



Natural spatial and temporal variations in groundwater chemistry in fractured, sedimentary rocks: scale and implications for solute transport

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Abstract

Natural tracers (major ions, $\delta^{18}\text{O}$, and O_2) were monitored to evaluate groundwater flow and transport to a depth of 20 m below the surface in fractured sedimentary (primarily shale and limestone) rocks. Large temporal variations in these tracers were noted in the soil zone and the saprolite, and are driven primarily by individual storm events. During nonstorm periods, an upward flow brings water with high TDS, constant $\delta^{18}\text{O}$, and low dissolved O_2 to the water table. During storm events, low TDS, variable $\delta^{18}\text{O}$, and high dissolved O_2 water recharges through the unsaturated zone. These oscillating signals are rapidly transmitted along fracture pathways in the saprolite, with changes occurring on spatial scales of several meters and on a time scale of hours. The variations decreased markedly below the boundary between the saprolite and less weathered bedrock. Variations in the bedrock units occurred on time scales of days and spatial scales of at least 20 m. The oscillations of chemical conditions in the shallow groundwater are hypothesized to have significant implications for solute transport. Solutes and colloids that adsorb onto aquifer solids can be released into solution by decreases in ionic strength and pH. The decreases in ionic strength also cause thermodynamic undersaturation of the groundwater with respect to some mineral species and may result in mineral dissolution. Redox conditions are also changing and may result in mineral dissolution/precipitation. The net result of these chemical variations is episodic transport of a wide range of dissolved solutes or suspended particles, a phenomenon rarely considered in contaminant transport studies.

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1. Introduction

While spatial variability in groundwater chemistry is frequently noted, temporal variability in chemistry re-

ceives less attention (Spalding and Exner, 1980; Bjerg and Christensen, 1992; Bourg and Richard-Raymond, 1994; Schreiber et al., 1999). When temporal variability is noted, it is often accompanied by the qualifying statement that it is small when compared to spatial variability. Rather than a comparison to spatial variability, it may be more appropriate to ask if the temporal variability is large enough to cause changes in the transport of dissolved or suspended solids.

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Hydrogeologic settings where temporal chemical variability have been well documented include karst (Jacobson and Langmuir, 1974), where surface water and groundwater interact (Bourg and Richard-Raymond, 1994; Malcom et al., 2003), and where groundwater has been impacted by anthropogenic activities (Nightingale and Bianchi, 1977). However, in many non-karst hydrogeologic investigations, groundwater chemistry is assumed to be temporally constant. The authors have not found literature that demonstrates temporal chemical variability on the storm event scale in a fractured rock setting.

A common hydrogeologic setting that has high potential for natural temporal chemical variability is where the water table is close to the surface (<10 m) and where preferential pathways for flow exist. In this setting, infiltrating precipitation can pass rapidly through the unsaturated zone, mixing to only a minor degree with the large volume of water stored in the unsaturated zone. This newly infiltrated water may also rapidly penetrate below the water table if a downward vertical hydraulic gradient is present.

The chemical composition of precipitation is usually significantly different from water in the unsaturated and saturated zones. Some important chemical differences include total dissolved solids (TDS) concentration that is generally an order of magnitude lower in precipitation, pH that is usually 1–3 units lower in precipitation, and dissolved O₂ that is higher in precipitation. The concentration of individual ions is usually higher in groundwater, although the concentration of some ions (SO₄²⁻, NO₃⁻, Cl⁻) may be higher in precipitation.

If temporal chemical variability exists, it can have a significant impact on the transport of solutes and contaminants. A decrease in TDS during a precipitation event can cause thermodynamic undersaturation that can result in mineral dissolution. Adsorption of charged species is a function of pH, ionic concentration, and ionic ratio, all of which can vary during a precipitation event. Decreases in TDS (and ionic strength) during a precipitation event can change the distribution of charge near mineral surfaces, resulting in conditions that promote the generation of suspended colloids. Changes in redox conditions due to variations in dissolved O₂ during precipitation events can result in dissolution or precipitation of redox sensitive minerals. In addition, the rate of natural attenuation of organic contaminants is in part dependent upon the redox conditions of the groundwater.

Although temporal chemical variability may exist in many water table situations, common monitoring well installation and sampling procedures may obscure the variations. Monitoring wells are typically screened over a 3-m interval or more. Significant spatial and temporal variability has been observed over distances of less than 3 m (Schreiber et al., 1999). As a result, samples col-

lected from a typical monitoring well are a complex mixture of the chemistry of water in that interval. Using an average chemistry to predict contaminant transport may ignore small, but important, zones where transport is occurring. Even if a well is screened over an interval <3 m, typical sampling procedures may not capture transient, precipitation driven variations. Given a choice, most hydrogeologists would prefer not to sample when it is raining. Therefore, the picture of groundwater chemistry may be biased towards non-storm conditions.

This investigation focuses on natural variability in groundwater chemistry in the soils, saprolite, and shallow fractured sedimentary rocks on the Oak Ridge Reservation (ORR), Tennessee. The presence of preferential pathways for flow on the ORR is well documented. Spatial variability in shallow groundwater chemistry was monitored on scales ranging from less than 1 m to over a km and temporal variability was monitored over periods ranging from several hours up to a year. The observed variations are used to test and refine the existing conceptual model of flow and transport on the ORR, to identify and group groundwater with similar geochemical history, and to evaluate the variability in flux of water from different flow paths that mix in discharge zones. The variations in water chemistry are also discussed in terms of the scale variability and the potential impact on solute transport.

2. Conceptual model of flow and transport

2.1. Geology

The field site is in the Appalachian Valley and Ridge Province of Tennessee, and is characterized by a series of imbricate thrust sheets which result in parallel valleys of less erosion-resistant bedrock (primarily shale) and intervening ridges of more resistant bedrock (sandstone or limestone/dolomite). Locally, bedrock is composed primarily of shale with occasional thin interbeds of limestone and sandstone. On a regional scale, groundwater recharges on the ridges and discharges in the valleys. Recharge also occurs locally on the valley floor. The conceptual model for flow and transport in the shallow subsurface of the ORR divides the shallow subsurface into 4 units based on hydrogeologic characteristics and position relative to the water table. Starting from the surface, the units are the stormflow zone, the saprolite, the transition zone and the intermediate zone (Fig. 2). The following sections outline the conceptual model of flow and transport in each unit.

2.2. Stormflow zone

The stormflow zone is a region just below land surface that is intermittently saturated and above the water

table. The hydraulic conductivity of the upper soil horizons is about 100X greater than the lower soil horizons. During storm events, the permeability contrast can result in saturation of the upper soil horizons (McKay and Driese, 1999).

