, and M.S. Redmond. 1990. The toxicity of cadmium in sediments: The role of acid volatile sulfide. *Environmental Toxicology and Chemistry* 9: 1487-1502.
- Di Toro, D.M., C.S. Zarba, D.J. Hansen, W.J. Berry, R.C. Swartz, C.E. Cowan, S.P. Pavlou, H.E. Allen, N.A. Thomas, and P.R. Paquin, 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environmental Toxicology and Chemistry*, 10: pp.1541-1583.
- Fetter, C.W., 1994. Applied Hydrogeology (3rd Edition). Prentice-Hall, Upper Saddle River, NJ., 691 pp.
- Gschwend, P.M. and S. Wu, 1985. On the constancy of sediment-water partition coefficients of hydrophobic organic pollutants, *Environmental Science and Technology*, 19:1, pp. 90-96.
- Hasset, J.L and W.L. Banwart, 1989. The sorption of nonpolar organics by soils and sediments. In Reaction and Movement of Organic Chemicals in Soils, B.L Sawhney and K. Brown (eds), SSSA Special Publication Number 22, Soil Science Society of America, Madison, WI, pp. 31-44.
- Hatzinger, P.B. and M. Alexander, 1995. Effect of aging of chemicals in soil on their biodegradability and extractability. *Environment Science and Technology*, 29:2, pp. 537-545.
- Harmon, T.C., W.P. Ball, and P.V. Roberts, 1989. Nonequilibrium transport of organic contaminants in groundwater. In Reaction and Movement of Organic Chemicals in Soils, B.L Sawhney and K. Brown (eds), SSSA Special Publication Number 22 Soil Science Society of America, Madison, WI, pp. 405-438.

- Hegeman, W.J., C.H. van der Weijden, and J.P. Gustav Loch, 1995. Sorption of benzo[a]pyrene and phenanthrene to suspended harbor sediment as a function of suspended sediment concentration and salinity: A laboratory study using the cosolvent partition coefficient. *Environment Science and Technology*, 29:2, pp. 363-371.
- Horne, R.A., 1969. Marine chemistry: The Structure Of Water And The Chemistry Of The Hydrosphere. Wiley-Interscience, NY, 568 pp.
- Johnston, R.K. 1995. Measurement and prediction of sediment assimilation capacity (abstract only). In Independent Research (IR) 1995 Annual Report, Technical Document 2868, Naval Command Control and Ocean Surveillance Center, RDT&E Division, San Diego, CA.
- Johnston, R.K. in prep. An evaluation of the assimilative and detoxifying capacity of aquatic sediments.
- Moore, W.S., 1996. Large groundwater inputs to coastal waters revealed by ^{226}Ra enrichments. *Nature*, 380 pp. 610-614.
- Pignatello, J.J., 1989. Sorption dynamics of organic compounds in soils and sediments. In Reaction and Movement of Organic Chemicals in Soils, B.L. Sawhney and K. Brown (eds), SSSA Special Publication Number 22, Soil Science Society of America, Madison, WI, pp. 45-80.
- Pignatello, J.J., 1991. Competitive effects in the sorption of nonpolar organic compounds by soils. In Organic Substances and Sediments in Water: Volume 1 Humics and Soils, R.A. Baker (ed), Lewis Publishers, Inc., Chelsea, MI, pp. 291-309.
- Pignatello, J.J. and B. Xing, 1996. Mechanisms of slow sorption of organic chemicals to natural particles. *Environment Science and Technology*, 30:1, pp. 1-11.
- Pilson, M.E.Q., 1998. An Introduction To The Chemistry Of The Sea. Prentice-Hall, Upper Saddle River, NY, 431 pp.
- Riley, J.P. and R. Chester, 1971. Introduction To Marine Chemistry. Academic Press, NY, 465 pp.
- Thurman, E.M., 1995. Organic Geochemistry of Natural Waters. Martinus Nijhoff/Dr. W. Junk Publishers, Boston, MA, 497 pp.
- Stumm, W. and J.J. Morgan, 1981. Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria In Natural Waters. John Wiley & Sons, NY, 780 pp.

Table 1. The average concentration (g/Kg seawater) of dissolved salts (major constituents) in seawater with a Salinity of 35. The molal concentration (moles/Kg seawater), the proportionality (g/g salt), and the ionic strength of the solution are calculated.

Species	Ion	charge	Conc. ⁹ (g/Kg Seawater)	Conc. ¹⁰ (mol/Kg Seawater)	proportion ¹¹ g/g salt	Ionic Strength ¹²
Sodium	Na ⁺	1	10.781	0.46896	0.30804	
Magnesium	Mg ²⁺	2	1.284	0.05283	0.03669	
Calcium	Ca ²⁺	2	0.412	0.01028	0.01177	
Potassium	K ⁺	1	0.399	0.01021	0.01140	
Strontium	Sr ²⁺	2	0.008	0.00009	0.00023	
Chloride	Cl ⁻	-1	19.353	0.54588	0.55294	
Sulfate	SO ₄ ²⁻	-2	2.712	0.02823	0.07749	
Bicarbonate	HCO ₃ ¹⁻	-1	0.126	0.00207	0.00360	
Bromide	Br ⁻	-1	0.067	0.00084	0.00192	
Borate	H ₂ BO ₃ ¹⁻	-1	0.026	0.00043	0.00075	
Fluoride	F ⁻	-1	0.001	0.00007	0.00004	
	total		35.170	1.1198		0.69705

⁹ Data from Pilson 1998, p59.

¹⁰ Calculated as Conc. g/Kg ÷ atomic weight of ion.

¹¹ Calculated as Conc. g/Kg ÷ S

¹² Calculated with Equation [5].

Table 2. Changes in salinity, molality, and ionic strength as seawater of salinity 35 is diluted by groundwater of salinity 0.

% Groundwater	Salinity	mol/Kg	Ionic Strength
5	33.25	1.0638	0.6622
10	31.50	1.0078	0.6273
20	28.00	0.8959	0.5576
50	17.50	0.5599	0.3485
75	8.75	0.2800	0.1743
90	3.50	0.1120	0.0697
95	1.75	0.0560	0.0349
98	0.70	0.0224	0.0139

Table 3. A. Density of seawater (S = 10 to 35, Pilson 1998) and absolute water (S = 0, Fetter 1994) as a function of temperature and salinity. B. Change in density of seawater from mixing with groundwater.

A. Density of seawater as a function of temperature and salinity.

Salinity (S)	Temperature (°C)				
	5	10	15	20	25
0	999.97	999.70	999.10	998.20	997.04
10	1007.91	1007.50	1006.78	1005.79	1004.56
20	1015.81	1015.27	1014.44	1013.36	1012.05
30	1023.71	1023.05	1022.12	1020.95	1019.57
35	1027.68	1026.95	1025.97	1024.76	1023.34

B. Density after seawater of salinity of 35 is diluted with groundwater.

%GW	Temperature (°C)				
	5	10	15	20	25
100	999.97	999.70	999.10	998.20	997.04
95	1001.35	1001.06	1000.44	999.53	998.36
90	1002.74	1002.43	1001.79	1000.86	999.67
80	1005.51	1005.15	1004.47	1003.52	1002.30
50	1013.82	1013.33	1012.54	1011.48	1010.19
20	1022.13	1021.50	1020.60	1019.45	1018.08
10	1024.91	1024.23	1023.29	1022.11	1020.71
5	1026.29	1025.59	1024.63	1023.44	1022.03

Table 4. Change in the pH of seawater (S=35, T=25, pH=8.2) as a function of mixing with groundwaters from different origins.

		pH		
		Initial Conditions of Groundwater to be mixed		
		Neutral Groundwater	Acidic Groundwater	Very Acidic Groundwater Isolated from Atmosphere
Percent of Ground Water Mixed	S	pH=7, T=5, S=0	pH=3, T=5, S=0	ppCO ₂ = 0.00346, T=5, S=0
0%	35.00	8.20	8.20	8.20
10%	31.50	8.17	8.17	8.18
20%	28.00	8.13	8.13	8.16
30%	24.50	8.09	8.08	8.14
40%	21.00	8.04	8.03	8.04
50%	17.50	7.98	7.95	7.84
60%	14.00	7.91	7.87	7.50
70%	10.50	7.80	7.76	7.15
80%	7.00	7.67	7.59	6.82
90%	3.50	7.45	7.29	6.41
95%	1.75	7.28	6.99	6.08
97%	1.05	7.19	6.77	5.84
99%	0.35	7.07	6.30	5.35

