Journal of Hydrology 209 (1998) 297–310

Modeling CO_2 degassing and pH in a stream–aquifer system

J. Choi[a], S.M. Hulseapple[a], M.H. Conklin[a,]*, J.W. Harvey[b]

[a]*University of Arizona, Department of Hydrology and Water Resources, Tucson, AZ 85721, USA*
[b]*United States Geological Survey, Reston, VA 20192, USA*

Received 13 March 1997; accepted 16 January 1998

Abstract

Pinal Creek, Arizona receives an inflow of ground water with high dissolved inorganic carbon (57–75 mg/l) and low pH (5.8–6.3). There is an observed increase of in-stream pH from approximately 6.0–7.8 over the 3 km downstream of the point of groundwater inflow. We hypothesized that CO_2 gas-exchange was the most important factor causing the pH increase in this stream–aquifer system. An existing transport model, for coupled ground water–surface water systems (OTIS), was modified to include carbonate equilibria and CO_2 degassing, used to simulate alkalinity, total dissolved inorganic carbon (C_T), and pH in Pinal Creek. Because of the non-linear relation between pH and C_T, the modified transport model used the numerical iteration method to solve the non-linearity. The transport model parameters were determined by the injection of two tracers, bromide and propane. The resulting simulations of alkalinity, C_T and pH reproduced, without fitting, the overall trends in downstream concentrations. A multi-parametric sensitivity analysis (MPSA) was used to identify the relative sensitivities of the predictions to six of the physical and chemical parameters used in the transport model. MPSA results implied that C_T and pH in stream water were controlled by the mixing of ground water with stream water and CO_2 degassing. The relative importance of these two processes varied spatially depending on the hydrologic conditions, such as stream flow velocity and whether a reach gained or lost stream water caused by the interaction with the ground water. The coupled transport model with CO_2 degassing and generalized sensitivity analysis presented in this study can be applied to evaluate carbon transport and pH in other coupled stream–ground water systems. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: CO_2 degassing; pH; Coupled stream–aquifer system

1. Introduction

Small streams are often the locations where ground water enters the surface drainage system. If the ground water contains elevated concentrations of carbon dioxide (CO_2) the degassing process can greatly affect the stream chemistry. Fischer et al. (1979) and McCutcheon (1989) described simple transport models for solute transport in rivers that consider a first-order reaction for solute and volatilization, respectively. Fewer studies and model applications have been undertaken in small streams. Several studies in streams receiving acid mine drainage (McKnight and Bencala, 1989; Broshears et al., 1996; Kimball et al., 1994b; Runkel et al., 1996) emphasized the importance of pH in controlling the transport and fate of metal contaminants. Broshears et al. (1996) described the effect of a pH modification experiment on an acidic mine drainage stream and attributed the resultant variations in iron and aluminum concentrations to their precipitation being enhanced by increasing pH. Also, they simulated the downstream pH variation as being caused by the

---

* Corresponding author. Fax: 001 520 621 1422; e-mail: martha@hwr.arizona.edu

PII S0022-1694(98)00093-6

hydrolysis of aluminum and iron, or the desorption of protons from the stream bed, under the assumption of CO_2 equilibration with the atmosphere. In this paper, the effect of CO_2 degassing in stream pH for a stream receiving ground water with an elevated concentration of CO_2 is examined.

Carbon dioxide (CO_2) is introduced into stream systems due to microbial respiration in soil and ground water systems caused by anthropogenic activities. Acid groundwater plumes, resulting from mining activities, often contain an elevated CO_2 concentration that resulted from geochemical neutralization reactions with aquifer materials. CO_2 in the stream may be lost by degassing, consumed by photosysnthesis or produced by biological respiration. The excess CO_2 introduced to stream water is likely to play an important role in the transport of various metals introduced from mining activities. For example, CO_2 concentration can control the in-stream pH, which is a key variable in metal chemistry affecting reactions, such as metal precipitation or dissolution. Improved models of CO_2 transport potentially could improve the understanding of metal transport in contaminated streams.

Loss by volatilization is often modeled as a first-order process with volatilization rate constants. Empirical correlations for determining volatilization rate constants have been typically developed from large streams and rivers (Rathbun, 1977; Duran, 1985). Genereux and Hemond (1990) developed a model for the transport of a volatile solute (such as naturally occurring radon-222) in a small stream in Massachusetts. Their model simulated the concentration of radon-222 in the groundwater inflow to a stream based on stream mass balance of water, propane tracer and naturally occurring radon-222. Heekyung et al. (1995) extended that approach to determine in situ biodegradation rates of toluene in the East Drainage Ditch in Massachusetts by a mass balance approach that distinguishes between toluene volatilization and biodegradation.

In this study, it was hypothesized that the mass-transfer limited CO_2 degassing is the key process in controlling the stream pH, in small stream system receiving groundwater inflow with high dissolved CO_2. In order to describe this system, we extended a transport model to include carbonate speciation and mass-transfer-limited CO_2 degassing and conducted volatile tracer experiments to determine volatilization rate constant. The model was used to predict in-stream pH changes for a small stream, Pinal Creek, Arizona, that receives CO_2-laden ground water. A sensitivity analysis approach was used to evaluate the relative significance of the processes involved in the coupled transport model. This generalized sensitivity analysis provides an integrated view of the system by

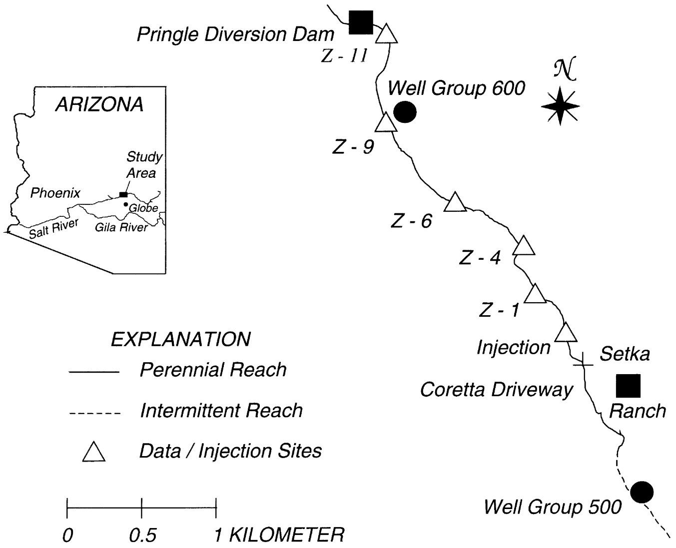

Fig. 1. The Pinal Creek study site with sampling locations Z1, Z4, Z6, Z9 and Z11.

considering the relative significances of parameters across the range of possible variation at the field site.

2. Field study

The Pinal Creek basin is within the upper Salt River basin in the central highlands of Arizona (Fig. 1). The Pinal Creek basin covers an area of 505 km^2 and ranges in elevation from 2400 m above mean sea level at its maximum, to 835 m at Inspiration Dam (Eychaner, 1991). The ground water aquifer, located in the drainage basin, comprises 170 km^2 including 17 km^2 of unconsolidated sand and gravel alluvium. The alluvium consists of material derived from the surrounding uplands and includes detritus of igneous, metamorphic, and sedimentary origin (Walter and Norris, 1991). Surrounding the alluvium is the Gila Conglomerate that is characterized by its calcareous cement (Walter and Norris, 1991). The surrounding uplands are comprised of Precambrian granite and younger Tertiary dacites (Wilson et al., 1959) and have been the source of copper and other metals for the mines in the region since the late 1800s (Peterson, 1962).

