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Geoderma 100 (2001) 303–319

GEODERMA

www.elsevier.nl/locate/geoderma

Elucidating the fundamental chemistry of soils: past and recent achievements and future frontiers

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Received 18 December 2000; received in revised form 8 January 2001; accepted 10 January 2001

This paper is dedicated with immense respect and fondness to Professor Grant W. Thomas, who taught me my first course in soil chemistry, and inspired me to pursue research and teaching in this wonderful field. For this, I am forever grateful.

Abstract

Contributions in the field of soil chemistry have immensely benefited humankind, including enhanced agricultural production and the quality of our environment. This review focuses on research breakthroughs since the mid-1970s and delineates frontiers in soil chemistry for the upcoming decade. However, early contributions in ion exchange, sorption phenomena, and soil acidity are highlighted. Beginning in the 1970s, soil chemistry paradigms shifted from the chemistry of plant nutrient reactions/processes in soils to studies on environmental soil chemistry. The latter included research on: acid rain effects on soils and waters; trace metal/metalloid, environmentally important plant nutrient, radionuclide, and organic chemical reaction mechanisms and retention; speciation of soil contaminants using chemical extraction and molecular scale analytical techniques; facilitated colloid transport of metals and organic chemicals; humic substance structure; kinetics of soil chemical processes; redox transformations of contaminants in soils; modeling of soil chemical reactions; and soil remediation. Frontiers in soil chemistry over the next decade will undoubtedly involve the use of advanced in situ technologies in combination with interdisciplinary research efforts to unlock important information on: speciation of contaminants in soils; cycling of trace elements and nutrients and impacts on global climate change; development of models to accurately predict the rate, fate, and transport of contaminants in the subsurface environment; elucidation of mechanisms for microbial transformations of contaminants; unraveling the precise structure of soil organic matter; and enhanced understanding of rhizosphere chemistry. In summary, the future of soil chemistry is bright for the 21st century. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: History of soil chemistry; Frontiers in soil chemistry

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1. Highlights in soil chemistry from the beginning to the 1970s

Soil chemistry, as a subdiscipline of soil science, had its roots in the mid-1850s in the seminal studies on ion exchange by J. Thomas Way (Thomas, 1977). Following Way's remarkable findings, which for the most part have stood the test of time, a plethora of studies ensued over the next 80 years on binary exchange processes on soils and soil components. Research by Hissink and Gedroiz seemed to show that ion exchange was rapid, almost instantaneous (Thomas, 1977). We shall see later that this was not entirely correct for all sorbents and ions.

In the early 20th century, many attempts were made to derive an equilibrium constant for a binary exchange reaction (Kerr, Gapon, Vanselow). However, from a thermodynamic standpoint, it was Vanselow (1932) who correctly established that a true exchange equilibrium constant should express the activity on the solid phase as the product of the mole fraction and the adsorbed phase activity coefficient. In the early 1950s, two seminal papers appeared (Argersinger et al., 1950; Gaines and Thomas, 1953) that provided a theoretical framework for determining a thermodynamic exchange constant, K_{ex} , for a binary process. All of the aforementioned landmark research laid the groundwork for numerous studies throughout the world on ion exchange processes in soils (Sparks, 1995a,b) and truly established ion exchange as one of the hallmarks of soil chemistry. The reader is referred to a number of reviews and books dealing with ion exchange history and developments in soil chemistry (Kelley, 1948; Thomas, 1977; Sposito and Matigod, 1979; Sposito, 1981a,b, 2000; Sparks, 1995a,b).

Another significant leitmotif in soil chemistry in the 20th century was the merry-go-round on soil acidity (Jenny, 1961). Intense arguments ensued about whether H or Al was the cause of soil acidity and the reason for the suspension effect. As Thomas (1977) has so elegantly and eruditely stated, some of the giants of soil chemistry were caught up in the arguments. The landmark studies of N.T. Coleman and C.I. Rich clearly established that Al, both exchangeable, monomeric, and nonexchangeable, polymeric, was the major culprit in soil acidity. H. Jenny, P.F. Low, N.T. Coleman, C.E. Marshall, M. Peech, and others vociferously argued over the suspension effect, and in the end, most agreed that a junction potential, due to differences in ion mobility on soil particle surfaces, was the primary reason for the suspension effect. Studies on the chemistry of Al and soil acidity reached their zenith in the 1950s and 1960s. In the 1970s and 1980s, as concerns about acid rain escalated, fundamental experiments employing NMR spectroscopy and other analytical techniques and methods were conducted to explore the speciation of Al in solution and soils (Barnhisel and Bertsch, 1982).