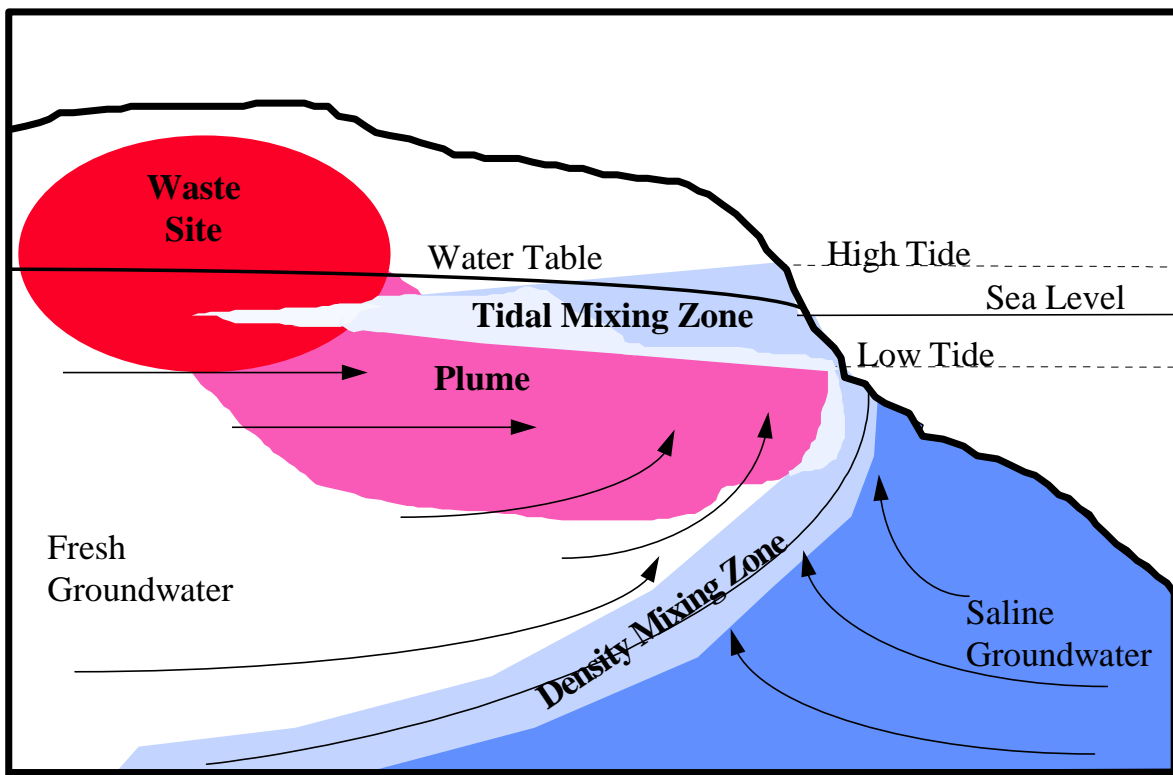


Figure 1. Diagram of a hazardous waste site located in a coastal area and its relationship to the water table, tidal level, and mixing between saline groundwater and fresh groundwater (Density Mixing Zone) and groundwater and seawater (Tidal Mixing Zone). Diagram not to scale (adapted from Fetter 1994).

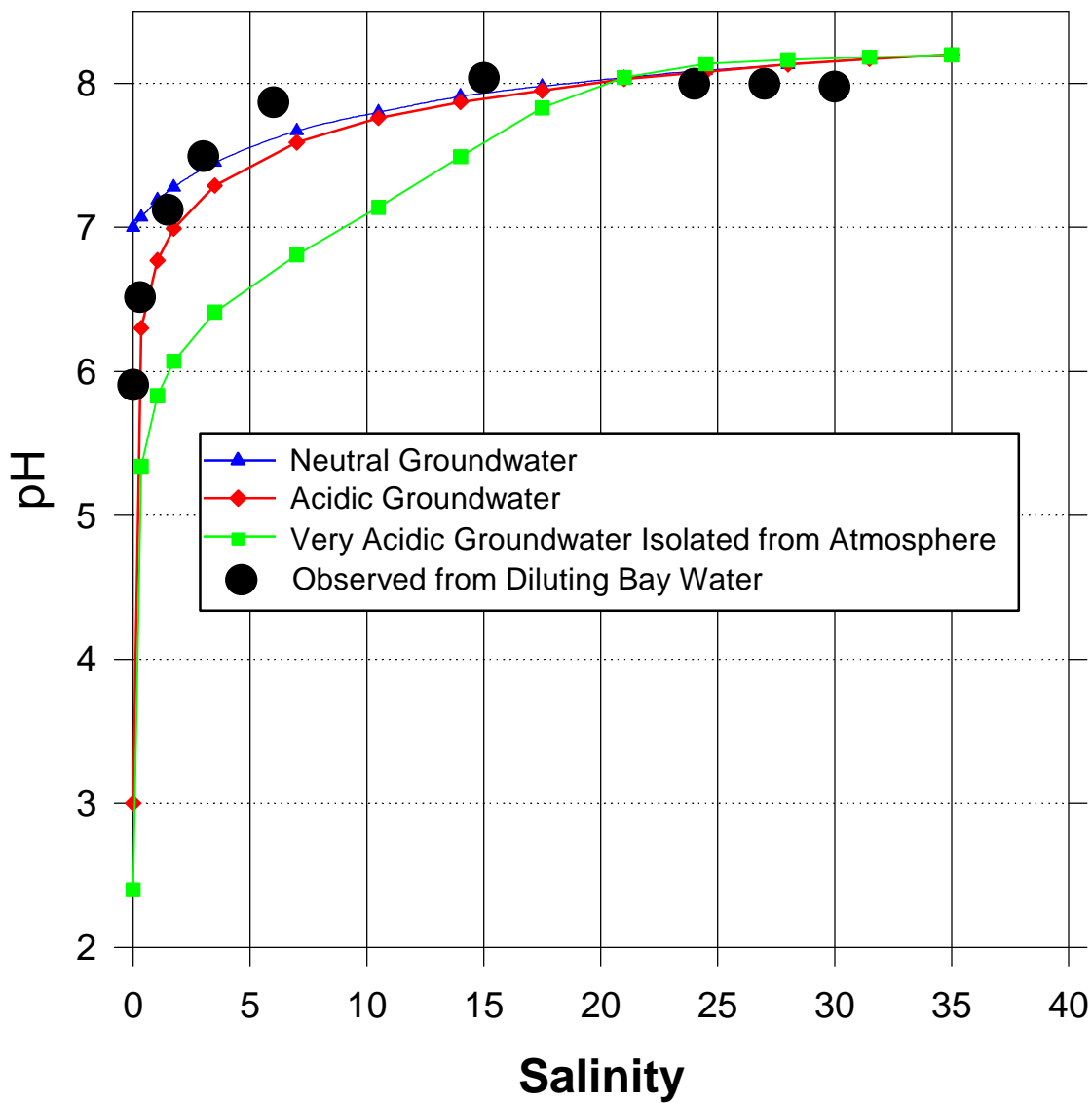
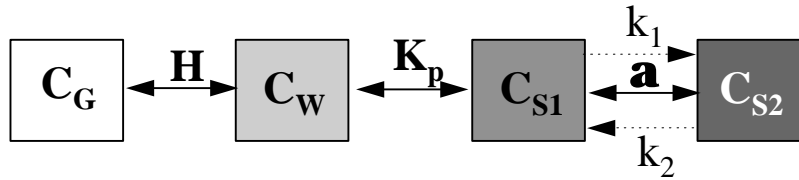


Figure 2. Change in pH as a function of seawater ($S=35$, $T=18^{\circ}\text{C}$) mixing with groundwater ($S=0$, $T=5^{\circ}\text{C}$) from different origins. The change in pH obtained from mixing Narragansett Bay water ($S=30$, $\text{pH}=7.97$, $T=22^{\circ}\text{C}$) with laboratory deionized water ($S=0$, $\text{pH}=5.91$, $T=22^{\circ}\text{C}$) is also shown.