2.3. Unsaturated and saturated saprolite

The saprolite results from in situ chemical weathering of the sedimentary (primarily shale and limestone) bedrock when primary minerals are dissolved and replaced by secondary minerals. This chemical transformation results in an increase in the matrix porosity from <5% to up to 50% (Davis et al., 1984). Although the bedrock is highly weathered, much of the original bedding structure and fractures are retained. Fracture spacing in some areas has been estimated to be 0.5 cm (Dreier et al., 1987); however, some fractures may be filled with translocated clays (McKay and Driese, 1999).

In the study area, the thickness of the saprolite ranges from 1 to 7 m. The saprolite is thinnest adjacent to streams and thickens rapidly away from them. The average saturated hydraulic conductivity is 2×10^{-4} cm/s (Rothschild et al., 1984). The water table fluctuates within the saprolite in response to individual storm events and seasonal changes.

Modeling studies (Gwo et al., 1995; Van der Hoven et al., 2003) indicate that advection is the dominant mechanism for exchange of solutes between the fractures and matrix in the unsaturated saprolite. During non-storm periods, slow vertical transport through the matrix is thought to occur (Solomon et al., 1992). Only a few studies have specifically targeted the saturated saprolite on the ORR. Several studies have demonstrated that transport is rapid along fracture pathways but that diffusive exchange of solutes between the fractures and saprolite matrix is a significant process (Lee et al., 1992; Stafford, 1996).

2.4. Transition zone

The majority of the water below the water table is thought to flow through the transition zone (Solomon et al., 1992). The rocks in the transition zone are thought to be moderately weathered and highly fractured because they cannot be penetrated by an auger and sample recovery is poor during coring. The spacing between fractures has not been measured, but is likely to be less than 10 cm, and the fractures are thought to be well connected. Samples of rock fragments removed from saprolite cores have an effective porosity of 10–15% (Dorsch and Katsube, 1996). Fractures dominate flow and transport; however, diffusion of solutes into the matrix is also a significant transport mechanism, as demonstrated by a He injection test (Moline et al., 1998).

2.5. Intermediate zone

The intermediate zone is defined by the depth below which competent core can be recovered. These rocks are unweathered and have low (<5%) matrix porosity and the spacing between fractures (or fracture zones) is estimated to be several meters near the water table. The fracture spacing increases to greater than 35 m at depths greater than 60 m below the surface (Solomon et al., 1992; Moline and Schreiber, 1996). The hydraulic conductivity of the intermediate interval measured by packer tests has a geometric mean of 5.8×10^{-6} cm/s with a standard deviation of 1.0 log unit (Solomon et al., 1992). The total flux of water through this zone is several orders of magnitude less than through the zones above it. Almost all flow occurs through the fractures and the low matrix porosity greatly reduces the significance of matrix diffusion.

2.6. Hydrochemistry

Precipitation samples collected at the site indicate that it contributes only a small fraction of the ions measured in the groundwater. Sulfate was detected in precipitation at 1–3 mg/L, while most other ions were <1 mg/L. Most groundwater passing through the stormflow zone and unsaturated saprolite can be characterized as having low but highly variable total dissolved solids (TDS), low Na/Ca ionic ratio, highly variable $\delta^{18}\text{O}$, and significant amounts of dissolved O_2 . The chemistry of the water in the saturated saprolite has the highest spatial and temporal variability of any of the geologic units in this investigation. All of the parameters that were monitored (TDS, $\delta^{18}\text{O}$, and O_2) were variable in both space and time within the saprolite.

Within the transition zone, there is significant spatial chemical variability throughout the study area, but only moderate temporal variability. In the intermediate zone, there is significant spatial variability and minor temporal variability. In general, water in both the transition and intermediate zones can be characterized as having high TDS, high Na/Ca ionic ratio, nearly constant $\delta^{18}\text{O}$ (–5.8‰ to –6.0‰), and low dissolved O_2 .

During nonstorm periods, there is upward flow to the water table throughout much of the study area, and the major ion chemistry and isotopic composition of water in the saprolite is similar to that of the underlying transition zone. During storm events, water recharging through the unsaturated zone causes a reversal in the vertical hydraulic gradient. As a result, the water in the saprolite has a major ion chemistry and isotopic composition similar to water in the stormflow zone.

3. Methods

3.1. Field methods

3.1.1. Monitoring well construction

The wells can be grouped into 3 types: transition and intermediate zone well pairs, intermediate zone multiport wells, and saprolite multiport wells (Fig. 1). The well pairs consist of a shallow well screened at the water table and a deeper well screened at a depth of between 12 and 18 m below the ground surface. Each of these wells is installed in a separate borehole and is constructed of 5 cm diameter PVC casing with a screened interval of 3 m.

The 3 multiport wells screened in the intermediate zone are located within 20 m of each other. Detailed description of drilling and installation of these wells is presented in Moline et al. (1998). Each well consists of a single borehole (total depth ranging from 15 to 21 m) with 5 screened intervals. The length of the screened intervals ranges from 0.3 to 0.6 m.

The multiport wells in the saprolite and transition zone consists of 4 or 5 sampling ports in a 20-cm diameter borehole. The screen length for each port is 10 cm, except for the bottom port where the screen length is 30 cm.

Water in the stormflow zone was monitored by 3, nested stormflow tubes that were 2.5 cm in diameter. A separate hole was hand-augered for each tube. A 5-cm screened section was placed at the bottom of the hole and blank casing extended above the land surface. The annular space around the screen was backfilled with

sand and compacted soil filled the remainder of the annular space to the surface.

3.1.2. Water sampling

Water samples were collected using a peristaltic pump or a down-hole centrifugal pump. Each well was purged of approximately one well volume of water at a rate of less than 100 ml/min. prior to sampling. Samples for major ion chemistry were collected in 500 ml polyethylene bottles. Sample bottles were rinsed with purge water, and then filled completely to minimize head space. A 30 ml aliquot for anion analysis was stored in a polyethylene bottle at 4 °C until analysis. Another 30 ml aliquot for cation analysis was passed through a 0.45 µm filter, acidified to pH 2 with ultra-pure HNO₃, and stored in a polyethylene bottle at 4 °C until analysis. Samples for O isotopic analysis were stored in 15 ml glass vials with teflon-lined caps at 4 °C until analysis.

