Grand challenges and opportunities in basic soil science research and the discipline of soil science

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Abstract

Contributions in basic soil science research have immensely benefited humankind, including enhanced agricultural production and the quality of our environment. This review focuses on recent breakthroughs in the fields of soil properties and processes and delineates frontiers for the present decade and beyond. Frontiers will undoubtedly involve multiple spatial and temporal scale investigations, elucidation of reactions at biological, chemical, and physical interfaces, and 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 field scale hydrologic and geochemical 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 various environmental settings.

The critical zone

Soil is part of the critical zone, "the heterogeneous, near surface environment in which complex interactions involving rock, soil, water, air and living organisms regulate the natural habitat and determine the availability of life sustaining resources" (NRC 2001). The critical zone is an interfacial region of mass and energy flux comprising terrestrial, lacustrine, and marine components of the continental crust and is one of two primary loci of life on Earth and for most of human activity.

The other major locus of life is the sun (NRC 2001). The critical zone is comprised of an array of spatial scales, ranging from the atomic to the global and temporal scales, ranging from seconds to eons. The physical, chemical, and biological processes within the critical zone mediate exchange of mass and energy which is required for biomass productivity, chemical recycling, and water storage. The critical zone is the most heterogeneous and abstruse portion of the entire Earth (NRC 2001). However, we must understand the physical, chemical, and biological processes and reactions in the critical zone over a range of spatial and temporal scales if we are going to sustain the planet for human habitation (NRC 2001; Hochella, 2002; Sparks 2004).

Molecular environmental soil science

The research challenges and questions we face in soil science occur over multiple scales (Fig. 1) and at physical, chemical, and biological interfaces where complex reactions occur involving inorganic and organic and microbial components of the soil. While we ultimately want to make accurate predictions at the field/landscape scale, fundamental mechanistic information at smaller scales, i.e., microscopic, molecular, and atomistic is required. Presently, one of the frontiers in the geosciences is the study of nanophases (Hochella 2002) which involves materials between one nanometer and 100 nm. The origins of nanoscience can be traced to clay mineralogy and crystallography (Lower *et al.* 2001) when it was discovered that clay minerals were crystalline and of micrometer size. Nanoparticles occur in weathering, soil forming, and surface and ground water environments. The properties of nanosized materials can behave quite differently than larger sized particles which is related to the notion of scaling first proposed by the quantum physicist, Richard Feynmann who noted that "all things do not simply scale down in proportion" (Hochella 2002). Small scale investigations, combined with macroscopic measurements, provides the level of chemical, biological, and physical detail to comprehend contaminant reactivity and bioavailability over a range of environmental conditions. This information then needs to be integrated into field scale hydrologic and geochemical models (O'Day 1999).

With the advent of state-of-the-art analytical techniques, some of which are synchrotron-based (see discussions that follow), one can elucidate reaction mechanisms at small scale. This has been one of the major advances in the soil and environmental sciences over the past decade. Undoubtedly, the molecular characterization of microenvironments and interfacial reactions will become increasingly significant in understanding the interactions between chemistry, physics, and biology in soil environments. The use of small scale techniques in environmental research has resulted in a new multidisciplinary field of study that soil scientists are actively involved in – molecular environmental science. Molecular environmental science can be defined as the study of the chemical and physical forms and distribution of contaminants in soils, sediments, waste materials, natural waters, and the atmosphere at the molecular level (Sparks 2002, 2004).

There are a number of areas in soil science where the application of molecular environmental science is resulting in major frontiers. These include: speciation of contaminants which is essential for understanding release mechanisms, spatial resolution, chemical transformations, toxicity, bioavailability, and ultimate impacts on human health; mechanisms of microbial transformations; development of predictive models; effective remediation and waste management strategies; and risk assessment. The application of molecular environmental science will be illustrated throughout the remainder of this paper.



Figure 1. Illustration of the various spatial scales that soil scientists are interested in. (Bertsch and Hunter 1998).