Certainly, there were many other major thrusts in soil chemistry from the 1850s to the early 1970s including the pioneering studies of Hendricks et al. and Kelley et al. who found that clay minerals in soils were crystalline and were an important source of negative charge due to ionic substitution in the clay mineral structures. Thereafter, X-ray diffraction studies were carried out to identify clay minerals and to determine their structures. Jackson et al. developed many standard procedures for soil particle fractionation and separation and phyllosilicate identification. Studies ensued on the sorption of ions on soils and soil minerals by S. Mattson, A. Mehlich, R. Schofield and others, and fundamental studies were conducted on clay mineralogy (Jackson, 1956), soil salinity

(Richards, 1954), organic matter and humic substances (Schnitzer and Khan, 1978; Stevenson, 1982), and redox chemistry (Ponnamepruma, 1972).

However, it is fair to say that the primary impetus in soil chemistry over the first 120 years was to better understand the reactions and processes of plant nutrients in soils. I shall not expand more on the historical aspects of soil chemistry prior to the early to mid-1970s as these are covered in a number of reviews, one of which appeared in “*Geoderma*” (Schuffelen, 1974). Rather, the emphasis of my review will focus on the advances in soil chemistry since the 1970s and on future frontiers.

2. Soil chemistry research themes during the period 1975–2000

In the 1970s, major societal concerns centered around the environment, including air, soil, and water quality as impacted by greenhouse gases, trace metals, radionuclides, pesticides and other organic chemicals, and nutrients such as nitrogen. As a result, the emphasis in soil chemistry shifted to studies on environmental soil chemistry/geochemistry. Over the past 25 years, major studies have been conducted on: acid rain effects on soils and waters; effects of trace metals/metalloids in land applied sludge materials and from other sources on metal/metalloid retention/release in soils, plant uptake and bioavailability; speciation of contaminants in soils using chemical extractions and molecular scale techniques; nitrate and phosphate, organic chemical, and radionuclide fate/transport in surface and groundwater; facilitated colloid transport of metals and organic chemicals; elucidation of humic substances structure; residence time effects on contaminant sequestration; redox transformations and mechanisms of inorganic and organic contaminants in soils; development of surface complexation models, based on classical double layer theory, to describe metal and ligand sorption on soils and soil components; soil remediation using chemical and phytoremediation approaches and microbially mediated transformations of contaminants.

Prior to the 1970s, macroscopic, equilibrium phenomena were emphasized in soils. However, it became apparent that the rates of soil chemical processes ranged over time scales of milliseconds to years and beyond. Thus, the often concluded assumption that soil chemical reactions reached equilibrium on fairly rapid time scales started to be investigated and questioned. As a result of these studies, some of which will be discussed below, and intense concern about the fate of contaminants over time, kinetics of soil chemical processes has become a major research thrust in soil chemistry.

In the 1970s, and particularly the 1980s, advanced analytical techniques became available for the study of reactions at the soil mineral/water interface. Of particular importance was the advent of molecular scale *in situ* techniques in which soil chemical reactions can be monitored in aqueous environments. In fact, a new multidisciplinary field of soil and environmental sciences, which often employs the aforementioned techniques, has been created—i.e., molecular environmental science. Molecular environmental science can be defined as the study of the physical and chemical forms and distribution of contaminants in soils, sediments, waste materials, natural waters, and the atmosphere at the molecular level. Without question, the employment of *in situ* molecular scale techniques, along with macroscopic, equilibrium and kinetic studies has

created a revolution in soil and environmental sciences research. Along with rapid developments in analytical tools, soil chemistry research is becoming highly multi- and inter-disciplinary. Soil chemists are collaborating with chemists, physicists, biologists, geochemists, engineers, material scientists and marine scientists like never before. These interactions and the breathtaking advances and developments in analytical techniques, information technology, and biotechnology will forever change the field of soil chemistry.