Active mining has taken place in the Globe area of the Pinal Creek drainage basin during most of the last century (Fig. 1). Mining activities in the basin have released acidic waste solutions that have initiated a complex series of geochemical reactions within the aquifer, resulting in the contamination of both ground and surface waters within the basin. Ground water that reaches the stream is partially neutralized resulting form the interaction with alluvial $CaCO_3$ (Eychaner, 1991).

The study area for this work was located in the upper 3 km of the perennial flow of Pinal Creek from Setka Ranch to the Pringle diversion dam (Fig. 1). Twelve measurement stations (Z-0–Z-11) were established in the study reach for hydrologic and water quality work. Five of the 12 sampling points (Z-1, Z-4, Z-6, Z-9 and Z-11) were used for the present work (Fig. 1).

To collect the chemical and physical data for the stream system, such as flow rate, groundwater exchange, gas exchange rate constant and stream chemistry (alkalinity and pH), we used the propane injection and bromide tracer injection tests. The point of injection for propane was made approximately 50 m upstream from Z-1. The propane injection began at approximately 1830 hours on 1st August 1994 and was maintained at a constant rate until 0430 hours on the morning of 2nd August 1994. Two propane sampling rounds were conducted during the injection period. At each round, triplicate samples were collected in 60 ml amber vials. Sample vials were sealed without any head-space using plastic screw-caps with Teflon coated silicon septa. Samples were immediately placed on ice until transported to the laboratory. Upon arrival at the laboratory at approximately 1100 hours, 2nd August, the samples were stored at 2°C until they were analyzed the following day.

Propane samples were analyzed using a Varian model 3740 gas chromatograph equipped with a flame ionization detector (GC/FID). The GC column consisted of 6 ft of 1/8 in ID brass tubing packed with Poropak Q (80/100 mesh). Instrument settings were as follows: column temperature, 80°C; injector temperature, 150°C; ion detector temperature, 210°C; and carrier gas (N_2) pressure, 30 psig. Propane retention time was approximately 1.2 min. The GC/FID was calibrated using head-space from the prepared aqueous standards. This method was verified using a 731 ppm propane–air mixture from Matheson Gas (Hulseapple, 1995).

Each propane sample vial was brought to room temperature 2 h prior to analysis. A 5 ml artificial head-space was injected into the sample vial 1 h prior to analysis and the sample was placed in an oven set at 30°C. A single 0.5 or 1.0 ml volume of head-space was withdrawn from each sample vial and injected into the GC. Head-space concentrations of propane were determined from calibration curves. Calculated concentrations were then averaged for each set of three samples.

The bromide tracer injection test was performed in June of 1994 to evaluate the stream flow rate and groundwater exchange with stream. The highly concentrated bromide solution was injected upstream and sampled from stream water downstream, such as Z1, Z4, Z9 and Z11. The breakthrough curves from the bromide tracer injection tests could provide the information of stream flow rate and groundwater exchange.

Alkalinity and pH were measured in stream water at each sampling point in June and August of 1994. June groundwater chemical data were used in the August simulations because previous work indicated that the variation of chemical concentrations in ground water beneath the stream is negligible over these months (Harvey and Fuller, 1994). The pH measurements were made using Orion model 231 pH meters with equipped with Orion Ross combination electrodes. Samples for alkalinity titration were collected at the time of the pH measurements. Alkalinity titration was conducted approximately 2 h after sample collection using 0.16 N H_2SO_4. Total dissolved inorganic carbon was calculated with MINTEQA2 using alkalinity, field measured pH and temperature (Table 3), and an average Pinal Creek background chemical composition (Table 1) as input parameters.

3. Modeling approach

Solute transport in Pinal Creek was simulated using a one-dimensional solute transport model that accounted for physical processes including advection, dispersion and groundwater inflow:

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}\left(AD\frac{\partial c}{\partial x}\right) + \frac{q_{\mathrm{LIN}}}{A}(C_{\mathrm{L}} - C) \qquad (1)$$

where A is the stream channel cross-sectional area [m^2], C is the in-stream solute concentration [gm^{-3}], C_L is the solute concentration in lateral inflow [gm^{-3}], D is the dispersion coefficient [$m^2\ s^{-1}$], Q is the volumetric flow rate [$m^3\ s^{-1}$], q_{LIN} is the groundwater inflow rate [$m^3\ s^{-1}\ m^{-1}$], t is time [s], and x is distance [m]. The one-dimensional physical transport model (OTIS), developed by Runkel and Broshears (1991), was used to solve Eq. (1).

Table 1

Background solute concentrations in mg/l from Longsworth and Taylor (1992) used in MINTEQA2 calculation

Species	Concentration (mg/l)
Mg	140
Na	100
K	5.3
Mn	61
Ca	619
SO_4	2300
Cl	115
SiO_2	56
Ba	27
Cd	5.0×10^{-3}
Cu	28×10^{-3}
Fe	81×10^{-3}
Ni	745×10^{-3}
Ag	14×10^{-3}
Sr	23×10^{-3}
Zn	48×10^{-3}
Li	270×10^{-3}

In order to simulate the transport of a non-conservative solute such as total inorganic carbon (C_T), OTIS was extended to include mass-transfer limited CO_2 degassing and aqueous carbonate equilibria. The analysis of the Pinal Creek stream water (Table 1) using the chemical equilibrium model MINTEQA2 (Allison et al., 1991) indicated that contribution of non-carbonate species to the alkalinity was less than 1%. As a result, the concentration of dissolved inorganic carbon could be used to calculate alkalinity. Also, the results from MINTEQA2 simulations indicated that for all sampling points, $H_2CO_3^*([CO_2(aq)^*] + [H_2CO_3])$ and HCO_3^- comprised approximately 95% of the total inorganic carbon. The remaining 5% consisted primarily of $CaHCO_3^+$ and $MgHCO_3^+$. Therefore, the total inorganic carbon concentration (C_T) was assumed to consist only of the following carbonate species:

$$C_T = [CO_2(aq)] + [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \qquad (2)$$

Based on MINTEQA2 simulations for alkalinity and carbonate speciation, the stream pH was calculated from the following relation (DiToro, 1976);

$$\mathrm{ALK} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$$
$$= \frac{{}^{c}K_1}{{}^{c}K_1 + [H^+]}C_T + \frac{{}^{c}K_w}{[H^+]} - [H^+] \qquad (3)$$

where ALK is alkalinity. Considering the ionic strength effect and measured pH range of the stream water, the $[CO_3^{2-}]$ can be neglected in Eq. (3). ${}^{c}K_1 = K_1/(\gamma_{HCO_3-}\gamma_{H+})$, ${}^{c}K_w = K_w/(\gamma_{OH-}\gamma_{H+})$, γ = activity coefficient, and K_1 is the carbonic acid dissociation constant. For this study, the first acid dissociation constant was corrected for temperature and ionic strength: $-\log(K_1) = 6.381$ and $-\log(K_w) = 14.17$ at 20°C and zero ionic strength (Stumm and Morgan, 1996).

