Mine Water Environ (2009) 28:84–93
DOI 10.1007/s10230-009-0064-x

TECHNICAL ARTICLE

Comparing Approaches for Simulating the Reactive Transport of U(VI) in Ground Water

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Received: 27 October 2008 / Accepted: 23 January 2009 / Published online: 20 February 2009

Abstract The reactive transport of U(VI) in a well-characterized shallow alluvial aquifer at a former U(VI) mill located near Naturita, CO, was predicted for comparative purposes using a surface complexation model (SCM) and a constant K_d approach to simulate U(VI) adsorption. The ground water at the site had U(VI) concentrations that ranged from 0.01 to 20 µM, alkalinities that ranged from 2.5 to 18 meq/L, and a nearly constant pH of 7.1. The SCM used to simulate U(VI) adsorption was previously determined independently using laboratory batch adsorption experiments. Simulations obtained using the SCM approach were compared with simulations that used a constant K_d approach to simulate adsorption using previously determined site-specific K_d values. In both cases, the ground water flow and transport models used a conceptual model that was previously calibrated to a chloride plume present at the site. Simulations with the SCM approach demonstrated that the retardation factor varied temporally and spatially because of the differential transport of alkalinity and dissolved U(VI) and the non-linearity of the U(VI) adsorption. The SCM model also simulated a prolonged slow decline in U(VI) concentration, which was not simulated using a constant K_d model. Simulations using the SCM approach and the constant K_d approach were similar after 20 years of transport but diverged significantly after 60 years. The simulations demonstrate the need for site-specific geochemical information on U(VI) adsorption to produce credible simulations of future transport.

Keywords Reactive transport · Uranium · Environmental geochemistry · Geochemical modeling

Introduction

Uranium contaminated ground water is a concern at many US Federal government sites (USDOE 1996; Crowley and Ahearne 2002) and at uranium mine and mill sites (Abdelouas et al. 1999). Assessing the mobility of uranium in ground water at these contaminated sites is often challenging because most aquifers are complex (Rubin 2003; Rubin and Hubbard 2005) and because the geochemistry of uranium is also complex (Grenthe et al. 1992; Langmuir 1997). Multi-component reactive transport simulations of U(VI) in ground water couple the effects of ground water flow and transport with geochemistry to provide an integrated framework for simulating future transport and possibly the effects of alternative remediation scenarios. These models can be used to support scientifically informed decisions related to site management activities.

Uranium occurs in the environment predominantly as U(IV) in reducing systems and U(VI) in oxic systems. In reducing environments, U(IV) forms insoluble phases that are relatively immobile (Gu et al. 2005; Vrionis et al. 2005). In oxic environments, U(VI) forms moderately soluble solid phases such that the mobility of U(VI) can be controlled by adsorption reactions at near-neutral pH values (Curtis et al. 2006; Davis et al. 2004; Kohler et al. 1996). The extent of adsorption onto a wide variety of geosorbents such as clays, iron oxides and soils is generally small at low pH values and increases with increasing pH

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usually in the pH range of 4 to 6 (Barnett et al. 2002; Davis et al. 2002; Fox et al. 2006; Pabalan et al. 1998; Waite et al. 1994). In the pH range of approximately 7–10, U(VI) is sensitive to the partial pressure of CO_2 because the formation of aqueous U(VI)-carbonate complexes can cause adsorption to be negligible (Davis et al. 2004; Fox et al. 2006; Um et al. 2007a, b; Waite et al. 1994).

A simple approach to describe U(VI) adsorption by sediment is to use a constant distribution coefficient defined by:

$$K_d = \frac{U_{ADS}}{U_{AQU}} \tag{1}$$

where K_d is the distribution coefficient (L/kg), U_{ADS} is the adsorbed U(VI) concentration (mol/kg), and U_{AQU} is the total dissolved U(VI) concentration in ground water (mol/L) (Davis and Kent 1990). However, U(VI) K_d values can vary by five orders of magnitude over the pH range of 6 to 9 and by four orders of magnitude at pH 8 over a CO_2 partial pressure range from its value in air (0.00038 atm) to 0.01 atm (Davis et al. 2004). Therefore, simulations with a constant K_d could introduce significant uncertainty into transport simulations. Constant K_d simulations also do not simulate the very slow decrease in U(VI) concentration after flushing with many pore volumes (i.e. tailing) caused by the nonlinear equilibrium adsorption isotherms (Bethke and Brady 2000; Glynn 2003; Kohler et al. 1996; Zhu 2003).

The semi-mechanistic surface complexation approach provides an efficient alternative approach for simulating sorption onto complex soils and sediments while simultaneously considering variable chemical conditions in the ground water (Davis et al. 1998, 2004; Kent et al. 2000, 2007, 2008; Curtis et al. 2006). In this approach, the adsorbing surface is considered to possess surface functional groups that can form surface complexes analogous to the formation of aqueous complexes in solution. For example, the formation of a surface complex of the uranyl cation, UO_2^{+2} can be described by the reaction:

$$>SOH + UO_2^{+2} + H_2O \Leftrightarrow\ >SOUO_2OH + 2H^+ \tag{2}$$

where >SOH is a protonated adsorption site on a mineral surface and $>SOUO_2OH$ is an adsorbed uranyl ion. The equilibrium expression (mass action expression) for this reaction is

$$K_S = \frac{(>SOUO_2OH)(H^+)^2}{(>SOH)(UO_2^{+2})} \tag{3}$$

where K_S is the equilibrium constant. In this semi-mechanistic modeling approach, adsorption is simulated as occurring on generic adsorption sites intended to represent average properties of the bulk sediment. Multiple site-types can be included in the semi-mechanistic modeling approach to simulate both the chemical heterogeneity of individual mineral surfaces and the heterogeneity of subsurface environments. This approach is practical and more accurate than the alternative approach that attempts to characterize each of the many adsorbing surfaces that may be present in sediment and then computing the total adsorption as sum of the adsorption onto all of the adsorbing surfaces (Davis et al. 2004).