Electromagnetic spectrum of light

The use of intense light to understand mechanisms of soil chemical reactions and processes has revolutionized the fields of soil science and the geosciences. The electromagnetic spectrum of light is shown in Fig. 2. Electromagnetic radiation has both particle and wave properties such that light at a particular wavelength correspond to a particular scale of detection (O'Day 1999). For example, longer wave radiation detects bigger objects while shorter wave radiation detects smaller objects. Light employed to see an object must have a wavelength similar to the object's size. Light has wavelengths longer or shorter than visible light. On the longer side are radio waves, microwaves, and infrared radiation. Shorter wavelength light includes ultraviolet, x-rays and gamma rays. The shorter the wavelength, the higher the frequency and the more energetic or intense is the light. Light generated at shorter wavelengths such as x-rays is not visible by the human eye and must be detected via special means (Sparks 2002).



Figure 2. Electromagnetic spectrum of light covering a wide range of wavelengths and photon energies. From advanced light source (Lawrence Berkeley Laboratory 2002).

Each region of the spectrum is characterized by a range of wavelengths and photon energies that will determine the degree to which light will penetrate and interact with matter. At wavelengths from 10⁻⁷ to 10⁻¹⁰ m, one can explore the atomic structure of solids, molecules, and biological structures. Atoms, molecules, proteins, chemical bond lengths and minimum distances between atomic planes in crystals fall within this wavelength range and can be detected. The binding energies of many electrons in atoms, molecules, and biological systems fall in the range of photon energies between 10-10,000 eV. When absorbed by an atom, a photon causes an electron to separate from the atom or can cause the release or emission of other photons. By detecting and analyzing such e⁻ or photon emissions, scientists can better understand the properties of a sample (Sparks 2002).

Synchrotron radiation

Intense light can be produced at a synchrotron facility. Synchrotron radiation is produced over a wide range of energies from the infrared region with energies < 1 eV, to the hard x-ray region with energies of 100 k eV or more. There are a number of synchrotron facilities throughout the world.

Synchrotrons are large machines (Fig. 3). In the synchrotron, charged particles either e⁻ or positrons, are injected into a ring-shaped vacuum chamber maintained at an ultra-high vacuum ($\sim 10^{-9}$ Torr). The particles enter the ring by way of an injection magnet and then travel around the ring at or near the speed of light, steered by bending magnets. Additional magnets focus and shape the particle beam as it travels around the ring. Synchrotron radiation or light is emitted when the charged particles go through the bending magnets, or through insertion devices which are additional magnetic devices called wigglers or undulators, which are inserted into straight sections of the ring. Beamlines allow the x-rays to enter experimental stations which are shielded rooms that contain instrumentation for conducting experiments (Schulze and Bertsch 1999; Sparks 2002).



Figure 3. Schematic diagram of a synchrotron x-ray source. Schulze and Bertsch 1999.

X-ray absorption spectroscopy

One of the most widely used synchrotron-based spectroscopic techniques is x-ray absorption spectroscopy (XAS). Its use has and will continue to revolutionize our understanding of important soil properties and processes. XAS can be used to study most elements in crystalline or non-crystalline solid, liquid or gaseous states over a concentration range of a few mg L⁻¹ to the pure element. XAS can be used to probe 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 science will surely occur over the next decade (Sparks 2002, 2004).

XAS is also an in-situ technique, which means that one can study reactions in the presence of water. This is a major advantage over many molecular scale techniques, which are ex-situ, often requiring drying of the sample material, placing it in an ultra-high vacuum (UHV), heating the sample or employing particle bombardment. Such conditions can alter the sample, creating artifacts, and do not simulate most natural soil conditions. It is important to study soil reactions in water as it is the principal medium of transport of inorganic and organic species and biochemical reactions take place in aqueous media and across biological membranes that are water-based (O'Day 1999; Sparks 2002, 2004).

XAS is an element specific, bulk method that yields information about the local structural and compositional environment of an absorbing atom. It "sees" only the 2 or 3 closest shells of neighbors around an absorbing atom (0.6nm) due to the short electron mean free path in most substances. Using XAS one can ascertain important soil chemical information such as the oxidation state, information on next nearest neighbors, bond distances (accurate to \pm 0.002nm), and coordination numbers (accurate to \pm 15-20%) (Brown *et al.* 1995).