Conceptual Model of Sediment Sorption Processes



STATE VARIABLES

C_G = Concentration in Gas Phase

C_W = Concentration in Water Phase

C_{S1} = Concentration Sorbed to Labile Phase

C_{S2} = Concentration Sorbed to Nonlabile Phase

TRANSFER COEFFICIENTS

H = Henry's Law Constant

K_p = Partition Coefficient

k_1 = Kinetic Uptake Rate

k_2 = Kinetic Release Rate

\mathbf{a} = First Order Sorption Rate Coefficient
(net effect of k_1 and k_2)

Figure 3. Conceptual model of sediment sorption processes.

Appendix A

To calculate the change in pH from mixing waters of different origins it was necessary to solve the carbonate system in terms of the partial pressure of CO₂ (ppCO₂) and total alkalinity (TA). The system was solved by relating the concentration of each of the species in terms of ppCO₂, TA, and H⁺ and then solving for the hydrogen ion concentration by iteration. The equation used to solve for H⁺ was obtained from the following relationships.

Substituting Equation 32 into Equation 37 and solving for bicarbonate, the concentration of bicarbonate can be expressed as a function of carbonate alkalinity.

$$[\text{HCO}_3^{1-}] = CA \frac{[H^+]}{([H^+] + 2K_2')} \quad [47]$$

From Equation 31, the concentration of bicarbonate can be expressed as a function of carbon dioxide and Equation 47 can be rearranged to obtain:

$$[\text{CO}_2] = \frac{CA[H^+]^2}{K_1'([H^+] + 2K_2')} \quad [48]$$

Equation 38 can then be used to relate the Equation 48 to the partial pressure of carbon dioxide:

$$\text{ppCO}_2 = \frac{CA[H^+]^2}{H_{\text{CO}_2} K_1'([H^+] + 2K_2')} \quad [49]$$

Additionally, carbonate alkalinity (CA) can be calculated as total alkalinity¹³ minus the contribution from borate alkalinity (Equation 35) where borate alkalinity is expressed as function of the borate concentration (Equations 34 and 36) to obtain:

$$CA = TA - \frac{K_B' \times [B]}{([H^+] + K_B')} \quad [50]$$

Substituting Equation 50 for carbonate alkalinity in Equation 49 and solving for the hydrogen ion concentration, the relationship between pH as a function of total alkalinity and the partial

¹³ Because the contribution of OH⁻ alkalinity (OH⁻ alk) is so small it was neglected from this analysis. The OH⁻ alk of seawater (S=35, T=18, pH=8.2) is 0.0000038 mole/Kg (Pilson 1998). The OH⁻ alk was subtracted from TA before calculating the concentrations of the other species (Table A-1 to A-6).

pressure of carbon dioxide was obtained:

$$\begin{aligned}
 0 = & -TA[H^+]^3 & [51] \\
 & + \left(H_{CO_2} ppCO_2 K_1' - (TA)K_B' + K_B'[B] \right) [H^+]^2 \\
 & + \left(2H_{CO_2} ppCO_2 K_1' K_2' + H_{CO_2} ppCO_2 K_1' K_B' \right) [H^+] \\
 & + \left(H_{CO_2} ppCO_2 K_1' K_2' K_B' \right)
 \end{aligned}$$

The carbonate species for seawater and groundwater were calculated as a function of diluting seawater with groundwater and recalculating the equilibrium with Equation 51 by iteration¹⁴.

The changes in pH as a function of ppCO₂ and TA were calculated for mixing seawater (S=35, T=18°C, pH=8.2, ppCO₂=0.0003806 atm) with neutral groundwater with the same ppCO₂ as the seawater (S=0, T=5°C, pH=7, ppCO₂=0.0003806 atm, Table A-1) acidic groundwater with and the same ppCO₂ as the seawater (S=0, T=5°C, pH=3, ppCO₂=0.0003806 mole/Kg, Table A-2), and very acidic groundwater isolated from the atmosphere with a much higher ppCO₂ than seawater (S=0, T=5°C, ppCO₂=0.0035182, Table A-3). The formulas (MS Excel[®]) used to calculate each species after mixing with groundwater s are provided in Table A-4, Table A-5, and Table A-6 for the results presented in Table A-1, Table A-2, and Table A-3, respectively.

For the very acidic groundwater isolated from the atmosphere, it was not possible to use Equation 51 to solve the pH concentration because ppCO₂ is nonconservative. In this case, the fact that T[CO₂] would be conservatively mixed was used to solve the equations. This was achieved by first calculating a target T[CO₂] concentration by conservatively mixing the T[CO₂] contributed from the seawater (T[CO₂]_S) and the groundwater (T[CO₂]_{GW}):

$$\text{Target T[CO}_2\text{]} = \text{T[CO}_2\text{]}_S(1-f) + \text{T[CO}_2\text{]}_{GW}(f) \quad [52]$$

where f is the fraction of groundwater mixed. Then the equations were solved by iterating the pH until the T[CO₂] of the mixture was equal to the target T[CO₂]. For the groundwater, Equation 51 was used to determine the initial using pH the initial [CO₂] and ppCO₂ determined for the groundwater (Table A-3 and Table A-6).

¹⁴ This was accomplished by entering a value for pH that would result in smallest absolute value for equation 51 that would not exceed 0.

Table A-1. Changes in carbonate species and pH as a result of mixing seawater with groundwater with pH=7 where TA was conservatively mixed and ppCO₂ was held constant. Units, unless otherwise noted, are moles/Kg. (See Table A-4 for equations).

