

Kinetics of Soil Chemical Phenomena: Future Directions

Donald L. Sparks

*Department of Plant and Soil Sciences
University of Delaware
Newark, Delaware*

4-1 INTRODUCTION

Historically, the emphasis in soil chemistry teaching and research has been on equilibrium processes and reactions. While these studies have been useful, they are not often relevant to field settings where chemical reactions are time-dependent.

In the late 1970s and certainly in the 1980s and 1990s the kinetics of environmentally important reactions on natural materials has become and will continue to be a major leitmotif in soil and environmental chemistry. This intense interest is in large part due to the recognition that to accurately predict the fate of contaminants in the subsurface environment, a knowledge of the reaction kinetics is imperative.

While major advances have been made in understanding time-dependent reactions on natural materials such as soils and sediments, there are still many unknowns that are complicated by the complex, heterogeneous nature of natural materials. This review will focus on future research needs, particularly in the area of sorption–release processes in the soil environment, and not on past findings and accomplishments. To learn about the latter, the reader can consult a number of books and reviews (Sparks, 1989, 1991, 1995; Sparks & Suarez, 1991). Future research needs that will be discussed in this review include: models that accurately describe both chemical kinetics and transport processes in multiple site, heterogeneous systems; more extensive studies on the effect of residence time or aging on contaminant retention–release; and mechanistic studies that employ both kinetic and in situ (drying and high vacuums are not employed; aqueous suspensions can be examined) microscopic and spectroscopic techniques.

4-2 KINETIC MODELS

While first-order models have been used widely to describe the kinetics of chemical reactions on natural materials, a number of other simple kinetic models also have been employed. These include various ordered equations such as zero-

order, second-order, and fractional-order, and Elovich, power function or fractional power, and parabolic diffusion models. For more complete details and applications of these models one should consult Sparks (1989).

4-2.1 $Z(t)$ and Diffusion Models

In a number of studies it has been shown that several simple kinetic models, as listed above, describe rate data well, based on correlation coefficients and standard errors of the estimate (Chien & Clayton, 1980; Onken & Matheson, 1982; Sparks & Jardine, 1984); however, some of the above kinetic models are empirical and no meaningful rate parameters can be obtained.

Aharoni and Ungarish (1976) and Aharoni (1984) noted that some simple kinetic models are approximations to which more general expressions reduce in certain limited time ranges. They suggested a generalized empirical equation by examining the applicability of power-function, Elovich, and first-order equations to experimental data. By writing these as the explicit functions of the reciprocal of the rate, Z , which is $(dq/dt)^{-1}$ where q is amount of sorbate sorbed and t is time, one can show that a plot of Z vs. t should be convex if the power-function equation is operational, linear if the Elovich equation is appropriate, and concave if the first-order equation is appropriate; however, Z vs. t plots for soil systems are usually S-shaped: convex at small t , concave at large t , and linear at some intermediate t . These findings suggest that the reaction rate can best be described by the power-function equation at small t , by the Elovich equation at an intermediate t , and by a first-order equation at large t . Thus, the S-shaped curve indicates that the above equations may be applicable, each at some limited time range.

One of the reasons a particular kinetic model appears to be applicable may be that the study is conducted during the time range when the model is most appropriate. While sorption, for example, decreases over many orders of magnitude before equilibrium is approached, with most methods and experiments, only a portion of the entire reaction is measured and over this time range the assumptions associated with a simple kinetic model (power function, Elovich, and first-order) are valid. Aharoni and Suzin (1982a,b) showed that the S-shaped curves could be well described using homogeneous and heterogeneous diffusion models. In homogeneous diffusion situations, the final and initial portions of the S-shaped curves (conforming to the power-function and first-order equations, respectively) predominated, whereas, in instances where the heterogeneous diffusion model was operational, the linear portion of the S-shaped curve, that conformed to the Elovich equation, predominated.

4-2.2 Implications of Diffusion Models

The finding that slower reactions at the soil particle-liquid interface can be described by diffusional models indicates that the kinetics of chemical processes cannot be considered separately from transport phenomena. Thus, such a combination of processes cannot be treated using first-order or other-order chemical kinetics equations. When one states that a reaction between the molecular species A and B is of first-order with respect to A, one assumes that the molecules of A

have equal chances of participating in the reaction and therefore the rate is proportional to the concentration C_A . This reasoning can be extended to a reaction between an adsorbing surface and an adsorptive solute. The concentration C_A , in this case, refers to the number of reactive sites per unit area, which corresponds to the number of unoccupied sites per unit area ($1 - \theta_A$); however, by using first-order kinetics (or other-order kinetics) one tacitly assumes that all of the surface sites are potential reactants at any time, and they have an opportunity of participating in the sorption process. If one assumes that there are sites that cannot be reached directly from the fluid phase, but can be reached after the sorbate has undergone sorption and desorption at other sites, one cannot separate chemical kinetics from transport kinetics. The overall kinetic process obeys a diffusion equation (Aharoni & Sparks, 1991).

4-2.3 Multiple Site Models

Based on the previous discussion, it is evident that simple chemical kinetics models such as ordered reaction models and the power function and Elovich models may not be appropriate to describe reactions in heterogeneous systems such as soils, sediments, and soil components. In these systems, where there is a range of particle sizes and multiple retention sites, both chemical kinetics and transport phenomena are occurring simultaneously, and a fast reaction is often followed by a slower reaction(s).

In such systems, nonequilibrium models that describe both chemical and physical nonequilibrium and that consider multiple components and sites are more appropriate. Physical nonequilibrium is ascribed to some rate-limiting transport mechanism such as film diffusion (FD) or particle diffusion (PD) while chemical nonequilibrium is due to a rate-limiting mechanism at the particle surface (i.e., the chemical reaction, CR). Nonequilibrium models include two-site, multiple site, radial diffusion (pore diffusion), surface diffusion, and multiprocess models (Table 4-1).

The term *sites* can have a number of meanings (Brusseau & Rao, 1989): (i) specific, molecular scale reaction sites; (ii) sites of differing degrees of accessibility (external, internal); (iii) sites of differing sorbent type (organic matter and inorganic mineral surfaces); and (iv) sites with different sorption mechanisms. With chemical nonequilibrium sorption processes, the sorbate may undergo two or more types of sorption reactions, one of which is rate-limiting. For example, a metal cation may sorb to organic matter by one mechanism and to mineral surfaces by another mechanism with one of the mechanisms being rate-limiting.

4-2.4 Chemical Nonequilibrium Models

Chemical nonequilibrium models describe time-dependent reactions at sorbent surfaces. The one-site model is a first-order approach that assumes that the reaction rate is limited by only one process or mechanism on a single class of sorbing sites and that all sites are of the time-dependent type (Table 4-1). In many cases this model appears to describe soil chemical reactions quite well; however, often it does not. This model would seem not appropriate for most heterogeneous

Conceptual model	Fitting parameter(s)	Model limitations
One-site model k_d $S \rightarrow C$	k_d	Cannot describe biphasic sorption-desorption
Two-site model $X_1 K_p, k_d$ $S_1 \rightarrow C \rightarrow S_2$	k_d, K_p, X_1, ξ	Cannot describe the bleeding or slow, reversible, nonequilibrium desorption for residual sorbed compounds (Karickhoff, 1980)
Radial diffusion penetration retardation (pore diffusion) model (Wu & Gschwend, 1986) K_p, D_{eff} $S' \rightarrow C' \rightarrow C$	$D_{\text{eff}} = f(n, r) D_{\text{in}} n / (1 - n) \rho_s K_p \eta$	Cannot describe instantaneous uptake without additional correction factor (Ball & Roberts, 1991); did not describe kinetic data for times $> 10^3$ min (Wu & Gschwend, 1986)
Dual-resistance surface diffusion model (Miller & Pedit, 1992) D_s, k_b $S' \rightarrow C' \rightarrow C$	D_s, k_b	Model calibrated with sorption data predicted more desorption than occurred in the desorption experiments (Miller & Pedit, 1992)
Multi-site continuum compartment model (Connaughton et al., 1993) $F(t) = 1 - [M(t)/M] = 1 - (\beta/\beta + t)^{\alpha}$	α, β	Model needs comparison to other models, α and β may vary with sorbent properties and model should be applied to sorption
Pore space diffusion model (Fuller et al., 1993) $\{\varepsilon + [S_d K_s C(r)^{1-1/n}] / n\} [\partial C(r) / \partial t]$ $= D_s [\partial^2 C(r) / \partial r^2] + [2\partial C(r) / r \partial r]$	$D_s, \varepsilon, K_s, 1/n, F_{\text{eq}}$	Assumption of homogeneous, spherical particles and diffusion only in aqueous phase
Multiple Particle Class Pore Diffusion Model (Pedit & Miller, 1995) $\{\theta'_p + \rho'_a [\partial q'_p(r, t) / \partial C'_p(r, t)]\} [\partial C'_p(r, t) / \partial t]$ $= (\theta'_p D'_p / r^2) (\partial / \partial r) (r^2 \partial C'_p(r, t) / \partial r)$ $- \theta'_p \lambda'_p C'_p(r, t) - \rho'_a \lambda'_1 q'_1(r, t)$	$\theta'_p, \rho'_a, D'_p, \lambda'_p, \lambda'_1$	Multiple fitting parameters; variations in sorption equilibrium and rates that might occur within a particle class or an individual particle grain are not addressed