In the remainder of this review, I want to focus on a few of the areas in soil chemistry where major activity and advances have occurred over the past 25 years. There have been several excellent special issues of “*Geoderma*” published in the last two decades on various aspects of soil chemistry, including ion transport in soils (Selim et al., 1986), physicochemical processes (Schweich and Sardin, 1989), environmental soil chemistry (Sparks, 1995a,b), applications of NMR spectroscopy in soil science (Hemminga and Buurman, 1987), contaminants in the soil environment (Naidu, 1998), and biochemistry of isotopes (Nordt et al., 1998) that the reader should consult. I would ask the reader to forgive me for omitting some areas, but space does not allow for definitive treatment of the field. At the end of the paper, I want to look into the future and offer my thoughts on soil chemistry in the 21st century.

3. Sorption processes and the advent of in situ molecular scale techniques

In the last 25 years, major advances have been made in modeling sorption reactions at the mineral/water interface and elucidating the kinetics and mechanisms of sorption/desorption phenomena in soils. In the past, soil chemists had employed classical adsorption models such as the Freundlich and Langmuir equations to describe an array of reactions on soils and soil components. While these models often describe experimental data quite well and can be useful in making comparisons about sorption behavior between soils, they provide no mechanistic information. Many investigators, based on parameters calculated from these equations, made conclusions about binding sites and strengths and types of sorption mechanisms (e.g., adsorption, precipitation).

However, in the 1970s and early 1980s, a number of investigators began to question whether the original assumptions of the Langmuir equation were valid for heterogeneous soil materials and the wisdom in making conclusions about sorption mechanisms (Harter and Baker, 1977; Veith and Sposito, 1977; Sposito, 1981b; Harter and Smith, 1981). In a landmark paper, Veith and Sposito (1977) showed that the Langmuir equation could equally well describe both adsorption (accumulation of a substance or material at an interface between the solid surface and the bathing solution) and precipitation (formation of three-dimensional products). Thus, one cannot differentiate between adsorption and other sorption processes, such as surface precipitation, using an “adsorption” isotherm and clearly mechanistic information cannot be derived from macroscopic models (Sposito, 1986; Scheidegger and Sparks, 1996).

To provide some molecular description to sorption processes at the soil mineral/water interface, a series of surface complexation models (SCM) were developed in the 1970s by Stumm and Schindler and their coworkers and others and included the constant

capacitance (Schindler and Gamsjager, 1972; Hohl and Stumm, 1976; Schindler et al., 1976; Stumm et al., 1976, 1980), and triple-layer (Davis and Leckie, 1978, 1980) models. Especially detailed reviews on the applications and theoretical aspects of other surface complexation models such as the Stern variable surface charge-variable surface potential (Bowden et al., 1977, 1980; Barrow et al., 1980, 1981), general two-layer model (Dzombak and Morel, 1990) and the one-pK and MUSIC models (Bolt and van Riemsdijk, 1982; Hiemstra et al., 1987) can be found in Davis and Kent (1990) and Goldberg (1992). Surface complexation models are chemical models that are based on molecular descriptions of the electric double layer model using equilibrium-based adsorption data (Goldberg, 1992). Differences in the SCM lie in the descriptions of the electrical double layer, i.e., in the definition and assignment of ions to the planes or layers of adsorption and in differences in the electrostatic equations and the relations between the surface potential and surface charge. They provide some information on the physical description of the electric double layer, including the capacitance and location of adsorbed ions, and they can describe data over a broad range of experimental conditions such as varying pH and ionic strength. Goldberg and Sposito (1984a,b) were among the first soil chemists to apply a SCM (i.e., constant capacitance model) to study the sorption of phosphate on goethite. Since that time, SCM have been widely used by soil chemists and other scientists to describe an array of chemical reactions including proton dissociation, metal cation and anion adsorption reactions on oxides, clay minerals, and soils, organic ligand adsorption on oxides, and competitive adsorption reactions on oxides. Many of these studies are described and alluded to by Goldberg (1992).

Surface complexation models have proved useful in soil chemical investigations, however, the limitations of the models must be appreciated. One of the major problems with many of the SCM is that multiple adjustable parameters are often used to fit the experimental data. Consequently, it may not be surprising that equilibrium data will fit a number of the models equally well as was beautifully illustrated by Westall and Hohl (1980). Additionally, as will be described later, it has been definitively shown that surface precipitation of metals can occur on soil minerals in addition to purely adsorption phenomena. Most of the SCM do not consider surface precipitation as a possible sorption mechanism. Some attempts have been made to include precipitation processes (Farley et al., 1985; Katz and Hayes, 1995a,b).