Davis et al. (2004) developed a semi-mechanistic U(VI) adsorption model for sediments collected up-gradient of a former uranium mill located near Naturita, CO, USA. This model, which is used in the work described below, was calibrated to batch experiments of U(VI) adsorption on Naturita aquifer background sediments (NABS) that was obtained from a gravel pit located up-gradient of well DOE547 (Fig. 1). The batch experimental conditions covered the range of geochemical conditions observed in the field and a semi-mechanistic SCM was fit to the adsorption data. The SCM consists of six reactions and three different site-types (Table 1). The three site-types are described as very strong (>SSOH), strong (>SOH), and weak (>WOH) sites, corresponding to their relative U(VI) binding strength. Curtis et al. (2006) previously used this adsorption model in a reactive transport modeling approach to match historical, site-wide geochemical data collected between 1984 and 2001 for the Naturita site. The purpose of this paper is to compare predictions of future U(VI) concentrations obtained using the SCM approach with results obtained using the constant K_d approach using the Naturita site as an example.

The former uranium mill site is approximately 3 km northwest of the town of Naturita and along the San Miguel River in southwestern Colorado (Fig. 1). The history and characteristics of this site have been presented previously (Davis and Curtis 2003; Curtis et al. 2006; USDOE 2008) and will only be briefly summarized here. Uranium ores were processed at the mill from 1939 to 1958 and mill tailings were stored onsite until 1979. Either process water from the mill or leachate that had contacted the tailings likely caused elevated U(VI) concentrations in the ground water. Contaminated soils were removed between 1993 and 1997 and replaced with clean sediments.

Hydrogeology and Geochemistry

Contaminated ground water at the Naturita site occurs in a thin alluvial aquifer adjacent to the San Miguel River (Fig. 1). The alluvial aquifer consists of sand, gravel, and cobbles; the mineralogy consists of primarily quartz with lesser amounts of detrital feldspars, carbonates, magnetite, and fine clay-size materials (Davis et al. 2004). Figure 1 shows the location of the former mill yard, the extent of the

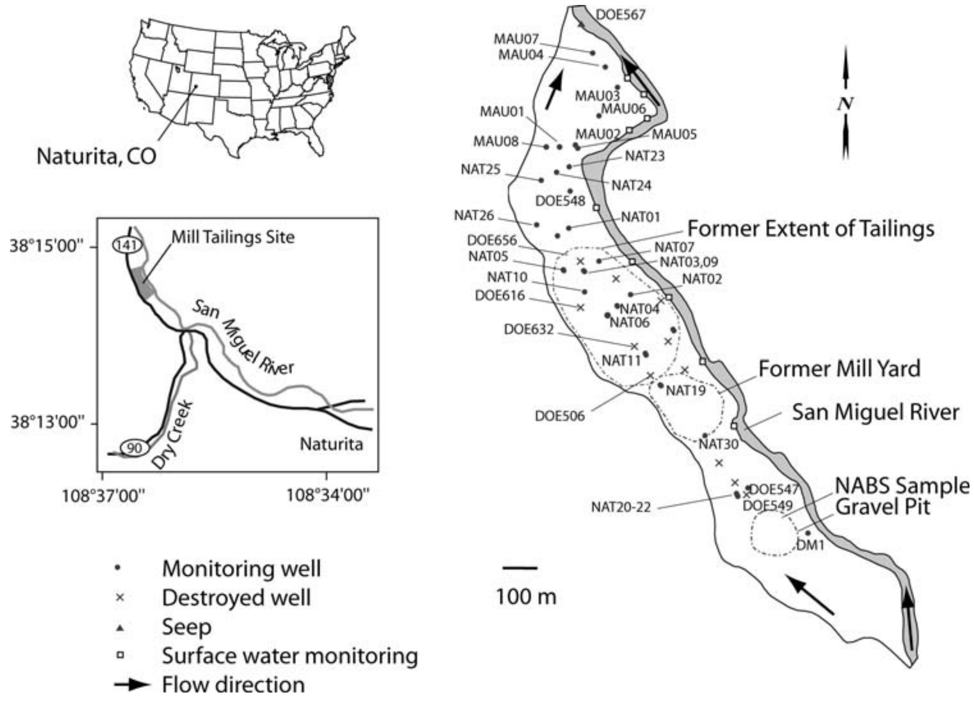

Fig. 1 Naturita field site location showing the location of the former mill yard, the extent of the tailings and the monitoring wells

Table 1 NABS surface complexation model (Davis et al. 2004)

Reaction	Log K[a]
$>SSOH + UO_2^{2+} = >SSOUO_2^{+} + H^{+}$	6.80
$>SOH + UO_2^{2+} = >SOUO_2^{+} + H^{+}$	5.82
$>WOH + UO_2^{2+} = >WOUO_2^{+} + H^{+}$	2.57
$>SSOH + UO_2^{2+} + H_2O = >SSOUO_2OH + 2H^{+}$	−0.67
$>SOH + UO_2^{2+} + H_2O = >SOUO_2OH + 2H^{+}$	−2.08
$>WOH + UO_2^{2+} + H_2O = >WOUO_2OH + 2H^{+}$	−5.32

The total site concentration was 1.92×10^{-6} moles of sites/m^2. The fraction of weak sites (>WOH) was 0.9989, the fraction of strong sites (>SOH) was 0.001 and the fraction of very strong sites (>SSOH) was 0.0001

[a] Log of apparent binding constant

former tailings pile, and all of the monitoring wells at the site.