† Partially adapted from Connaughton et al. (1993).

‡ Abbreviations used are as follows: S , concentration of the bulk sorbed contaminant (g g^{-1}); S_2 , concentration of the sorbed contaminant that is rate limited (g g^{-1}); S_1 , concentration of the contaminant that is in equilibrium with the bulk aqueous concentration (g g^{-1}); X_1 , fraction of the bulk sorbed contaminant that is in equilibrium with the aqueous concentration; K_p , sorption equilibrium partition coefficient (mL g^{-1}); D_{eff} , effective diffusivity of sorbate molecules or ions in the particles ($\text{cm}^2 \text{s}^{-1}$); S' , concentration of contaminant in immobile bound state (mol g^{-1}); C' , concentration of contaminant free in the pore fluid (mol cm^{-3}); n , porosity of the sorbent (cm^3 of fluid cm^{-3} total); D_m , pore fluid diffusivity of the sorbate ($\text{cm}^2 \text{s}^{-1}$); ρ_s , specific gravity of the sorbent (g cm^{-3}); $f(n, t)$, pore geometry factor; k_b , boundary layer mass transfer coefficient (m s^{-1}); R , radius of the spherical solid particle, assumed constant (m); ρ , macroscopic particle density of the solid phase (g m^{-3}); C'_s , solution-phase solute concentration corresponding to an equilibrium with the solid-phase solute concentration at the exterior of the particle (g L^{-1}); D_s , surface diffusion coefficient (m s^{-1}).

§ K_p can be determined independently.

¶ K_p , D_m , and ρ_s can be determined independently; $F(t)$, fraction of mass released through time t ; $M(t)$, mass remaining after time t ; M , total initial mass; β , scale parameter necessary for determination of mean and standard deviation of k_s ; α , shape parameter; ϵ , internal porosity of sorbent; $C(r)$, concentration of sorptive in the aqueous phase in the pore fluid at radial distance r ; S_a is the surface of sorbent per unit volume of solid; $1/n$, the adsorption isotherm slope; K_s , adsorption isotherm intercept; D_e , effective diffusion coefficient; a , radius of the aggregate, F_{eq} , equilibrium fraction of adsorption sites; θ_p , intraparticle porosity of particle class i ; ρ'_{i1} , apparent particle density of particle class i ; r , radial distance; $C_p^i(r, t)$, intraparticle fluid-phase solute concentration of the particle class i ; D_p , pure diffusion coefficient for particle class i ; λ_p^i , intraparticle fluid-phase first-order reaction rate coefficient for particle class i ; λ_r^i , intraparticle solid-phase first-order reaction rate coefficient for particle class i ; $q_r^i(r, t)$, intraparticle solid-phase solute concentration of particle class i .

systems since multiple sorption sites exist. The two-site (two compartment, two box) or bicontinuum model has been widely used to describe chemical nonequilibrium (Leenheer & Ahlrichs, 1971; Hamaker & Thompson, 1972; Karickhoff, 1980; Karickhoff & Morris, 1985; McCall & Agin, 1985; Jardine et al., 1992) and physical nonequilibrium (Nkedi-Kizza et al., 1984; Lee et al., 1988; van Genuchten & Wagenet, 1989). This model assumes that there are two reactions occurring, one that is fast and reaches equilibrium quickly and a slower reaction that can continue for long time periods (Table 4-1). The reactions can occur in either series or in parallel (Brusseau & Rao, 1989).

In describing chemical nonequilibrium with the two-site model it is assumed that the sorbent has two types of sites. One site involves an instantaneous equilibrium reaction and the other site involves the time-dependent reaction. The instantaneous equilibrium reaction is described by an equilibrium isotherm equation while a first-order equation is usually employed to describe the time-dependent reaction.

Jardine et al. (1985) modeled the transport of Al through Ca-saturated kaolinite columns using a two-site nonequilibrium transport process. They assumed type-1 sites were in local equilibrium with the solution phase and involved an instantaneous Ca-Al exchange mechanism. Type-2 sites involved a time-dependent Al polymerization reaction mechanism and were described by first-order kinetics.

The polymerization mechanism was indirectly confirmed by investigating the effect of influent pH on Al transport. When influent pH was lowered, the slower kinetic reaction was eliminated and the Al breakthrough curve was described with a one-site equilibrium model.

With the two-site model there are two adjustable or fitting parameters, the fraction of sites at local equilibrium (X_1) and the rate constant (k). A distribution (K_d) or partition coefficient (K_p) is determined independently from a sorption-desorption isotherm. Connaughton et al. (1993) used a two-site model to describe naphthalene desorption from contaminated soil (Fig. 4-1a). The model did not describe the data well and fitted and estimated desorption rate coefficients (k_d) did not agree, with the estimated k_d values being higher than the values obtained from fitting. The estimated k_d values were based on the relation $\log k_d = 0.301 - 0.688 \log K_p$ (Brusseau & Rao, 1989). Connaughton et al. (1993) related this discrepancy to the greater desorption times of their experiments and to the use of the two-site model to describe the entire desorption process. The two-site model, that the $K_p - k_d$ relationship was based on, assumes that the initial desorption is instantaneous, which is not the case for naphthalene desorption. One major disadvantage in using the two-site model to describe heterogeneous systems such as soil is the assumption that only two sorptive sites are present. Thus, the fitting parameters in the two-site model probably do not conform to actual reaction rates on multiple sites in soils. Moreover, it is difficult to relate the fitting parameters to known properties of the sorbent. For example Wu and Gschwend (1986) found two different sets of fitting parameters described tetrachlorobenzene sorption on a Charles River sediment if different sediment mean aggregate sizes were used. Consequently, the parameters had to be experimentally determined for each sediment size.

To account for the multiple sites that may exist in heterogeneous systems Connaughton et al. (1993) developed a multi-site compartment model (Γ) that incorporates a continuum of sites or compartments with a distribution of rate coefficients that can be described by a gamma density function. A fraction of the sorbed mass in each compartment is at equilibrium and there is a desorption rate coefficient or distribution coefficient for each compartment or site (Table 4-1). The multisite model has two fitting parameters α , a shape parameter, and $1/\beta$, which is a scale parameter that determines the mean standard deviation of the rate coefficients. Figure (4-1B) shows application of the Γ model to desorption of