Over the past 15 years, major advances have occurred in elucidating sorption mechanisms at the mineral/water interface. Based on pioneering studies by Stumm and Schindler and their coworkers, it was assumed that major adsorption complexes were outer-sphere (a water molecule is present between the surface functional group and the bound ion or molecule) and inner-sphere (no water molecule is present between the ion or molecule and the surface functional group to which it is bound). However, until molecular scale studies were performed, conclusions about sorption mechanisms were purely speculative. With the advent of *in situ* molecular scale techniques such as Fourier-transform infrared (FTIR), nuclear magnetic resonance (NMR), and X-ray absorption (XAS) spectroscopies and scanning probe microscopy (SPM), definitive information on sorption products and mechanisms have been gleaned.

XAS requires intense X-rays that are generated by electrons/positrons that circulate in a storage ring of a synchrotron facility at energies of 1 to 6 GeV in paths curved by a

magnetic field (Fendorf et al., 1994a,b; Schulze and Bertsch, 1995; Scheidegger and Sparks, 1996). XAS has been one of the most widely used molecular scale techniques employed by soil chemists to ascertain information at the mineral/water interface such as oxidation state, number and type of near neighbors, coordination state, and bond distances. This information can be determined at low concentration levels (depending on element and matrix as low as 0.03% to 0.05% per weight). XAS can be used to probe most types of phases (crystalline or amorphous solids, liquids, and gases) and at structural sites ranging from those in crystals and glasses to those at interfaces such as the mineral/water interface. With second- and third-generation synchrotron light sources that provide X-ray energies ranging from the infrared to the hard X-ray regions, higher flux and higher brightness, beamline optics that produce microfocused beams for spectromicroscopy and imaging studies, and state-of-the-art X-ray detectors, important advances in soil chemistry will surely occur over the next decade.

Perhaps the first application of XAS to study sorption mechanisms of ions on natural surfaces was the research of Hayes et al. (1987) who studied selenate and selenite adsorption on goethite. They showed that selenate was adsorbed as an outer-sphere complex and selenite was adsorbed as an inner-sphere complex. These findings were later questioned by Manceau and Charlet (1994), who found that selenate ions form binuclear bidentate surface complexes on goethite. However, as others have recently shown, the type of sorption mechanism for a particular ion is greatly affected by environmental factors such as ionic strength and pH (Hug, 1997; Peak et al., 1999; Strawn and Sparks, 1999). Numerous studies have appeared in the soil and geochemistry literature over the past 10 years employing XAS and other *in situ* spectroscopic techniques to elucidate metal/metalloid adsorption complexation mechanisms at the soil mineral/water interface. Many of the XAS studies are reported in Scheidegger and Sparks (1996).

Recently, a number of soil chemists and geochemists have shown that sorption of metals such as Co, Cr, Mn, Ni, and Zn on soil components and soils results in the formation of metal hydroxide precipitate phases (Chisholm-Brause et al., 1990a,b; Charlet and Manceau, 1992; Fendorf et al., 1994a,b; O'Day et al., 1994a,b; Scheidegger et al., 1997,1998; Towle et al., 1997; Roberts et al., 1999; Thompson et al., 1999; Ford and Sparks, 2000). In the case of Al-bearing soil mineral sorbents, the precipitates are metal-Al hydroxides (hydrotalcite type, layered double hydroxide [LDH] structure) while with non-Al bearing soil minerals, the precipitate phases are metal hydroxides (Scheinost et al., 1999). The surface precipitates occur at metal loadings far below a theoretical monolayer coverage, in a pH-range well below the pH where the formation of metal hydroxide precipitates would be expected according to the thermodynamic solubility product, and at time scales as fast as 15 min (Scheidegger and Sparks, 1996; Scheidegger et al., 1998). Using XAS, in combination with diffuse reflectance spectroscopy (DRS) and high resolution thermogravimetric analysis (HRTGA), Ford et al. (1999) found that mixed Ni–Al (LDH) precipitates transform over time to a precursor Ni–Al phyllosilicate phase, which greatly enhances the stability of the metal. For example, Scheckel and Sparks (2001) investigated Ni sorption on several phyllosilicates, gibbsite, amorphous silica, and a mixture of gibbsite and amorphous silica for residence times of 1 h to 2 years and subsequent Ni release using an array of dissolution agents. As

