

**It's about scale and interfaces:
frontiers in basic soil science research**

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Our future as a discipline and Scientific Union is indeed bright. Soil scientists are major players in the research frontiers of molecular environmental science, nanoscience, carbon sequestration, and biocomplexity. Our efforts in these areas will most certainly benefit humankind. However, we face challenges in the next decade. We must preserve the identity of our discipline, but increasingly interact with colleagues in other fields. Additionally, we must become more proactive in communicating to policymakers and the public about the importance of soils and excite young persons about soil science as a career. We must stay ahead of the curve on developing issues that we need to be a major player in and identify emerging issues in soil science. We must all let our legislators and policymakers know that funding for soil science, and indeed for all of science, is absolutely essential if we are to continue to have a strong economy and a superb quality of life.

I am confident that we can meet these and other challenges and build on the remarkable successes we have had as a discipline and a Union.

It's about scale and interfaces: frontiers in basic soil science research

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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.

Keywords: molecular scale, macroscopic scale, landscape scale, soil processes, kinetics

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 (Figure 1).

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 (Hochella, 2002). Processes within the critical zone can be divided into four categories. Each of these affects the other and includes: biologic activity, weathering, fluid transport, and near-surface tectonics. Examples of critical zone processes that are important frontiers in soil science are: the terrestrial C cycle and its relation to global climate change, including the temporal and spatial variability of C sources and sinks and the influence of weathering reactions; and microbial interactions with minerals and their role in mineral weathering, soil formation, accumulation of natural resources, and mobilization of nutrients and contaminants (NRC, 2001).

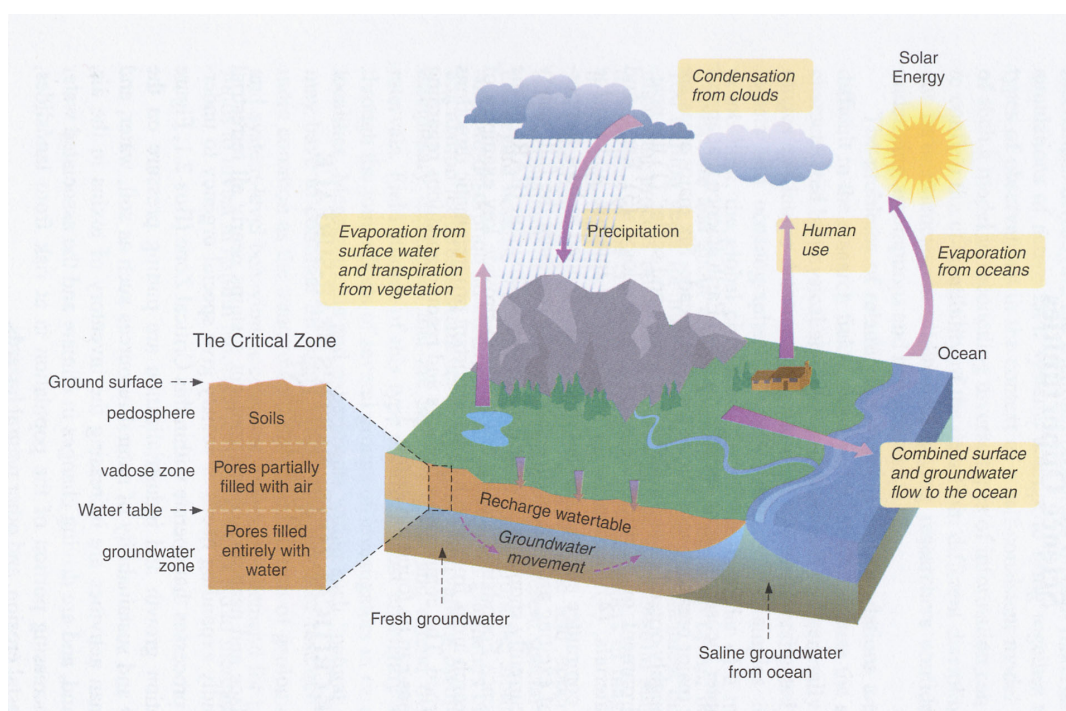


Figure 1 The Critical Zone includes the land surface and its canopy of vegetation, rivers, lakes, and shallow seas, and it extends through the pedosphere, unsaturated vadose zone, and saturated groundwater zone. Interactions at this interface between the solid Earth and its fluid envelopes determine the availability of nearly every life-sustaining resource (National Research Council, 2001).

Molecular Environmental Soil Science

The research challenges and questions we face in soil science occur over multiple scales (Figure 2) and at 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).

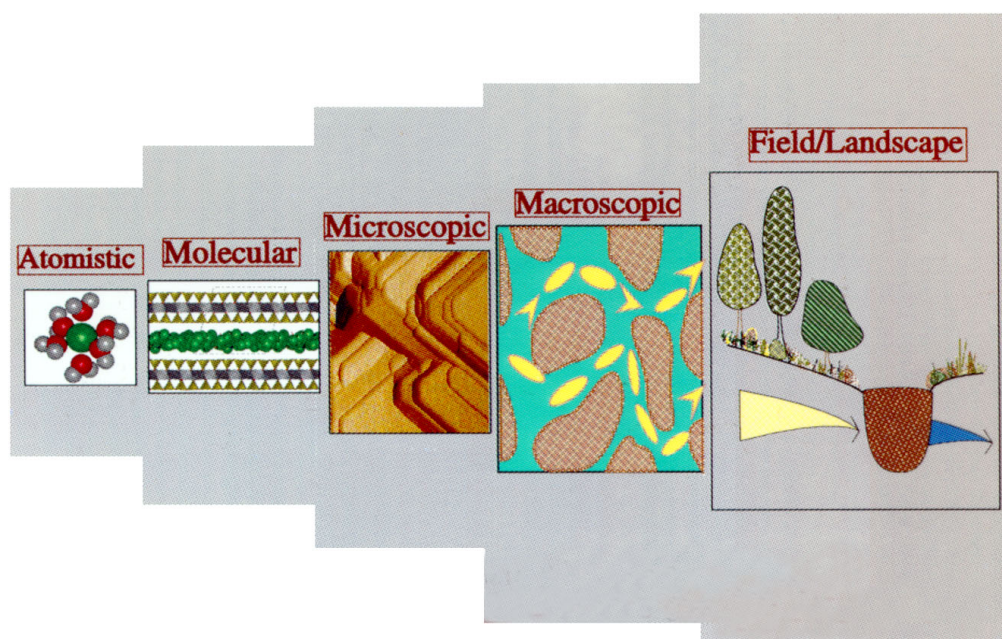


Figure 2 Illustration of the various spatial scales that soil scientists are interested in (Bertsch and Hunter, 1998).