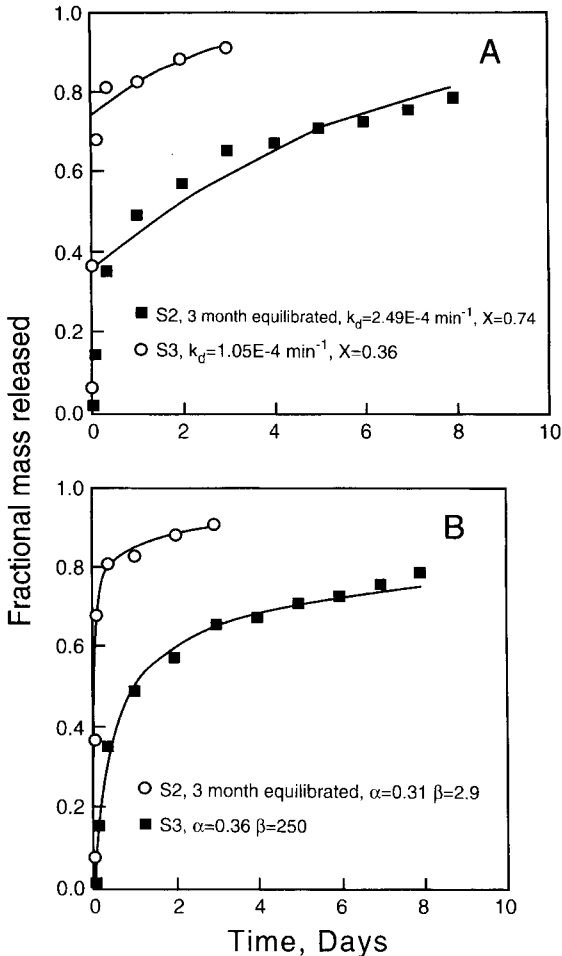


Fig. 4-1. (A) Fitted two-site model with release profiles of naphthalene from two soils, S2 and S3; $R^2 = 0.88$ and 0.91 for S2 and S3 regression fits, respectively, where X is the fraction of sites at instantaneous equilibrium and k_d is the desorption rate coefficient. (B) Mass fractional release of naphthalene from S2 and S3 soils with fitted multisite continuum compartment (Γ) model. (from Connaughton et al., 1993).

naphthalene from contaminated soils. The entire desorption process was described well with this model.

4-2.5 Physical Nonequilibrium Models

There are a number of physical models that can be used to describe nonequilibrium reactions. Since transport processes in the mobile phase are not usually rate-limiting, physical nonequilibrium models focus on diffusion in the immobile phase or intra-aggregate-diffusion processes (e.g., pore and/or surface diffusion). The transport between mobile and immobile regions is accounted for in physical nonequilibrium models in three ways (Brusseau & Rao, 1989): (i) explicitly with Fick's law to describe the physical mechanism of diffusive transfer; (ii) explicitly by using an empirical first-order mass-transfer expression to approximate solute transfer; and (iii) implicitly by using an effective or lumped dispersion coefficient that includes the effects of sink-source differences and hydrodynamic dispersion and axial diffusion.

A pore diffusion model (Table 4-1) has been used by a number of investigators to study sorption processes using batch systems (Wu & Gschwend, 1986; Steinberg et al., 1987; Ball & Roberts, 1991; Harmon et al., 1992; Pignatello et al., 1993). Wu and Gschwend (1986) successfully used the pore diffusion model to describe chlorobenzene congener sorption-desorption on soils and sediments. Figure 4-2 shows experimental and model fits for tetrachlorobenzene and pentachlorobenzene sorption on soils. The sole fitting parameter in this model is the effective diffusion coefficient (D_e). This parameter can be estimated a priori from chemical and colloidal properties; however, this estimation is only valid if the sorbent material has a narrow particle size distribution such that an accurate, average particle size can be defined. Moreover, in the pore diffusion model it is assumed that there is an average representative D_e , which means there is a continuum in properties across an entire pore size spectrum. This is not a valid assumption for micropores (<2.0 nm) since there are higher adsorption energies

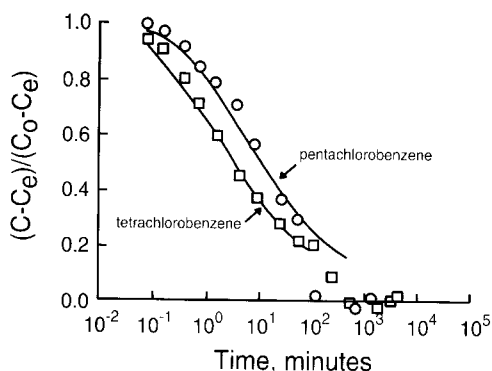


Fig. 4-2. Experimental and model-fitting results for pentachlorobenzene and tetrachlorobenzene sorption on Iowa soils where C is the dissolved concentration of organic chemical in the bulk solution, C_0 is the initial concentration and C_e is the equilibrium concentration. The points represent experimental data and the solid lines represent fit of the data to the radial diffusion (pore diffusion) model (from Wu & Gschwend, 1986).

of sorbates in micropores, which causes increased sorption. The increased sorption causes reduced diffusive transport rates and nonlinear isotherms for sorbents with pores < several sorbate diameters in size. Other factors can cause reduced transport rates in micropores including steric hindrance that increases as the pore size approaches the solute size and greatly increased surface area to pore volume ratios, which occurs as pore size decreases. Another problem with the pore diffusion model is that sorption and desorption kinetics may have been measured across a narrow concentration range. This is a problem since a sorption-desorption mechanism in micropores at one concentration may be insignificant at another concentration.

Fuller et al. (1993) used a pore space diffusion model (Table 4-1) to describe arsenate adsorption on ferrihydrate that included a subset of sites whereby sorption was at equilibrium. A Freundlich model was used to describe sorption on these sites. Diffusion into the particle was described by Fick's second law of diffusion and homogeneous, spherical aggregates, and diffusion only in the aqueous phase were assumed.

Figure 4-3 shows the fit of the model when sorption at all sites was controlled by intra-aggregate diffusion. The fit was better when sites that had attained sorption equilibrium were included (Fig. 4-3). The latter model assumed that there was an initial rapid sorption on external surface sites before intra-aggregate diffusion.

Pedit and Miller (1995) have developed a general multiple-particle class pore diffusion model that accounts for differences in physical and sorptive properties for each particle class (Table 4-1). The model includes both instantaneous equilibrium sorption and time-dependent pore diffusion for each particle class. The pore diffusion portion of the model assumes that solute transfer between the intra-particle fluid and the solid phases is fast vis a' vis intra-particle pore diffusion processes.

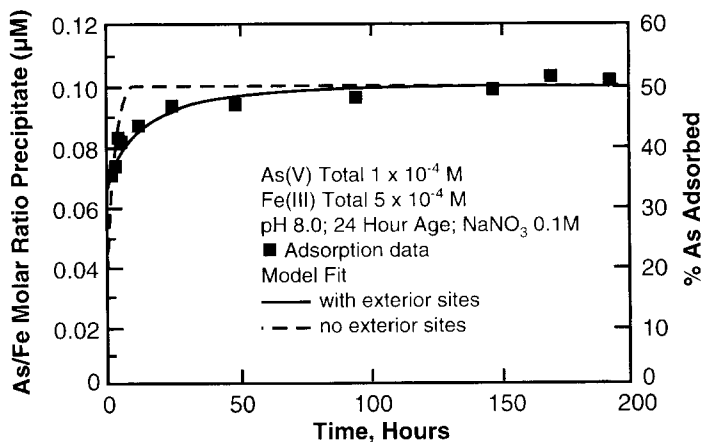


Fig. 4-3. Comparison of pore space diffusion model fits of As (V) sorption with experimental data (dashed curve represents sorption where all surface sites are diffusion-limited and the solid curve represents sorption on equilibrium sites plus diffusion-limited sites; from Fuller et al., 1993).

Surface diffusion models, assuming a constant surface diffusion coefficient, have been used by a number of researchers (Weber & Miller, 1988; Miller & Pedit, 1992). The dual resistance model (Table 4-1) combines both pore and surface diffusion.

4-3 RESIDENCE TIME EFFECTS ON REACTION RATES

While some soil chemical reactions are rapid, such as some ion exchange and adsorption reactions, it is well known that many reactions are quite slow. There also is good evidence that as the time of contact between the sorbate and sorbent (residence time) increases, the rate of many soil chemical reactions become increasingly retarded. The slow kinetics have been attributed to intraparticle and interparticle diffusion processes, sites of differing reactivity and surface precipitation phenomena; however, the mechanisms are not well understood and mechanistic conclusions have primarily been based on macroscopic and kinetic studies. To definitively understand the mechanism(s), in-situ spectroscopic and microscopic studies, along with kinetic investigations, are needed.