Elevated concentrations of U(VI) and alkalinity were observed below and down-gradient of the former uranium mill tailings. The concentration of both species were generally lower near the San Miguel River and higher near the highway (Fig. 2) and had a peak concentration of 10 µM at well NAT26. In September 1999, the average U(VI) concentration in the up-gradient wells (e.g. wells DM1, DOE547, and NAT20-22) was 0.02 µM. The alkalinity had a similar spatial pattern as U(VI) but the range in concentrations was smaller (Fig. 2b). The alkalinity values ranged from 4.5 meq/L near well DOE547 to a peak value of 12 meq/L at well NAT26. The elevated alkalinity occurred widely across the field site and extended farther down-gradient than the uranium concentration. The pH values ranged from 7.0 to 7.3, did not exhibit any significant spatial structure (Curtis et al. 2006), and were probably controlled by calcite, which is present in the aquifer.

Speciation calculations (Davis and Curtis 2003) showed that the $Ca_2UO_2(CO_3)^0_{3(aq)}$ and $CaUO_2(CO_3)_3^{2-}$ aqueous species (Bernhard et al. 2001; Kalmykov and Choppin 2000) accounted for more than 95% of the total dissolved U(VI) in all ground water samples. Saturation indices (SI) indicated that uranophane ($Ca(UO_2)_2SiO_3(OH)_2 \cdot 5H_2O$); soddyite ($(UO_2)_2SiO_4 \cdot 2H_2O$), schoepite ($UO_2(OH)_2 \cdot H_2O$), and rutherfordine ($UO_2CO_3$) were at least four orders of magnitude below saturation.

Uranium(VI) Adsorption

The semi-mechanistic SCM described by Davis et al. (2006) (Table 1) was used to simulate adsorption in the reactive transport simulations. The simulations also used all of the aqueous U(VI) speciation reactions listed in Davis et al. (2004). Although the adsorption model was developed for a single sediment that was collected from an up-gradient location, the application of this model to the entire Naturita site is supported by previous investigations of the effects of both spatially varying uranium and alkalinity concentrations and the effects of spatially varying sediment characteristics. It was found that the spatial variability in alkalinity was more important in controlling U(VI) adsorption than the geologic heterogeneity, as represented by 15 samples (Curtis et al. 2006). In addition, the semi-mechanistic model generally predicted U(VI) adsorption by