bold = conservative mixing; pptCO ₂ held constant	Seawater to be mixed (<u>underline</u> = input, others calculated)	Groundwater to be mixed: pH=7, Temp=5, Sal=0	mixture 10% ground water, ppCO ₂ held constant	mixture 20% ground water, ppCO ₂ held constant	mixture 30% ground water, ppCO ₂ held constant	mixture 40% ground water, ppCO ₂ held constant	mixture 50% ground water, ppCO ₂ held constant	mixture 60% ground water, ppCO ₂ held constant	mixture 70% ground water, ppCO ₂ held constant	mixture 80% ground water, ppCO ₂ held constant	mixture 90% ground water, ppCO ₂ held constant	mixture 95% ground water, ppCO ₂ held constant	mixture 97% ground water, ppCO ₂ held constant	mixture 99% ground water, ppCO ₂ held constant
pH as a function of TA and ppCO ₂			10%	20%	30%	40%	50%	60%	70%	80%	90%	95%	97%	99%
S (psu)	<u>35</u>	<u>0</u>	31.5	28	24.5	21	17.5	14	10.5	7	3.5	1.75	1.05	0.35
t (C)	<u>18</u>	<u>5</u>	16.7	15.4	14.1	12.8	11.5	10.2	8.9	7.6	6.3	5.65	5.39	5.13
T (Kelvin)	291.15	278.15	289.85	288.55	287.25	285.95	284.65	283.35	282.05	280.75	279.45	278.8	278.54	278.28
[CO ₂]	1.30494E-05	2.4384E-05	1.3829E-05	1.4973E-05	1.587E-05	1.688E-05	1.789E-05	1.872E-05	2.043E-05	2.14E-05	2.322E-05	2.401E-05	2.416E-05	2.451E-05
[HCO ₃]	0.001877539	0.000115973	0.00175185	0.001622896	1.47E-03	1.31E-03	1.14E-03	9.47E-04	7.51E-04	5.46E-04	3.33E-04	2.25E-04	1.82E-04	1.38E-04
[CO ₃₂₋]	<u>0.0001835</u>	1.7779E-07	0.000139794	0.000102768	7.42E-05	5.12E-05	3.36E-05	2.08E-05	1.11E-05	5.20E-06	1.66E-06	7.07E-07	4.50E-07	2.52E-07
OH- alk	<u>0.0000038</u>													
BA	<u>0.0000816</u>	0	7.37754E-05	5.57944E-05	4.11E-05	2.87E-05	1.88E-05	1.14E-05	5.73E-06	2.36E-06	5.48E-07	1.52E-07	6.56E-08	1.37E-08
CA	0.0022446	0.000116328	0.002031437	0.001828431	1.62E-03	1.41E-03	1.20E-03	9.89E-04	7.74E-04	5.56E-04	3.37E-04	2.27E-04	1.83E-04	1.38E-04
TA	0.0023262	0.000116328	0.002105213	0.001884226	1.66E-03	1.44E-03	1.22E-03	1.00E-03	7.79E-04	5.58E-04	3.37E-04	2.27E-04	1.83E-04	1.38E-04
%TA			86.19%	77.14%	68.09%	59.05%	50.00%	40.95%	31.91%	22.86%	13.81%	9.29%	7.48%	5.67%
[B]	0.0004158	0	0.00037422	0.00033264	0.0002911	0.0002495	0.0002079	0.0001663	0.0001247	8.316E-05	4.158E-05	2.079E-05	1.247E-05	4.158E-06
T[CO ₂]	<u>0.002074089</u>	0.000140534	0.001905473	0.001740636	0.001564	0.001379	0.001187	0.000987	0.000783	0.000572	0.000358	0.0002500	0.0002063	0.000163
ppCO ₂ (atm)	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>
lnHco ₂	-3.373003474	-2.74782088	-3.315877693	-3.257545977	-3.20E+00	-3.14E+00	-3.08E+00	-3.01E+00	-2.95E+00	-2.88E+00	-2.82E+00	-2.78E+00	-2.77E+00	-2.75E+00
pKB'	8.738667533	9.73911267	8.78085278	8.825646782	8.87E+00	8.93E+00	8.98E+00	9.04E+00	9.12E+00	9.21E+00	9.32E+00	9.41E+00	9.47E+00	9.55E+00
pK1	6.041958708	6.322750041	6.068294319	6.09501738	6.12E+00	6.15E+00	6.18E+00	6.21E+00	6.23E+00	6.26E+00	6.29E+00	6.31E+00	6.31E+00	6.32E+00
pK2	9.209881192	9.814448411	9.269009884	9.328433693	9.39E+00	9.45E+00	9.51E+00	9.57E+00	9.63E+00	9.69E+00	9.75E+00	9.78E+00	9.80E+00	9.81E+00
Hco ₂	0.034286504	0.06406732	0.036302172	0.03848272	4.08E-02	4.34E-02	4.62E-02	4.92E-02	5.24E-02	5.60E-02	5.99E-02	6.19E-02	6.28E-02	6.36E-02
KB'	1.82529E-09	1.82342E-10	1.65633E-09	1.49401E-09	1.34E-09	1.19E-09	1.04E-09	9.02E-10	7.63E-10	6.24E-10	4.74E-10	3.85E-10	3.41E-10	2.80E-10
K1'	9.07907E-07	4.75609E-07	8.54487E-07	8.03494E-07	7.55E-07	7.09E-07	6.64E-07	6.23E-07	5.83E-07	5.45E-07	5.09E-07	4.92E-07	4.86E-07	4.79E-07
K2'	6.16764E-10	1.53303E-10	5.38258E-10	4.69425E-10	4.09E-10	3.56E-10	3.10E-10	2.70E-10	2.34E-10	2.04E-10	1.77E-10	1.65E-10	1.60E-10	1.56E-10
pH	<u>8.2</u>	<u>7</u>	8.171	8.13	8.09	8.04	7.98	7.91	7.80	7.67	7.45	7.28	7.19	7.07
[H+]	6.30957E-09	0.0000001	6.74528E-09	7.4131E-09	8.13E-09	9.12E-09	1.05E-08	1.23E-08	1.58E-08	2.14E-08	3.55E-08	5.25E-08	6.46E-08	8.51E-08
A	-0.0023262		-0.002105213	-0.001884226	-1.66E-03	-1.44E-03	-1.22E-03	-1.00E-03	-7.79E-04	-5.58E-04	-3.37E-04	-2.27E-04	-1.83E-04	-1.38E-04
B	8.36064E-12		8.93902E-12	9.45031E-12	9.90E-12	1.03E-11	1.06E-11	1.09E-11	1.11E-11	1.13E-11	1.15E-11	1.15E-11	1.15E-11	1.16E-11
C	3.62399E-20		3.22643E-20	2.86308E-20	2.53E-20	2.22E-20	1.94E-20	1.68E-20	1.43E-20	1.20E-20	9.61E-21	8.29E-21	7.67E-21	6.86E-21
D	2.66756E-29		2.10511E-29	1.65069E-29	1.28E-29	9.91E-30	7.55E-30	5.67E-30	4.16E-30	2.95E-30	1.95E-30	1.47E-30	1.27E-30	1.01E-30
[H+]	6.30957E-09		6.74528E-09	7.4131E-09	8.13E-09	9.12E-09	1.05E-08	1.23E-08	1.58E-08	2.14E-08	3.55E-08	5.25E-08	6.46E-08	8.51E-08
O=	3.8621E-30		-6.96882E-31	-1.95129E-29	-2.07E-29	-2.56E-29	-2.67E-29	-1.39E-31	-7.40E-29	-2.15E-29	-2.90E-28	-6.15E-28	-5.44E-28	-1.02E-27

Table A-2. Changes in carbonate species and pH as a result of mixing seawater with groundwater with pH=3 where TA was conservatively mixed and ppCO₂ was held constant. Units, unless otherwise, noted are moles/Kg. (See Table A-5 for equations)