4-3.1 Metal Reactions

Ainsworth et al. (1994) studied the adsorption-desorption of Co^{2+} , Cd^{2+} , and Pb^{2+} on hydrous ferric oxide (HFO) as a function of oxide aging and metal-oxide residence time (aging). Oxide aging did not cause hysteresis of metal cation sorption-desorption. Aging the oxide with the metal cations resulted in hysteresis with Cd^{2+} and Co^{2+} but little hysteresis was observed with Pb^{2+} . With Pb^{2+} , between pH 3 and 5.5 there was slight hysteresis during a 21-wk aging process (hysteresis varied from <2% difference between sorption and desorption to $\approx 10\%$). At pH 2.5 Pb desorption was complete within a 16 h desorption period

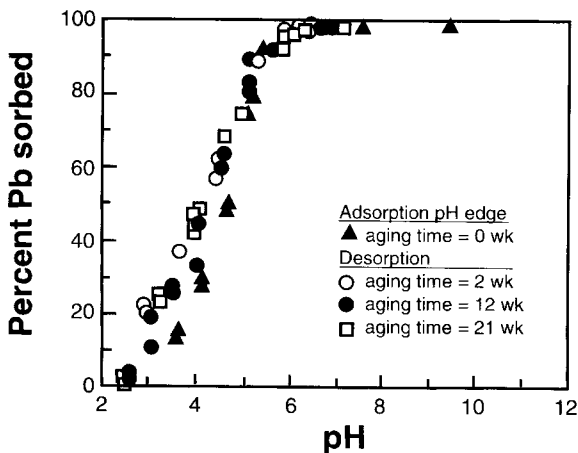


Fig. 4-4. Fractional sorption-desorption of Pb^{2+} to hydrous Fe-oxide (HFO) as a function of pH and HFO- Pb^{2+} aging time (from Ainsworth et al., 1994).

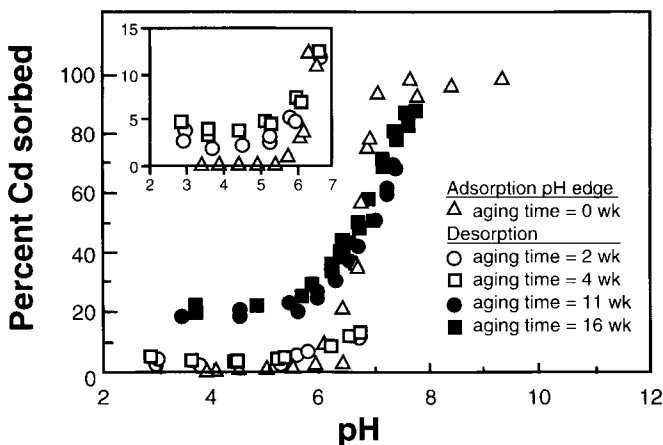


Fig. 4-5. Fractional sorption-desorption of Cd²⁺ to hydrous Fe-oxide (HFO) as a function of pH and HFO-Cd²⁺ aging time; insert shows adsorption-desorption of Cd²⁺ to HFO at 2- and 4-wk aging times (from Ainsworth et al., 1994).

and was not affected by aging time (Fig. 4-4); however, with Cd and Co, extensive hysteresis was observed during a 16 wk aging period and the hysteresis increased with aging time (Fig. 4-5 and 4-6). After 16 wk of aging 20% of the Cd and 53% of the Co was not desorbed, and even at pH 2.5, hysteresis was observed. Ainsworth et al. (1994) attributed the hysteresis to Co and Cd incorporation into a recrystallizing solid (probably goethite) via isomorphous substitution and not to micropore diffusion.

Bruemmer et al. (1988) studied Ni²⁺, Zn²⁺, and Cd²⁺ adsorption on goethite, and found at pH 6 that as reaction time increased from 2 h to 42 d (at

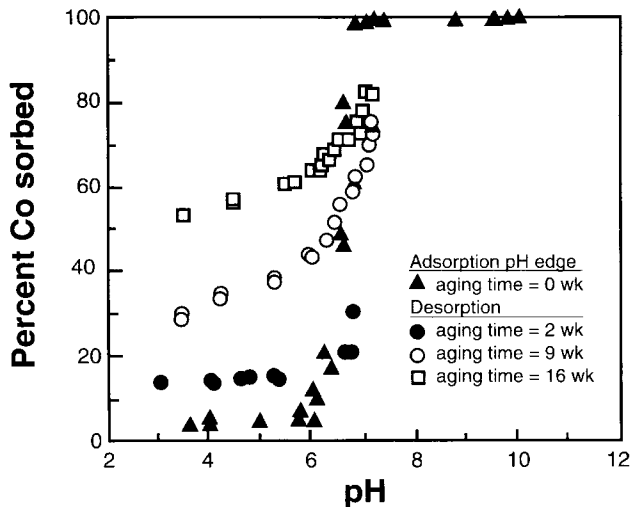


Fig. 4-6. Fractional adsorption of Co²⁺ to hydrous Fe-oxide (HFO) as a function of pH and HFO-Co²⁺ aging time (from Ainsworth et al., 1994).

293 K), adsorbed Ni^{2+} increased from 12 to 70% of total adsorption, and total increases in Zn^{2+} and Cd^{2+} adsorption over this time increased 33 and 21%, respectively. Bruemmer et al. (1988) attributed the slow kinetics to diffusion-controlled reactions on external and internal surface sites.

Backes et al. (1995) did not observe an increase in Co^{2+} or Cd^{2+} adsorption on Fe- and Mn-oxides as the sorption period increased from 12 to 15 wk; however, increased sorption time did result in a decrease in the rate and amount of desorption of Co^{2+} and Cd^{2+} from goethite, Co^{2+} from hausmannite and Cd^{2+} from crystomelane.

4-3.2 Organic Chemical Reactions

There have been a number of studies on the kinetics of organic chemical sorption-desorption with soils and soil components. Many of these investigations have shown that sorption-desorption is characterized by a rapid, reversible stage followed by a much slower, nonreversible stage (Karickhoff et al., 1979; DiToro & Horzempa, 1982; Pavlostathis & Mathavan, 1992) or biphasic kinetics. The rapid phase has been ascribed to retention of the organic chemical in a labile form that is easily desorbed; however, the much slower reaction phase involves the entrapment of the chemical in a nonlabile form that is difficult to desorb. This slower sorption-desorption reaction has been described to diffusion of the chemical into micropores of organic matter and inorganic soil components (Wu & Gschwend, 1986; Steinberg et al., 1987; Ball & Roberts, 1991). The labile form of the chemical is available for microbial attack while the nonlabile portion is resistant to biodegradation.

An example of the biphasic kinetics that is observed for many organic chemical reactions in soils-sediments is shown in Fig. 4-7. In this study 55% of the labile polychlorinated biphenyls (PCBs) were desorbed from sediments in a 24-h period, while little of the remaining 45% nonlabile fraction was desorbed in 170 h (Fig. 4-7a). During another 1-yr period about 50% of the remaining nonlabile fraction was desorbed (Fig. 4-7b).

In another study with volatile organic compounds (VOCS), Pavlostathis and Mathavan (1992) observed a biphasic desorption process for field soils contaminated with trichloroethylene (TCE), tetrachloroethylene (PCE), toluene (TOL), and xylene (XYL). A fast desorption reaction occurred in 24 h followed by a much slower desorption reaction beyond 24 h. In 24 h, 9-29%, 14-48%, 9-40%, and 4-37% of the TCE, PCE, TOL, and XYL, respectively, were released.

A number of studies have also shown that with aging the nonlabile portion of the organic chemical in the soil-sediment becomes more resistant to release (McCall & Agin, 1985; Steinberg et al., 1987; Pavlostathis & Mathavan, 1992; Scribner et al., 1992; Pignatello et al., 1993); however, Connaughton et al. (1993) did not observe the nonlabile fraction increasing with age for naphthalene contaminated soils.