The stream pH can be calculated from Eq. (3), using the concentrations of alkalinity and total inorganic carbon obtained from the simulations. Assuming that precipitation of carbonate minerals is insignificant to the stream carbon balance, alkalinity can be considered a conservative quantity, since the loss or addition of dissolved CO_2 does not change the charge balance of the system (Stumm and Morgan, 1996). Because there is no reactive production or loss in alkalinity, the governing transport equation for alkalinity is given by Eq. (1).

The governing transport equation for C_T including the loss of dissolved inorganic carbon from stream to atmosphere by degassing can be expressed by:

$$\frac{\partial C_T}{\partial t} = -\frac{Q}{A}\frac{\partial C_T}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}\left(AD\frac{\partial C_T}{\partial x}\right) + \frac{q_{LIN}}{A}(C_{T_L} - C_T) + r_{C_T} \quad (4)$$

where C_{T_L} is the concentration of total dissolved inorganic carbon in groundwater inflow, and r_{C_T} is a reaction term. Exchange of CO_2 across the air–water interface was modeled as a simple mass-transfer limited process dependent on a rate constant and the difference between the saturated concentration and actual concentration of the solute (Bennett and Rathbun, 1972):

$$r_{C_T} = k(\alpha_0 C_T - [CO_2(aq)^*]) \quad (5)$$

where α_0 is the fraction of total inorganic carbon in $H_2CO_3^*\{\alpha_0 \cong [H^+]/([H^+] + {}^cK_1)\}$ and $CO_2(aq)^*$ is the equilibrium saturation concentration and k is the gas exchange rate constant [s^-]. By incorporating this CO_2 degassing reaction, the transport Eq. (4) for C_T can be rewritten as:

$$\frac{\partial C_T}{\partial t} = -\frac{Q}{A}\frac{\partial C_T}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}\left(AD\frac{\partial C_T}{\partial x}\right) + \frac{q_{LIN}}{A}(C_{T_L} - C_T) - k\{\alpha_0 C_T - [CO_2(aq)^*]\} \quad (6)$$

Because the pH is an unknown variable (pH = $-\log[H^+]$) and can be calculated only through the alkalinity–C_T–pH relationship Eq. (3), the transport Eq. (6) for C_T is non-linear due to the ionization fraction (α_0), which depends on pH. In order to simulate the pH, both governing equations for alkalinity and C_T were solved simultaneously. Based on the implicit Crank–Nicolson discretization (Runkel and Chapra, 1993) of the governing equation, we implemented the numerical iteration method to solve the non-linearity in the transport equation of C_T.

The chemical and physical parameters involved in the model were estimated based on the field studies such as bromide tracer injection test and propane injection test. Stream flow rate (Q) and groundwater inflow (q_{LIN}) were determined by tracer dilution gaging (Kilpatrick and Cobb, 1985). Groundwater exchange with stream in this study were evaluated based on both velocity meter gaging measurements and analysis of the June bromide tracer injection test. Velocity meter gaging in the stream in August 1994 provided data to calculate the net exchange of ground water and stream water in each reach. Dilution gaging in June 1994 provided an estimate of groundwater inflow to each reach. We combined both data sets and computed, by difference, stream water loss to ground water in each reach.

A non-linear regression approach (Wagner and Gorelick, 1986) was used to estimate the other parameters of the physical transport model, i.e. the cross-sectional area of the main channel and the longitudinal dispersion coefficient. This technique yielded estimates of the optimal values of parameters associated with the transport model by matching simulated and observed concentration of the injected Br tracer. The solute concentration in the groundwater inflow (C_L) was measured in shallow groundwater (2 m), collected using drive-point samplers.

To simulate the total inorganic carbon, the gas exchange rate constants should be evaluated for every reach. The gas exchange rate constant, k, was estimated from a tracer experiment involving the injection of a volatile and a conservative solute tracer (Tsivoglou et al., 1965). We used the constant rate injection method (Tsivoglou, 1967; Bennett and Rathbun, 1972; Genereux and Hemond, 1990), which has the advantage of requiring fewer samples. Tsivoglou et al. (1965) provided an equation to compute k_P based on dilution of a conservative tracer such as chloride (Cl^-),

$$k_P = \frac{1}{t_t}\ln\frac{(C_P/C_C)_A}{(C_P/C_C)_B} \quad (7)$$

where C_C is the concentration of the conservative tracer, C_P is the concentration of the volatile tracer (propane), and k_P is the gas exchange rate constant for propane.

In the determination of the propane degassing rate, it was assumed that no losses of stream water to ground water occurred in reaches that gained water by ground water inflow. In that case, $(C_{C}Q)_{A}$ = $(C_{C}Q)_{B}$ for a conservative solute injected upstream of point A, and Eq. (7) becomes

$$k_{P} = \frac{1}{t_{t}}\ln\frac{(C_{P}Q)_{A}}{(C_{P}Q)_{B}} \tag{8}$$

For a reach that loses water on a net basis, it was assumed that no inflow occurred at any point along the reach. Therefore, C_{C} does not change along the stream reach and Eq. (7) becomes

$$k_{P} = \frac{1}{t_{t}}\ln\frac{C_{PA}}{C_{PB}} \tag{9}$$

The ratio of exchange rate constants for two gases has been shown to be constant. Kilpatrick et al. (1989) reported the constant for propane and carbon dioxide,

$$\frac{k_{CO_2}}{k_{P}} = 1.24 \tag{10}$$

The mathematical models may include ill-defined parameters that cannot be measured with a high degree of accuracy in the field or in the laboratory. These ill-defined parameters will severely limit the accuracy of any single simulation and increase the difficulty of assessing the applicability and utility of a model to a physical situation. In an attempt to overcome this difficulty, it has been proposed that the sensitivities of parameters in the model be evaluated by assigning a degree of uncertainty to each parameter (Hornberger and Spear, 1981; Chang and Delleur, 1992). This multi-parametric sensitivity analysis (MPSA) followed the procedure proposed by Chang and Delleur (1992). The procedure is given in the following:

1. Select the parameters to be tested.
2. Set the range of each selected parameter to include the variations experienced in field measurements.
3. For each selected parameter, generate a series of, for example, 500 independent random numbers with a uniform distribution within the design range.
4. Run the model using selected 500 parameter sets and calculate the objective function values.
5. Determine whether the parameter set is acceptable or unacceptable by comparing the objective function value to a given criterion (R).
6. Statistically evaluate parametric sensitivity. For each parameter, compare the distributions of the parameter values associated with the acceptable and unacceptable results. If the two distributions are not statistically different, the parameter is classified as insensitive, otherwise, the parameter is classified as sensitive.

The objective function values of the sensitivity analysis were calculated from the sum of squared errors between observed and modeled values:

$$f = \sum_{i=1}^{n} [x_{o}(i) - x_{c}(i)]^{2} \tag{11}$$

where f is the objective function value and $x_{c}(i)$ and $x_{o}(i)$ are calculated and observed values, respectively. Observed values were calculated from simulations that used the mid-points of the characteristic ranges for each parameter. The ranges for each parameter were determined from minimum to maximum values that were obtained from parameter estimations and field measurements through reaches (1–4). If the objective function value obtained from the simulation was less than a subjective criterion then the result was acceptable, otherwise the result was unacceptable.