bold = conservative mixing; pptCO ₂ held constant	Seawater to be mixed (<u>underline</u> = input, others calculated)	Groundwater to be mixed: pH=7, Temp=5, Sal=0	mixture 10% ground water, ppCO ₂ held constant	mixture 20% ground water, ppCO ₂ held constant	mixture 30% ground water, ppCO ₂ held constant	mixture 40% ground water, ppCO ₂ held constant	mixture 50% ground water, ppCO ₂ held constant	mixture 60% ground water, ppCO ₂ held constant	mixture 70% ground water, ppCO ₂ held constant	mixture 80% ground water, ppCO ₂ held constant	mixture 90% ground water, ppCO ₂ held constant	mixture 95% ground water, ppCO ₂ held constant	mixture 97% ground water, ppCO ₂ held constant	mixture 99% ground water, ppCO ₂ held constant
pH as a function of TA and ppCO ₂			10%	20%	30%	40%	50%	60%	70%	80%	90%	95%	97%	99%
S (psu)	<u>35</u>	<u>0</u>	31.5	28	24.5	21	17.5	14	10.5	7	3.5	1.75	1.05	0.35
t (C)	<u>18</u>	<u>5</u>	16.7	15.4	14.1	12.8	11.5	10.2	8.9	7.6	6.3	5.65	5.39	5.13
T (Kelvin)	291.15	278.15	289.85	288.55	287.25	285.95	284.65	283.35	282.05	280.75	279.45	278.8	278.54	278.28
[CO ₂]	1.30494E-05	2.4384E-05	1.38239E-05	1.47825E-05	1.593E-05	1.673E-05	1.833E-05	1.917E-05	2.011E-05	2.15E-05	2.322E-05	2.409E-05	2.436E-05	2.434E-05
[HCO ₃]	0.001877539	1.15973E-08	0.001743157	0.001602247	1.45E-03	1.27E-03	1.09E-03	8.85E-04	6.74E-04	4.56E-04	2.31E-04	1.16E-04	6.96E-05	2.33E-05
[CO ₃ ²⁻]	<u>0.0001835</u>	1.7779E-15	0.000138461	0.00010146	7.11E-05	4.85E-05	3.00E-05	1.77E-05	9.10E-06	3.61E-06	7.95E-07	1.86E-07	6.56E-08	7.22E-09
OH- alk	<u>0.0000038</u>													
BA	<u>0.0000816</u>	0	7.3503E-05	5.57944E-05	4.03E-05	2.82E-05	1.77E-05	1.04E-05	5.25E-06	1.97E-06	3.81E-07	7.80E-08	2.50E-08	2.33E-09
CA	0.0022446	1.15973E-08	0.002020078	0.001805168	1.59E-03	1.37E-03	1.15E-03	9.20E-04	6.93E-04	4.63E-04	2.32E-04	1.16E-04	6.98E-05	2.33E-05
TA	0.0023262	1.15973E-08	0.002093581	0.001860962	1.63E-03	1.40E-03	1.16E-03	9.30E-04	6.98E-04	4.65E-04	2.33E-04	1.16E-04	6.98E-05	2.33E-05
%TA			90.00%	80.00%	70.00%	60.00%	50.00%	40.00%	30.00%	20.00%	10.00%	5.00%	3.00%	1.00%
[B]	0.0004158	0	0.00037422	0.00033264	0.0002911	0.0002495	0.0002079	0.0001663	0.0001247	8.316E-05	4.158E-05	2.079E-05	1.247E-05	4.158E-06
T[CO ₂]	<u>0.002074089</u>	2.43956E-05	0.001895441	0.001718490	0.0015328	0.0013358	0.0011338	0.0009215	0.0007036	0.0004812	0.0002547	0.0001401	0.0000941	0.0000476
ppCO ₂ (atm)	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>
lnHco ₂	-3.373003474	-2.74782088	-3.315877693	-3.257545977	-3.20E+00	-3.14E+00	-3.08E+00	-3.01E+00	-2.95E+00	-2.88E+00	-2.82E+00	-2.78E+00	-2.77E+00	-2.75E+00
pKB'	8.738667533	9.73911267	8.78085278	8.825646782	8.87E+00	8.93E+00	8.98E+00	9.04E+00	9.12E+00	9.21E+00	9.32E+00	9.41E+00	9.47E+00	9.55E+00
pK1	6.041958708	6.322750041	6.068294319	6.09501738	6.12E+00	6.15E+00	6.18E+00	6.21E+00	6.23E+00	6.26E+00	6.29E+00	6.31E+00	6.31E+00	6.32E+00
pK2	9.209881192	9.814448411	9.269009884	9.328433693	9.39E+00	9.45E+00	9.51E+00	9.57E+00	9.63E+00	9.69E+00	9.75E+00	9.78E+00	9.80E+00	9.81E+00
Hco ₂	0.034286504	0.06406732	0.036302172	0.03848272	4.08E-02	4.34E-02	4.62E-02	4.92E-02	5.24E-02	5.60E-02	5.99E-02	6.19E-02	6.28E-02	6.36E-02
KB'	1.82529E-09	1.82342E-10	1.65633E-09	1.49401E-09	1.34E-09	1.19E-09	1.04E-09	9.02E-10	7.63E-10	6.24E-10	4.74E-10	3.85E-10	3.41E-10	2.80E-10
K1'	9.07907E-07	4.75609E-07	8.54487E-07	8.03494E-07	7.55E-07	7.09E-07	6.64E-07	6.23E-07	5.83E-07	5.45E-07	5.09E-07	4.92E-07	4.86E-07	4.79E-07
K2'	6.16764E-10	1.53303E-10	5.38258E-10	4.69425E-10	4.09E-10	3.56E-10	3.10E-10	2.70E-10	2.34E-10	2.04E-10	1.77E-10	1.65E-10	1.60E-10	1.56E-10
pH	<u>8.2</u>	<u>3</u>	8.169	8.13	8.08	8.03	7.95	7.87	7.76	7.59	7.29	6.99	6.77	6.30
[H ⁺]	6.30957E-09	0.001	6.77642E-09	7.4131E-09	8.32E-09	9.33E-09	1.12E-08	1.35E-08	1.74E-08	2.57E-08	5.13E-08	1.02E-07	1.70E-07	5.01E-07
A	-0.0023262		-0.002093581	-0.001860962	-1.63E-03	-1.40E-03	-1.16E-03	-9.30E-04	-6.98E-04	-4.65E-04	-2.33E-04	-1.16E-04	-6.98E-05	-2.33E-05
B	8.36064E-12		8.95829E-12	9.48507E-12	9.95E-12	1.03E-11	1.07E-11	1.10E-11	1.12E-11	1.14E-11	1.15E-11	1.16E-11	1.16E-11	1.16E-11
C	3.62399E-20		3.22643E-20	2.86308E-20	2.53E-20	2.22E-20	1.94E-20	1.68E-20	1.43E-20	1.20E-20	9.61E-21	8.29E-21	7.67E-21	6.86E-21
D	2.66756E-29		2.10511E-29	1.65069E-29	1.28E-29	9.91E-30	7.55E-30	5.67E-30	4.16E-30	2.95E-30	1.95E-30	1.47E-30	1.27E-30	1.01E-30
[H ⁺]	6.30957E-09		6.77642E-09	7.4131E-09	8.32E-09	9.33E-09	1.12E-08	1.35E-08	1.74E-08	2.57E-08	5.13E-08	1.02E-07	1.70E-07	5.01E-07
0=	3.8621E-30		-4.12997E-31	-8.1259E-30	-2.57E-29	-1.62E-29	-7.28E-29	-5.65E-29	-2.76E-29	-7.11E-29	-5.97E-28	-2.69E-27	-6.58E-27	-1.46E-26

Table A-3. Changes in carbonate species and pH as a result of mixing seawater with very acidic groundwater isolated from the atmosphere¹⁵, where TA and T[CO₂] were conservatively mixed. Units, unless otherwise specified, are moles/Kg. (See Table A-6 for equations)