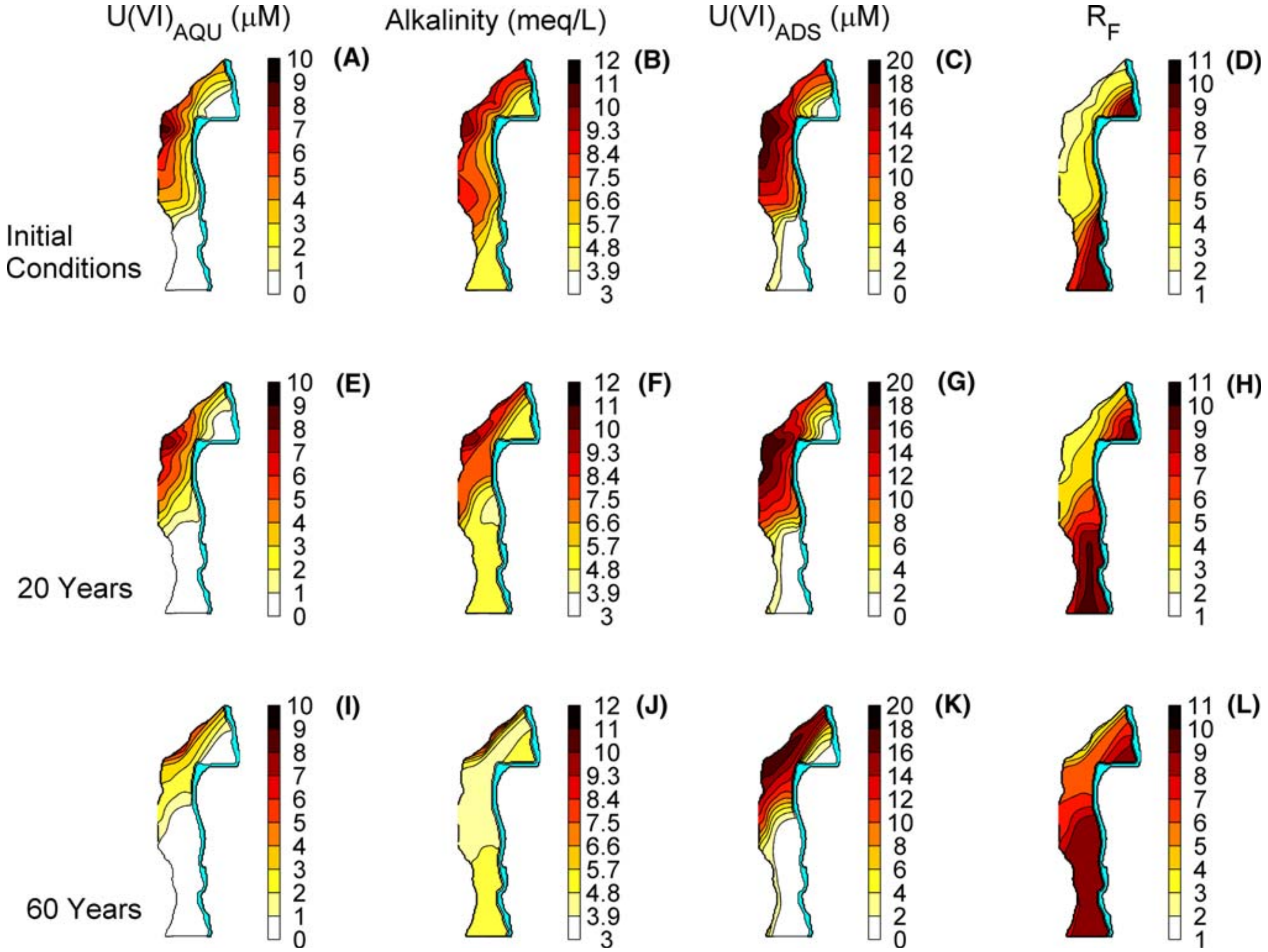

Fig. 2 Initial conditions and predicted temporal evolution of dissolved uranium ($U(VI)_{AQU}$), alkalinity, adsorbed uranium ($U(VI)_{ADS}$), and the simulated retardation factor (R_F) calculated using the surface complexation model

both contaminated sediments and uncontaminated sediments suspended in ground water wells within a factor of three or less (Curtis et al. 2004). In addition, predictions that used the SCM to simulate U(VI) desorption agreed well with field-scale U(VI) desorption experiments (Curtis and Davis 2006) suggesting that desorption is reversible. Although this SCM performs well for the Naturita site, its applicability has not been demonstrated for simulations involving geochemical changes outside the range of calibration, such as a significant pH change. The SCM is also not applicable to other U(VI) contaminated sites.

The semi-mechanistic adsorption model was used to compute total adsorbed U(VI) (U_{ADS}) from the known concentrations in solution, i.e., total dissolved U(VI) (U_{AQU}), alkalinity, pH, total concentration of adsorbed sites as well as the major ions in ground water (e.g. Ca, Mg, and Na). The calculated adsorbed U(VI) concentrations used the reactions listed in Table 1 and the aqueous speciation reactions listed in Davis et al. (2004). The peak simulated adsorbed concentration is located at well NAT-26 (Fig. 2c). However, there is a region up-gradient of well NAT-26 that has predicted adsorbed U(VI) concentrations that remain high even though the dissolved U(VI) concentrations are half of the maximum value in the ground water. This occurs because the alkalinity is a second important factor that controls the shape of the initial adsorbed U(VI) distribution in the aquifer. In contrast, if the adsorbed U(VI) had been calculated from a constant K_d value, the initial adsorbed U(VI) distribution would have had an identical distribution as in Fig. 2a, except that it would have been scaled by the K_d value.

Reactive Transport Modeling Approaches

One approach for simulating the reactive transport of an adsorbing species is to assume that adsorption is linear and independent of all other solutes. In this case, the mobility can be estimated from the retardation factor (R_F), defined by:

$$R_F = 1 + \frac{\rho_b}{\theta} K_d \qquad (4)$$

where ρ_b is the bulk density (kg/L), θ is the effective porosity (L/L), and K_d is the distribution coefficient defined by Eq. 1. In many instances, it is assumed that the values of ρ_b, θ, and K_d are spatially and temporally constant, which results in a constant R_F value.

Literature K_d Values

Krupka et al. (1999) summarized measured U(VI) K_d values determined in single mineral studies and in soil/sediment studies; solution pH and alkalinity were identified as key variables that determine K_d values. However, even with this understanding, K_d values at pH 7 ranged from 63 to 630,000 L/kg, which are generally much higher than values at the Naturita field site. The US Nuclear Regulatory Commission code DandD (McFadden et al. 2001) is intended to perform screening analyses of dose associated with exposure to radionuclides, including U. This code contains a default distribution of K_d values for U(VI); the default distribution is a log normal distribution with a mean log K_d value of approximately 2.1 and a standard deviation of 1.4. It is recognized in the screening level calculations that there is considerable uncertainty associated with the K_d value for any particular field site and therefore most screening level applications involve sampling the entire distribution of K_d values. The screening level distribution (Fig. 3) has K_d values that range from 0.1 to 100,000 L/kg.

Site-specific K_d Values

The application of K_d values at many sites, including the Naturita site, needs to account for the large fraction of cobbles in the aquifer. This has been done by assuming that the <3 mm fraction accounts for all of the sorption capacity of the aquifer. Under these assumptions, the gravel-corrected K_d values are approximated by (Kaplan et al. 2000):

$$K_{d-c} = (1 - \mathrm{f})K_d(<3\,\mathrm{mm}) \qquad (5)$$

where $K_{d\text{-}c}$ is a gravel-corrected K_d value, *f* is the fraction of gravel and cobbles, and K_d (<3 mm) is the K_d of the less than 3 mm fraction of the sediment. In was previously estimated that the cobbles and gravels greater than 2 mm (the closest measured size fraction to 3 mm) accounted for 85% of the aquifer sediments (Davis et al. 2004). Consequently, the gravel-corrected K_d values for the aquifer equal 0.15 times the K_d values for the NABS sample.