Three different objective function values were tested for a subjective criterion. Those values defined the 33, 50 and 66% divisions of 500 sorted objective functions. A test indicated that MPSA results were not affected by the choice of the subjective criterion. The 50% criterion was used for the further analysis in this paper.

A reactive solute, such as C_{T} and pH, can be affected by both physical and chemical parameters. In this study, MPSA was performed for the selected physical parameters of ground water inflow/outflow, cross-sectional area of main channel and CO_2 degassing rate constant, and chemical parameters of solute concentrations of ground water inflow. We executed 500 simulations using randomly chosen parameter sets having uniform distribution.

4. Results

The net balance of stream flow at each reach indicated a net loss of stream flow from Z9 to Z11 and a net gain of stream flow in the other three, from Z1 to Z9 for June 1994. In contrast, the net balance of stream flow obtained from August 1994 showed a net loss of stream flow from Z1 to Z4 and Z9 to Z11, and a net gain from Z4 to Z6 and Z6 to Z9 (Table 2).

Temperature corrected propane gas exchange rate constants calculated for both rounds ($k_{p,20}$) ranged from 6.8 h^{-1} (Z-l–Z-4, period 2) to 1.2 h^{-1} (Z-6–Z-11, period 2) (Table 4). Standard deviations of measurements of propane at each sampling point during each sampling round were generally less than 25% of the mean. Exceptions include Z-9 samples from both sampling periods, which had standard deviations of 47.5 and 40.7%, and period 2 samples from Z-6 with a standard deviation of 32%. The high variability in propane results was probably due to sampling and/or analytical errors. For reach Z-6 to Z-9, the difference between estimates for the two periods suggested that the variability of the propane analysis was too great to predict k_p with reasonable accuracy between these two sampling points. As a result, Z-9 was discarded as a reach endpoint in subsequent gas-exchange calculations. Gas exchange rate constants for CO_2 calculated using Eqs. (8)–(10) and corrected to 20°C (Metzger, 1968) ranged from 6.3 to 1.8 h^{-1} for the first period and 8.5 to 1.5 h^{-1} for period 2, respectively (Table 4). The gas exchange rate constants for CO_2 calculated from k_p were within the range of reported values from similar field studies conducted on other streams (Genereux and Hemond, 1990, 1992; Parker and Gay, 1987; Longsworth, 1991).

Fig. 2 shows the observed alkalinity, total inorganic carbon, pH and the results of simulations conducted under the physical and chemical conditions described in Tables 2, 3 and 4. The potential error from measurements of alkalinity (±15%) and degassing rate constant (one standard deviation) were considered in the simulations, and is indicated by error bars on simulation results and ranges of observed concentration on Fig. 2. The simulated concentration of alkalinity showed gradual downstream increase and agreed 6.9% and 5.0% of the field measurements of June and August, respectively.

The modeling results of total inorganic carbon followed the trends of measurements with some deviation and were within 8.4% and 11.4% of the measurements of June and August, respectively. The C_T concentrations along the study reaches were almost constant, even though there was continuous groundwater inflow with higher C_T into stream water.

Based on the simulation results of alkalinity and total inorganic carbon along the entire reach, the pH was calculated for each observation station by using the alkalinity–C_T–pH relationship given in Eq. (3). The calculated pH values are plotted on Fig. 2 with the observed pH from June and August field measurements. Although there were minor deviations between observations and simulations, the simulated pH

Table 2
Summary of physical and chemical parameters

Reach	Length [m]	A [m^2]	$q^a_{L,IN}$ [$m^3\,s^{-1}\,m^{-1}$]	$q^a_{L,OUT}$ [$m^3\,s^{-1}\,m^{-1}$]	D [$m^2\,s^{-1}$]	k^b [s^{-1}]	$C_{L,ALK}$ [$meql^{-1}$]	$C_{L,TIC}$ [mgl^{-1}]	Temp. [°C]
June 1994									
No. 1 (Z1–Z4)	303	0.40	3.71×10^{-5}	2.24×10^{-5}	0.676	1.92×10^{-3}	1.44	57.46	25.0
No. 2 (Z4–Z6)	588	0.48	7.71×10^{-5}	0.00	0.492	1.41×10^{-3}	1.53	68.07	25.0
No. 3 (Z6–Z9)	572	0.38	5.40×10^{-5}	0.00	2.163	4.87×10^{-4}	2.44	65.49	25.0
No. 4 (Z9–Z11)	1520	0.35	1.20×10^{-5}	2.95×10^{-5}	0.619	4.87×10^{-4}	3.12	65.49	25.0
August 1994									
No. 1 (Z1–Z4)	303	0.22	3.15×10^{-5}	5.39×10^{-5}	based on June data	1.82×10^{-3}	based on June data		22.0
No. 2 (Z4–Z6)	588	0.28	9.69×10^{-5}	0.00		1.42×10^{-3}			26.0
No. 3 (Z6–Z9)	572	0.34	4.81×10^{-5}	0.00		4.77×10^{-4}			23.7
No. 4 (Z9–Z11)	1520	0.41	3.01×10^{-6}	3.25×10^{-5}		4.77×10^{-4}			23.7

[a] The volumetric flow rate at Z1 (upper boundary) was 0.126 m^3/s and 0.118 m^3/s for June and August, respectively. Based on $q_{L,IN}$ and $q_{L,OUT}$, the volumetric flow rate at each end-point was calculated.

[b] Degassing rate constants were corrected for temperature dependence.