bold = conservative mixing;	Seawater to be mixed (<u>underline</u> = input, others calculated)	Groundwater to be mixed: pH=7, Temp=5, Sal=0	mixture 10% ground water	mixture 20% ground water	mixture 30% ground water	mixture 40% ground water	mixture 50% ground water	mixture 60% ground water	mixture 70% ground water	mixture 80% ground water	mixture 90% ground water	mixture 95% ground water	mixture 97% ground water	mixture 99% ground water
f			0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	0.95	0.97	0.99
S (psu)	<u>35</u>	<u>0</u>	31.5	28	24.5	21	17.5	14	10.5	7	3.5	1.75	1.05	0.35
t (C)	<u>18</u>	<u>5</u>	16.7	15.4	14.1	12.8	11.5	10.2	8.9	7.6	6.3	5.65	5.39	5.13
T (Kelvin)	291.15	278.15	289.85	288.55	287.25	285.95	284.65	283.35	282.05	280.75	279.45	278.8	278.54	278.28
[CO ₂]	1.30494E-05	0.00022168	1.33848E-05	1.35174E-05	1.383E-05	1.632E-05	2.397E-05	4.624E-05	8.405E-05	0.0001287	0.0001775	0.0001965	0.0002078	0.0002172
[HCO ₃]	0.001878951	2.65446E-08	0.001735074	0.001584435	1.42E-03	1.27E-03	1.10E-03	9.10E-04	6.92E-04	4.64E-04	2.32E-04	1.16E-04	6.98E-05	2.33E-05
[CO ₃ ²⁻]	<u>0.0001835</u>	1.02454E-15	0.00014168	0.000108503	7.95E-05	4.95E-05	2.36E-05	7.76E-06	2.29E-06	6.24E-07	1.06E-07	2.30E-08	7.73E-09	8.11E-10
OH- alk	<u>0.0000038</u>													
BA	<u>0.0000816</u>	0	7.51488E-05	5.95249E-05	4.49E-05	2.87E-05	1.40E-05	4.61E-06	1.33E-06	3.41E-07	5.06E-08	9.63E-09	2.94E-09	2.61E-10
CA	0.0022446	2.65446E-08	0.002018434	0.00180144	1.58E-03	1.37E-03	1.15E-03	9.26E-04	6.97E-04	4.65E-04	2.33E-04	1.16E-04	6.98E-05	2.33E-05
TA	0.0023262	2.65446E-08	0.002093583	0.001860965	1.63E-03	1.40E-03	1.16E-03	9.30E-04	6.98E-04	4.65E-04	2.33E-04	1.16E-04	6.98E-05	2.33E-05
%TA			90.00%	80.00%	70.00%	60.00%	50.00%	40.00%	30.00%	20.00%	10.00%	5.00%	3.00%	1.00%
[B]	0.0004158	0	0.00037422	0.00033264	0.0002911	0.0002495	0.0002079	0.0001663	0.0001247	8.316E-05	4.158E-05	2.079E-05	1.247E-05	4.158E-06
Target T[CO₂]			0.001890	0.001705	0.001519	0.001334	0.001149	0.000963	0.000778	0.000592	0.000407	0.000314	0.000277	0.000240
T[CO₂]	0.002075501	0.000221707	0.001890	0.001706	0.001518	0.001334	0.001149	0.000964	0.000778	0.000593	0.000410	0.000313	0.000278	0.000240
%T[CO ₂]			82.28%	74.28%	66.07%	58.06%	50.04%	41.98%	33.88%	25.82%	17.85%	13.62%	12.08%	10.47%
ppCO ₂ (atm)	<u>0.0003806</u>	0.00346011	0.000368706	0.000351258	0.0003386	0.000376	0.0005191	0.0009401	0.0016025	0.0022989	0.0029647	0.0031729	0.0033101	0.0034134
lnH _{CO₂}	-3.373003474	-2.74782088	-3.315877693	-3.257545977	-3.20E+00	-3.14E+00	-3.08E+00	-3.01E+00	-2.95E+00	-2.88E+00	-2.82E+00	-2.78E+00	-2.77E+00	-2.75E+00
pKB'	8.738667533	9.73911267	8.78085278	8.825646782	8.87E+00	8.93E+00	8.98E+00	9.04E+00	9.12E+00	9.21E+00	9.32E+00	9.41E+00	9.47E+00	9.55E+00
pK1	6.041958708	6.322750041	6.068294319	6.09501738	6.12E+00	6.15E+00	6.18E+00	6.21E+00	6.23E+00	6.26E+00	6.29E+00	6.31E+00	6.31E+00	6.32E+00
pK2	9.209881192	9.814448411	9.269009884	9.328433693	9.39E+00	9.45E+00	9.51E+00	9.57E+00	9.63E+00	9.69E+00	9.75E+00	9.78E+00	9.80E+00	9.81E+00
H _{CO₂}	0.034286504	0.06406732	0.036302172	0.03848272	4.08E-02	4.34E-02	4.62E-02	4.92E-02	5.24E-02	5.60E-02	5.99E-02	6.19E-02	6.28E-02	6.36E-02
KB'	1.82529E-09	1.82342E-10	1.65633E-09	1.49401E-09	1.34E-09	1.19E-09	1.04E-09	9.02E-10	7.63E-10	6.24E-10	4.74E-10	3.85E-10	3.41E-10	2.80E-10
K1'	9.07907E-07	4.75609E-07	8.54487E-07	8.03494E-07	7.55E-07	7.09E-07	6.64E-07	6.23E-07	5.83E-07	5.45E-07	5.09E-07	4.92E-07	4.86E-07	4.79E-07
K2'	6.16764E-10	1.53303E-10	5.38258E-10	4.69425E-10	4.09E-10	3.56E-10	3.10E-10	2.70E-10	2.34E-10	2.04E-10	1.77E-10	1.65E-10	1.60E-10	1.56E-10
pH	<u>8.198</u>	<u>2.40</u>	8.181	8.164	8.14	8.04	7.84	7.50	7.15	6.82	6.41	6.08	5.84	5.35
[H ⁺]	6.3387E-09	0.003971915	6.59174E-09	6.85488E-09	7.328E-09	9.12E-09	1.45E-08	3.16E-08	7.08E-08	1.51E-07	3.89E-07	8.32E-07	1.45E-06	4.47E-06

¹⁵ The [CO₂] for groundwater was obtained by assuming equilibrium with the atmosphere (ppCO₂=354 μatm) at the time of formation (S=0, t=1, [CO₂]=22.68 μmol/Kg) and adding the CO₂ produced by the consumption of all the available O₂ by microbes (199 μmol CO₂/Kg) to obtain the value of 221.68 μmol/Kg.

Table A-4. The variables, equations, and calculations (MS Excel® formulas) to determine carbonate species from mixing seawater with groundwater with pH=7 where TA was conservatively mixed and ppCO₂ was held constant (see Table A-1). Units, unless otherwise noted, are moles/Kg.

	A		B	C	D
1	Variable (Units)	Equation	Seawater (<u>underline</u> = input)	Groundwater to be mixed: (<u>underline</u> = input)	Mixture
2	f	fraction of groundwater mixed			0.1
3	S (psu)	$S_s(1-f) + S_{GW}(f)$	<u>35</u>	<u>0</u>	=B3*(1-D\$2)+\$C3*D\$2
4	t (C)	$t_s(1-f) + t_{GW}(f)$	<u>18</u>	<u>5</u>	=B4*(1-D\$2)+\$C4*D\$2
5	T (Kelvin)	t + 273.15	=273.15+B4	=273.15+C4	=273.15+D4
6	[CO ₂]	H _{CO2} × ppCO ₂	=B17*B23	=C17*C23	=D17*D23
7	[HCO ₃]	$CA \left(\frac{[H^+]}{[H^+] + 2K_2'} \right)$	=B11*(B29/(B29+2*B26))	=C11*(C29/(C29+2*C26))	=D11*(D29/(D29+2*D26))
8	[CO ₃ ²⁻]	$CA \left(\frac{K_2'}{[H^+] + 2K_2'} \right)$	=0.0001835	=C11*(C26/(C29+2*C26))	=D11*(D26/(D29+2*D26))
9	OH ⁻ alk (Eq)		<u>0.0000038</u>		
10	BA (Eq)	$\frac{K_B' \times [B]}{([H^+] + K_B')}$	<u>0.0000816</u>	=(C24*C15)/(C29+C24)	=(D24*D15)/(D29+D24)
11	CA (Eq)	[HCO ₃ ⁻] + 2[CO ₃ ²⁻] TA - BA	=B12-B10	=C7+2*C8	=D12-D10
12	TA (Eq)	CA + BA - [OH ⁻ alk] $TA_s(1-f) + TA_{GW}(f)$	=0.00233 - B9	=C11+C10	=B12*(1-D\$2)+\$C12*D\$2
13	%TA (%)	(TA _{mixture} /TA _(S+GW))×100			=D12/(\$B12+\$C12)
14					
15	[B]	0.00001188S	=0.00001188*B3	=0.00001188*C3	=0.00001188*D3
16	T[CO ₂]	$H_{CO_2} ppCO_2 + [HCO_3^{2-}] + [CO_3^{2-}]$ $[CA] \frac{[H^+]^2 + [H^+]K_1' + K_1'K_2'}{K_1'([H^+] + 2K_2')}$	<u>0.002013</u>	=C23*C17+C7+C8	=D11*((D29^2+D29*D25+D25*D26)/(D25*(D29+2*D26)))
17	ppCO ₂ (atm)		<u>0.0003806</u>	<u>0.0003806</u>	<u>0.0003806</u>