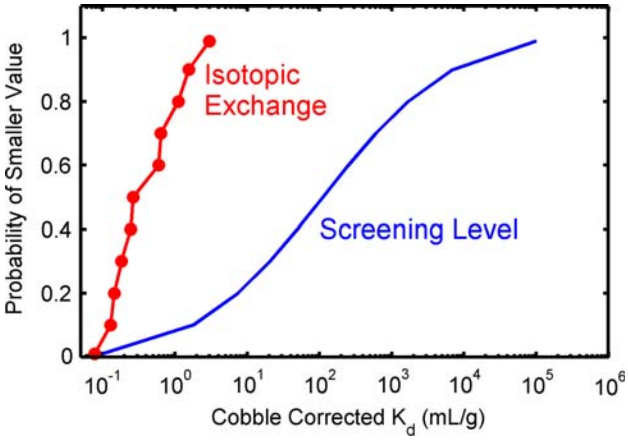

Fig. 3 Distribution of K_d values determined experimentally by isotopic exchange and a screening level distribution

Kohler et al. (2004) measured K_d values for contaminated sediment samples collected at the site during well installation and on the Naturita aquifer background sediment (NABS) sample. Ground water samples from each location had variable U(VI) concentration, alkalinity, and pH. Field K_d values were calculated from the observed total U(VI) concentrations in ground water and from the amount of "labile" U(VI) associated with the sediment samples. The sediment-associated labile U(VI) was estimated by both an isotopic exchange approach and by extraction of U(VI) with a pH 9.45, 20 meq/L sodium bicarbonate solution (Kohler et al. 2004). The two methods gave nearly identical results. The gravel-corrected K_d values determined with the isotopic exchange method had a mean value of 0.62 L/kg and the K_d values ranged from 0.08 to 3.0 L/kg (Fig. 3). This distribution does not include the previously reported K_d values for sediments from wells MAU-03 and MAU-04 (Kohler et al. 2004) because it is likely that local reducing conditions at these wells caused the sediment-associated U to be a mixture of U(VI) and U(IV) (Davis et al. 2006).

Surface Complexation Simulations

Simulated R_F values were calculated from the SCM using the U(VI) and alkalinity concentrations shown in Figs. 2a and b and the results are shown in Fig. 2d. The simulations assumed a uniform pH equal to 7.1 and that the ground water was in equilibrium with calcite. A total adsorption site concentration of 0.02 moles/L, which includes a correction for the gravel (Eq. 5), was used as described previously (Curtis et al. 2006). The simulated R_F values near NAT26 are smaller than values farther down-gradient (Fig. 2d). In the up-gradient areas of the aquifer, the R_F values are approximately an order of magnitude larger that the values near NAT26. These results show that both the U(VI) concentration and alkalinity are important in controlling spatially-varying R_F in this aquifer.

Reactive Transport Simulations

Reactive transport simulations were conducted to compare the spatial distribution of U(VI) at selected times and to compare the simulated breakthrough at selected observation points (NAT11, NAT05, and MAU01) in the aquifer. The total mass of U(VI) remaining in the aquifer over time was also compared. The simulations compared results obtained with three selected constant K_d values with results obtained using the semi-empirical SCM approach to simulate U(VI) adsorption. In both cases, the steady state ground water flow model described previously (Curtis et al. 2006) was used. Simulations were performed using RATEQ (Curtis 2005), which couples reactive transport to MODFLOW 2000 (Harbaugh et al. 2000) and MT3DMS (Zheng and Wang 1999).

Initial and Boundary Conditions

Two-dimensional reactive transport simulations were conducted to illustrate the key differences that result when adsorption is modeled using the K_d approach versus the SCM approach. For both sets of reactive transport simulations, the U(VI) observed in ground water in 1999 (Fig. 2a) was used as the initial conditions. The only boundary condition that had a solute source was along the San Miguel River, which had a constant U(VI) concentration of 0.065 μM. For the SCM simulations, the initial conditions also used the observed alkalinity (Fig. 2b), a spatially uniform initial pH of 7.1 and the assumption that the ground water was in equilibrium with calcite. The river water was assumed to have a pH of 7.1, an alkalinity of 4.5 meq/L, and to be in equilibrium with calcite. The ground water flow model was the same as in previous simulations (Curtis et al. 2006).

Comparison of Simulated U(VI) Plumes

Figure 2 shows the predicted evolution of the dissolved U(VI) and alkalinity plumes after 20 and 60 years of transport simulated using the SCM approach. The computed R_F values are also shown. After 20 years of transport, the highest predicted U(VI) and alkalinity concentrations are still present adjacent to the northwestern side of the aquifer. However, after 60 years of transport, the simulated alkalinity has nearly reached background values, whereas a U(VI) plume with concentrations from 1 to 5 μM remains along the northwestern side of the aquifer. These dissolved U(VI) concentrations are approximately 100 times above background concentrations. Over the 60 year simulation period, the adsorbed U(VI) concentrations change relatively little compared to the dissolved U(VI) and alkalinity. Even after 60 years of transport, the peak adsorbed U(VI) concentrations are 85% of the initial values (Fig. 2k), although the location of the peak values has moved slightly down-gradient. This relatively small change in adsorbed concentration results from the inherent nonlinearity of the adsorption model and the variable chemical conditions. The adsorption model consists of U(VI) adsorption reactions occurring on three different adsorption site types; weak, strong, and very strong. The weak sites are the most abundant and bind U(VI) relatively weakly, whereas the very strong sites are least abundant and bind U(VI) very strongly. This distribution of adsorption affinity causes the percent of adsorbed U(VI) to increase as the total U(VI) concentration decreases.