One way to gauge the effect of time on organic contaminant retention in soils is to compare K_d (sorption distribution coefficient) values for freshly aged

and aged soil samples. In most studies, K_d values are measured based on a 24 h equilibration between the soil and the organic chemical. When these values are compared to K_d values for field soils previously reacted with the organic chemical (aged samples) the latter have much higher K_d values, indicating that much more of the organic chemical is in a sorbed state. For example, Pignatello and Huang (1991) measured K_d values in freshly aged (K_d) and aged soils (K_{app} , apparent sorption distribution coefficient) reacted with atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,2,5-triazine) and metolachlor [2-chloro-N-(2-thyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide], two widely used herbicides. The aged soils had been treated with the herbicides 15 to 62 mo before sampling. The K_{app} values ranged from 2.3 to 42 times higher than the K_d values (Table 4-2).

Scribner et al. (1992), studying simazine (a widely used triazine herbicide for broadleaf and grass control in crops) desorption and bioavailability in aged

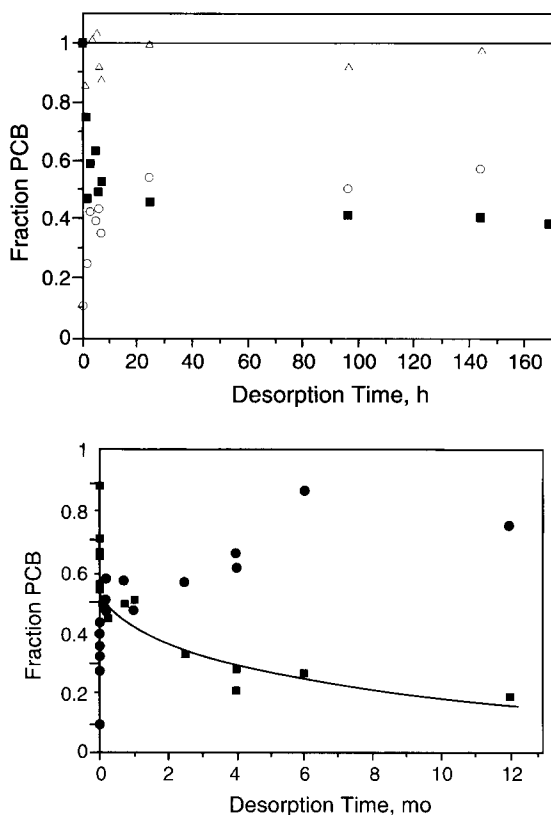


Fig. 4-7. (A) Short-term polychlorinated biphenyl (PCB) desorption in hours from Hudson River sediment contaminated with 25 mg kg^{-1} PCB. Distribution of the PCB between the sediment (■) and XAD-4 resin (○) is shown, as well as the overall mass balance (Δ). The resin acts as a sink to retain the PCB that is desorbed (from Carroll et al., 1994). (B) Long-term PCB desorption in months (mo) from Hudson River sediment contaminated with 25 mg kg^{-1} PCB. Distribution of the PCB between the sediment (■) and XAD-4 resin (○) is shown. The line represents a nonlinear regression of the data by a two-site model (from Carroll et al., 1994).

Table 4-2. Sorption distribution coefficients for herbicides in freshly aged and aged soils.†

Herbicide	Soil	K_d ‡	K_{app} §
Metolachlor	CVa	2.96	39
	CVb	1.46	27
	W1	1.28	49
	W2	0.77	33
Atrazine	CVa	2.17	28
	CVb	1.32	29
	W3	1.75	4

† Adapted from Pignatello and Huang (1991); herbicides had been added to soils 31 mo prior to sampling for CVa and CVb soils, 15 mo for the W1 and W2 soils, and 62 mo for the W3 soil.

‡ Sorption distribution coefficient of freshly aged soil based on a 24-h equilibration period.

§ Apparent sorption distribution coefficient in contaminated soil (aged soil) determined using a 24-h equilibration period.

soils, found that K_{app} values were 15 times higher than K_d values. Scribner et al. (1992) also showed that 48% of the simazine added to the freshly aged soils was biodegradable during a 34-d incubation period while none of the simazine in the aged soil was biodegraded.

4-3.3 Implications of Aging Studies

One of the implications of the above studies on the effects of residence time on metal and organic chemical reactions on natural materials is that while many transport and degradation models for contaminants in soils and waters assume that the sorption process is an equilibrium process, the studies clearly show that kinetic reactions must be considered when making predictions about the mobility and fate of organic pollutants. Moreover, calculation of K_d values based on a 24-h equilibration period, which are commonly used in fate and risk assessment models, can be inaccurate since 24-h K_d values often overestimate the amount of contaminant in the solution phase.

The findings that many contaminants are quite persistent in the soil environment have both good and bad features. The beneficial aspect is that the contaminants are less mobile and may not be readily transported in groundwater supplies. The negative aspect is that their persistence and inaccessibility to microbes may make decontamination more difficult, particularly if in-situ remediation techniques such as biodegradation are employed.

4-4 USE OF MOLECULAR APPROACHES TO CONFIRM REACTION MECHANISMS

Kinetic studies, particularly if energies of activation are calculated and stopped-flow or interruption techniques are employed (Sparks, 1989), can reveal information about reaction mechanisms at the soil particle-solution interface; however, to definitively confirm the mechanism, molecular and/or atomic reso-

lution surface techniques should be employed to corroborate the proposed mechanism hypothesized from kinetic studies. These techniques can be either used separately or preferably, simultaneously with the kinetic investigations. While the latter approach is preferable, only limited studies have been reported in the literature. Examples of both approaches will be cited in the following discussions.

There are a plethora of surface probe techniques—both spectroscopic and microscopic. These will not be reviewed in detail here. The reader should consult a number of monographs and textbooks for extensive details on these techniques (Hawthorne, 1988; Hochella & White, 1990; Charlet & Manceau, 1993; Fendorf et al., 1994; Schulze & Bertsch, 1995). Many of the surface techniques are non-in situ, meaning that the sorbent must be examined dry and/or under vacuum. The effects of these treatments on the surface chemistry of the sorbent and of the contrast between such a system and what would be found in the natural environment are not well understood.

Magnetic [nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR)] and vibrational [Fourier transform infrared (FTIR) and Raman] spectroscopies can be used to study reactions in situ. While these methods provide atomic level information, they do not always provide precise information on the local structural environment of a species. X-ray absorption fine structure (XAFS) spectroscopy is an in situ technique that can provide direct information on the local structural environment, e.g., surface complexed and/or surface precipitated metals, and oxidation states of metals (Charlet & Manceau, 1993; Fendorf et al., 1994; Schulze & Bertsch, 1995; Sparks, 1995).

While XAFS provides local chemical information, it yields no spatial resolution information. Transmission electron microscopy can provide spatial resolution of surface changes and can be combined with electron spectroscopies to determine elemental analysis; however, electron microscopies require a vacuum environment that may cause an alteration in the solid sample. Also, bombardment of the sample with electrons could damage the sample. To avoid these problems, atomic force microscopy (AFM) or other surface probing microscopies (SPM) can be used.

4-4.1 Use of Kinetic and Spectroscopic Approaches

There are a few examples in the literature of studies where mechanisms of metal reactions on soil components have been hypothesized via kinetic experiments and verified in separate spectroscopic investigations (Fuller et al., 1993; Waychunas et al., 1993). An example of this approach can be found in the recent research of Fuller et al. (1993) and Waychunas et al. (1993), who studied the kinetics and mechanisms of As(V) sorption on ferrihydrite. Adsorption was investigated during coprecipitation, in which As(V) was present in solution during the hydrolysis and precipitation of Fe, and after coprecipitation (post-synthesis adsorption). In the post-synthesis adsorption studies, As(V) uptake was initially rapid and then slowly increased for up to 8 d. The rapid uptake was ascribed to adsorption on surface sites near the outside of aggregates, while the slower adsorption was attributed to diffusion of As(V) to adsorption sites on ferrihydrite surfaces within aggregates of colloidal particles. The latter were caused by coag-

ulation and crystallite growth processes. These processes resulted in a decrease in the number of adsorption sites, and as aggregates formed, adsorption sites were buried in large clusters of the particles (Fuller et al., 1993). In the coprecipitation studies, initial As(V) uptake was much greater than observed for the post-synthesis adsorption studies, and the uptake rate was not diffusion-controlled as As(V) was coordinated by surface sites before crystallite growth.