	A	B	C	D	
19	$\ln H_{CO_2}^*$	$9345.17/T - 167.8108 + 23.3585 \times \ln(T) + [0.023517 - 0.00023656(T) + 0.00000047036(T^2)] \times S$	$=9345.17/B5 - 167.8108 + 23.3585 \times \ln(B5) + (0.023517 - (0.00023656 \times B5) + 0.00000047036 \times B5^2) \times B3$	$=9345.17/C5 - 167.8108 + 23.3585 \times \ln(C5) + (0.023517 - (0.00023656 \times C5) + 0.00000047036 \times C5^2) \times C3$	$=9345.17/D5 - 167.8108 + 23.3585 \times \ln(D5) + (0.023517 - (0.00023656 \times D5) + 0.00000047036 \times D5^2) \times D3$
20	pK_B^*	$2291.9/T + 0.01756(T) - 3.3850 - 0.26316(S^{1/3})$	$=(2291.9/B5 + 0.01756 \times B5 - 3.385 - 0.26316 \times B3^{1/3})$	$=(2291.9/C5 + 0.01756 \times C5 - 3.385 - 0.26316 \times C3^{1/3})$	$=(2291.9/D5 + 0.01756 \times D5 - 3.385 - 0.26316 \times D3^{1/3})$
21	pK_1^*	$17.788 - 0.073104(T) - 0.0051087(S) + 0.00011463(T^2)$	$=17.788 - 0.073104 \times B5 - 0.0051087 \times B3 + 0.00011463 \times B5^2$	$=17.788 - 0.073104 \times C5 - 0.0051087 \times C3 + 0.00011463 \times C5^2$	$=17.788 - 0.073104 \times D5 - 0.0051087 \times D3 + 0.00011463 \times D5^2$
22	pK_2^*	$20.919 - 0.064209(T) - 0.011887(S) + 0.000087313(T^2)$	$=20.919 - 0.064209 \times B5 - 0.011887 \times B3 + 0.000087313 \times B5^2$	$=20.919 - 0.064209 \times C5 - 0.011887 \times C3 + 0.000087313 \times C5^2$	$=20.919 - 0.064209 \times D5 - 0.011887 \times D3 + 0.000087313 \times D5^2$
23	H_{CO_2}	$e^{\ln H_{CO_2}}$	$=EXP(B19)$	$=EXP(C19)$	$=EXP(D19)$
24	K_B'	$10^{-pK_B'}$	$=10^{-(1 \times B20)}$	$=10^{-(1 \times C20)}$	$=10^{-(1 \times D20)}$
25	K_1'	$10^{-pK_1'}$	$=10^{-(1 \times B21)}$	$=10^{-(1 \times C21)}$	$=10^{-(1 \times D21)}$
26	K_2'	$10^{-pK_2'}$	$=10^{-(1 \times B22)}$	$=10^{-(1 \times C22)}$	$=10^{-(1 \times D22)}$
27					
28	pH		<u>8.2</u>	<u>7</u>	8.174
29	$[H^+]$	10^{-pH}	$=10^{-B28}$	$=10^{-C28}$	$=10^{-D28}$
30				$=C29/B29$	
31	A	$-1(TA)$	$=-1 \times B12$		$=-1 \times D12$
32	B	$+ (H_{CO_2} ppCO_2 K_1' - (TA) K_B' + K_B'[B])$	$=B23 \times B17 \times B25 - B12 \times B24 + B24 \times B15$		$=D23 \times D17 \times D25 - D12 \times D24 + D24 \times D15$
33	C	$+ (H_{CO_2} ppCO_2 (K_1' 2K_2' + K_1' K_B'))$	$=B23 \times B17 \times (B25^2 \times B26 + B25 \times B24)$		$=D23 \times D17 \times (D25^2 \times D26 + D25 \times D24)$
34	D	$+ (H_{CO_2} ppCO_2 K_1' 2K_2' K_B')$	$=B23 \times B17 \times B25^2 \times B26 \times B24$		$=D23 \times D17 \times D25^2 \times D26 \times D24$
35	$[H^+]=$	10^{-pH}	$=10^{-(1 \times B28)}$		$=10^{-(1 \times D28)}$
36	0=	$A[H^+]^3 + B[H^+]^2 + C[H^+]$	$=B31 \times B35^3 + B32 \times B35^2 + B33 \times B35 + B34$		$=D31 \times D35^3 + D32 \times D35^2 + D33 \times D35 + D34$

* Equation from Pilson (1998).

Table A-5. The variables, equations, and calculations (MS Excel® formulas) to determine carbonate species from mixing seawater with groundwater with pH=3 where TA was conservatively mixed and ppCO₂ was held constant (see Table A-2). Units, unless otherwise noted, are moles/Kg.

	A		B	C	D
1	Variable (Units)	Equation	Seawater (<u>underline</u> = input)	Groundwater to be mixed: (<u>underline</u> = input)	Mixture
2	f	fraction of groundwater mixed			0.1
3	S (psu)	$S_s(1-f) + S_{GW}(f)$	<u>35</u>	<u>0</u>	=B3*(1-D\$2)+\$C3*D\$2
4	t (C)	$t_s(1-f) + t_{GW}(f)$	<u>18</u>	<u>5</u>	=B4*(1-D\$2)+\$C4*D\$2
5	T (Kelvin)	t + 273.15	=273.15+B4	=273.15+C4	=273.15+D4
6	[CO ₂]	H _{CO2} × ppCO ₂	=B17*B23	=C17*C23	=D17*D23
7	[HCO ₃]	$CA \left(\frac{[H^+]}{[H^+] + 2K_2'} \right)$	=B11*(B29/(B29+2*B26))	=C11*(C29/(C29+2*C26))	=D11*(D29/(D29+2*D26))
8	[CO ₃ ²⁻]	$CA \left(\frac{K_2'}{[H^+] + 2K_2'} \right)$	=0.0001835	=C11*(C26/(C29+2*C26))	=D11*(D26/(D29+2*D26))
9	OH ⁻ alk (Eq)		<u>0.0000038</u>		
10	BA (Eq)	$\frac{K_B' \times [B]}{([H^+] + K_B')}$	<u>0.0000816</u>	=(C24*C15)/(C29+C24)	=(D24*D15)/(D29+D24)
11	CA (Eq)	[HCO ₃ ⁻] + 2[CO ₃ ²⁻] TA - BA	=B12-B10	=C7+2*C8	=D12-D10
12	TA (Eq)	CA + BA - [OH ⁻ alk] TA _s (1-f) + TA _{GW} (f)	=0.00233 - B9	=C11+C10	=B12*(1-D\$2)+\$C12*D\$2
13	%TA (%)	(TA _{mixture} /TA _(S+GW))×100			=D12/(\$B12+\$C12)
14					
15	[B]	0.00001188S	=0.00001188*B3	=0.00001188*C3	=0.00001188*D3
16	T[CO ₂]	$H_{CO_2} ppCO_2 + [HCO_3^{2-}] + [CO_3^{2-}]$ $[CA] \frac{[H^+]^2 + [H^+]K_1' + K_1'K_2'}{K_1'([H^+] + 2K_2')}$	<u>0.002013</u>	=C23*C17+C7+C8	=D11*((D29^2+D29*D25+D25*D26)/(D25*(D29+2*D26)))
17	ppCO ₂ (atm)		<u>0.0004001</u>	<u>0.0004001</u>	0.0004001