The temporal and spatial distributions of the simulated alkalinity also affect the distribution of the adsorbed U(VI). The alkalinity is transported nearly conservatively in the simulations whereas U(VI) is slightly retarded by adsorption. This differential transport accentuates the concentration tailing of U(VI) because the relative percent of adsorbed U(VI) increases as the high alkalinity water is displaced by up-gradient water having relatively low alkalinity.

Figure 2h and l also illustrate the simulated R_F values in the aquifer after 20 and 60 years. Initially, approximately 70% of the aquifer had R_F values that ranged from 1 to 3 and corresponded to regions where the U(VI) and alkalinity values were greatest. Most of the remaining R_F values ranged from 7 to 11 and were in the up-gradient areas or in the down-gradient areas adjacent to the river. After a simulation period of 60 years, greater than 80% of the aquifer had R_F values that exceeded 7; the exception was a relatively small area in the downstream portion of the aquifer. Thus, the initial R_F values ranged from nearly uniform values ranging from 1 to 3, whereas after 60 years of transport, the R_F had increased and most ranged from approximately 7–11. However, at the intermediate time scale (20 years), the simulated R_F values show significant spatial character.

U(VI) transport simulations were also conducted with the constant K_d approach using cobble-corrected K_d values of 0.08, 0.14, and 1.5 L/kg. The K_d of 0.08 L/kg is the minimum K_d value measured on the contaminated sediments after correction for gravel and cobbles. Therefore, using this low K_d value represents a scenario of uniform, low U(VI) sorption. The K_d value of 0.14 L/kg was chosen for illustrative purposes. In addition, this K_d value agrees very closely with the minimum K_d calculated from the SCM, which equals 0.17 L/kg and occurs near NAT26, which has both high U(VI) concentration and alkalinity. The value of 1.5 L/kg was selected because it equals the 90th percentile value of the experimentally determined values. The K_d values of 0.08, 0.14, and 1.5 L/kg correspond to retardation factors of 1.8, 2.5, and 17, respectively, assuming an effective porosity of 0.2 and a bulk density of 2.1 kg/L (Curtis et al. 2006).

Figure 4 illustrates predicted U(VI) concentrations for simulations that used the three constant-K_d values. The simulation with a constant-K_d value equal to 0.08 L/kg showed that after 20 years, the U(VI) concentrations were all less than 1 μM and most of the U(VI) has been transported into the river. Similarly, the simulation for the K_d value of 0.14 L/kg showed that U(VI) concentrations were less than 1 μM everywhere except near the northwestern border of the aquifer. Neither of these two cases agrees with the SCM results, which simulated dissolved U(VI) concentrations that ranged from 1 to 6 μM after 60 years.

Simulations using a K_d value of 1.5 L/kg gave plume shapes that were roughly similar to the predictions that used the SCM after 20 years of transport. Specifically, the shape of the U(VI) plume after 20 years generally agrees in the two simulations, suggesting a similar extent of transport. After 60 years of transport, however, the U(VI) plume simulated with the K_d value of 1.5 L/kg was slightly larger than the plume simulated with the SCM approach and the U(VI) concentration in the ground water is also slightly higher. The larger plume probably results from the nearly conservative transport of the alkalinity plume in the SCM approach, which leads to an increased percentage of adsorbed U(VI) with increasing time as the alkalinity is transported down-gradient; this causes U(VI) to transfer from the dissolved to adsorbed phase. Although the simulations with a K_d value of 1.5 L/kg ($R_F = 17$) are generally similar to the SCM results, there are significant differences between the two simulation results. First, it is difficult to explain the high concentrations of U(VI) at the northern boundary of the aquifer with a R_F value equal to 17; the ground water ages near NAT25 and NAT26 are approximately 35 to 45 years (Curtis et al. 2006) old, suggesting slow ground water transport, which would be considerably slower after retardation was included in the estimation of U(VI) transport. Second, Davis et al. (2006) reported that sediment collected from the aquifer near NAT25, which is near the center of the U(VI) plume in Fig. 4f, had a gravel-corrected K_d of 0.16 L/kg. This measured K_d value agreed well with a simulated value using the SCM and was significantly smaller than the value of 1.5 L/kg used in the simulations. A simulation using the measured K_d of 0.16 L/kg would be very similar to the constant K_d simulation that used a K_d value of 0.14 L/kg (Figs. 4c and f).

The total simulated mass of U(VI) in the aquifer predicted by the SCM approach and the 3 K_d simulations is shown in Fig. 5. The total mass of U(VI) estimated from the SCM approach was 400 kg and is probably the best available total mass estimate given it is based on a geochemical model that predicted K_d values within a factor of three or less. This suggests that the initial mass estimated using a K_d value of 1.5 L/kg, which was approximately 4 times larger, is slightly too large. Similarly, the initial total mass calculated using the K_d values equal to 0.08 and 0.14 L/kg were a factor of 2 to 2.3 smaller than the mass calculated from the SCM model but possibly within error. The simulations with the two smaller K_d values show that nearly all of the mass should have been flushed into the river within approximately 60 years. If the average K_d from the screening distribution (125 L/kg) had been used in the simulations, the initial total mass in the aquifer would have been approximately 100 times larger than the mass estimated from the SCM and would not have agreed well with the observed values reported by Kohler et al. (2004). In addition, the model simulations with the average screening distribution K_d show negligible U(VI) migration (results not shown) and are inconsistent with observed elevated U(VI) in the most down-gradient wells.