The mechanistic hypotheses, based on the kinetic studies, were verified with companion XAFS studies (Waychunas et al., 1993). Analyses of the XAFS data provided no evidence for surface precipitation, one possible mechanism that has been proposed for slow metal sorption processes. Arsenate retention in both the coprecipitation and post-synthesis adsorption studies involved primarily an inner-sphere bidentate and monodentate binding on sites initially adsorbing arsenate. Waychunas et al. (1993) hypothesized that these defect sites probably adsorb As(V) as a bidentate complex first, and then sorb as a monodentate complex. Monodentate complexes accounted for about 30% of all As-Fe correlations and occurred at only low As loading levels. Recently, Manceau (1995) has questioned some of the As-Fe distances and pointed out the importance of edge linkages between Fe octahedra and arsenate tetrahedra.

Ideally, one would prefer to study reaction mechanisms by following reaction rates spectroscopically (time-resolved or real-time studies) using in-situ approaches. Such studies are scarce in the literature. The quick EXAFS (extended x-ray fine structure spectroscopy) technique, abbreviated QEXAFS, depends on a constant monochromator scan rate and fast array deflectors to obtain a full EXAFS spectrum in a fraction of a second compared to tens of minutes in a traditional EXAFS method. Thus, ms or μ s reactions could be spectroscopically monitored (Frahm, 1991; Lytle & Greegar, 1991; Dobson, 1994; Schulze & Bertsch, 1995). Such studies would be very useful for many soil particle-solution reactions that are rapid. Energy dispersive EXAFS, abbreviated DEXAFS, also can be used to determine a full EXAFS spectrum in a fraction of a second (Baker et al., 1991); however, detection can only be determined in the transmission mode. For slower reactions, it should be possible to follow the reaction mechanisms over time using standard XAFS techniques.

A recent example of time-resolved in-situ spectroscopic analyses is the research of Hunter and Bertsch (1994). They employed attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) to quantitatively measure the degradation kinetics of tetraphenylboron (TPB) on clay minerals. The mechanisms of degradation were ascribed to surface-facilitated oxidation at Lewis acid and Bronsted acid sites. First-order models, based on these mechanisms, described the time-dependent data quite well.

4-4.2 Use of Kinetic and Microscopic Approaches

Scanning force microscopy (SFM) is being used increasingly as an in situ technique for imaging mineral surfaces immersed in aqueous solution and studying the kinetics of dissolution, precipitation, and heterogeneous nucleation reactions (Dove & Hochella, 1993; Gratz & Hillner, 1993; Bosbach & Rammensee, 1994; Junta & Hochella, 1994; Stipp et al., 1994; Maurice et al., 1995; Fendorf

Table 4-3. Studies on the kinetics of mineral reactions using scanning force microscopy (SFM).†

Dove et al., 1992	Calcite precipitation
Hellman et al., 1992	Albite dissolution
Hillner et al., 1992a,b	Calcite growth and dissolution
Johnsson et al., 1992	Muscovite dissolution
Dove & Hochella, 1993	Calcite precipitation mechanisms and inhibition by orthophosphate
Gratz & Hillner, 1993	Step dynamics and spiral growth on calcite
Bosbach & Rammensee, 1994	Gypsum growth and dissolution
Junta & Hochella, 1994	Mn(II) oxidation on hematite, goethite and albite
Stipp et al., 1994	Calcite surface structure
Maurice et al., 1995	Dissolution of hematite in organic acids
Fendorf et al., 1996	Precipitation kinetics of chromium hydroxide on goethite and silica

† Studies are listed in chronological order.

et al., 1996). SFM permits a direct measure of surface-controlled growth and dissolution rates by providing three-dimensional data on changes in microtopography. In situ SFM has the perhaps unique ability to detect different processes, such as dissolution and secondary phase formation, occurring simultaneously on a mineral surface (Maurice, 1998). Some of the studies in which SFM have been used to study the kinetics of mineral reactions are reported in Table 4-3.

Recently, Fendorf et al. (1996) studied the kinetics of Cr(III) reactions on single goethite and silica particles using a flow-cell mounted in a SFM. This procedure enabled one to study the reactions in an aqueous environment (in situ) and to react the surface while imaging (real-time measurements). Figure 4-8 shows an image of the unreacted silica in an aqueous environment. The surface is mostly flat and smooth with no island outcroppings. One hour after a 1 mM Cr(III) solution at pH 6 was introduced into the flow cell one sees that the Cr(III) solution caused a dramatic change in the surface morphology of silica (Fig. 4-8). Surface clusters have formed on the surface and within 2 h (figure not shown) the clusters have expanded in width and girth. The precipitates form as discrete surface clusters on the silica surface rather than distributing across the surface (Fendorf et al., 1996).

4-5 CONCLUSIONS AND FUTURE RESEARCH NEEDS

Research on the kinetics and mechanisms of reactions at the soil particle-solution interface will be a common theme in soil and environmental sciences for decades to come. This research emphasis is in large part due to the recognition that reactions controlling the fate and transport of contaminants in the subsurface environment are time-dependent. To accurately predict contaminant behavior in soils over time, one must understand the kinetics of the reactions. For further advancement to occur in this area the following research is needed: (i) more accurate kinetic models that describe reactions on multireactive, heterogeneous particle surfaces; (ii) long-term sorption-desorption rate studies; (iii) a better understanding of residence time effects on nutrient, radionuclide, metal, and organic retention-release mechanisms on soils and other natural materials, (iv) an increased knowledge of nucleation-precipitation and dissolution reaction rates at the mineral-water interface and their effect on nutrient-contaminant mobility in

the soil environment; (v) increased studies on the kinetics and mechanisms of redox processes in soils, particularly the role that soil components such as Mn-oxides have on oxidation-reduction of inorganic and organic pollutants; and (vi) increased use of time-resolved, in situ spectroscopic and microscopic techniques to confirm reaction mechanisms.