An XAS experiment which results in a spectrum (Fig. 4), consists of exposing a sample to an incident monochromatic beam of synchrotron x-rays, which is scanned over a range of energies below and above the absorption edge (K, L, M) of the element of interest. When x-rays interact with matter a number of processes can occur: x-ray scattering production of optical photons, production of photoelectrons and Auger electrons, production of fluorescence X-ray photons, and position-electron pair production (Sparks 2002).

The energy region extending from just above to about 50 eV above the absorption edge is the XANES (x-ray absorption near edge structure) portion of the spectrum (Fig. 4). Fingerprint information, such as oxidation states, can be gleaned from this portion of the XAS spectrum. The energy region from 50 to 1,000 eV above the absorption edge is the EXAFS (extended x-ray absorption fine structure) portion (Fig. 4) of the spectrum (Brown *et al.* 1995). Analyses of the EXAFS spectrum provides information on bond distances, coordination number, and next nearest neighbors (Sparks 2002). More detail on XAS methodology, sample preparation, and data analyses can be found in a number of excellent sources (Brown 1990; Brown *et al.* 1995; Fendorf and Sparks 1996; Bertsch and Hunter 1998; Fendorf 1999; O'Day 1999; Schulze and Bertsch 1999; Brown and Sturchio 2002; Sparks 2002).





Sorption processes and in situ molecular scale techniques

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 XAS spectroscopies, definitive information on sorption products and mechanisms have been gleaned. Many of these XAS studies are reported in several reviews and books (Brown and Parks 2001, Brown and Sturchio 2002; Sparks 2002). From these studies one can conclude that sorption of alkali and alkaline earth elements primarily occurs via outer-sphere complexes while for most other cations and anions, such as most heavy metals and oxyanions (exceptions being sulfate and selenate in some cases), inner-sphere sorption complexes result. However, bulk XAFS analyses provides only the average local chemical environment, meaning that while a particular surface complex, e.g., inner-sphere complex, may predominate, this does not mean that outer-sphere complexes are not present. In fact, recent studies have clearly shown that as environmental factors change, e.g., pH, ionic strength, and time, the predominate surface complex/product can change (Peak et al. 1999; Strawn and Sparks 1999).

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 (Scheidegger et. al. 1997, 1998; 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 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. 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 since sorption is often a continuum. At low sorption densities, mononuclear, monodentate and bidentate inner-sphere complexes occur and at higher sorption densities, multinuclear clusters and surface precipitates can form (Sparks 2002, 2004).

New frontiers

In the remaining section of this review, I want to focus on what I believe are some of the future research frontiers in soil science, with emphasis on soil properties and processes. 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 science. These include: speciation of contaminants in soils and other heterogeneous systems; 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 on soil components; unraveling the precise structure of soil organic matter; and understanding plant/soil interfacial reactions that are important in rhizosphere chemistry and soil remediation. For the purposes of this paper, I want to focus on metal speciation in contaminated soils, and mineral/microbial and plant/soil interfacial reactions.

Speciation of metals in soils

Standard XAS techniques probe an area of several square mm. However, the most reactive sites in soils have particle sizes in the micrometer range and metal speciation may vary over regions of a few $100 \,\mu m^2$. Therefore, the derived structural information may be only an average of several contaminant species. With the advent of third generation synchrotron radiation facilities, which afford enhanced spatial resolution (<5 µm) and sensitivity, one can speciate metals in soils using micro-XAS and determine elemental distributions and associations using micro-X-ray fluorescence (micro-XRF) spectroscopy. An example of the use of these techniques is shown in Fig. 5 from the research of Nachtegaal et al. (2004). They investigated the speciation, distribution, and association of Zn and their relation to mobility and bioavailability of Zn in a nonremediated and a remediated smelter contaminated soil from Belgium. Overall, the researchers found that there were no significant differences in Zn speciation between samples of the two soils. Thirty percent of Zn was in smelter related minerals, mainly willemite, 10% of Zn was chemisorbed to Fe- and Mn-oxides, and 60% of Zn was incorporated into newly formed mixed Zn-Al layered double hydroxides (LDH) in the nonremediated and a Zn-phyllosilicate in the remediated soil. Macroscopic desorption and biosensor studies were conducted on the soils to assess bioavailability of Zn. At the pH of the soils (6.4-6.7), these studies showed that the presence of the LDH phases greatly diminished the bioavailability of Zn in the soils. Desorption of Zn, and consequently bioavailability, was enhanced at lower pHs. The results of this investigation indicate that at higher pHs the formation of (mixed) metal hydroxide precipitates could be an important means of sequestering toxic metals such as Zn, as well as Co and Ni, in the soil environment.