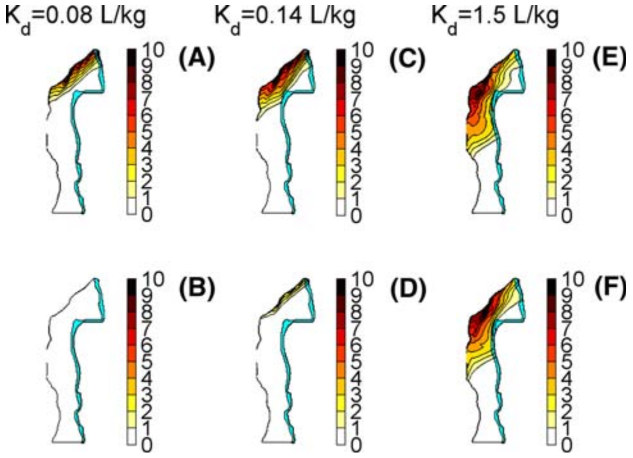

Fig. 4 Spatial distributions of dissolved U(VI) concentrations after 20 and 60 years simulated using the constant-K_d approach

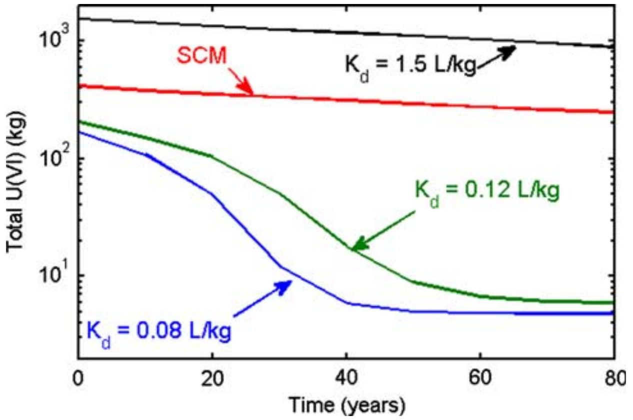

Fig. 5 Simulated total mass of U(VI) present in the aquifer simulated using the SCM and constant-K_d approaches

Comparison of Concentration Breakthrough

Another method for comparing simulations using the SCM and the K_d approach is to consider the concentration of U(VI) at selected points over a 60 year period. Figure 6 shows the simulated concentration using the SCM at well NAT11, which is shown in Fig. 1. The dissolved and adsorbed U(VI) concentrations computed using the SCM approach are illustrated along with alkalinity values. At the beginning of the simulation, the dissolved U(VI) concentration equals 3.5 µM and the adsorbed U(VI) concentration is 13 µM; together, these values correspond to a K_d value of 0.35 L/kg and an R_F value of 4.7. The simulations show that the alkalinity, which behaves nearly conservatively in this system, decreased to the background concentration (4.5 meq/L) in less than 10 years. In contrast, both the dissolved and adsorbed U(VI) decreased more slowly, and the dissolved U(VI) does not meet the U. S. drinking water standard (0.12 µM) for approximately 40 years. In addition, the adsorbed U(VI) concentrations decreased even more slowly than the dissolved concentrations as a consequence of the non-linear, multi-site adsorption model and variable alkalinity. Consequently, after 40 years of natural flushing, the K_d value at this location increased to 10.2 L/kg.

Breakthrough curves obtained using both the SCM and the constant-K_d approaches were simulated at wells NAT11, which is an up-gradient well, NAT05, which is slightly up-gradient of the peak U(VI) concentration, and at well MAU01, which is slightly down-gradient of the peak U(VI) concentration. All of the experimentally determined K_d values shown in Fig. 3 were used in the constant-K_d simulations. Predicted breakthrough curves for both modeling approaches are illustrated in Fig. 7. The simulations with the complete distribution of K_d values at NAT11 show that at early times, the K_d simulations with the smallest K_d values agree well with the SCM approach but that at the longest simulation times, the simulation using the largest K_d agreed better with the SCM approach. At NAT05, which is located up-gradient of the peak dissolved U(VI) concentration, most of the constant-K_d simulations yielded results where U(VI) concentrations decreased sharply to 0.2 µM, followed by a slower rate of concentration decrease. The change in slope of the elution curves is a consequence of the initial conditions used in the simulations; the same type of behavior was observed when U(VI) transport was assumed to be conservative (results not shown). Because increased retardation slows the rate of down-gradient transport, the time required to reduce the U(VI) concentration to a specific concentration increases with increasing K_d value. The simulated U(VI) concentration using the SCM approach was initially similar to those simulations with smaller K_d values. However, at longer times, the SCM results significantly diverged from 10 of the 11 constant-K_d simulations, because model-calculated K_d values increased during the simulation period to values as high as 1.0 L/kg. Only the constant-K_d simulation, which used the maximum value, gave U(VI) concentrations that were consistently above the SCM simulation at longer times.

The simulation results at MAU01 were significantly different from the results described for NAT05 and especially NAT11. MAU01 is located down-gradient of the maximum initial U(VI) concentration and, as a result, the simulated dissolved U(VI) concentration initially increased as the peak passed the observation point. The SCM results show that the predicted increase in U(VI) concentration is damped relative to the constant-K_d simulations. This damping is caused by the nonlinearity of the adsorption model and variations in alkalinity. The simulations imply that relatively high concentrations of U(VI) could persist at MAU01 for a prolonged time.