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 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).

There are a number of areas in environmental 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.

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 Figure 3. Electromagnetic radiation has both particle and wave properties such that light at a particular wavelength corresponds 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).

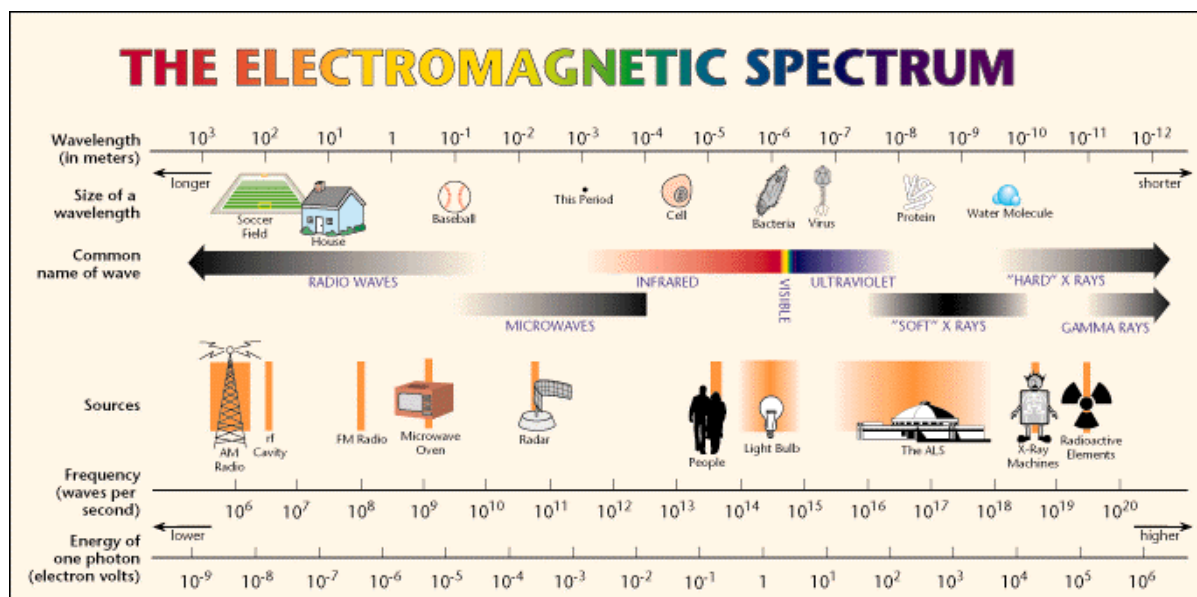


Figure 3 Electromagnetic spectrum of light covering a wide range of wavelengths and photon energies. From Advanced Light Source (Lawrence Berkeley Laboratory, 2002).

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 keV or more. There are a number of synchrotron facilities throughout the world (Table 1). In the USA major facilities are found at National Laboratories.

Table 1 Selected first, second, and third generation synchrotron research facilities (Schulze and Bertsch, 1999).

Acronym	Facility	Location
	First generation sources	
SSRL	Stanford Synchrotron Radiation Laboratory	Stanford, CA, USA
CHESS	Cornell High Energy Synchrotron Source	Ithaca, NY, USA
LURE	Laboratoire pour l'Utilisation de Rayonnement Electromagnétique	Orsay, France
HASYLAB	Hamburger Synchrotronstrahlungs Labor	Hamburg, Germany
	Second generation sources	
SRS	Synchrotron Radiation Source	Daresbury, United Kingdom
KEK	Photon Factory	Tsukuba, Japan
NLS	National Synchrotron Light Source	Upton, NY, USA
BESSY	Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung	Berlin, Germany
	Third generation sources	
APS	Advanced Photon Source	Argonne, IL, USA
ALS	Advanced Light Source	Berkeley, CA, USA
ESRF	European Synchrotron Radiation Facility	Grenoble, France
SPring-8	Super Photon ring – 8GeV	Nishi Harima, Japan

Synchrotrons are large machines (Figure 4). 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).

Synchrotron radiation has enabled soil and environmental scientists to employ a number of spectroscopic and microscopic analytical techniques to understand chemical reactions and processes at molecular and smaller scales. Spectroscopies (Table 2) reveal chemical information and deal with the interaction of electromagnetic radiation with matter. A large number of spectroscopic techniques are a function of both large frequency or energy ranges of electromagnetic radiation involved and the approach used for probing the interaction over a given frequency range (Bertsch and Hunter, 1998). Microscopic techniques (Table 2) provide spatial information and arise from the

interaction of energy with matter that either focuses or rasters radiation in some way to produce an image (Sparks, 2002).

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).