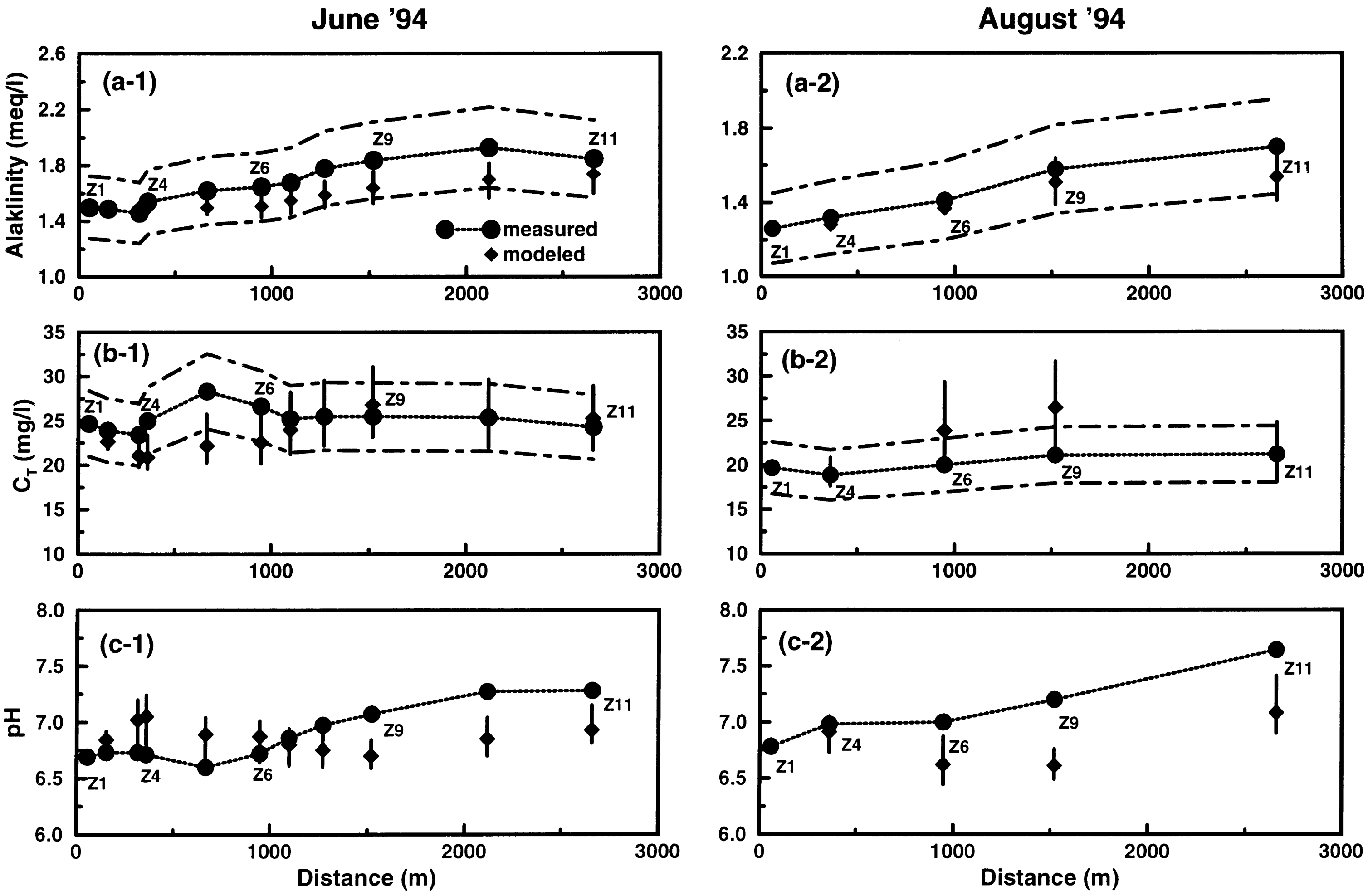

Fig. 2. Comparison of modeled alkalinity, C_T and pH to measured concentrations for June and August 1994. The error bars on modeled concentrations and upper and lower ranges of measured concentrations (dashed line) indicate the potential error from measurements of alkalinity in field.

Table 3
Pinal Creek surface water and groundwater chemistry. C_T values of surface and ground water were calculated from measured pH and alkalinity

	Surface water				Groundwater		
	Reach endpoint	pH	ALK. [meq/L]	C_T [mg/L]	pH	ALK. [meq/L]	C_T [mg/l]
June 1994	Z1	6.69	1.50	24.70	5.87	1.32	69.33
	Z4	6.71	1.54	25.05	5.88	1.30	57.43
	Z6	6.72	1.65	26.68	6.04	1.75	59.93
	Z9	7.07	1.84	25.50	6.31	3.12	74.69
	Z11	7.28	1.85	24.32	6.31	3.12	74.69
August 1994	Z1	6.78	1.26	19.70		based on June data	
	Z4	6.98	1.32	18.86			
	Z6	7.00	1.41	20.00			
	Z9	7.20	1.58	21.14			
	Z11	7.64	1.70	21.25			

followed the general trend of increasing stream pH, and agreed within 3.8% and 5.4% of observed pH of June and August, respectively.

From the results of MPSA with the selected six physical and chemical parameters, the cumulative frequency distributions of equal acceptable–unacceptable cases are shown in Fig. 3 for alkalinity, C_T and pH. The modeling results of stream alkalinity were very sensitive with respect to the alkalinity and the inflow rate of ground water [Fig. 3(a)]. We infer, therefore, that the stream alkalinity was controlled by the interaction between groundwater and stream water. However, the pH and C_T in stream water were sensitive with respect to CO_2 degassing rate constant as well as interaction between groundwater and stream water [Fig. 3(b),(c)]. The modeling of stream pH was also sensitive to the alkalinity and C_T concentrations of groundwater [Fig. 3(c)].

5. Discussion

Previous work on reactive solutes transported in streams have been focussed either on solute uptake or production caused by the interaction with sediments or shallow ground water (Bencala et al., 1984; Kimball et al., 1994a), or on volatile solutes (Genereux and Hemond, 1992). A more recent study determined the rates of volatilization of a volatile organic compound, independently of the rate of loss of that compound by interaction with sediments (Heekyung et al., 1995). The present study combined the general approach of the previous works with thermodynamic equilibrium considerations for carbonate chemistry and CO_2 degassing.

We supplemented the OTIS transport model with carbonate equilibrium speciation and mass transfer limited CO_2 degassing. The extended model reproduced the major trends in concentrations of both C_T

Table 4
Calculated gas exchange rates for propane and CO_2 corrected to 20°C with range. Range based on ±1 standard deviation of propane data

Reach	$k_{P,20}(h^{-1})$	Range	$k_{CO2,20}(h^{-1})$	Range
Round 1 Z1–Z4	3.42	2.71–4.05	4.25	3.37–5.04
Z4–Z6	5.03	4.93–5.13	6.25	6.13–6.38
Z6–Z9	1.43	1.39–1.48	1.78	1.73–1.84
Z9–Z11	1.43	1.39–1.48	1.78	1.73–1.84
Round 2 Z1–Z4	6.83	6.53–7.12	8.49	8.11–8.85
Z4–Z6	2.47	2.13–2.79	3.08	2.64–3.46
Z6–Z9	1.18	1.10–1.25	1.46	1.36–1.57
Z9–Z11	1.18	1.10–1.25	1.46	1.36–1.57