3.2. Laboratory methods

Alkalinity titrations were performed in the laboratory within several hours of collection using a Fischer Titrimeter II Automatic System. The titration was conducted to an endpoint of pH 4.5 and it was assumed that all alkalinity was due to the HCO₃⁻ ion. Anion analysis was performed at Oak Ridge National Laboratory, Environmental Sciences Division using a Dionex DX-120 ion chromatograph with an AS4A-SC column. Cation analysis was performed at Oak Ridge National Laboratory, Chemical and Analytical Division using a Thermo Jarrell Ash IRIS ICAP. Oxygen isotopic analy-

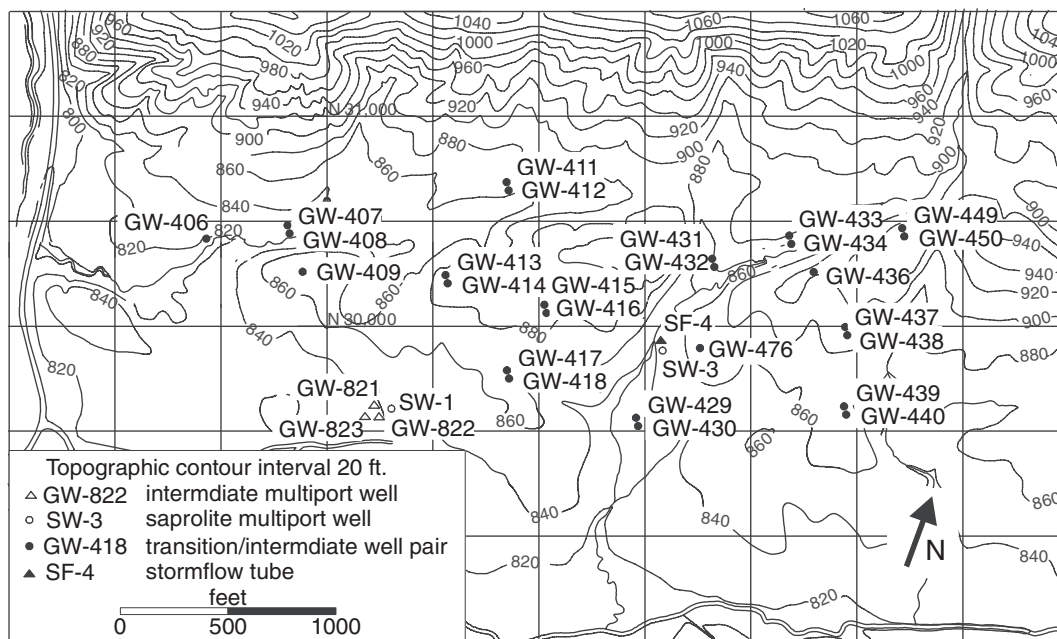


Fig. 1. Map of the study area showing well locations.

ses were performed in the Department of Geologic Sciences at the University of Tennessee on a Finnigan Delta Plus gas source mass spectrometer with a HDO Equilibrator for automated analysis of water samples. Dissolved gas analyses were performed on a Stanford Research quadrupole gas source mass spectrometer in the Department of Geology and Geophysics at the University of Utah.

4. Results and discussion

The presence of preferential pathways for groundwater flow are well established in the soils, saprolite, and bedrock on the ORR (Solomon et al., 1992; Gwo et al., 1995). The data presented in this section are consistent with the existing conceptual model of subsurface flow and transport. While spatial and temporal variability in groundwater chemistry has been addressed in some studies conducted on the ORR (Wilson et al., 1993; Schreiber et al., 1999), the scale associated with variability in the saturated zone has not been approached in a systematic manner. The focus of this discussion will be on the chemistry of water in the saturated zone, however, data from the unsaturated zone will also be presented where it is important to the understanding of saturated zone processes.

4.1. Saturated saprolite

Chemical variability in the shallow subsurface was evaluated by sampling during storm events. These data represent the highest resolution (<1 m spatial and 6–8 h temporal) data collected during this investigation. Data were collected from a number of storm events at two different sites. While the response to an individual

storm event was dependent on precipitation rate/amount and antecedent moisture conditions, the data from an April–May, 1998 storm event are presented as representative of the observations and interpretations from most of the storm events. The sampling locations and the geologic setting of the data collected during this storm event are shown on Fig. 2.

Water in the saturated saprolite has the greatest amount of chemical variability of the units studied in this investigation. This variability is a result of the presence of preferential pathways for flow and the frequent reversals in hydraulic gradient generated by storm events. It is assumed that the majority of water collected during sampling comes from the preferential pathways, and not from the less permeable matrix. The chemical variability within the matrix is likely to be lower, and advective/diffusive exchange of solutes may buffer the magnitude of changes along the preferential pathways.

Fig. 3(a) shows the precipitation rate and isotopic composition of the precipitation that fell during the April–May, 1998 storm event. The largest changes occur between Days 120 and 122, when a total of 40.2 mm of precipitation fell. Fig. 3(b) shows a typical gradient reversal, lasting for several days during and after the storm event.

Fig. 3(c) shows the $\delta^{18}\text{O}$ of water in the stormflow and shallow saturated zones during the April–May, 1998 storm event. Prior to the storm, the ^{18}O of all the wells is relatively constant (between -5.5‰ and -5.8‰). This is similar to $\delta^{18}\text{O}$ of water in the intermediate zone, indicating an upward vertical gradient. The weighted average of $\delta^{18}\text{O}$ of precipitation falling on Day 120 is -3.3‰ . The $\delta^{18}\text{O}$ in the stormflow zone (well SF-4A on Fig. 3(c)) is initially -4.4‰ , indicating that it is a mixture of new precipitation and water stored in the subsurface. The $\delta^{18}\text{O}$ of water in the shallowest port in

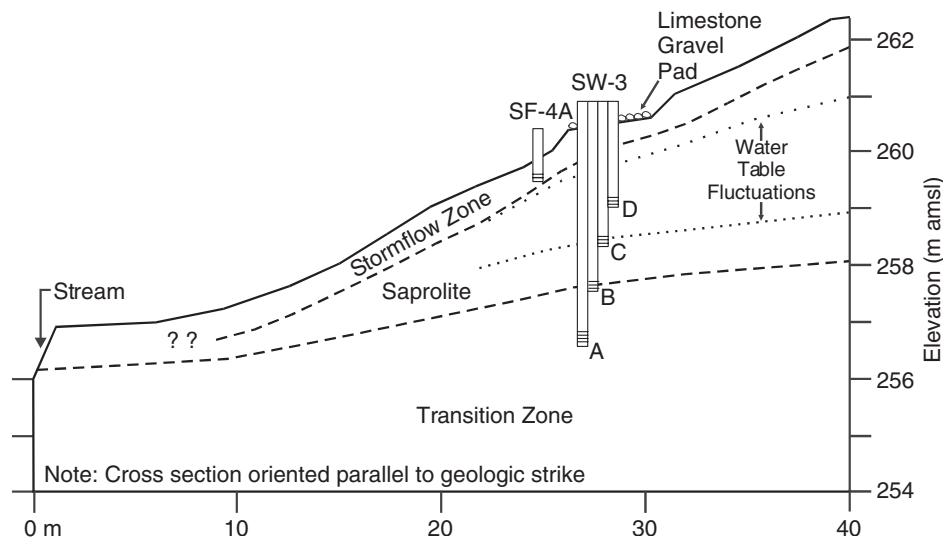


Fig. 2. Geologic cross section of the shallow subsurface showing construction of multiport wells.