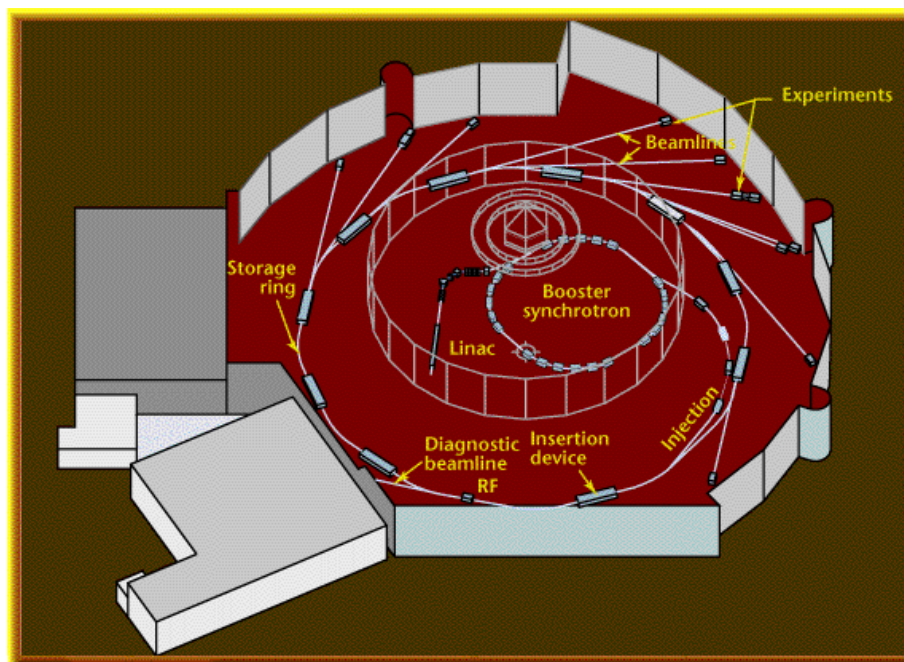


Figure 4 Schematic diagram of a synchrotron x-ray source (Schulze and Bertsch, 1999).

Table 2 Summary of Selected Analytical Methods for Molecular Soil Science^a.

Analytical Method	Type of Energy	
	Source	Signal
Absorption, emission, and relaxation spectroscopies IR ^b and FTIR	infrared radiation	transmitted infrared radiation
Synchrotron XAS (XANES and EXAFS)	synchrotron X-rays	transmitted or fluorescent X-rays; electron yield
Synchrotron microanalysis (XRF, XANES)	synchrotron X-rays	fluorescent X rays
EELS (also called PEELS)	electrons	electrons
XPS and Auger spectroscopy	X-rays	Electrons
Resonance spectroscopies NMR	radio waves (+ magnetic field)	radio waves
ESR (also called EPR)	microwaves	microwaves
Scattering and ablation	(+ magnetic field)	
X-ray scattering (small angle, SAXS; wide angle, WAXS)	X-rays (synchrotron or laboratory)	scattered X-rays
SIMS	charged ion beam	atomic mass
LA-ICP-MS	laser	atomic mass
Microscopies STM	tunneling electrons	electronic perturbations
AFM (also called SFM)	electronic force	force perturbation
HR-TEM and STEM	electrons	transmitted or secondary electrons
SEM/EM with EDS or WDS chemical analysis	electrons	secondary, or backscattered electrons; fluorescent X-rays

^a From (O'Day, 1999).

^b Abbreviations are: IR, infrared; FTIR, Fourier transform infrared; XAS, X-ray absorption spectroscopy; XANES, X-ray absorption near-edge structure; EXAFS, extended X-ray absorption fine structure; XRF, X-ray fluorescence; EELS, electron energy loss spectroscopy; PEELS, parallel electron energy loss spectroscopy; XPS, X-ray photoelectron spectroscopy; NMR, nuclear magnetic resonance; ESR, electron spin resonance (also known as EPR); EPR, electron paramagnetic resonance (also known as ESR); SAXS, small-angle X-ray scattering; WAXS, wide-angle X-ray scattering; SIMS, secondary ion mass spectrometry; LA-ICP-MS, laser ablation inductively coupled plasma mass spectrometry; STM, scanning tunneling microscopy; AFM, atomic force microscopy (also known as scanning force microscopy, SFM); HR-TEM, high-resolution transmission electron microscopy; STEM, scanning transmission electron microscopy; SEM, scanning electron microscopy; EM, electron microscopy; EDS, energy dispersive spectrometry; WDS, wavelength dispersive spectrometry.

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).

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 $\pm 0.002\text{nm}$), and coordination numbers (accurate to $\pm 15\text{-}20\%$) (Brown *et al.*, 1995).

An XAS experiment which results in a spectrum (Figure 5), 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 positron-electron pair production (Sparks, 2002).

In the x-ray energy range of 0.5 to 100 keV, photoelectron production dominates and causes x-ray attenuation by matter. When the energy of the incident x-ray beam ($h\nu$) < binding energy (E_b) of a core electron on the element of interest, absorption is minimal. However, when $h\nu \approx E_b$, electron transitions to unoccupied bound energy levels arise, contributing the main absorption edge and causing features below the main edge, referred to as the pre-edge portion of the spectrum (Figure 5).

As $h\nu$ increases beyond E_b , electrons can be ejected to unbound levels and stay in the vicinity of the absorber for a short time with excess kinetic energy. In the energy region extending from just above to about 50 eV above E_b and the absorption edge electrons are multiply scattered among neighboring atoms which produces the XANES (x-ray absorption near edge structure) portion of the spectrum (Figure 5). Fingerprint information, such as oxidation states, can be gleaned from this portion of the XAS spectrum. When $h\nu$ is about 50 to 1,000 eV above E_b and the absorption edge, electrons are ejected from the absorber, singly or multiply scattered from first- or second-neighbor atoms back to the absorber, and then leave the vicinity of the absorber, creating the EXAFS (extended x-ray absorption fine structure) portion (Figure 5) of the spectrum (Brown *et al.*, 1995). The EXAFS spectrum is caused by interference between outgoing and backscattered photoelectrons, which modulates the atomic

absorption coefficient (Figure 5). 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).