residence time increased from 1 h to 2 years, the amount of Ni released from the precipitates decreased from 98% to 0% indicating an increase in stability with aging time regardless of sorbent and dissolution agent. This enhanced stability is due to a combination of substitution of Al for Ni in the octahedral layers of the LDH, takovite-like precipitate phase in the case of Al-bearing sorbents, Si incorporation into the interlayers of the precipitates due to weathering of the sorbent, and perhaps Ostwald ripening (Ford et al. 1999; Scheckel et al., 2000). The formation of metal hydroxide precipitates could be an important mechanism for sequestering metals in soil and water environments such that they are less mobile and bioavailable. It is also apparent that to accurately model metal retention/release in soil environments, one must employ sorption models that can describe both adsorption and precipitation phenomena.

4. Kinetics of soil chemical processes

During the late 1970s, and particularly in the 1980s, soil chemists increasingly realized that while the study of equilibrium processes and reactions in soils were important, that most field reactions were seldom at equilibrium. It became apparent that one needed to understand the rates of soil chemical processes to accurately predict the fate/transport of ions and organic compounds in soil and water environments, including the development of predictive models.

Perhaps there are two reasons why equilibrium approaches dominated soil chemistry for so long. J. Thomas Way had conducted some kinetic studies during his classic ion exchange research and concluded that the rate of exchange was almost instantaneous. This was later verified by Hissink and Gedroiz. However, Kelley (1948), in his beautiful book, *Cation Exchange in Soils*, had clearly raised the point that perhaps ion exchange and sorption processes would not be so rapid on soil minerals like mica and vermiculite where ion diffusion could occur, resulting in slow reaction rates. However, few soil chemists appeared to have paid attention to Kelley's perceptive observations.

It was left to the classic study of Boyd et al. (1947) and later the seminal studies of Helfferich (1962) and coworkers who demonstrated that diffusion was the rate-limiting process for ion exchange. Later, Scott and Reed (1962), Scott and Smith (1966, 1967), Mortland (1958) and Mortland and Ellis (1959) clearly showed that K release from soil minerals was diffusion-controlled. I recall quite vividly that during my PhD research, a number of scientists questioned my findings that K sorption on soils was quite slow, which I attributed to interparticle diffusion into micropores of soil clay minerals. With time, my results were accepted, and many other soil chemists began to study the kinetics of soil chemical reactions.

Another major impediment in promotion of kinetics as a major area in soil chemistry was the complexity of the topic, particularly as kinetics is applied to heterogeneous soil systems, and the lack of good methods to measure both rapid and slow soil chemical reactions. Over the past two decades, soil chemists have developed and employed an array of batch and flow methods to measure reactions over time scales of minutes and longer, and have used chemical relaxation methods, such as pressure-jump and concentration-jump, to study reaction rates on millisecond time scales. These methods are

discussed in a number of books and reviews (Sparks, 1989; Amacher, 1991; Sparks and Zhang, 1991; Sparks et al., 1996). Without question, in the last two decades, kinetics has become a major theme in soil chemistry. There is no space to discuss all the significant contributions that soil chemists have made in the area of kinetics; however, the reader can consult a number of references authored by soil chemists (Sparks, 1989, 1999, 2000; Sparks and Suarez, 1991; Sposito, 1994). I want to highlight a very few studies on kinetics in the following discussion.

We now know that the time scales for soil chemical reactions range from milliseconds to years. Certainly, the chemical exchange reaction occurs almost instantaneously and cannot be measured using batch and flow techniques. Often, the majority of ion or organic chemical sorption occurs over a time scale of a few hours. This can be attributed to chemical reaction rates, surface precipitation, and diffusion processes such as film and macropore diffusion (Sparks, 1999). However, we know that there are many slow processes in soils that are usually ascribed to interparticle (pore) and intraparticle diffusion (within the soil particles). Thus, clearly there is a residence time effect, i.e., the longer the contact time between the sorbent and the sorptive, the greater the sorbate uptake. This can be one of the causes for the frequently reported observation that the forward and backward rate processes are not the same.