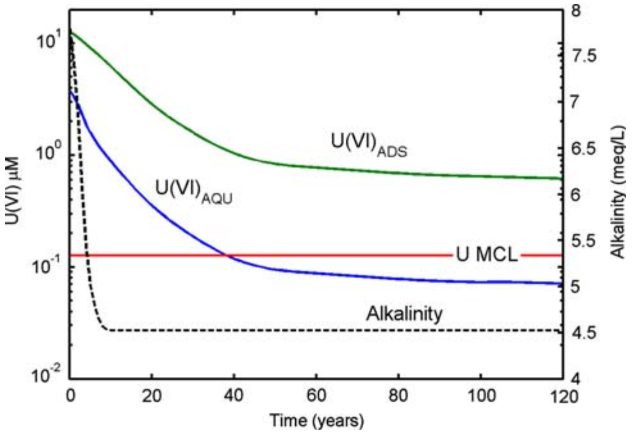

Fig. 6 Simulated concentrations of dissolved and adsorbed U(VI) and alkalinity at NAT11

Summary and Conclusions

Future transport of U(VI) at the Naturita site was simulated using the constant-K_d and semi-mechanistic surface complexation modeling approaches. The U(VI) K_d values used in the predictions were selected from experimentally determined values measured with contaminated Naturita sediments and values computed from a surface complexation model (SCM) calibrated with data from U(VI) adsorption experiments with uncontaminated Naturita sediments. In addition, U(VI) K_d values were compared to those from screening level distributions. Concentration data from ground water samples collected from monitoring wells distributed across the site were used for the initial conditions in the simulations.

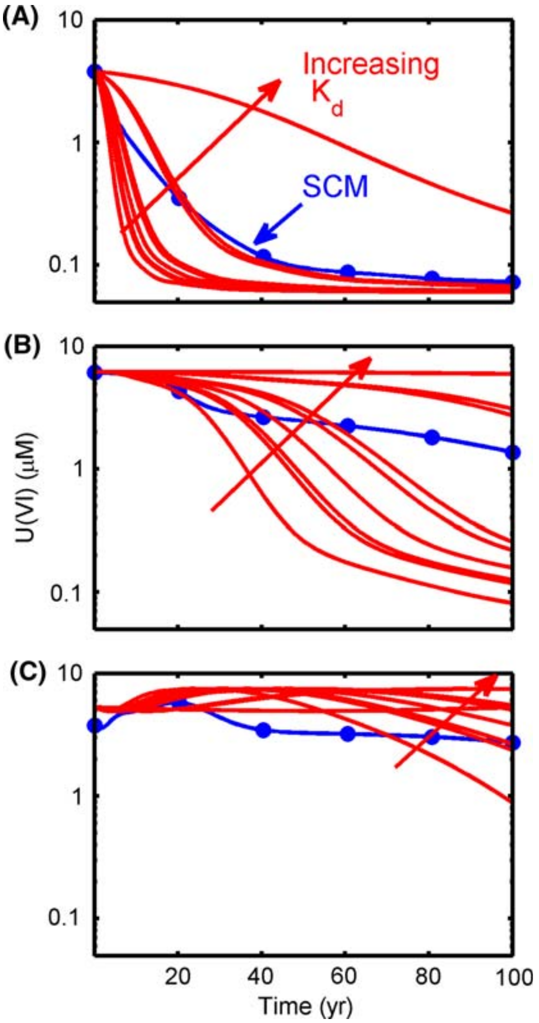

Fig. 7 Comparison of U(VI) concentration histories at observation wells **a** NAT11, **b** NAT05 and **c** MAU01 simulated with the surface complexation model and the observed constant-K_d distribution

Predictions that used small U(VI) K_d values (0.08 to 0.14 L/kg) gave U(VI) breakthrough curves that were similar to SCM simulations for short times, but the constant-K_d simulations did not reproduce the long concentration tails of the SCM approach that was evident in both the breakthrough curves and the two-dimensional plumes. In addition, predictions with small K_d values yielded a total initial mass of U(VI) in the aquifer that was approximately half of the mass simulated with the surface complexation modeling approach. The total mass of U(VI) that was flushed into the river simulated using small K_d values was considerably faster than predicted with the SCM approach. Predictions with larger constant-K_d values resulted in higher dissolved U(VI) concentrations at longer times. However, the assumed K_d value was approximately ten times larger than a measured K_d value for a location near the center of the simulated plume. A major distinction between the constant-K_d and SCM simulations was that the latter approach predicted a much greater degree of concentration tailing in the U(VI) breakthrough curves, especially in the up-gradient wells. This predicted tailing significantly affects the time required for a contaminated site to reach background concentrations by natural ground water flushing.

The observed K_d distribution had significantly smaller K_d values than the screening distribution. This suggests that K_d values selected from the screening distribution or from the literature have limited applicability to a contaminated site. In the Naturita study, it was found that considerably more reliable K_d values were obtained by conducting a site-specific geochemical investigation of a contaminated site. The simulations with the minimum and maximum measured K_d values taken from the measured distribution tended to bracket the simulation obtained using the SCM approach. The simulation using the SCM approach, however, has the advantage that it does not simulate the rapid flushing of contaminated ground water into the adjacent river for the low K_d simulations nor simulate very slow transport for the large K_d values, and it can consider the effects of variable alkalinity on U(VI) adsorption and transport.

Acknowledgments This work was supported by the US Nuclear Regulatory Commission (Interagency Agreement RES-97-009) and the US Geological Survey Toxic Substances Hydrology program. We thank David Naftz for field assistance and David Meece for laboratory assistance. We also thank Christopher Green, Michael Hay, and two anonymous reviewers for their valuable comments on the manuscript.

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