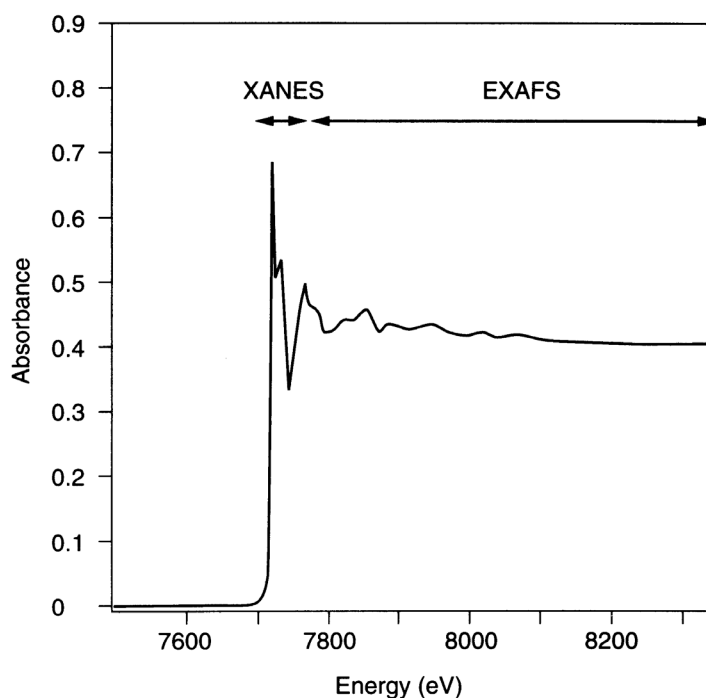


Figure 5 Co K-edge x-ray absorption spectrum of CaCO_3 recorded in the transmission mode showing the XANES and EXAFS regions. The pre-edge region is from a few eV to ~ 10 eV below the main absorption edge and shows a small pre-edge feature due to a $1s \rightarrow 3d$ bound – state electron transition (Xu, 1993).

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 co-workers, 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. We now know 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.

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, 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; 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 *et al.* (2000) 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.

New Frontiers

In the remaining section of this review, I want to focus on what I believe are some of the future frontiers in 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; unraveling the precise structure of soil organic matter; and understanding the chemistry of the rhizosphere.

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 $100 \mu\text{m}^2$. 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 ($<5 \mu\text{m}$) and sensitivity, one can speciate metals in soils at the micro-scale. Thus, one can determine all potential species within a small area in the soil matrix. An example of this capability is shown in Figure 6 where Zn and other metals were mapped (micro-synchrotron X-ray fluorescence spectroscopy, μ -SXRF) and speciated (micro-extended X-ray absorption fine structure spectroscopy, μ -EXAFS) in a contaminated subsoil sample collected around the Palmerton, Pennsylvania, USA smelting facility near Palmerton, Pennsylvania, USA (Roberts, 2001).

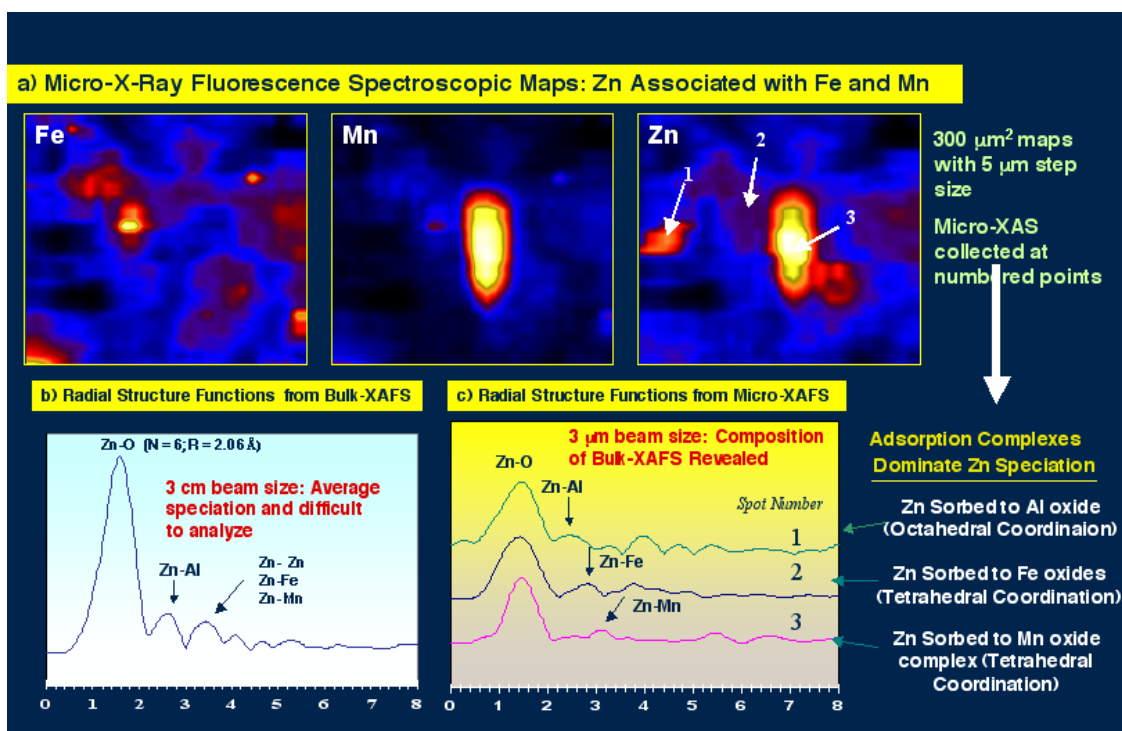


Figure 6 Synchrotron – based speciation of Zn in a smelter-contaminated subsurface soil using a) μ -Synchrotron x-ray fluorescence (μ -SXRF) spectroscopy, b) bulk XAFS, and c) μ -XAFS techniques (Roberts, 2001).

Zn concentrations were several thousand parts per million in the soil. From the μ -SXRF maps one sees that Zn is strongly associated with Mn in the center of the samples, with Fe in other portions of the sample, and with neither Mn or Fe in some portions of the sample (Figure 6a). This micro-scale heterogeneity in elemental associations suggests that Zn could be present in different phases over a small sample area. Bulk XAFS analyses suggested that Zn was bound as an inner-sphere complex to Al, Fe, and Mn oxides but the data interpretation was difficult (Figure 6b).