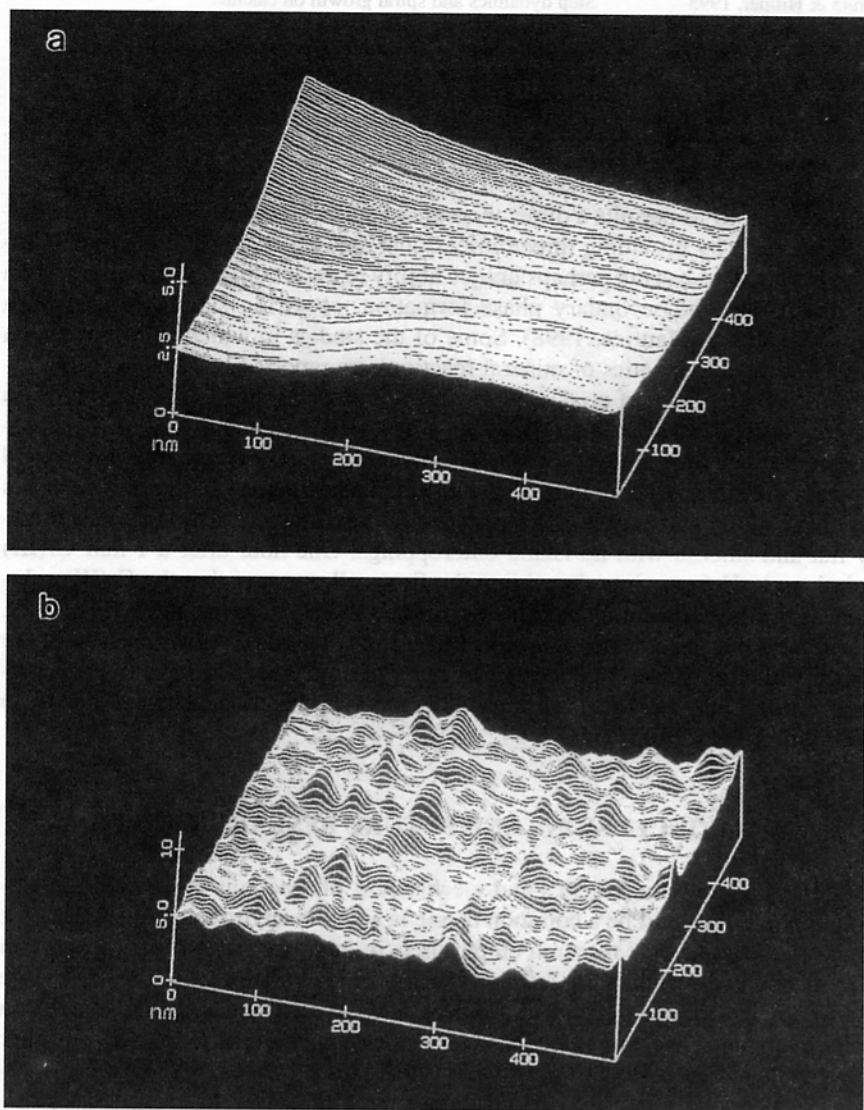


Fig. 4-8. Using a flow cell a single-particle of silica was imaged in an aqueous environment. The unreacted silica (a) is relatively flat and smooth across the 500×500 nm scan region; no pronounced outcroppings from the surface are observed. After reacting with 1 mM Cr(III) for 1 h at pH 6.0 (b) a different surface morphology is apparent: distinct surface clusters have formed that protrude away from the silica surface. These clusters continue to expand away from the surface and fuse together after 2 h (not shown) of reacting with Cr(III) (from Fendorf et al., 1996).

REFERENCES

- Aharoni, C. 1984. Kinetics of adsorption: The S-shaped $Z(t)$ plot. *Adsorpt. Sci. Technol.* 1:1–29.
- Aharoni, C., and D.L. Sparks. 1991. Kinetics of soil chemical reactions: A theoretical treatment. p. 1–18. *In* D.L. Sparks and D.L. Suarez (ed.) Rates of soil chemical processes. SSSA Spec. Publ. 27. SSSA, Madison, WI.
- Aharoni, C., and Y. Suzin. 1982a. Application of the Elovich equation to the kinetics of occlusion: 1. Homogenous microporosity. *J. Chem. Soc., Faraday Trans.* 178: 2313–2320.
- Aharoni, C. and Y. Suzin. 1982b. Application of the Elovich equation to the kinetics of occlusion: 3. Heterogenous microporosity. *J. Chem. Soc., Faraday Trans.* 178: 2329–2336.
- Aharoni, C., and M. Ungarish. 1976. Kinetics of activated chemisorption. 1. The non-Elovichian part of the isotherm. *J. Chem. Soc., Faraday Trans.* 172:400–408.
- Ainsworth, C.C., J.L. Pilou, P.L. Gassman, and W.G. Van Der Sluys. 1994. Cobalt, cadmium, and lead sorption to hydrous iron oxide: Residence time effect. *Soil Sci. Soc. Am. J.* 58:1615–1623.
- Backes, C.A., R.G. McLaren, A.W. Rate, and R.S. Swift. 1995. Kinetics of cadmium and cobalt desorption from iron and manganese oxides. *Soil Sci. Soc. Am. J.* 59:778–785.
- Baker, G., A.J. Dent, G. Derbyshire, G.N. Greaves, C.R.A. Catlow, J.W. Couves, and J.M. Thomas. 1991. Time resolved structural studies of nickel exchanged zeolite and nickel oxide using energy dispersive EXAFS. p. 738–741. *In* S.S. Hasnain (ed.) X-ray absorption fine structure. Ellis Harwood, New York.
- Ball, W.P., and P.V. Roberts. 1991. Long-term sorption of halogenated organic chemicals by aquifer material: 1. Equilibrium. *Environ. Sci. Technol.* 25(7):1223–1236.
- Bernasconi, C.F. 1976. Relaxation kinetics. Academic Press, New York.
- Bosbach, D., and W. Rammensee. 1994. In situ investigation of growth and dissolution on the (010) surface of gypsum by scanning force microscopy. *Geochim. Cosmochim. Acta.* 58:843–849.
- Bruemmer, G.W., J. Gerth, and K.G. Tiller. 1988. Reaction kinetics of the adsorption and desorption of nickel, zinc and cadmium by goethite: 1. Adsorption and diffusion of metals. *J. Soil Sci.* 39:37–52.
- Brusseau, M.L., and P.S.C. Rao. 1989. Sorption nonideality during organic contaminant transport in porous media. *CRC Crit. Rev. Environ. Control* 19:33–99.
- Carroll, K.M., M.R. Harkness, A.A. Bracco, and R.B. Balcarel. 1994. Application of a permeant/polymer diffusion model to the desorption of polychlorinated biphenyls from Hudson River sediments. *Environ. Sci. Technol.* 28:253–258.
- Charlet, L., and A. Manceau. 1993. Structure, formation, and reactivity of hydrous oxide particles: Insights from x-ray absorption spectroscopy. p. 117–164. *In* J. Buffle and H.P. van Leeuwen (ed.) Environmental particles. Lewis Publ., Boca Raton, FL.
- Chien, S.H., and W.R. Clayton. 1980. Application of Elovich equation to the kinetics of phosphate release and sorption in soils. *Soil Sci. Soc. Am. J.* 44:265–268.
- Connaughton, D.F., J.R. Stedinger, L.W. Lion, and M.L. Shuler. 1993. Description of time-varying desorption kinetics: Release of naphthalene from contaminated soils. *Environ. Sci. Technol.* 27:2397–2403.
- DiToro, D.M., and L.M. Horzempa. 1982. Reversible and resistant components of PCB adsorption–desorption: Isotherms. *Environ. Sci. Technol.* 16:594–602.
- Dobson, B.R. 1994. Quick scanning EXAFS facilities at Daresbury. *SRS Synchrotron Radiat. News* 7(1):21–24.
- Dove, P.M., and M.F. Hochella, Jr. 1993. Calcite precipitation mechanisms and inhibition by orthophosphate: In situ observations by scanning force microscopy. *Geochim. Cosmochim. Acta.* 57:705–714.
- Dove, P.M., M.F. Hochella, Jr., and R.J. Reeder. 1992. In situ investigation of near-equilibrium calcite precipitation by atomic force microscopy. p. 141–144. *In* Y.K. Kharaka and A.S. Maest (ed.) Water–rock interaction VII. A.A. Balkema, Rotterdam.
- Fendorf, S.E., G. Li, and M.E. Gunter. 1996. Micromorphologies and stabilities of chromium (III) surface precipitates elucidated by scanning force microscopy. *Soil Sci. Soc. Am. J.* 60:99–106.
- Fendorf, S.E., D.L. Sparks, G.M. Lamble, and M.J. Kelley. 1994. Applications of x-ray absorption fine structure spectroscopy to soils. *Soil Sci. Soc. Am. J.* 58:1583–1595.
- Frahm, R. 1991. Quick XAFS: Potentials and practical applications in materials science. p. 731–737. *In* S.S. Hasnain (ed.) X-ray absorption fine structure. Ellis Harwood, New York.
- Fuller, C.C., J.A. Davis, and G.A. Waychunas. 1993. Surface chemistry of ferrihydrite: 2. Kinetics of arsenate adsorption and coprecipitation. *Geochim Cosmochim. Acta* 57:2271–2282.