Figure 5. a) micro-XRF tricolor maps showing the distribution of Zn, Fe, and Cu in a remediated soil from Belgium. The numbers indicate the spots where micro-EXAFS spectra were collected to determine the direct speciation of Zn in the soil. Red is indicative of the distribution of Fe, green of copper, and blue of Zn b) micro-EXAFS spectra from selected spots on the thin sections of the remediated soil. The solid line indicates the raw chi data and the dotted line indicates the best fits obtained with a linear fitting approach. Percentages of the various Zn species at each spot were determined through principal component (PCA) and linear combination fitting (LCF) analyses. (Nachtegaal *et al.* 2004).

Plant/soil interfacial reactions

Better understanding plant/soil interfacial reaction mechanisms could significantly advance efforts to enhance environmental sustainability and quality. 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 possible relations to rhizosphere speciation and biochemistry, and the chemical structure of metal binding synchrotron based techniques, and plant physiologists can work closely with plant molecular biologists, who are employing state-of-the-art genomic, proteomic, and bioinformatic approaches, to produce better metal accumulating plants, enhancing remediation efforts (Tonner and Traina 1998). Such collaborations can also advance our understanding of biogeochemical interactions and cycling among organisms, ecosystems, and the environment (Sparks 2004).

With the advent of micro-XAS and XRF techniques, and the use of synchrotron microtomography techniques, which provides three dimensional information, we can gain precise information on elemental distribution and speciation in plants. An example of this is shown in Fig. 6, illustrating the distribution of Ni, Mn, and Ca in the leaf of a Ni hyperaccumulator, *"Alyssum murale"*.



Figure 6. Synchrotron micro-XRF (SXRF) images of a leaf edge from the Ni hyperaccumulator *Alyssum murale* showing the distribution of a) Ni (red) throughout the leaf with b) discrete regions of Mn (blue) enrichment at the base of c) the calcium (green) rich trichome. Elemental maps are superimposed resulting in a metal correlation relative to that depicted in the color correlation triangle. Plants were grown in loam soils collected form an area adjacent to a Nickel refinery in Port Colborne, Ontario, Canada. The soils contained approximately 2-3000 mg/kg Ni. From McNear and Sparks (2004 unpublished data).

Mineral/bacterial interfacial reactions

In soils, it is well known that reactions at soil interfaces are greatly impacted by microbes. A recent example of the use of synchrotron radiation to follow the real-time biodegradation of organic chemicals on mineral surfaces is the research of Holman *et al.* (2002). It was hypothesized that humic acid accelerates the degradation of polyaromatic hydrocarbons (PAHs) by enhancing the solubility of the PAH, thus increasing PAH bioavailability to microorganisms. However, there was no direct evidence that this indeed occurred until the research of Holman *et al.* (2002). In the latter study, the researchers employed synchrotron radiation-based Fourier transform infrared (SR-FTIR) spectromicroscopy to study the effect of HA (Elliott

soil HA; abbreviated ESHA) on the degradation kinetics of pyrene by *Mycobacterium* sp. JLS on a magnetite surface. In Figure 7, time series spectra are shown by measuring the same location on each pyrene coated sample for greater than 1 month.



Figure 7: Time series of SR-FTIR absorption bands corresponding to pyrene and biomass formation following the degradation of pyrene by *Mycobacterium* sp. JLS on magnetite surfaces. Panels a and b are spectra from a sample without ESHA; panels c and d are from a sample with ESHA. The time at which each spectrum was acquired is labeled. Panels a and c are centered on a pyrene absorption band at 1185cm⁻¹. Panels b and d show a pyrene doublet at 3044 and 3027 cm⁻¹ and biomass IR absorption bands at 2921 and 2850 cm⁻¹. Inserts are time series from abiotic control experiments (Holman *et al.* 2002).