	A	B	C	D	
19	$\ln H_{CO_2}^*$	$9345.17/T - 167.8108 + 23.3585 \times \ln(T) + [0.023517 - 0.00023656(T) + 0.00000047036(T^2)] \times S$	$=9345.17/B5 - 167.8108 + 23.3585 \times \ln(B5) + (0.023517 - (0.00023656 \times B5) + 0.00000047036 \times B5^2) \times B3$	$=9345.17/C5 - 167.8108 + 23.3585 \times \ln(C5) + (0.023517 - (0.00023656 \times C5) + 0.00000047036 \times C5^2) \times C3$	$=9345.17/D5 - 167.8108 + 23.3585 \times \ln(D5) + (0.023517 - (0.00023656 \times D5) + 0.00000047036 \times D5^2) \times D3$
20	pK_B^*	$2291.9/T + 0.01756(T) - 3.3850 - 0.26316(S^{1/3})$	$=(2291.9/B5 + 0.01756 \times B5 - 3.3850 - 0.26316 \times B3^{1/3})$	$=(2291.9/C5 + 0.01756 \times C5 - 3.3850 - 0.26316 \times C3^{1/3})$	$=(2291.9/D5 + 0.01756 \times D5 - 3.3850 - 0.26316 \times D3^{1/3})$
21	pK_1^*	$17.788 - 0.073104(T) - 0.0051087(S) + 0.00011463(T^2)$	$=17.788 - 0.073104 \times B5 - 0.0051087 \times B3 + 0.00011463 \times B5^2$	$=17.788 - 0.073104 \times C5 - 0.0051087 \times C3 + 0.00011463 \times C5^2$	$=17.788 - 0.073104 \times D5 - 0.0051087 \times D3 + 0.00011463 \times D5^2$
22	pK_2^*	$20.919 - 0.064209(T) - 0.011887(S) + 0.000087313(T^2)$	$=20.919 - 0.064209 \times B5 - 0.011887 \times B3 + 0.000087313 \times B5^2$	$=20.919 - 0.064209 \times C5 - 0.011887 \times C3 + 0.000087313 \times C5^2$	$=20.919 - 0.064209 \times D5 - 0.011887 \times D3 + 0.000087313 \times D5^2$
23	Hco2	$e^{\ln H_{CO_2}}$	=EXP(B19)	=EXP(C19)	=EXP(D19)
24	K_B'	$10^{-pK_B'}$	=10 ^(-1*B20)	=10 ^(-1*C20)	=10 ^(-1*D20)
25	K_1'	$10^{-pK_1'}$	=10 ^(-1*B21)	=10 ^(-1*C21)	=10 ^(-1*D21)
26	K_2'	$10^{-pK_2'}$	=10 ^(-1*B22)	=10 ^(-1*C22)	=10 ^(-1*D22)
27					
28	pH		<u>8.2</u>	<u>3</u>	8.172
29	[H+]	10^{-pH}	=10 ^{-B28}	=10 ^{-C28}	=10 ^{-D28}
30				=C29/B29	
31	A	-1(TA)	=-1*B12		=-1*D12
32	B	$+ (H_{CO_2} ppCO_2 K_1' - (TA) K_B' + K_B' [B])$	=B23*B17*B25 - B12*B24 + B24*B15		=D23*D17*D25 - D12*D24 + D24*D15
33	C	$+ (H_{CO_2} ppCO_2 (K_1' 2K_2' + K_1' K_B'))$	=B23*B17*(B25*2*B26 + B25*B24)		=D23*D17*(D25*2*D26 + D25*D24)
34	D	$+ (H_{CO_2} ppCO_2 K_1' 2K_2' K_B')$	=B23*B17*B25*2*B26*B24		=D23*D17*D25*2*D26*D24
35	[H+]=	10^{-pH}	=10 ^(-1*B28)		=10 ^(-1*D28)
36	0=	$A [H^+]^3 + B [H^+]^2 + C [H^+] + D$	=B31*B35^3 + B32*B35^2 + B33*B35 + B34		=D31*D35^3 + D32*D35^2 + D33*D35 + D34

* Equation from Pilson (1998).

Table A-6. The variables, equations, and calculations (MS Excel® formulas) to determine carbonate species from mixing seawater with very acidic groundwater that was isolated from the atmosphere and had increased dissolved CO₂ from microbial consumption all the available. TA and T[CO₂] were conservatively mixed and ppCO₂ was allowed to vary and (see Table A-3). Units, unless otherwise noted, are moles/Kg.

	A		B	C	D
1	Variable (Units)	Equation	Seawater (<u>input</u>)	Groundwater to be mixed: (<u>input</u>)	Mixture
2	f	fraction of groundwater mixed			0.1
3	S (psu)	$S_s(1-f) + S_{GW}(f)$	<u>35</u>	<u>0</u>	=B3*(1-D\$2)+C3*D\$2
4	t (C)	$t_s(1-f) + t_{GW}(f)$	<u>18</u>	<u>5</u>	=B4*(1-D\$2)+C4*D\$2
5	T (Kelvin)	t + 273.15	=273.15+B4	=273.15+C4	=273.15+D4
6	[CO ₂]	HCO ₂ × ppCO ₂	=B17*B23	= <u>0.000225399166498365</u>	=D17*D23
7	[HCO ₃]	$CA \left(\frac{[H^+]}{[H^+] + 2K_1'} \right)$ $\frac{K_1' [CO_{2(f)}}{[H^+]}$	=B11*(B29/(B29+2*B26))	=C25*C6/C29	=D11*(D29/(D29+2*D26))
8	[CO ₃ ²⁻]	$CA \left(\frac{K_2'}{[H^+] + 2K_2'} \right)$ $\frac{K_2' [HCO_3^{1-}]}{[H^+]}$	= <u>0.0001835</u>	=C26*C7/C29	=D11*(D26/(D29+2*D26))
9	OH ⁻ alk (Eq)		<u>0.0000038</u>		
10	BA (Eq)	$\frac{K_B' \times [B]}{([H^+] + K_B')}$	<u>0.0000816</u>	=(C24*C15)/(C29+C24)	=(D24*D15)/(D29+D24)
11	CA (Eq)	[HCO ₃ ⁻] + 2[CO ₃ ²⁻] TA - BA	=B12-B10	=C7+2*C8	=D12-D10
12	TA (Eq)	CA + BA - [OH ⁻ alk] $TA_s(1-f) + TA_{GW}(f)$	= <u>0.00233</u> - B9	=C11+C10	=B12*(1-D\$2)+C12*D\$2
13	%TA (%)	(TA _{mixture} /TA _(S+GW))×100			=D12/(\$B12+\$C12)
14	[B]	0.00001188S	=0.00001188*B3	=0.00001188*C3	=0.00001188*D3

		A	B	C	D
15	Target T[CO2]	$T[CO_2]_s(1-f) + T[CO_2]_{GW}(f)$			=B16*(1-D\$2)+\$C16*D\$2
16	T[CO2]	$H_{CO_2} ppCO_2 + [HCO_3^{2-}] + [CO_3^{2-}]$ $[CA] \frac{[H^+]^2 + [H^+]K_1' + K_1'K_2'}{K_1'([H^+] + 2K_2')}$	=B6+B7+B8	=C11*((C29^2+C29*C25+C25*C26)/(C25*(C29+2*C26)))	=D11*((D29^2+D29*D25+D25*D26)/(D25*(D29+2*D26)))
17	%T[CO2]				=D16/(\$B16+\$C16)
18	ppCO2 (atm)	ppCO2/Hco2	<u>0.0003806</u>	=C6/C23	=D6/D23
19	lnHco2 *	$9345.17/T - 167.8108 + 23.3585 \times \ln(T) + [0.023517 - 0.00023656(T) + 0.00000047036(T^2)] \times S$	=9345.17/B5-167.8108 +23.3585*LN(B5)+ (0.023517-(0.00023656*B5)+ 0.00000047036*B5^2)*B3	=9345.17/C5-167.8108 +23.3585*LN(C5)+ (0.023517-(0.00023656*C5)+ 0.00000047036*C5^2)*C3	=9345.17/D5-167.8108 +23.3585*LN(D5)+ (0.023517-(0.00023656*D5)+ 0.00000047036*D5^2)*D3
20	pKB' *	$2291.9/T + 0.01756(T) - 3.3850 - 0.26316(S^{1/3})$	=(2291.9/B5+0.01756*B5-3.385-0.26316*B3^(1/3))	=(2291.9/C5+0.01756*C5-3.385-0.26316*C3^(1/3))	=(2291.9/D5+0.01756*D5-3.385-0.26316*D3^(1/3))
21	pK1' *	$17.788 - 0.073104(T) - 0.0051087(S) + 0.00011463(T^2)$	=17.788-0.073104*B5-0.0051087*B3 +0.00011463*B5^2	=17.788-0.073104*C5-0.0051087*C3 +0.00011463*C5^2	=17.788-0.073104*D5-0.0051087*D3 +0.00011463*D5^2
22	pK2' *	$20.919 - 0.064209(T) - 0.011887(S) + 0.000087313(T^2)$	=20.919-0.064209*B5-0.011887*B3 +0.000087313*B5^2	=20.919-0.064209*C5-0.011887*C3 +0.000087313*C5^2	=20.919-0.064209*D5-0.011887*D3 +0.000087313*D5^2
23	HCO2	$e^{\ln H_{CO_2}}$	=EXP(B19)	=EXP(C19)	=EXP(D19)
24	KB'	$10^{-pK_B'}$	=10^(-1*B20)	=10^(-1*C20)	=10^(-1*D20)
25	K1'	$10^{-pK_1'}$	=10^(-1*B21)	=10^(-1*C21)	=10^(-1*D21)
26	K2'	$10^{-pK_2'}$	=10^(-1*B22)	=10^(-1*C22)	=10^(-1*D22)
27					
28	pH		<u>8.198</u>	<u>2.4</u>	7.96
29	[H+]	10^{-pH}	=10^-B28	=10^-C28	=10^-D28
30					

* Equation from Pilson (1998).