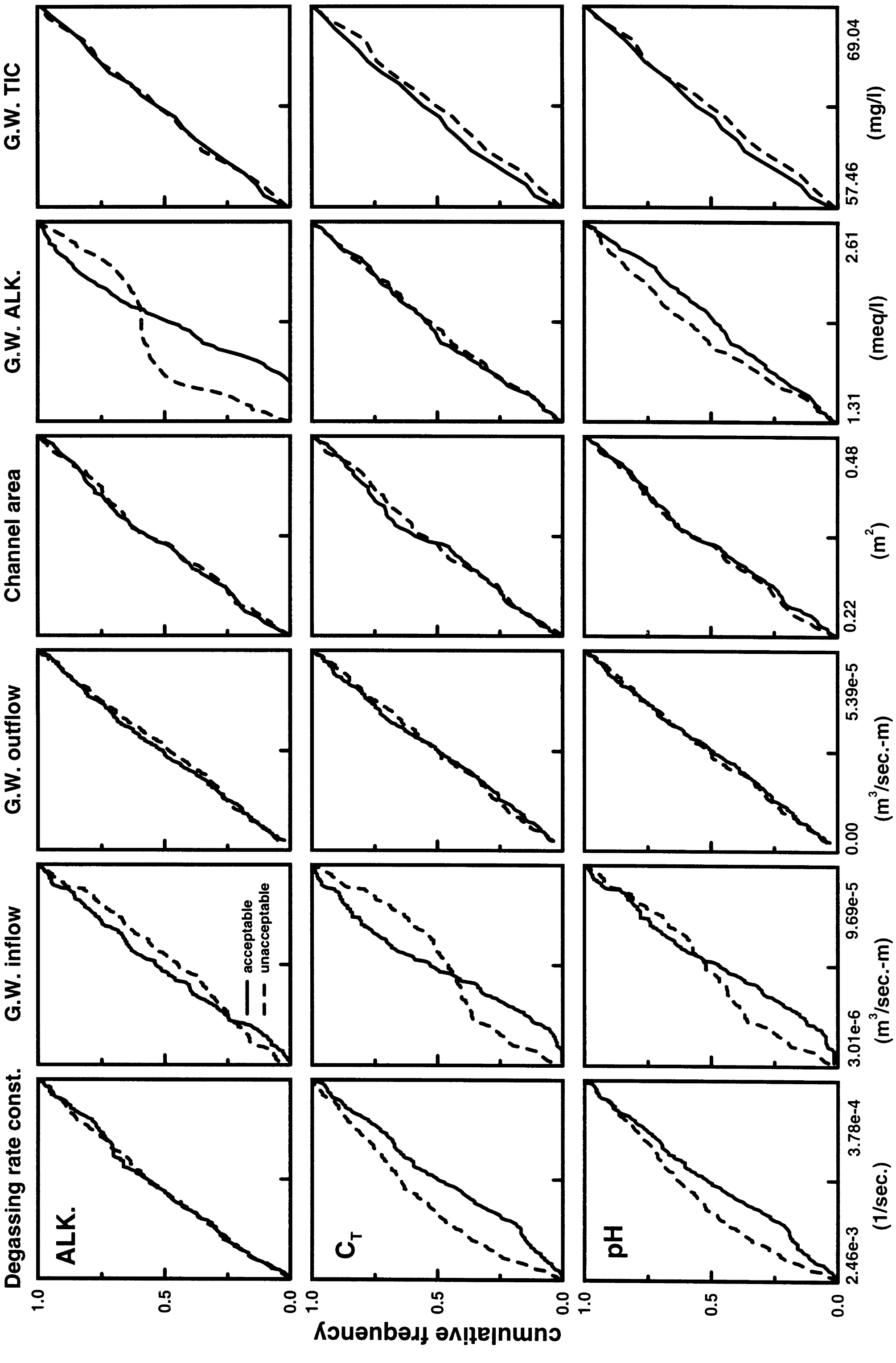

Fig. 3. MPSA results for alkalinity (upper row), C_T (middle row), and pH (low row) modeling. Solid and dotted lines indicate acceptable and unacceptable cases, respectively.

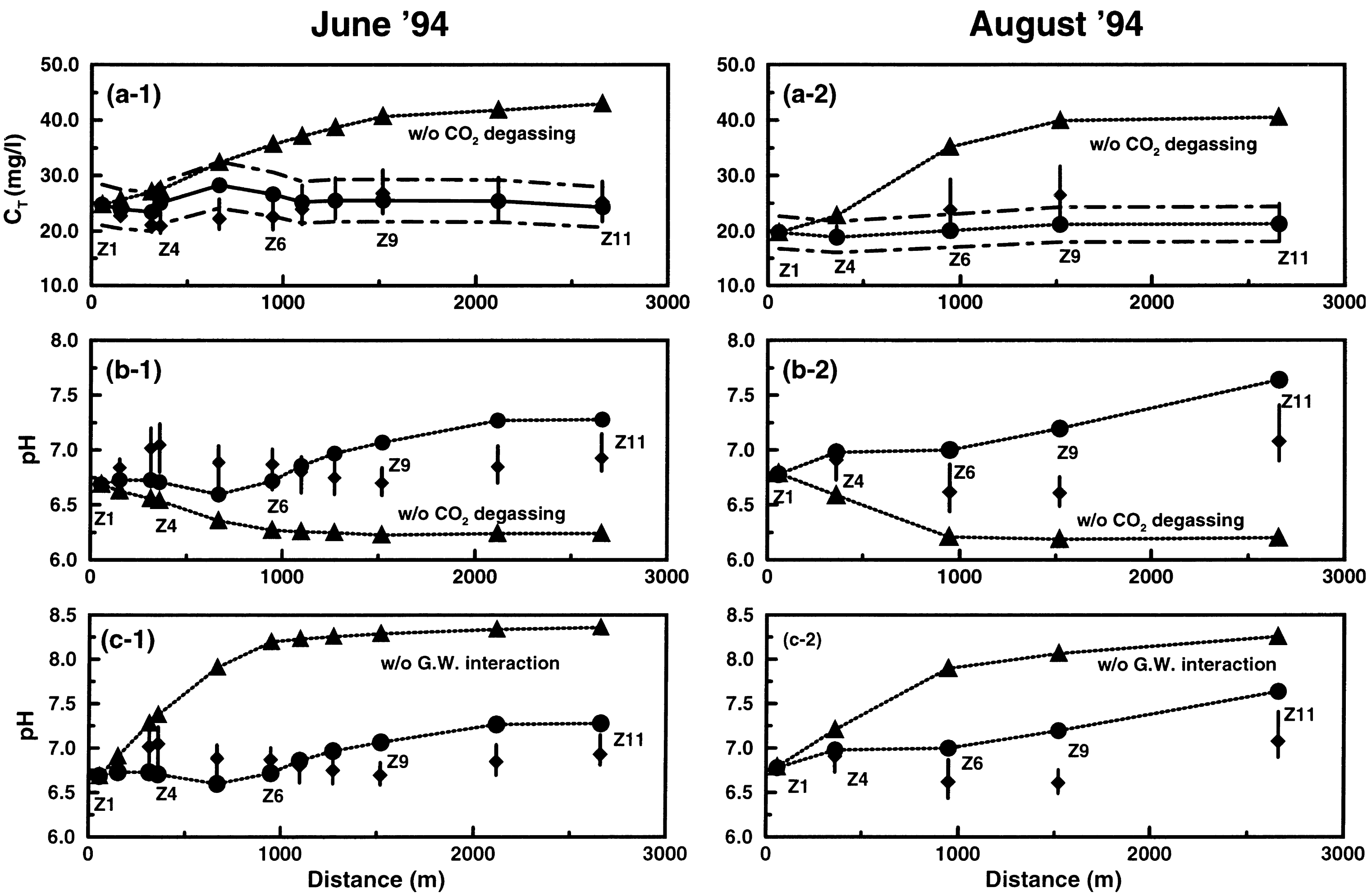

Fig. 4. The effects of CO_2 degassing (a and b) and groundwater interaction (c) on C_T and pH modeling for both June and August 1994. The results (closed triangle) from modeling without CO_2 degassing (a and b) and groundwater interaction (c) are compared to the measurements (closed circle) and simulation results (closed diamond) from model including the both processes.

and pH as a function of distance downstream (Fig. 2). The differences between observation and simulation were most likely because of the uncertainties in estimating the parameters, such as groundwater inflow rate and/or the rate of gas exchange. Also, we can not exclude the possibility that other processes (e.g. plant respiration or carbonate precipitation) which are not included in the model, may have affected the pH of stream water. In order to identify the significance of CO_2 degassing and interaction between ground water and surface water, we compared the results obtained from simulations that include and exclude CO_2 degassing (Fig. 4). As we can see from Fig. 4, the effect of CO_2 degassing is necessary to account for observed trend of C_T and pH [Fig. 4(a),(b)]. In addition, the interaction between ground water and surface water played an important role in controlling the stream pH [Fig. 4(c)]. The simulation results without the groundwater interaction showed that the simulated pH of June and August displayed the discrepancies of 14.8% and 9.1% from the observed ranges of pH, respectively [Fig. 4(c)].