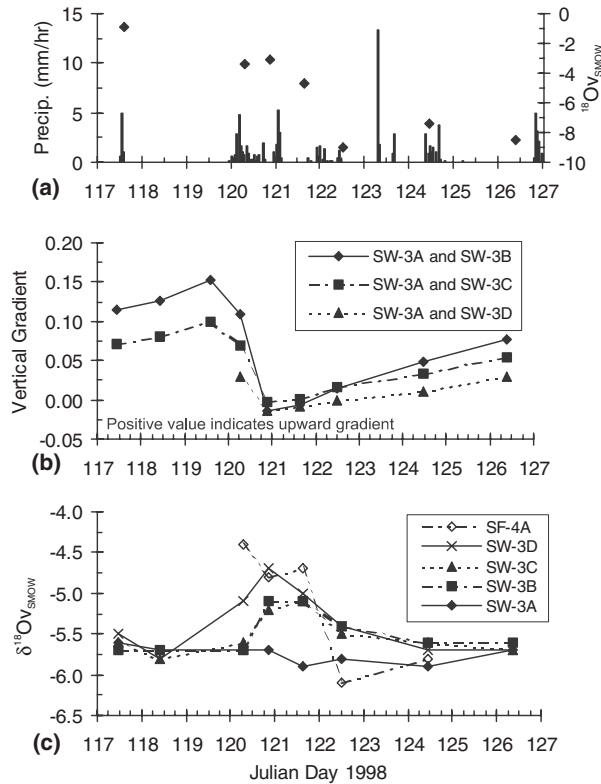


Fig. 3. (a) Precipitation rate and the $\delta^{18}\text{O}$ composition of precipitation, (b) variations in vertical hydraulic gradient, and (c) variations in ^{18}O of shallow groundwater over the course of a storm event in April–May, 1998.

the saprolite well (SW-3D) increases to a value nearly identical to the stormflow zone. This indicates that water passes along preferential pathways in the unsaturated saprolite with only minor mixing with water stored in the saprolite matrix. The response in the deeper saprolite ports (SW-3B and SW-3C) is also evident, but is lagged by about 12 h and subdued compared to the shallowest port. These data indicate that while flow along preferential pathways is still important, the percentage of stored water mixing with the new water increases. The $\delta^{18}\text{O}$ of water from the port in the transition zone (SW-3A) varies only 0.2‰ over the monitoring period, and does not appear to respond to the storm event. At the end of the monitoring period, the $\delta^{18}\text{O}$ in all the ports in the saturated zone converges to the pre-storm value as the vertical hydraulic gradient becomes upward again.

The variations in major ion chemistry in these wells (Fig. 4) supports the interpretation of flow along preferential pathways and gradient reversals made from the hydraulic head and $\delta^{18}\text{O}$ data. It should be noted here that the patterns just described are applicable to areas that have not been significantly impacted by human activities. At the site where this data was collected, a limestone gravel pad (shown on Fig. 2) was installed to facilitate access by vehicles. The impact of dissolution

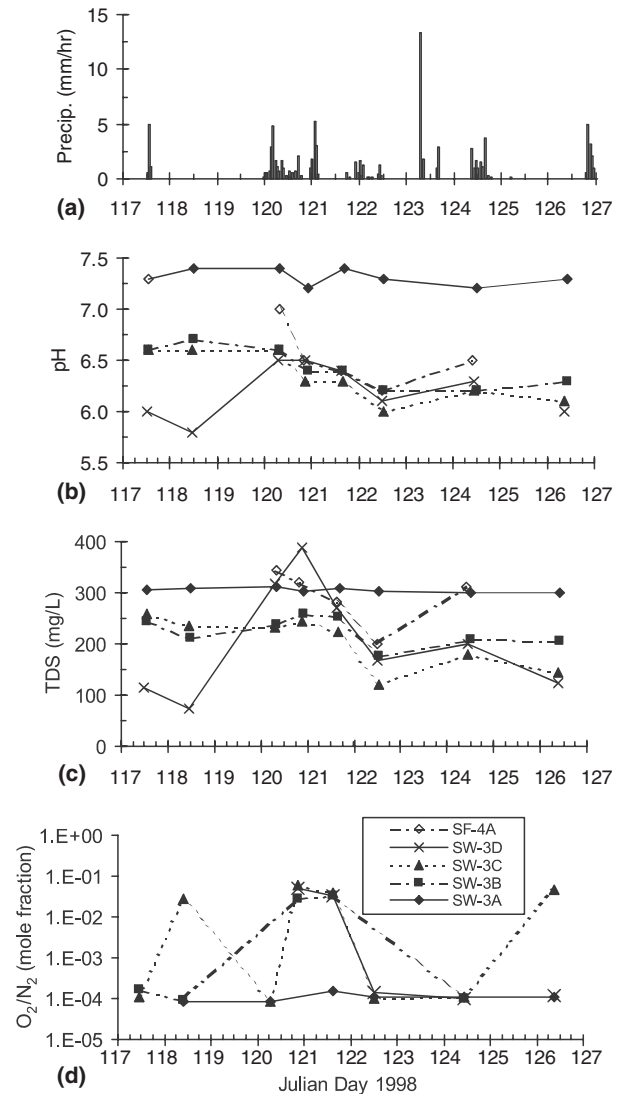


Fig. 4. (a) Precipitation rate, (b) variations in pH, (c) TDS, and (d) O_2/N_2 mole fractions of shallow groundwater over the course of a storm event in April–May, 1998.

of carbonate minerals from the limestone gravel will be discussed, however, the conceptual model and interpretations are not altered by the presence of the gravel.

The pH of groundwater is highest prior to the beginning of the storm event, and pH increases with depth (Fig. 4(b)). In the ports in the saprolite, the pH decreases 0.5–0.75 pH units in response to the storm event, and the pH remains at around 6 for the rest of the monitoring period. The pH in the transition zone does not appear to respond to the storm event.

The TDS of groundwater is highest prior to the beginning of the storm event, and increases with depth (Fig. 4(c)). The initial response in the saprolite ports is a large increase in SW-3D and a slight increase in SW-3B and SW-3C. Note also that the TDS is high in the stormflow zone, even higher than in the transition zone.