- Gratz, A.J., and P.E. Hillner. 1993. Poisoning of calcite growth viewed in the atomic force microscope (AFM). *J. Cryst. Growth* 129:789–793.
- Hamaker, J.W., and J.M. Thompson. 1972. Adsorption. p. 39–151. *In* C.A.I. Goring and J.W. Hamaker (ed.) *Organic chemicals in the environment*. Marcel Dekker, New York.
- Harmon, T.C., L. Semprini, and P.V. Roberts. 1992. Simulating solute transport using laboratory-based sorption parameters. *J. Environ. Eng.* 118:666–689.
- Hawthorne, F.C. (ed.) 1988. Spectroscopic methods in mineralogy and geology. *Rev. Mineral.* Vol. 18. Mineral. Soc. Am., Washington, DC.
- Hellman, R., B. Drake, and K. Kjoller. 1992. Using atomic force microscopy to study the structure, topography and dissolution of albite surfaces. p. 149–152. *In* Y.K. Kharaka and A.S. Maest (ed.) *Water-rock interaction VII*. A.A. Balkema, Rotterdam.
- Hillner, P.E., A.J. Gratz, S. Manne, and P.K. Hansma. 1992a. Atomic-scale imaging of calcite growth and dissolution in real-time. *Geology* 20:359–362.
- Hillner, P.E., S. Manne, A.J. Gratz, and P.K. Hansma. 1992b. AFM images of dissolution and growth on a calcite crystal. *Ultramicroscopy* 44:1387–1393.
- Hochella, M.F., Jr., and A.F. White (ed.) 1990. Mineral-water interface geochemistry. *Rev. Mineral.* Vol. 23. Ann Arbor Sci., Ann Arbor, MI.
- Hunter, D.B., and P.M. Bertsch. 1994. *In situ* measurements of tetraphenylboron degradation kinetics on clay mineral surfaces by FTIR. *Environ. Sci. Technol.* 28:686–691.
- Jardine, P.M., F.M. Dunnivant, H.M. Selim, and J.F. McCarthy. 1992. Comparison of models for describing the transport of dissolved organic carbon in aquifer columns. *Soil Sci. Soc. Am. J.* 56:393–401.
- Jardine, P.M., J.C. Parker, and L.W. Zelazny. 1985. Kinetics and mechanisms of aluminum adsorption on kaolinite using a two-site nonequilibrium transport model. *Soil Sci. Soc. Am. J.* 49:867–873.
- Johnsson, P.A., M.F. Hochella, Jr., G.A. Parks, A.E. Blum, and G. Sposito. 1992. Direct observation of muscovite basal-plane dissolution and secondary phase formation: An XPS, LEED, and SFM study. p. 159–162. *In* Y.K. Kharaka and A.S. Maest (ed.) *Water-rock interaction VII*. A.A. Balkema, Rotterdam.
- Junta, J.L., and M.F. Hochella, Jr. 1994. Manganese (II) oxidation at mineral surfaces: A microscopic and spectroscopic study. *Geochim. Cosmochim. Acta* 58:4985–4999.
- Karickhoff, S.W. 1980. Sorption kinetics of hydrophobic pollutants in natural sediments. p. 193–205. *In* R.A. Baker (ed.) *Contaminants and sediments*. 2. Ann Arbor Sci., Ann Arbor, MI.
- Karickhoff, S.W., D.S. Brown, and T.A. Scott. 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Res.* 13:241–248.
- Karickhoff, S.W., and K.R. Morris. 1985. Sorption dynamics of hydrophobic pollutants in sediment suspensions. *Environ. Toxicol. Chem.* 4:469–479.
- Lee, L.S., P.S.C. Rao, M.L. Brusseau, and R.A. Ogwada. 1988. Nonequilibrium sorption of organic contaminants during flow through columns of aquifer materials. *Environ. Toxicol. Chem.* 7:779–793.
- Leenheer, J.A., and J.L. Ahlrichs. 1971. A kinetic and equilibrium study of the adsorption of carbaryl and parathion upon soil organic matter surfaces. *Soil Sci. Soc. Am. Proc.* 35:700–704.
- Lytle, F.W., and R.B. Greeger. 1991. New developments in XAS experiments. p. 625–633. *In* S.S. Hasnain (ed.) *X-ray absorption fine structure*. Ellis Harwood, New York.
- Manceau, A. 1995. The mechanism of anion adsorption on iron oxides: Evidence of the bonding of arsenate tetrahedra on free Fe(O,OH)₆ edge. *Geochim. Cosmochim. Acta* 59:3647–3653.
- Maurice, P.A. 1998. Scanning probe microscopy of environmental surfaces. p. 109–153. *In* P.M. Huang et al. (ed.) *Structure and surface reactions of soil particles*. JohnWiley & Sons, New York.
- Maurice, P.A., M.F. Hochella, Jr., G.A. Parks, G. Sposito, and U. Schwertmann. 1995. Evolution of hematite surface microtopography upon dissolution by simple organic acids. *Clays Clay Miner.* 43(1):29–38.
- McCall, P.J., and G.L. Agin. 1985. Desorption kinetics of picloram as affected by residence time in the soil. *Environ. Toxicol. Chem.* 4:37–44.
- Miller, C.T., and J. Pedit. 1992. Use of a reactive surface-diffusion model to describe apparent sorption-desorption hysteresis and abiotic degradation of lindane in a subsurface material. *Environ. Sci. Technol.* 26(7):1417–1427.
- Nkedi-Kizza, P., J.W. Biggar, H.M. Selim, M. Th. van Genuchten, P.J. Wierenga, J.M. Davidson, and D.R. Nielsen. 1984. On the equivalence of two conceptual models for describing ion exchange during transport through an aggregated Oxisol. *Water Resour. Res.* 20:1123–1130.

- Onken, A.B., and R.L. Matheson. 1982. Dissolution rate of EDTA-extractable phosphate from soils. *Soil Sci. Soc. Am. J.* 46:276-279.
- Pavlostathis, S.G., and G.N. Mathavan. 1992. Desorption kinetics of selected volatile organic compounds from field contaminated soils. *Environ. Sci. Technol.* 26:532-538.
- Pedit, J.A., and C.T. Miller. 1995. Heterogenous sorption processes in subsurface systems: 2. Diffusion modeling approaches. *Environ. Sci. Technol.* 29(7):1766-1772.
- Pignatello, J.J., and L.Q. Huang. 1991. Sorptive reversibility of atrazine and metolachlor residues in field soil samples. *J. Environ. Qual.* 20:222-228.
- Pignatello, J.J., F.J. Ferrandino, and L.Q. Huang. 1993. Elution of aged and freshly added herbicides from a soil. *Environ. Sci. Technol.* 27:1563-1571.
- Schulze, D.G., and P.M. Bertsch. 1995. Synchrotron x-ray techniques in soil, plant, and environmental research. *Adv. Agron.* 55:1-66.
- Scribner, S.L., T.R. Benzing, S. Sun, and S.A. Boyd. 1992. Desorption and bioavailability of aged simazine residues in soil from a continuous corn field. *J. Environ. Qual.* 21:115-120.
- Sparks, D.L. 1989. *Kinetics of soil chemical processes.* Academic Press, San Diego, CA.
- Sparks, D.L. 1991. Chemical kinetics and mass transfer processes in soils and soil constituents. p. 585-637. *In* J. Bear and M.Y. Corapcioglu (ed.) *Transport processes in porous media.* Kluwer Academic Publ., Dordrecht, the Netherlands.
- Sparks, D.L. 1995. *Environmental soil chemistry.* Academic Press, San Diego, CA.
- Sparks, D.L., and P.M. Jardine. 1984. Comparison of kinetic equations to describe K-Ca exchange in pure and in mixed systems. *Soil Sci.* 138:115-122.
- Sparks, D.L., and D.L. Suarez (ed.). 1991. *Rates of soil chemical processes.* SSSA Spec. Publ. 27. SSSA, Madison, WI.
- Steinberg, S.M., J.J. Pignatello, and B.L. Sawhney. 1987. Persistence of 1,2 dibromoethane in soils: Entrapment in intra particle micropores. *Environ. Sci. Technol.* 21:1201-1208.
- Stipp, S.L.S., C.M. Eggleston, and B.S. Nielsen. 1994. Calcite surface structure observed at microtopographic and molecular scales with atomic force microscopy (AFM). *Geochim. Cosmochim. Acta* 58:3023-3033.
- van Genuchten, M.Th., and R.J. Wagenet. 1989. Two-site/two-region models for pesticide transport and degradation: Theoretical development and analytical solutions. *Soil Sci. Soc. Am. J.* 53:1303-1310.
- Waychunas, G.A., B.A. Rea, C.C. Fuller, and J.A. Davis. 1993. Surface chemistry of ferrihydrite: 1. EXAFS studies of the geometry of coprecipitated and adsorbed arsenate. *Geochim. Cosmochim. Acta* 57:2251-2269.
- Weber, W.J., Jr., and C.T. Miller. 1988. Modeling the sorption of hydrophobic contaminants by aquifer materials: 1. Rates and equilibria. *Water Res.* 22:457-464.
- Wu, S., and P.M. Gschwend. 1986. Sorption kinetics of hydrophobic organic compounds to natural sediments and soils. *Environ. Sci. Technol.* 20:717-725.