μ -EXAFS data were collected on the three regions of the sample (labeled 1, 2, and 3 on the Zn map, Figure 6a). Spot 1 on the map showed that Zn was octahedrally coordinated and sorbed to an Al-oxide phase (Figure 6c). Spots 2 and 3, with Zn in a tetrahedral coordination, revealed that Zn was primarily sorbed to Fe-oxide (spot 2) and to Mn-oxide (Spot 3) (Figure 6c). These results suggest that Zn^{2+} could have been released from Zn bearing mineral phases in the topsoil (containing mainly sphalerite, ZnS and franklinite, $ZnFe_2O_4$) and transported to the subsoil where the Zn^{2+} was partially readsorbed to both Al, Fe, and Mn oxides.

Structure and Chemistry of Soil Organic Matter

With the development of *in situ* x-ray spectromicroscopy and other state-of-the-art techniques, major advances are and will continue to occur in

unraveling the structure of soil organic matter and the interaction of humic substances with soil minerals. This has been an enigmatic area that has baffled soil chemists/biochemists since the inception of our discipline. 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. 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 macromolecular structure (size and shape) of humic substances (Figure 7).

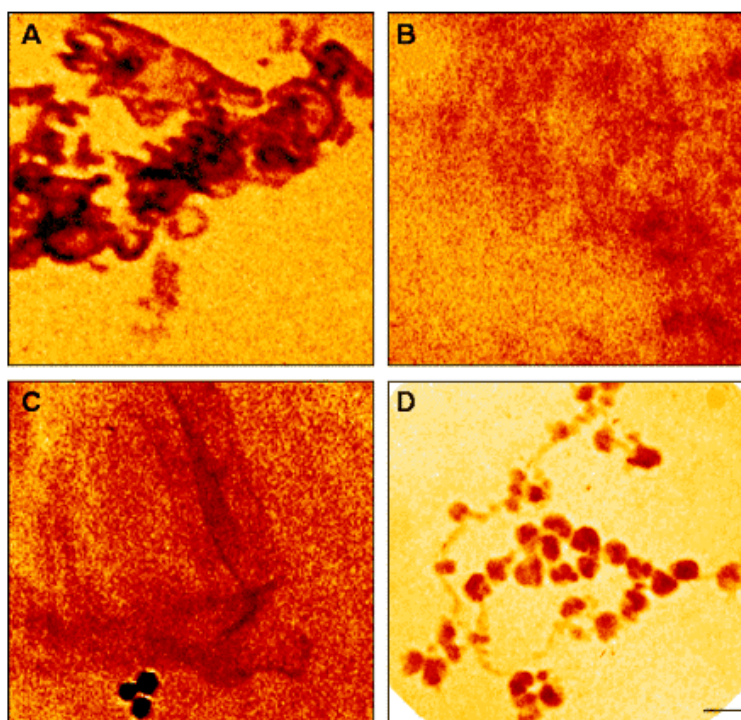


Figure 7 Influence of pH, ionic strength, and complexing cations on the macromolecular structures of isolated fluvial fulvic acid. (A) pH is 3.0 ± 1.0 , NaCl is 1.0 M, and C is $\sim 1.5 \text{ g liter}^{-1}$. The average sizes of globular and ringlike structures were $0.3 \mu\text{m}$ (range 0.2 to $0.45 \mu\text{m}$) and $0.65 \mu\text{m}$ (range 0.3 to $1.2 \mu\text{m}$), respectively. The ratio of globular to ring structures was 70:30. In addition, sheetlike structures (average of $3 \mu\text{m}$, range 2 to $8 \mu\text{m}$) were also noticed in concentrated HS solutions. (B) pH is 9.0 ± 1.0 , NaCl is 0.5 M, and C is ~ 1.2 to 1.5 g liter^{-1} . Average aggregate size is $<0.1 \mu\text{m}$ with little deviation size. In concentrated HS solutions, globular (average of $0.3 \mu\text{m}$, range of 0.2 to $0.5 \mu\text{m}$) and sheetlike structures (average of $1.5 \mu\text{m}$, range of 1 to $5 \mu\text{m}$) were also formed. (C) pH is $\sim 4.0 \pm 1.0$, CaCl_2 is 0.018 M, and C is $\sim 1.0 \text{ g liter}^{-1}$. The threadlike structures had an average length of $\sim 3 \mu\text{m}$ (range of 2 to $6 \mu\text{m}$) and a width of $<0.15 \mu\text{m}$. (D) pH is $\sim 4.0 \pm 1.0$, Fe^{3+} is 1 mM, and C is $\sim 0.1 \text{ g liter}^{-1}$. The average sizes of globular and threadlike structures were $0.3 \mu\text{m}$ (range of 0.25 to $0.4 \mu\text{m}$) and $0.8 \mu\text{m}$ (range of 0.5 to $1.3 \mu\text{m}$), respectively. Scale bar, 500 nm (Myneni *et al.*, 1999).

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.

In our own group (Nachtegaal and Sparks, unpublished data), we have been using soft x-ray spectromicroscopy to obtain physical (using scanning transmission x-ray microscopy, STXM) and chemical (using carbon-near edge x-ray absorption spectroscopy, CNEXAS) information on metal-humic acid complexation in soils. The two micrographs in Figure 8 show a natural humic acid in solution (pH=5 and I=0.1 M NaNO₃) and a natural humic acid complexed with a Cu solution (also at pH=5 and 1.0 M NaNO₃).

Two images are taken below the C edge (280 eV), where C will not absorb any energy, and thus only the distribution of elements with L and M edges at lower energies become visible. The other two images are taken above the C edge (288 eV) where the distribution of the humic acid or more precisely the distribution of certain functional groups of the humic acid are visible (Figure 8). From the Cu-humic acid images (the two on the right), a strong correlation between Cu (left) and C (right) is observed and indicates that all the Cu in solution is complexed by the humic acid. The humic acid also tends to contract upon reaction with Cu (compare the 288 eV images of HA and Cu-HA), confirming the observations of Myneni *et al.* (1999) cited above. Figure 9 shows preliminary results of the CNEXAFS studies on metal complexation with HA.