Water in the stormflow zone is in continual contact with the limestone gravel pad, dissolving CaCO_3 between storm events. Over the course of the storm event, the TDS in the stormflow zone decreases as it is diluted with low TDS precipitation. After the initial increase, the TDS in all the saprolite ports decreases to as much as half the pre-storm values, and remains relatively low for the rest of the monitoring period.

The variations in the amount of dissolved O_2 (expressed as the ratio of the mole fraction of dissolved O_2 over the mole fraction of dissolved N_2) in the saturated saprolite and upper transition zone are shown on Fig. 4(d). Dissolved O_2 is reported as the mole fraction of O_2 to N_2 because the total pressure inside the diffusion sampler was not known and therefore the concentration of dissolved gases could not be calculated. However, since the concentration of N_2 does not vary significantly in groundwater, the variations in O_2/N_2 are primarily a result of changes in O_2 . Groundwater that is in equilibrium with atmospheric O_2 and N_2 would have a mole fraction ratio of 0.27.

Prior to the storm event there is very little O_2 (O_2/N_2 ratio of around 10^{-4}) in the shallow groundwater except in one sample from SW-3C. After the main pulse of precipitation on Day 120, the O_2/N_2 ratio of the 3 ports in the saprolite (SW-3B, SW-3C, and SW-3D) increases to between 0.01 and 0.06. Field observations also support the storm-driven variations in dissolved O_2 . The walls

of fractures in the saprolite are commonly coated with Fe and Mn oxides. Fe and Mn are more soluble in reducing conditions. Water recharging through the vadose zone during storm events moves primarily along the fractures. The oxidizing conditions in the fractures cause precipitation of the Fe and Mn oxides.

4.2. Transition zone

Data for water chemistry in the transition zone come primarily from the water table wells of the shallow and intermediate depth well pairs (Fig. 1). These wells have a screen length of 3 m and are likely to reflect water chemistry in the upper part of the transition zone as well as the lower part of the saprolite. The previous section presented data from a discreet interval in the transition zone over the course of a storm event that indicate there is not much change over the course of a storm event. However, variability was noted in the water table wells when sampled on a monthly basis. This variability was initially hypothesized to be due to seasonal changes in the relative flux of water from the overlying saprolite and the underlying intermediate zone. While seasonal trends were observed in a few wells, there was a weak or no seasonal trend in most wells.

Since seasonal flux variations appear to be minor, the possibility that individual storm events can influence groundwater chemistry in the transition zone was

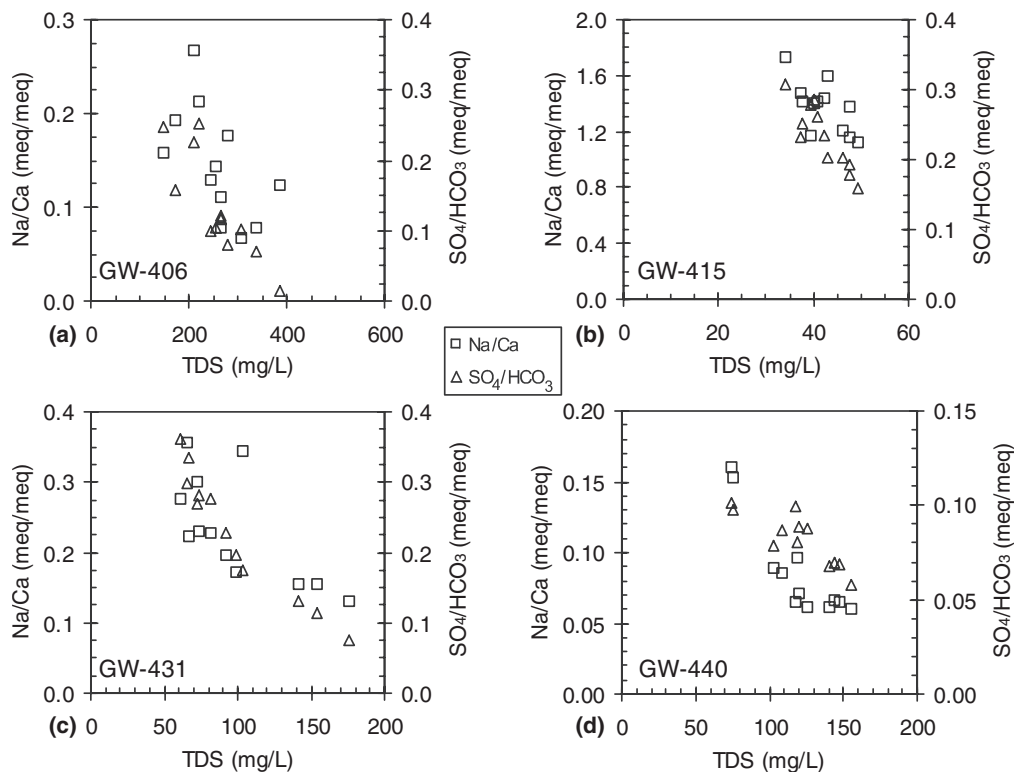


Fig. 5. Correlation between TDS, Na/Ca and SO_4/HCO_3 ratios for selected water table wells sampled on a monthly basis.

further evaluated. In general, water in the intermediate zone has higher TDS, Ca^{2+} , Na^+ , and HCO_3^- concentrations, and Na/Ca ionic ratios and lower SO_4/HCO_3 ionic ratios than water in the transition zone. If the change in TDS were controlled by variations in the flux of water from the intermediate zone, Na/Ca ratios would be positively

correlated with TDS, and SO_4/HCO_3 ratios would be negatively correlated with TDS. In two thirds of the water table wells, both Na/Ca and SO_4/HCO_3 ratios are negatively correlated with TDS (Fig. 5). In most of the other water table wells there is low variability and little correlation between ionic ratios and TDS. Exam-

Table 1
Major ion chemistry and ionic ratios for selected water table wells sampled on a monthly basis