One of the first reports in the soil science literature on the effect of residence time with metals was that of McKenzie (1967). He observed that manganese nodules present in Australian soils accumulated a large quantity of Co. McKenzie (1967) speculated that this was due to a continuous sorption reaction. To test this hypothesis, he determined both sorption and desorption kinetics of Co on manganese nodules isolated from soils. He showed that uptake of Co from solution slowed dramatically after two days, but the degree of desorption decreased greatly with increasing residence times. Bruemmer et al. (1988) found that over a period of 2 h to 42 days, Ni sorption increased from 12% to 70% of total sorption, and total increases in Zn and Cd sorption over this time period increased 33% and 21%, respectively. The slow kinetics were attributed to diffusion-controlled reactions on external and internal surface sites. Other work by Barrow (1986, 1998) and Barrow et al. (1989) also investigated the effect of residence time and temperature on metal uptake/release and concluded that diffusion processes were most important in effecting a residence time effect and slow rate processes in soils. Ainsworth et al. (1994) studied the sorption of Co, Cd, and Pb on hydrous ferric oxide as a function of oxide aging and metal-oxide residence time. Oxide aging did not cause hysteresis of metal cation sorption/desorption. Aging the oxide with the metal cations resulted in hysteresis with Cd and Co, but little hysteresis with Pb. With Pb, there was slight hysteresis over a 21-week aging process between pH 3 and 5.5. At pH 2.5, Pb desorption was complete within a 16-h desorption period and was not affected by aging time. However, with Cd and Co, extensive hysteresis was observed over a 16-week aging period, and the hysteresis increased with aging time. After 16 weeks of aging, 20% of the Cd and 53% of the Co was not desorbed, and hysteresis was even observed at pH 2.5. Ainsworth et al. (1994) attributed the hysteresis to Co and Cd incorporation into a recrystallizing solid via isomorphic substitution and not to micropore diffusion.

Another reason for the marked residence time effect that is observed with metals such as Co, Mn, Ni, and Zn is the formation of surface precipitates on soil mineral surfaces.

These precipitates have been shown to occur at pHs > 6.8 and at higher metal loading levels (Roberts et al., 1999). While the kinetics of surface precipitate formation can be quite rapid (Scheidegger et al., 1998), once the precipitates form, sequestration of the metal is enhanced as residence time increases (Ford et al., 1999; Scheckel et al., 2000). It appears that such precipitates do not occur as readily with metals such as Pb, which is related to the larger hydrated radius of Pb relative to Co, Mn, Ni, and Zn, which are smaller and similar in size to ions like Al that occur in mineral structures. Scheidegger et al. (1997, 1998) have theorized that ions such as Co, Mn, Ni, and Zn substitute for Al in mineral structures by promoting dissolution of the Al. This reaction drives the formation of mixed metal-Al precipitates that greatly enhance the sequestration of the metal with increasing residence time.

In soils, organic matter also seems to greatly affect residence time effects with metals. For example, Strawn et al. (1998), employing macroscopic kinetics and molecular scale XAS, did not observe an effect of residence time on the type of Pb surface complex (bidentate, inner-sphere complex) on γ -AlO₂ or significant hysteresis after a 48-h sorption residence time. However, when soils were investigated, increased residence time caused increased Pb sorption and marked hysteresis occurred (Strawn and Sparks, 2000). The hysteresis in the soils was ascribed to diffusion of Pb into soil organic matter void spaces that have been described by Schulten and Schnitzer (1993) and Schnitzer and Schulten (1995).

The kinetics of organic chemical sorption is also characterized by a rapid, often reversible stage, followed by a much slower, nonreversible stage (Karickhoff et al., 1979). The rapid phase has been ascribed to retention of the organic chemical in a labile form that is easily desorbed and bioavailable. The much slower reaction is thought to involve the entrapment of the organic chemical in a nonlabile form, primarily in micropores and void spaces of humic materials, that is difficult to desorb and not readily bioavailable (Steinberg et al., 1987; Ball and Roberts, 1991; Pignatello and Huang, 1991; Scribner et al., 1992). Steinberg et al. (1987) were the first to show, that similarly to metals, that residence time had a marked effect on organic chemical release from soils. Comparing laboratory and field-contaminated soils, they found that little EDB in field-contaminated soils was released, while considerably more EDB was released from laboratory-contaminated soils. This was ascribed to diffusion processes. An especially good review on the kinetics of organic chemical reactions in soils is that of Pignatello (2000).

The kinetics of soil mineral weathering and redox reactions were also investigated by a number of soil chemists in the past two decades. The former studies are discussed in a number of reviews (Bloom and Nater, 1991; Sparks, 2000). I will highlight some of the kinetic studies dealing with redox reactions.