The assignment of peaks is based on studies of polymers and small organic acids. Upon metal sorption, both the phenolic (around 287 eV) and the carboxylic (around 288.39 eV) peaks decrease in intensity compared to the unreacted HA samples. Also, upon reaction of the HA with Al and Ni, the peaks shift about 0.1 eV to the right. This shift is due to the metals attracting electron density from the carboxyl group.

Light Element Chemistry

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. For example, the precise speciation of Al in soils can be gleaned, an enigma that has perplexed soil scientists since the early part of the 20th century. Such information would address important questions concerning soil acidity and its effects on plant life.

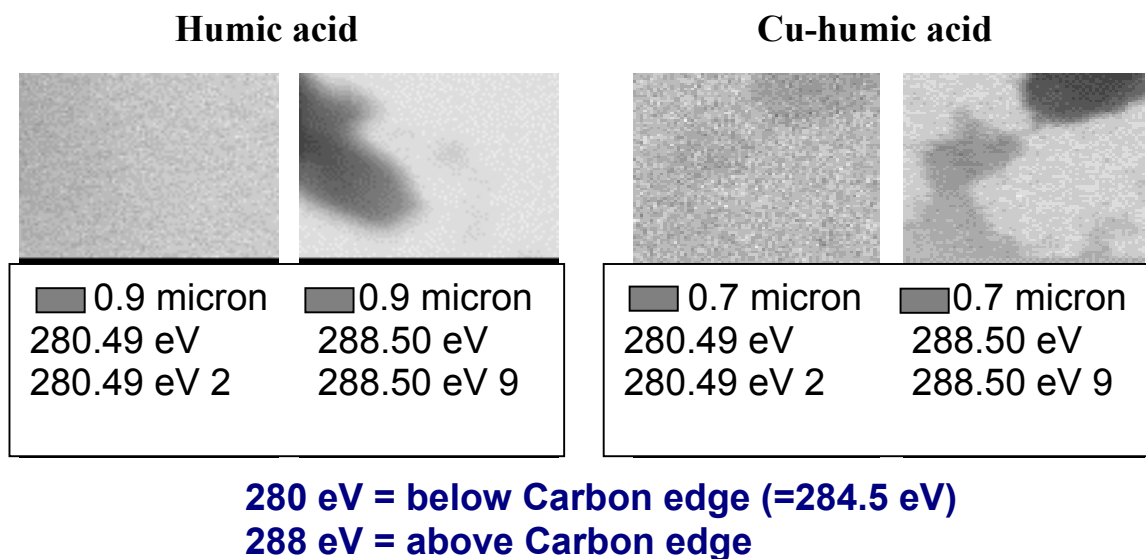


Figure 8 Synchrotron-based scanning transmission x-ray microscopic (STXM) images of natural humic acid (two images on the left) in solution (pH=5 and I=0.1 M NaNO₃) and the natural humic acid complexed with a copper solution (two images on the right) at pH=5 and I = 0.1 M NaNO₃. From Nachtegaal and Sparks, (unpublished data).

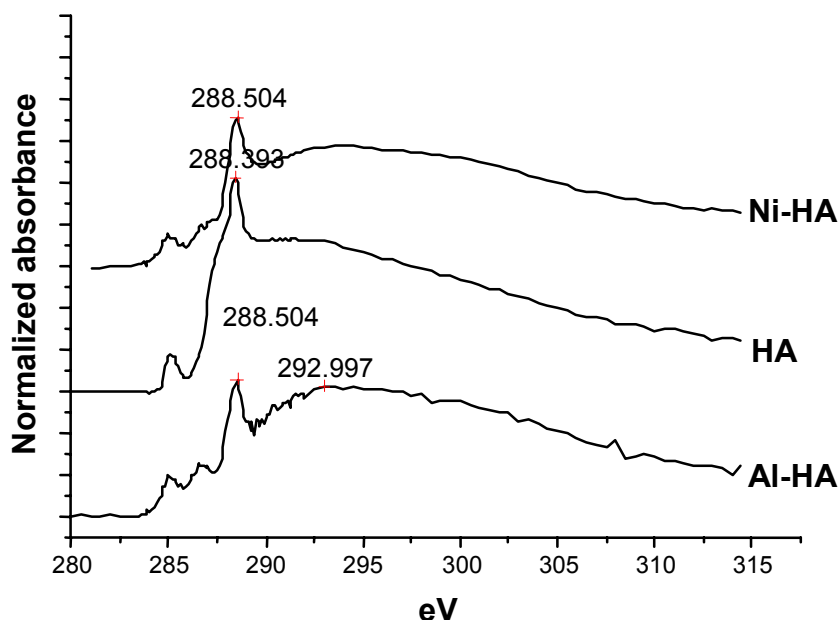


Figure 9 CNEXAFS analyses of natural humic acid and natural humic acid complexed with Ni and Al. The peak around 287 eV represents phenolic carbon and 288.39 eV represents carboxyl carbon.

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).

Environmental Molecular Biology

The field of environmental molecular biology could significantly advance efforts to enhance environmental 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 the chemical structure of metal binding proteins is needed. These are areas where soil biochemists, soil chemists, and geochemists, using 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.

A fine example of using *in situ* synchrotron based techniques to study metal speciation on plant roots is the study by Hansel *et al.* (2002). They investigated spatial and temporal associations of As and Fe species on aquatic plant roots. The soil/root interface is very complex, containing both reduced and oxidized mineral species and organic-metal complexes. It is known that Fe (hydr) oxide precipitates, or plaques, appear on the surfaces of aquatic plants. These probably result from the radial oxygen diffusion and subsequent oxidation of ferrous iron. The Fe-plaques could serve as a substrate for metalloid retention and sequestration. Associated with the plaques are iron-oxidizing bacteria. However, the role of bacteria in iron oxidation within the rhizosphere is not well understood. The nature of the plaque mineralogy should indicate the biochemical conditions within the rhizosphere which may be dependent on plant species and/or site specific soil and aqueous chemistry (Hansel *et al.*, 2002).