Well	Date	Na (mg/L)	Ca (mg/L)	HCO_3^- (mg/L)	SO_4 (mg/L)	TDS (mg/L)	Na/Ca (meq/meq)	SO_4/HCO_3 (meq/meq)
GW-411	12/10/96	3.2	9.4	38.4	8.6	64.4	0.30	0.28
	1/28/97	3.2	8.2	35.5	8.5	59.8	0.34	0.30
	2/20/97	2.8	7.7	34.5	8.4	58.4	0.31	0.31
	4/15/97	3.0	8.5	35.7	8.4	59.7	0.30	0.30
	5/22/97	3.9	7.1	31.7	7.5	54.0	0.48	0.30
	6/27/97	3.7	6.7	30.4	7.8	52.8	0.49	0.32
	7/29/97	4.0	6.1	29.0	7.3	50.9	0.57	0.32
	9/2/97	4.1	7.9	31.5	8.6	58.1	0.45	0.35
	10/6/97	4.0	7.6	30.5	10.0	59.0	0.46	0.41
	12/2/97	3.1	6.4	25.3	8.7	48.8	0.42	0.44
1/21/98	2.8	6.0	24.9	8.2	46.5	0.41	0.42	
GW-415	11/7/96	5.8	4.2	29.3	4.7	46.1	1.204	0.202
	12/11/96	4.4	2.2	20.3	4.9	34.1	1.729	0.307
	1/28/97	5.2	3.2	23.8	5.3	40.1	1.403	0.284
	3/3/97	4.1	3.1	23.7	5.2	39.3	1.171	0.279
	4/15/97	5.4	3.3	24.4	5.0	40.7	1.419	0.261
	5/21/97	5.9	3.6	25.4	4.7	42.2	1.435	0.234
	6/25/97	5.4	3.3	22.2	4.4	37.8	1.420	0.252
	7/29/97	6.7	4.3	29.5	4.5	47.5	1.376	0.193
	9/10/97	6.1	4.7	31.6	4.0	49.3	1.127	0.159
	10/6/97	6.0	3.3	26.6	4.2	43.0	1.592	0.202
11/20/97	6.1	4.6	29.9	4.2	47.4	1.158	0.177	
1/21/98	5.2	3.1	22.4	4.1	37.4	1.470	0.232	
GW-431	11/11/96	2.6	10.1	38.4	10.1	66.7	0.222	0.334
	12/10/96	3.2	14.4	57.6	10.3	91.8	0.196	0.227
	2/2/97	3.5	13.2	48.7	10.6	81.4	0.228	0.275
	3/3/97	3.2	7.9	39.8	9.4	66.0	0.356	0.299
	4/15/97	3.0	11.3	45.1	10.0	74.1	0.231	0.280
	5/21/97	4.1	23.3	95.0	9.7	140.9	0.155	0.130
	6/27/97	5.1	12.9	69.2	9.5	103.4	0.345	0.173
	7/30/97	4.3	24.1	108.0	9.6	154.3	0.155	0.113
	9/2/97	3.8	25.7	128.1	7.5	175.6	0.130	0.074
	10/6/97	3.1	15.7	63.3	9.8	98.6	0.172	0.196
11/24/97	2.7	8.6	34.8	9.9	60.8	0.277	0.360	
1/21/98	3.4	9.8	43.6	9.2	72.1	0.301	0.268	
GW-440	11/10/96	1.7	22.7	82.8	6.5	118.0	0.065	0.099
	12/9/96	1.7	22.1	109.7	6.0	143.6	0.067	0.069
	1/28/97	2.6	14.3	50.4	4.0	74.0	0.160	0.101
	3/6/97	2.3	13.0	53.1	4.1	75.6	0.153	0.097
	4/16/97	1.7	24.1	89.3	6.2	125.3	0.061	0.088
	5/22/97	1.9	22.8	85.8	6.0	120.1	0.071	0.089
	6/30/97	2.0	20.3	77.0	5.3	108.4	0.085	0.087
	8/1/97	2.4	21.7	86.0	5.5	119.3	0.096	0.081
	9/4/97	1.9	27.7	101.0	5.4	140.2	0.061	0.068
	10/7/97	2.1	27.6	107.5	5.8	147.1	0.066	0.069
12/2/97	2.1	30.1	113.6	5.1	155.1	0.060	0.058	
1/26/98	2.0	19.6	72.8	4.5	102.3	0.089	0.078	

nation of the changes in concentration for the individual ions (Table 1) indicates that there is higher variability in Ca^{2+} and HCO_3^- and lower variability in Na^+ and SO_4^{2-} concentrations.

This pattern of variability can be explained by an increased recharge flux during precipitation events rather than variations in the flux from the underlying intermediate zone. One explanation is that during storm events, low TDS water that is undersaturated with respect to calcite passes through the saprolite and enters the transition zone. The thermodynamic undersaturation may cause calcite dissolution, resulting in a gradual rise in the concentration of Ca^{2+} and HCO_3^- and TDS after the storm. Alternatively, the rise in Ca^{2+} and HCO_3^- after the storm event could be explained by a flux of solutes stored in the micropores of the matrix into the fracture pathways that have been diluted by infiltrating precipitation. In contrast to Ca^{2+} and HCO_3^- , concentrations of Na^+ and SO_4^{2-} do not vary as much, nor do they correlate with changes in TDS as would be expected from a variable flux from the intermediate zone.

4.3. Intermediate zone

Data from the intermediate zone come from two different types of wells. The first type is the deeper wells in the well pairs. These wells are constructed with a screened interval of 3 m and are located throughout

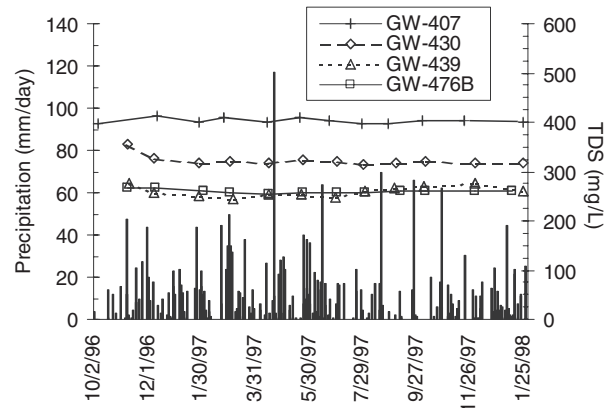


Fig. 6. Variations in TDS in selected intermediate depth wells sampled on a monthly basis and daily precipitation.

the study area (Fig. 1). There are also 3 multiport wells located within 20 m of each other (GW-821, GW-822, GW-823 on Fig. 1). Each multiport well has 4 or 5 screened sections that are 0.5 m in length.

Based on the data from the 3-m screened wells, the major ion chemistry of the intermediate zone groundwater can be divided into two groups related to their topographic position. Along the small streams which cut diagonally across the valley and near the center of the valley, the water is Na– HCO_3 or Na–Ca– HCO_3 type.