In soils, Mn-oxides are extremely important in effecting oxidation of both inorganic and organic species, as was shown in the classic study of Bartlett and James (1979). They showed that Cr(III) could be oxidized to Cr(VI) by Mn(III/IV) oxides. Subsequently, a number of studies were conducted by soil chemists on the oxidation kinetics of As, Cr, and Pu by Mn(III/IV) oxides and whole soils (Amacher and Baker, 1982; Oscarson et al., 1980, 1983; Fendorf and Zamoski, 1992). Fendorf and Zamoski (1992) found that Cr(III) oxidation on γ -MnO₂ was more rapid at pH 5 than 3 with overall

production of Cr(VI) being greater at pH 3 at a Cr(III) concentration of 770 μM . The rate and extent of Cr(III) oxidation was affected by a number of factors including formation of surface precipitates at higher pHs and Cr(III) concentrations that effectively inhibited oxidation (Fendorf et al., 1992). Oscarson et al. (1980) studied the oxidation of As(III) to As(V) in sediments from five lakes in Saskatchewan, Canada. Oxidation of As(III) to As(V) occurred within 48 h. In general, > 90% of the added As was sorbed on the sediments within 72 h. For general reviews on chemistry of redox reactions and processes in soils, the reader can consult some excellent reviews published in the last 25 years (Huang, 1991; Bartlett and James, 1993; James and Bartlett, 2000).

Ideally, one should couple macroscopic, kinetic studies with molecular scale studies. In recent years, a number of papers, authored by soil chemists, have appeared employing this multi-scale approach (e.g., Hunter and Bertsch, 1994; Fendorf et al., 1997; Grossl et al., 1997; Scheidegger et al., 1998; Strawn et al., 1998; Ford et al., 1999; Roberts et al., 1999; Scheckel et al., 2000).

5. New frontiers

In the remaining section of this review, I want to focus on what I believe are some of the future frontiers in our field. In my view, the combination of advanced technologies and interdisciplinary research will dominate our field and lead to major discoveries and even greater respect and recognition. Molecular-scale investigations have and will open new frontiers in soil chemistry. These include: speciation of contaminants, providing useful information on release mechanisms, spatial distribution, chemical transformations, toxicity, bioavailability, remediation strategies, and ultimate impact on human health; cycling of trace elements and nutrients such as C, N, and S and impacts on global climate change; development of models that will accurately predict the rate, fate, and transport of contaminants in the subsurface environment; elucidation of mechanisms for microbial transformations of contaminants; unraveling the precise structure of soil organic matter; and understanding the chemistry of the rhizosphere.

5.1. *Speciation of metals / oxyanions*

As noted earlier, major advances have occurred over the past 15 years in definitively identifying the type of ion surface product, i.e., outer-sphere and inner-sphere complexes and surface precipitates that form on an array of model soil minerals, combining macroscopic and novel in situ molecular scale techniques, particularly XAS.

Standard (bulk) XAS techniques probe an area of several square millimeters. However, the most reactive sites in soils have particle sizes in the micrometer range and metal speciation may vary over regions of a few 100 μm^2 . With the advent of third generation synchrotron radiation facilities, which afford enhanced spatial resolution (< 5 μm) and sensitivity, one can speciate metals in soils at the micro-scale. This has been recently accomplished in the research of Manceau et al. (2000) and in my own group (Roberts et al., 2001). In the latter study, Zn and other metals were mapped (micro X-ray fluorescence spectroscopy, $\mu\text{-XRF}$) and speciated (micro X-ray absorption near

edge structure, μ -XANES) in a contaminated topsoil collected around the Palmerton, PA, USA smelting facility. Zn concentrations were several thousand parts per million in the surface horizon. In the surface horizon, Zn was present as Zn-sulfide (sphalerite) and Zn ferrite mineral phases (ZnFe_2O_4). In the subsurface soil, Zn was predominately sorbed to Fe and Mn oxides, with little secondary precipitate formation.

5.2. Soil organic matter structure

With the development of in situ X-ray spectromicroscopy, other state-of-the-art analytical techniques and employment of computational chemistry (Schulten and Schnitzer, 1993; Schnitzer and Schulten, 1995) major advances will continue to occur in unraveling the structure of soil organic matter and the interaction mechanisms of humic substances with soil minerals and inorganic and organic species. The structure of organic matter has been an enigmatic area that has baffled soil chemists/biochemists since the inception of our discipline (Schnitzer, 2000).