Hansel *et al.* (2002) used x-ray fluorescence microprobe and microtomography to study Fe plaque mineralogy and As speciation on the roots

of two aquatic plant species, *P. arundinacea* (reed canarygrass) and *T. latifolia* (cattail). The microprobe analyses provides a vertical average of As and Fe through the plaque and microtomography gives a cross sectional slice through the plant root- from the interior of intact roots through the epidermis and plaque. Figures 10a and b shows microtomographic images of reed canarygrass roots.

As exists as isolated hot spots on the root surface and interior. High levels of As do not seem to correspond to higher levels of Fe (Figures 10a and b). X-ray microprobe images of the plaque show heterogeneous precipitation of As and Fe on the surface of the plant root and elevated levels of As correspond with higher Fe concentrations (Figure10b). Using linear combination analyses, the Fe plaque on reed canarygrass was 63% ferrihydrite, 32% goethite, and 5% siderite (Hansel *et al.*, 2002). XANES analyses of As in the plaque of reed canarygrass showed that As(V) predominated with some As(III). The As appeared to be as a sorbed species on Fe(III) hydroxides.

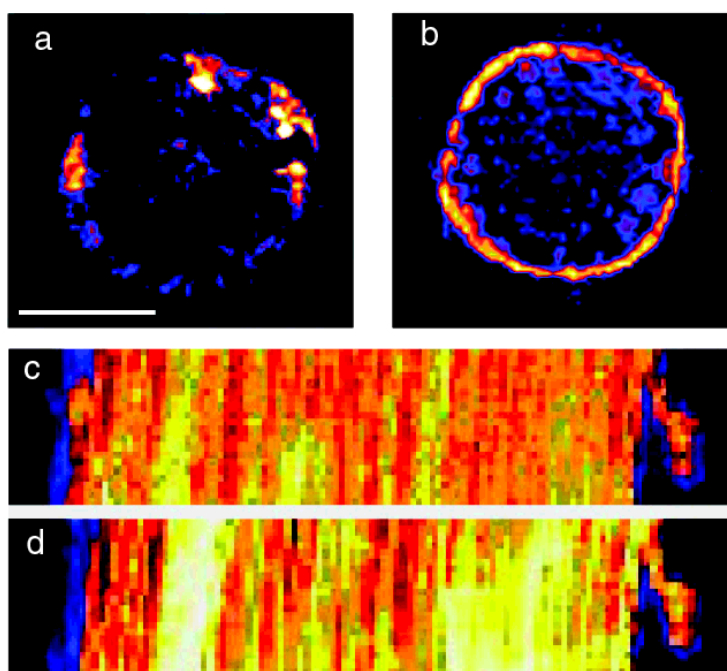


Figure 10 X-ray fluorescence microtomographic images of (a) As and (b) Fe distributions within *P. arundinacea* root cross-sections (slices). X-ray microtomography images were obtained by translating an unaltered (intact) root through an X-ray beam and collecting the fluorescence in order to reconstruct the root cross-section. X-ray microprobe image of (c) As and (d) Fe distributions on the surface of *P. arundinacea* roots. (X-ray microprobe analysis was conducted by physically slicing off a thin film of the Fe plaque from the surface of the root and obtaining a vertical average of the As and Fe concentrations within the plaque.) Scale bar represents 300 μm (Hansel *et al.*, 2002).

Other soil chemical-biological research areas that will be prominent in the future include: understanding the transport and sorption kinetics and mechanisms of contaminants on nanoparticles; mechanisms of microbial-mineral interactions using *in situ* nanoscale techniques such as biologic force microscopy (BFM) [Lower *et al.* 2000, 2001, 2002]; elucidating microbially mediated redox reactions; effect of biofilms on soil minerals, and metal and oxyanion speciation and retention; the role of biogenically derived minerals on contaminant transport and solubility; redox transformations of C, N, P, and S over different redox boundaries; and real-time biodegradation mechanisms of contaminants.

A recent example of the use of synchrotron radiation to follow the real-time biodegradation of organic chemicals 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 11, time series spectra are shown by measuring the same location on each pyrene coated sample for greater than 1 month.

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 $5\text{ }\mu\text{m}$ across the center of the bacterial colony containing ESHA

(Figures 11c and d). Figure 12 shows contour maps of spatial distribution of measured infrared absorbances corresponding to the bacteria, ESHA, and pyrene.