From the multi-parametric sensitivity analysis for the simulation of alkalinity, the groundwater inflow rate and alkalinity were identified as the most important parameters (Fig. 3). The transport of alkalinity was controlled mainly by the dilution and/or concentration process through groundwater inflow into stream water. C_T was highly sensitive to CO_2 degassing as well as interaction between ground water and stream water. Because of the interdependency between pH, alkalinity and C_T, pH was

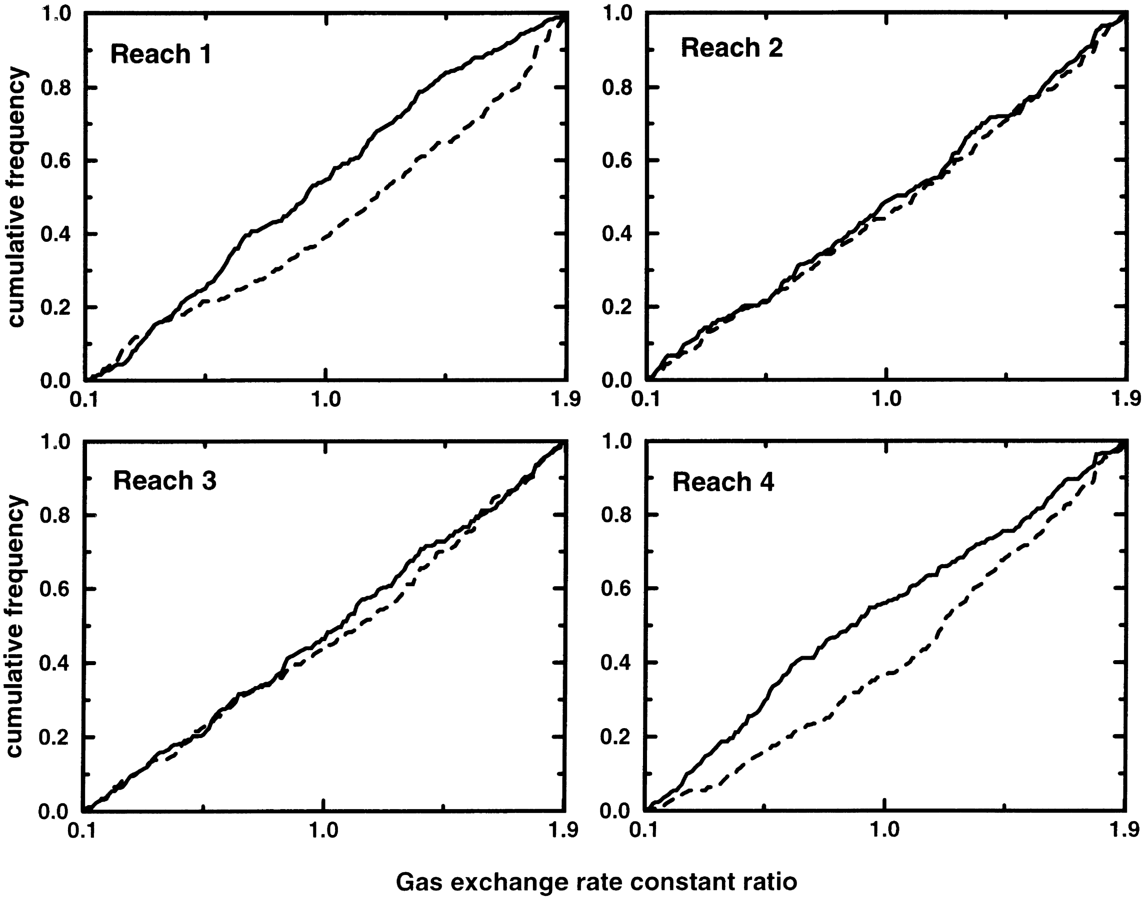

Fig. 5. Spatial variation of sensitivity in pH modeling to the CO_2 degassing process. Solid and dotted lines indicate acceptable and unacceptable cases, respectively. Abscissa represents the ratio of the gas exchange rate constant randomly chosen for MPSA to the midpoint (standard) of its range.

sensitive to both physical and chemical parameters: CO_2 degassing rate, groundwater inflow rate and concentrations of alkalinity and C_T in ground water.

The relative sensitivity of a particular model parameter varied between reaches depending on the other processes that were active and on the hydrological conditions. In order to identify the spatial variations of the relative sensitivities of the selected parameters, MPSA was applied for each study reach (reach 1 to 4), which have their own specific hydrologic conditions: gaining/losing reach, flow rate and channel cross-sectional area. The results from these localized MPSA showed that the relative sensitivities of parameters varied from reach to reach. For example, CO_2 degassing was not sensitive in reach 2 and 3, but it was in reach 1 and 4 (Fig. 5). The relatively high sensitivity of CO_2 degassing in reach 1 and 4 could be explained by the lower groundwater inflow rate, which caused a decrease in the sensitivity to groundwater interaction. In addition, the sensitivity to CO_2 degassing at reach 1 was enhanced by the longer travel time per unit length resulting from the slower stream velocity. The amount of CO_2 degassed from stream water to the atmosphere was sensitive to the travel time of stream water and degassing rate, which vary spatially according to the geometry of reach. Our interpretation from localized MPSA is that the relative sensitivity of a process depends on the significances of other processes that occur simultaneously.

6. Conclusions

Discharge of chemically distinct ground water to stream water can affect the stream pH, which is very important in the chemistry and ecology of a stream system. For example, an inflow of ground water with high dissolved inorganic carbon into a small stream system can change the stream pH. Degassing of CO_2 can also affect pH. The balance between these processes in addition to biological activity and carbonate precipitation and their effects on pH, influence chemical transformations of solutes such as metals whose mobility in the stream water is affected by pH. In the case of Pinal Creek, the ground water also contains elevated concentration of dissolved Mn(II) and trace amount of other metals. Precipitation and/or dissolution of of the Mn(II) and other trace metals in a stream system is generally controlled by the stream pH. Stream pH also has a strong influence on ecological environments for micro-organisms, which can mediate biochemical transformations through oxidation and reduction of heavy metals. Therefore, improved understanding and modeling of the processes that control stream pH is key to being able to predict the fate and transport of many heavy metals in Pinal Creek and other small stream systems with similar hydrological and geochemical conditions.

Acknowledgements

This project was made possible by grant number EAR-9523881 from National Science Foundation and grant number ES04949 from the National Institute of Environmental Health Sciences, NIH and by funding from the Toxic Substances Hydrology Program, USGS. We appreciate the help in collecting field data and for laboratory analysis from: Tim Corley, Justin Marble (The University of Arizona) and Chris Fuller, Sheryl Ferguson, Dorrie Gellenbeck, James Brown and Henry Sanger (USGS). We would like to thank the Journal of Hydrology reviewers Robert Runkel, Kenneth Bencala and an anonymous reviewer for their constructive comments. Reference to trade names, commercial products, manufacturers, or distributors in this paper is for identification purposes only and does not constitute an endorsement or a recommendation for use by the US Geological Survey.

References

Allison, J.D., D.S. Brown, K.J. Novo-Gardac, 1991. MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 Manual, US EPA, p. 106.