Panels a and c show IR spectra centered on the C-H bending mode of pyrene at 1185 cm⁻¹. Panels b and d show the pyrene C-H stretching doublet at 3044 and 3027 cm⁻¹ plus peaks from biomass methyl groups at 2921 and 2850 cm⁻¹. Panels a and b spectra do not contain ESHA and panels c and d spectra contain ESHA. Insets on all panels show spectra for abiotic corresponding samples. With the bacteria present, the intensities of the 1185, 3044, and 3027 cm⁻¹ peaks decrease over time, showing a reduction in the amount of pyrene on the surface. In the abiotic systems, irrespective of whether ESHA was added, only small changes in pyrene absorption peaks occurred over time. For samples without ESHA, the degradation of pyrene is slow at first and about 168 hours passes before changes in the spectra are noted. Then, biodegradation increases rapidly and all the pyrene is degraded in nearly 35 hours. As pyrene peaks disappear, the biomass IR peaks appear, showing biomass formation while pyrene is being consumed. Biodegradation of pyrene on samples with

ESHA starts immediately (about 1 hour) after the bacteria are added and is complete in 4 hours. During the latter part of the pyrene degradation, an increase in biomass absorption is noted, again indicating that biomass formation occurs at the same time as pyrene consumption.

At the end of the time resolved studies (about 460 hours), the spatial distribution of pyrene, bacteria, and the ESHA were determined by taking spectra every 5 μ m across the center of the bacterial colony containing ESHA (Fig. 7 c, d). Figure 8 shows contour maps of spatial distribution of measured infrared absorbances corresponding to the bacteria, ESHA, and pyrene.



Figure 8: Contour diagrams from infrared mapping obtained at the end of the experiment showing the spatial distribution of the infrared absorption peaks corresponding to (top) *Mycobacterium* sp. JLS bacteria, (middle) ESHA, and (bottom) pyrene. Appropriate spectral regions were integrated for each point on the maps. The color scales for each contour plot are red for high integrated IR peak area (high concentration of the corresponding component) and blue for low peak area (low concentration); black is an out-of-focus region of the sample. The center of the map shows a region with high density of bacteria and high concentration of ESHA where pyrene has been completely degraded (Holman et. al. 2002).

The center of the maps shows a region that contains a high population density of the bacteria and a high concentration of ESHA. Also, at the initiation of the experiment there was a high concentration of pyrene in

this central region (the reason this region was studied). At the end of the study, pyrene in the central region was entirely degraded. Where pyrene was present without the bacteria, degradation was insignificant.

Need for multidisciplinary, interdisciplinary and multifaceted approaches

The future of basic soil science research and the discipline of soil science 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, physicists, and biologists must and will increasingly collaborate with other soil scientists, and with geochemists, chemists, microbiologists, molecular biologists, environmental and chemical engineers, and material scientists. I predict that one of the major leitmotifs of the field in the 21st century will be the study of biological effects on soil chemical and physical reactions and processes. This provides soil scientists with a unique opportunity to combine their expertise with that of molecular biologists. We must also employ an array of multiple, molecular scale techniques over a range of temporal scales in combination with macroscopic approaches and computational modeling to solve complex questions concerning soil properties and processes.

In a recent issue of "Science", soil science research was highlighted and referred to on the cover as the last frontier. If we are going to remain viable and flourish as scientists and as an important scientific discipline, we must take a number of pivotal steps in the years ahead. These include: becoming more proactive and effective in communicating to policymakers and the public about issues that we are experts in, and being more aggressive in seeking and advocating for funding to address important agricultural and environmental issues and to enhance the global economy; improving our "image" with scientists in allied fields by publishing and presenting papers in an array of journals and scientific venues; preserving the identity of our discipline, but increasing interactions and collaborations with colleagues in other fields; becoming more active in disseminating educational materials and providing training workshops to teachers and students in K-12 so that more students can be attracted to and excited about soil science as an academic major and career; enhancing student recruiting and training efforts at the graduate level; and increasing the diversity of our professional societies in terms of gender, ethnicity, gender, and type of member (we need to reach out more to practicing professionals and ensure that we provide them with membership services that meet their needs).

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