Using macroscopic solution factors such as viscosity and vapor pressure osmometry, researchers predicted that humic substances (HS) coil at low pHs and high ionic strengths while forming linear strands at high pH and low ionic strengths (Ghosh and Schnitzer, 1980). Recent studies on soil and fluvial humic substances using X-ray microscopy do indeed show that pH and ionic strength of the solutions change the micro-molecular structure (size and shape) of humic substances. For example, fulvic acid unwinds and disperses as the two solution parameters increase. Additionally, different types of structural shapes are possible at the same solution conditions, and the major factor controlling the behavior is the concentration of the humic substances (Myneni et al., 1999). The macromolecular structural changes of HS can significantly affect contaminant solubility, biotransformation, and C cycling in soils and sediments.

Soft X-ray spectromicroscopy has recently been used to image and speciate C in the colloidal fractions of soils (Scheinost, unpublished data; Nachttegaal, unpublished data). Soft X-ray spectromicroscopy uses X-rays with an energy of 100–1000 eV, or a wavelength of about 1–10 nm. The wavelength is much lower than that of visible light, providing enhanced spatial resolution (up to 3 nm) imaging. The photon energy is well matched to inner-shell electron energies of low-Z elements. By operating between the K edges of C and O, one can contrast between organic matter and water. Additionally, one can study the morphology of HS in situ, without the need to apply high vacuum.

5.3. Other frontiers

There are a number of other new frontiers on the soil chemistry horizon. With the advent of in situ soft X-ray spectromicroscopy, we will be able to obtain unique information on many important low atomic number elements, such as Al, B, C, Cl, Mg, N, Na, P, and S, that are important both agriculturally and environmentally. Such studies will yield significant information on nutrient cycling in soils, which affects global climate change, nutrient uptake by plants, and remediation of degraded land. The precise speciation of Al in soils could be gleaned, an enigma that has perplexed soil chemists since the early part of the 20th century. Such information would address important questions concerning soil acidity and its effects on plant life.

Boron, a critical element for plants and animals, is a toxicant at elevated concentrations, with a narrow range between deficiency and toxicity. The speciation of B on mineral and organic component surfaces in soils is poorly understood. Using elemental mapping at small spatial scales, and spectromicroscopy and microdiffraction coupled with FTIR and pressure-jump relaxation kinetics, one could understand B speciation over a range of environmental conditions. Such information would be invaluable in developing strategies for reducing or managing hazards related to high B concentrations (Bertsch and Sayers, 1998).

The uptake and biochemical transformations of trace elements by plants are important in the production of food and fiber and in soil remediation. One area that will continue to be of great interest to soil and environmental scientists is the study of phytoremediation processes in hyperaccumulating plants. These plants may transform a toxic species into a less toxic form or produce a volatile species of the toxic element. However, we do not understand the chemical composition of metal binding sites within the plant materials. The speciation of the trace elements within the plants and the chemical structure of metal binding proteins is needed. These are areas where soil chemists, biochemists, and plant physiologists can work closely with plant molecular biologists to produce better metal accumulating plants, enhancing remediation efforts (Tonner and Traina, 1998).

Other soil chemical–biological research areas that will be prominent in the future include: effects and mechanisms of microbial–mineral interactions; microbially mediated redox reactions; effect of biofilms on soil minerals; metal and oxyanion speciation and retention; the role of biogenically derived minerals on contaminant transport and solubility; and redox transformations of C, N, P, and S over different redox boundaries. The latter could yield information on abiotic and biotic processes.

5.4. Need for multidisciplinary, interdisciplinary and multifaceted approaches

The future of soil chemistry is exceedingly bright. However, to successfully address and fund the major research needs that have been alluded to, and others that were not mentioned, multidisciplinary and interdisciplinary and multifaceted approaches must be carried out. Soil chemists must and will increasingly collaborate with other soil scientists, and with geochemists, chemists, biologists, engineers, and material and marine scientists. I predict that one of the major leitmotifs of soil chemistry in the 21st century will be the study of biological effects on soil chemical reactions and processes. This provides soil chemists a unique opportunity to combine their expertise with that of molecular biologists. We must also employ an array of multiple, molecular scale techniques in combination with macroscopic approaches and computational modeling to solve complex soil chemical questions.

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