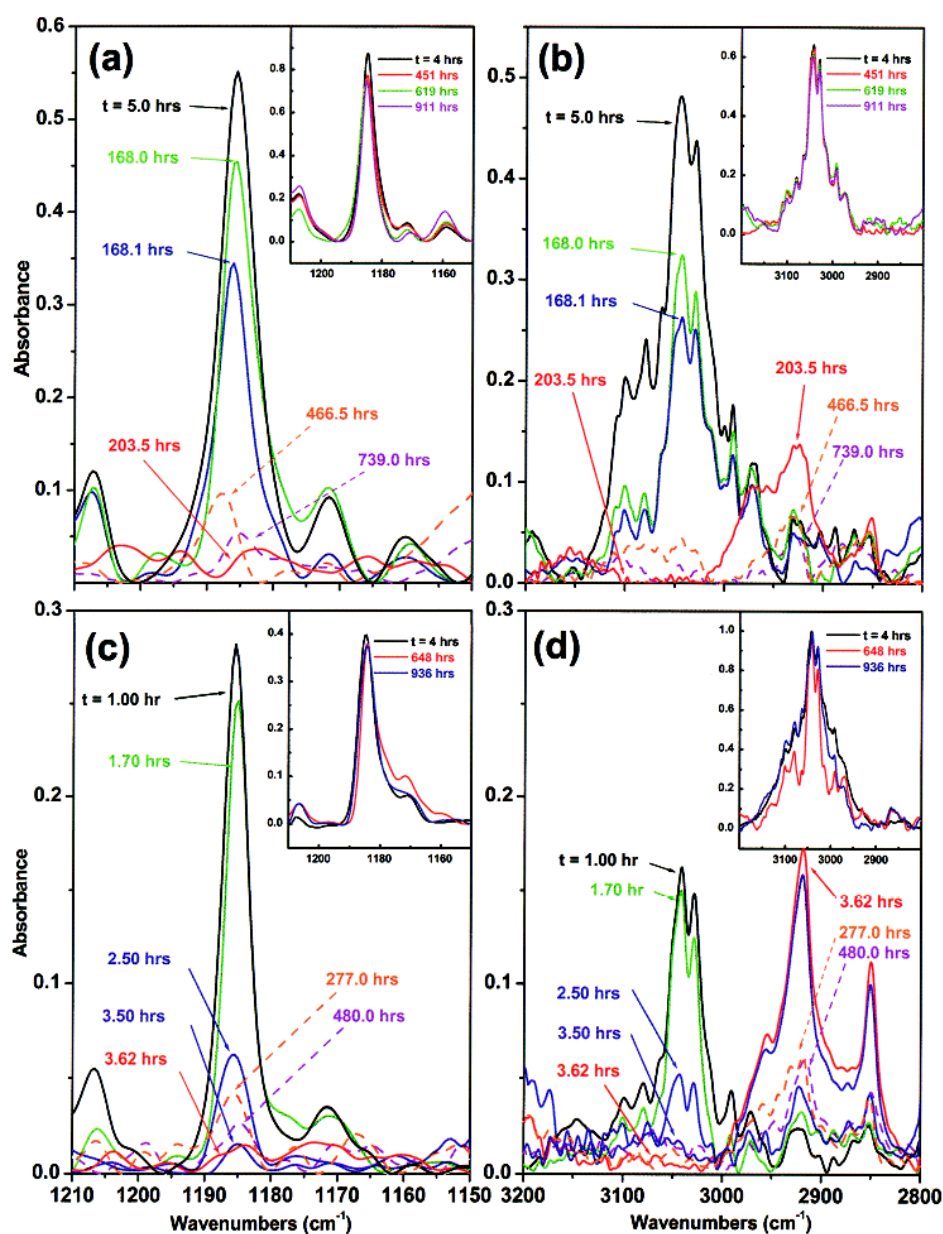


Figure 11 Time series of SR-FTIR absorption bands corresponding to pyrene and biomass formation following the degradation of pyrene by *Mycobacterium* sp. JLS on magnetite surfaces. Panels a and b are spectra from a sample without ESHA; panels c and d are from a sample with ESHA. The time at which each 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 3027cm^{-1} and biomass IR absorption bands at 2921 and 2850cm^{-1} . Inserts are time series from abiotic control experiments (Holman *et al.*, 2002).

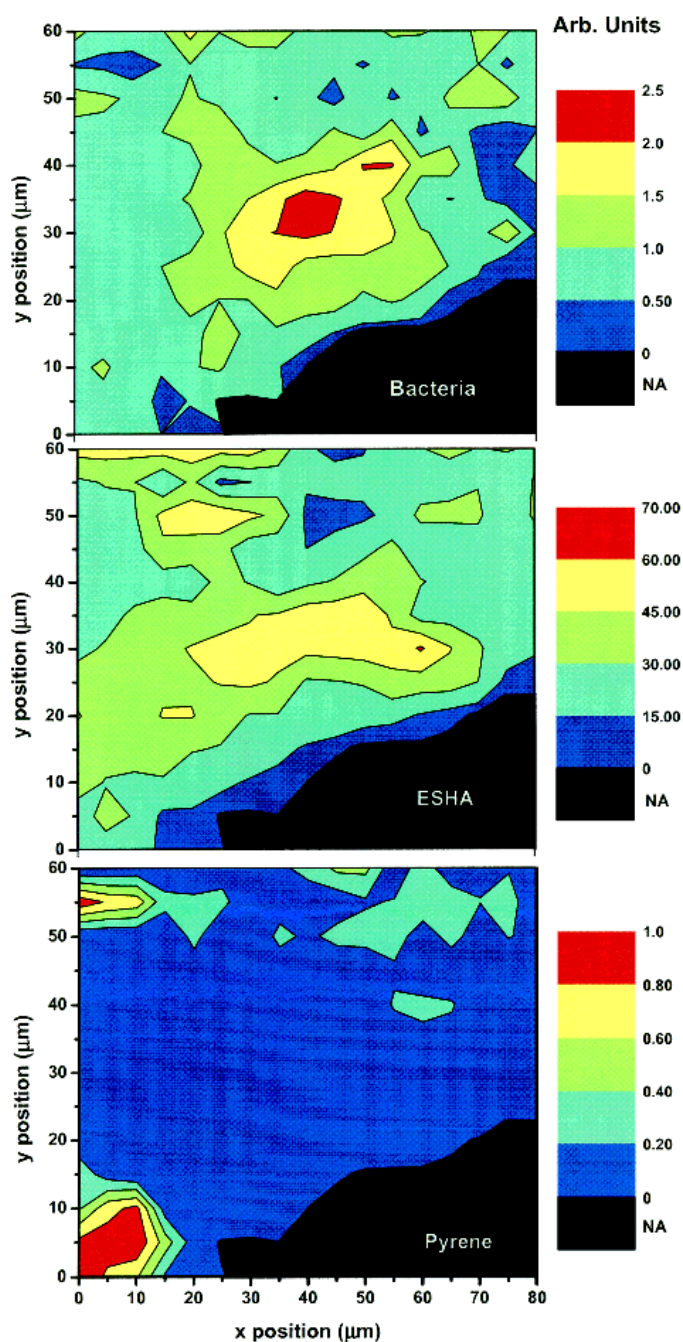


Figure 12 Contour diagrams from infrared mapping obtained at the end of the experiment showing the spatial distribution of the infrared absorption peaks corresponding to (top) *Mycobacterium* sp. JLS bacteria, (middle) ESHA, and (bottom) pyrene. Appropriate spectral regions were integrated for each point 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 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.

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