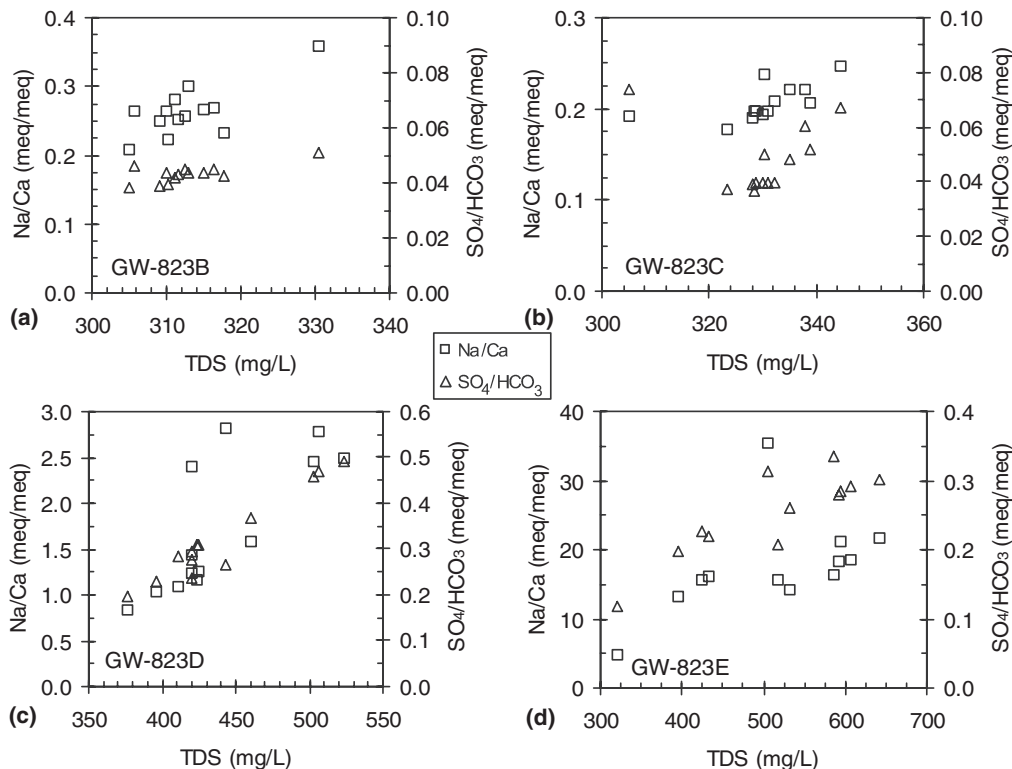


Fig. 7. Correlation between TDS, Na/Ca and SO_4/HCO_3 ratios for selected intermediate zone multiport wells sampled on a monthly basis.

Away from the streams the water is Ca–HCO₃ type. There are only small variations in water chemistry in these wells, and no correlation was found between TDS and seasons (Fig. 6).

In the multiport wells, there is greater chemical variability. When these variations are plotted against the date of collection or water levels (evaluation of seasonal trends), no apparent patterns were noted. When TDS is plotted against Na/Ca and SO₄/HCO₃ ionic ratios, a positive correlation is seen in a number of the ports (Fig. 7). In other ports, there is chemical variability, but no correlation exists between TDS and the ionic ratios. In the ports where there is a positive correlation, the concentrations of Na⁺, Ca²⁺, SO₄²⁻, and HCO₃⁻ are generally increasing with increasing TDS. However, there is a larger relative increase in the concentration of Na⁺ and SO₄²⁻ than in Ca²⁺ and HCO₃⁻ resulting in higher ionic ratios. In general, the relative concentrations of Na⁺ and SO₄²⁻ increase with depth in these wells are interpreted to be changes in the relative flux of groundwater from flow paths within the intermediate zone.

The data from the multiport wells clearly indicate that the temporal variations in chemistry extend into the intermediate zone groundwater and suggest that the flow path of groundwater to a specific location changes through time. Since the variations were not correlated with seasons, the authors hypothesize that storm events cause changes in the relative flux of groundwater from shallower and deeper flow paths. This is consistent with data for the same site for He tracer test data reported by Moline et al. (1998) and major ion chemistry data reported by Schreiber et al. (1999). An explanation for the lack of variability in the long screened wells is that they intersect multiple flow zones, while the screened interval in the multiport wells may intersect a discrete flow zone. The integration of multiple flow zones may result in an averaging of the water chemistry that masks temporal changes in a discrete flow zone.

5. Spatial and temporal scales of variability

Spatial and temporal variability in groundwater chemistry was observed at all scales explored during this investigation. The greatest amount of variability was seen in the saturated saprolite, where on a temporal scale of hours, changes occur on a spatial scale of up to several meters below the ground surface. The chemical variations are driven by individual storm events and are also influenced by antecedent moisture conditions.

In the transition zone, between 3 and 5 m below the ground surface, chemical variation occurred on temporal scales of days. Chemical variability appears to be driven by storm events, although the signal is damped and lagged by days when compared to changes in the overlying saprolite. Spatial variability in the transition zone on

a scale of 100s of m was controlled by topographic position. These spatial variations are interpreted to be due to topographic control of groundwater flow paths, and were temporally constant over the 1.5-a investigation.

In the intermediate zone, almost no temporal chemical variability was observed in wells where the screen length is 3 m. However, in intermediate zone wells where the screen length is 0.5 m, significant temporal variability was observed to a depth of at least 20 m below the surface. The magnitude and temporal scale of variability is similar to the transition zone. The variability is interpreted to be due to shifts in flow paths within the intermediate zone driven by storm events.

6. Impact of chemical variations on solute transport

Spatial and temporal variations in groundwater chemistry can have significant impacts on the transport of solutes. Variables that control the adsorption of solutes and colloids to the surface of aquifer solids include ionic strength and pH. The dissolution and precipitation of minerals is controlled by the concentration of dissolved ions or compounds. The dissolution and precipitation of other minerals is controlled by the redox state of the water. All of these parameters have been shown to vary significantly in the saprolite on the ORR. The following sections will discuss in more detail how these variations can affect transport of solutes and colloids.

6.1. Adsorption

It is well known that the adsorption of dissolved solutes, colloidal material, and dissolved organic matter are influenced by solution chemistry. For some materials (e.g., oxides of Si, Al, Fe, Mn and organic matter), the surface charge is pH dependent (Stumm and Morgan, 1970). Brooks and Carroll (2002) studied the transport of Co with chelating agents in undisturbed cores of saprolite from the ORR. They found that at a pH of 4, Co transport occurred predominately as the Co²⁺ ion. The prolonged tailing of Co eluting from the column was attributed to release of adsorbed Co. At a pH of 6.6, the chelating agent decreased the adsorption of Co. Although Brooks and Carroll (2002) used a range of pH twice that observed in this field investigation, their conclusions illustrate the influence of pH on adsorption.