Bencala, K.E., Kennedy, V.C., Zellweger, G.W., Jackman, A.P., Avanzino, R.J., 1984. Interactions of solutes and streambed sediments 1. An experimental analysis of cation and anion transport in a mountain stream, Water Resources Research, 20, 1797–1803.

Bennett, J.P., Rathbun, R.E., 1972. Reaeration in open channel flow. Technical report, US Geological Survey Professional Paper 737, p. 63.

Broshears, R., Runkel, R., Kimball, B., McKnight, D., Bencala, K., 1996. Reactive solute transport in an acidic stream: experimental pH increase and simulation of controls of pH, aluminum and iron, Environmental Science and Technology, 30, 3016–3024.

Chang, F., Delleur, J., 1992. Systematic parameter estimation of watershed acidification model, Hydrological Processes, 6, 29–44.

DiToro, D.M., 1976. Combining chemical equilibrium and phytoplankton models—a general methodology. In: Canale, R.P. (Eds), Modeling Biochemical Processes in Aquatic Ecosystems. Ann Arbor Science, New York.

Duran, A.P., 1985. Nitrous oxide production in nitrogen-rich river sediments. Ph.D. thesis, Department of Civil Engineering, Massachusetts Institute of Technology, Cambridge, MA.

Eychaner, J.H., 1991. The Globe, Arizona research site-contaminants related to copper mining in a hydrologically integrated environment. In: Mallard, G., Aronson, D. (Eds.), USGS Toxic Substances Hydrology Program, vol. U.S. Geological Survey Water Resources Investigations Report, 91-4034, pp. 439–447.

Fischer, H.B., List, E.J., Koh, R.C.Y., Imberger, J., Brooks, N.H., 1979. Mixing in Inland and Coastal Waters. Academic Press, San Diego, CA.

Genereux, D.P., Hemond, H.F., 1990. Naturally occurring radon-222 as a tracer for streamflow generation: steady-state methodology and field example, Water Resources Research, 26, 3065–3075.

Genereux, D.P., Hemond, H.F., 1992. Determination of gas exchange rate constants for a small stream on Walker Branch watershed Tennessee, Water Resources Research, 28, 2365–2374.

Harvey, J., Fuller, C., 1994. Hydrologic controls on manganese transport in a contaminated stream–aquifer system, Pinal Creek Basin, Arizona, EOS Transactions American Geophysical Union, 75, 293.

Heekyung, K., Hemond, H.F., Krumholz, L.R., Cohen, B.A., 1995. In situ biodegradation of toluene in a contaminated stream. 1. Field studies, Environmental Science and Technology, 29, 108–116.

Hornberger, G., Spear, R., 1981. An approach to the preliminary analysis of environmental systems, Journal of Environmental Management, 12, 7–18.

Hulseapple, S.M., 1995. A field study of reaeration and solute transport at Pinal Creek, Globe, Arizona. Master's thesis, Department of Hydrology and Water Resources, University of Arizona, Tucson, AZ, p. 96.

Kilpatrick, F., Cobb, E., 1985. Measurement of discharge using tracers: US Geological Survey Techniques of Water Resources Investigations, Book 3, Chapter A16, 52 p.

Kilpatrick, F.A., Rathbun, R.E., Yotsukura, N., Parker, G.W., DeLong, L.L., 1989. Determination of stream reaeration coefficients by use of tracers: US Geological Survey Techniques of Water-Resources Investigations, Book 3, Chapter A18, 55 p.

Kimball, B.A., Broshears, R.E., Bencala, K.E., McKnight, D.M., 1994. Coupling of hydrologic transport and chemical reactions in a stream affected by acid mine drainage, Environmental Science and Technology, 28, 2065–2073.

Kimball, B., Broshears, R., Bencala, K., 1994. Environmental geochemistry of sulfide oxidation, effects of instream pH modification on transport of sulfide-oxidation products, ACS Symposium Series 550, American Chemical Society, 224–243.

Longsworth, S.A., 1991. Measurement of stream reaeration at Pinal Creek, Arizona. In: Mallard, G., Aronson, D. (Eds.), USGS Toxic Substances Hydrology Program. US Geological Survey Water Resources Investigations Report 91-4034, pp. 492–497.

Longsworth, S.A., Taylor, A.M., 1992. Hydrologic data from the study of acidic contamination in the Miami Wash-Pinal Creek area, Arizona, water years 1990–91, U.S. Geological Survey, Open-file report 92-468, 48–55.

McCutcheon, S.C., 1989. Water quality modeling. In: Transport and Surface Exchange in Rivers, vol. 1. CRC Press, Boca Raton, FL.

McKnight, D.M., Bencala, K.E., 1989. Reactive iron transport in an acidic mountain stream in Summit County, Colorado: a hydrologic perspective, Geochimica et Cosmochimica Acta, 53, 2225–2234.

Metzger, I., 1968. Effects of temperature on stream reaeration, Journal of the Sanit Engineering Division, American Society of Civil Engineering, 94 (SA-6), 1153–1159.

Parker, G.W., Gay, F.B., 1987. A procedure for estimating reaeration coefficients for Massachusetts streams. Technical report Water Resources investigations Report 86-4111, US Geological Survey, p. 34.

Peterson, N.P., 1962. Geology and ore deposits of the globe–Miami district, Arizona. Technical report Professional Paper 342, US Geological Survey, p. 151.

Rathbun, R.E., 1977. Reaeration coefficients of streams: state of the art, Journal of Hydraulics Division of the American Society of Civil Engineers, 103 (HY4), 409–424.

Runkel, R.L., Broshears, R.E., 1991. One-dimensional transport with inflow and storage (OTIS): A solute transport model for small streams, Technical Report 91-01, Cent. for Adv. Dec. Support for Water and Environ. Sys., Univ. of Colo., Boulder.

Runkel, R., Chapra, S., 1993. An efficient numerical solution of the transient equations for solute transport in small streams, Water Resources Research, 29, 211–215.

Runkel, R.L., Bencala, K.E., Broshears, R.E., Chapra, S.C., 1996. Reactive solute transport in streams, 1. Development of an equilibrium-based model, Water Resources Res., 32(2), 409–418.

Stumm, W., Morgan, J., 1996. Aquatic Chemistry: An Introduction with an Emphasis on Chemical Equilibria in Natural Waters. Wiley, New York.

Tsivoglou, E.C., 1967. Tracer measurement of stream reaeration. Technical report Federal Pollution Control Federation Report, US Department of the Interior, p. 86.

Tsivoglou, E.C., O'Connell, R.L., Walter, C.M., Godsil, P.J., Logsdon, G.S., 1965. Tracer measurement of atmospheric reaeration, Journal of the Water Pollution Control Federation, 37, 1343–1362.

Wagner, B.J., Gorelick, S.M., 1986. A statistical methodology for estimating transport parameters: theory and applications to one-dimensional advective–dispersive systems, Water Resources Research, 22, 1303–1315.

Walter, G.R., Norris, J.R., 1991. Hydrochemical zoning in the Pinal Creek alluvium. In: Mallard, G., Aronson, D. (Eds.), USGS Toxic Substances Hydrology Program. US Geological Survey Water Resources Investigations Report 91-4034, pp. 516–519.

Wilson, E.D., Moore, R.T., Pierce, H.W.. 1959. Geologic Map of Gila County, Arizona, Arizona Bureau of Mines.