6.1.1. Mineral dissolution and precipitation

The presence of low TDS waters in the shallow groundwater during precipitation events may cause thermodynamic undersaturation with respect to some solid phases, particularly calcite and silica minerals. In order to evaluate the saturation state of these minerals over the course of a storm event the equilibrium geochemical modeling program PHREEQC (Parkhurst, 1995) was

used. The program calculates the degree of thermodynamic equilibrium with respect to certain minerals based on the water chemistry data. The degree of thermodynamic equilibrium is reported as a saturation index. A negative saturation index indicates that the solution is undersaturated with respect to that mineral whereas a positive saturation index indicates that the solution is oversaturated with respect to that mineral. A saturation index near zero indicates that the mineral is at or near equilibrium and no net dissolution/precipitation is occurring.

The saturation indices for calcite from well SW-3 are plotted on Fig. 8. Just prior to the beginning of the storm event, calcite is at or close to thermodynamic equilibrium. After the start of precipitation, the saturation index for both minerals becomes negative, and gradually approaches equilibrium over a several day period. This may be due to mineral dissolution or discharge of water up through the transition zone that is in equilibrium with respect to calcite.

Undersaturation is significant because of the potential for release of contaminants when these minerals dissolve. On the ORR, radioactive ^{90}Sr is a contaminant of concern whose mobility may be retarded by precipitation as a carbonate mineral.

The authors also explored the possibility that conservative mixing of two water types could produce the observed changes without invoking mineral reactions. It was not possible to simulate any of the observed changes using simple mixing models.

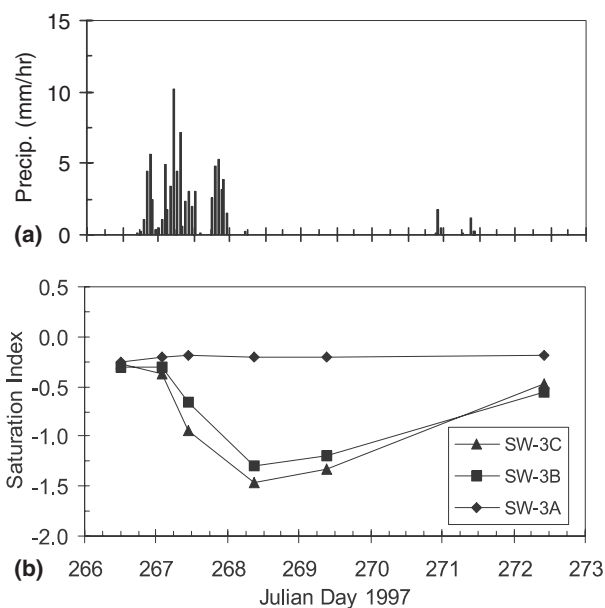


Fig. 8. (a) Precipitation rate and (b) saturation indices for calcite in well SW-3 over the course of a September, 1997 storm event.

6.1.2. Mineral oxidation and reduction

In the discussion of solute transport up to now, recharge of low TDS, low pH water may increase the mobility of many solutes. For minerals and solutes subject to redox reactions, the opposite may be true. During nonstorm periods, reducing water (no dissolved O_2 , Fig. 4) discharges up through the transition zone. Reducing conditions tend to result in dissolution of Fe and Mn minerals. Some contaminants (metals) tend to co-precipitate or adsorb on the surface of these minerals, and therefore dissolution would increase their mobility. In addition, Ryan and Gschwend (1994) have shown that clay colloids can be generated by the dissolution of Fe minerals. Recharge during storm events brings water with dissolved O_2 (Fig. 4) into the saturated saprolite. The oxidizing conditions will tend to cause precipitation of Fe and Mn oxides and reduce the mobility of contaminants that co-precipitate or adsorb to the surface of these minerals.

6.1.3. Kinetics

From an equilibrium thermodynamics point of view, it is possible for adsorption, dissolution, and redox reactions discussed in the previous sections to occur. However, because of the short time scales involved, one could ask if it is possible from a kinetics point of view. Adsorption has been demonstrated to be a rapid kinetic process, occurring on the time scale of hours (Glover et al., 2002). The precipitation and dissolution of carbonate minerals has also been demonstrated to occur on the time scale of hours (Ferris et al., 2004). Both of these processes appear to be kinetically possible on the time scales of the present investigation. It is also seen from field evidence that redox reactions involving Fe and Mn are occurring. Many of the fractures within the saprolite are coated with secondary Fe/Mn oxides/hydroxides. In order for these secondary precipitates to form, the Fe and Mn must first be dissolved under reducing conditions and then precipitated under oxidizing conditions. This is consistent with the field data of alternating oxidizing and reducing conditions on a storm event scale.

7. Conclusions

Based on their chemical characteristics, subsurface waters in the study area can be divided into 4 zones: the stormflow zone which is in the unsaturated zone, the saprolite which is in both the unsaturated and saturated zone, and the transition and intermediate zones which are fully saturated. Temporal variability is highest in the unsaturated zone and shallow groundwater, but decreases rapidly with depth below the water table.

Within the saturated saprolite, measurements of hydraulic head, major ion chemistry, and dissolved O_2

all indicate that reversals in the vertical hydraulic gradient are driven by storm events. The storm signals are rapidly transmitted through the saturated saprolite along relict fractures, bypassing the bulk of water and solutes stored in the matrix. Within the saturated saprolite, changes occur on the time scale of hours. At this temporal scale, changes can be propagated a distance of several meters below the ground surface.

In the transition and intermediate zones of the bedrock units, temporal variability was observed to a depth of at least 20 m below the surface. These chemical changes occurred on a time scale of days and are also interpreted to be driven by individual storm events. Spatial variability in chemistry of groundwater from the bedrock units on a scale of 100s of m is present. This large scale variability is interpreted to be due to topographic control on flow paths and is temporally invariant on a time scale of years.

The large temporal changes in water chemistry in the shallow subsurface are likely to have significant impact on the transport of contaminants. The adsorption of dissolved solutes and colloidal material is largely controlled by ionic strength and pH. Decreases in both of these parameters are hypothesized to result in increased desorption and transport of contaminants. The decrease in TDS and pH during storm events is also hypothesized to cause dissolution of some mineral phases. If dissolution occurs, contaminants that are co-precipitated with or adsorbed on these mineral phases may be released to solution, and additional colloidal material may be generated. The transport of chemical species that are controlled by the redox state of the water may also be affected by storm event changes. During nonstorm periods, reducing conditions prevail and transport of many common metals may increase. During storm events, dissolved O₂ is introduced and these metals may be precipitated as oxides.

The overall result of temporal changes in chemistry driven by precipitation events will be episodic transport of contaminants. This conclusion has practical implication for the conceptual understanding and numerical modeling of contaminant transport. An assumption of constant groundwater chemistry in setting like the one in this study will lead to errors when evaluating contaminant transport. The importance of variability in groundwater chemistry can only be evaluated through high resolution spatial and temporal sampling.

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