Reflective Essay

Pursuant to Application for Promotion to Professor

[redacted]

1. Personal vision of the problems and approaches

Farmers, industrial producers, and even home consumers of chemicals face social problems that have emerged over the past generation involving management of anthropogenic chemicals released to the environment, and how to optimize future applications of beneficial compounds. Neither cynical laissez faire approaches nor superstitiously prohibitive attitudes are tenable, but reasonable and sustainable approaches should be based upon cost-benefit analyses of risk, which depend in turn on a scientific understanding of chemical transport and fate. I am proud to work as a scientist at this interface where we are finding the ever-shifting balance between human needs to feed ourselves and otherwise shape our environment versus our self-realization that we must preserve the essence of this environment for the next human generations. My mandate at Michigan State is to devote 70% of my effort to research in this area, and 30% of effort toward teaching these concepts to students.

Since many chemicals are released into soil, optimizing the management of both chemical application and remediation demands deep insight into the operant chemical processes in soils and aquifers. With fundamental understanding of these processes, rational new technologies can be efficiently developed and then flexibly adapted to site-specific needs. Without fundamental knowledge, a new approach is occasionally discovered by trial and error, but often fails elsewhere because no one understood *why* it worked. The necessary depth of insight into chemical transport in the soil environment requires the synthesis of data across many spatial scales, ranging from field-scale plume migration through lab-scale transport and transformation phenomena to molecular-scale binding mechanisms.

Chemicals of special interest are those posing risks of unintended adverse consequences. In particular, persistent organic pollutants (POPs) such as pesticides, organic solvents, and industrial by-products such as dioxins are risks to both human and ecosystem health through exposure of organisms to contaminated soil, water, or air.

2. What am I trying to accomplish?

My goal as a soil chemist is to integrate spatio-temporally diverse data into a coherent understanding of solute sorption (binding) in soils, and thereby enable detailed predictions of soil system responses to chemical management decisions. The tools of computational chemistry provide an efficient platform for attempting such a synthesis because molecular simulations can predict a variety of bulk properties of chemical systems at the same time that they give very detailed atomic-scale mechanistic information. Available data can be used to constrain the molecular simulations, and the simulations can then be used to integrate data across scales, to observe the relevant processes in mechanistic detail, to propose hypotheses, and thereby to derive more information from both bulk and spectroscopic experimentation. Early in my career, I became fascinated by problems of contamination by pesticides and organic solvents, and I continue to find that understanding the fate of POPs in soil is intriguing, important, and a source of both challenges and discoveries.

3. What have I done?

In soils and sediments, the fate, transport, and bioavailability of many plant nutrients and pollutants are controlled largely by interactions with clay mineral surfaces. Clay minerals are layer aluminosilicates, most with structural negative charges and large surface areas. Due to their abundance and reactivity, attempts to understand solute movement through soils must include a model for the energetics and kinetics of solute reactions with clay surfaces.

Since 1992, I have worked to apply a number of tools from computational chemistry to study problems involving clay minerals. One such tool is simulation by molecular dynamics, in which force fields (collections of potential energy functions and parameters) are used to compute the forces on a collection of atoms and thereby use Newtonian physics to determine the system evolution. By 1997, I had developed the **first** force field methods for molecular dynamics simulations of clay-water-solute systems in which all atoms were given full conformational freedom. Furthermore, this was the first force field that was able to simulate clay interactions with organic solutes, which had been my goal since my graduate work on pesticide transport. Subsequent studies in 1998 (by Exxon Mobil Corporation) and 2001 [redacted] University of London) to find which of the five or six existing methods could best be used to model the interlayer properties of clay minerals, showed that my methods best predicted the experimental phenomena at clay surfaces. Given this independently validated method, I began to apply it to problems of practical interest.

Theoretical chemists with passion for applied environmental problems are rare, and can probably maximize their impacts by teaming with experimentalists, so I sought a position in which that goal could be achieved. I was very lucky to come to Michigan State where I could work for the past ten years with [redacted] collaborators at other institutions to investigate the broad problem "What controls POP sorption to soil clay minerals?" The typical view in the soil chemistry community was that minor sorption to clays may occur, but it is dwarfed in topsoils by POP sorption to soil organic matter. We had seen enough anomalous data that we challenged this view for certain classes of organics, and we wanted to understand the operative mechanisms that drive such sorption.

The team approach we have developed has been very successful (more than 25 joint papers and six competitive USDA/NSF/NIH grants over the past six years), and combines experimental data at several different scales with molecular simulations that I contribute. [redacted] groups screen POP compounds to find which ones sorb strongly to swelling clay minerals, and they then quantify the sorption response to several geochemical variables. We measure swelling of the clays in my lab by X-ray diffraction, and we added [redacted] Iowa State University to our team because he had developed techniques for measuring the swelling of clays in very wet systems corresponding to our sorption experiments. Meanwhile, [redacted] (at Purdue University) and I team up to investigate the molecular mechanisms operant in these systems: [redacted] uses experimental methods (Fourier transform infrared (FTIR) and Raman spectroscopies) and I use molecular simulations.

In a typical scenario, my students or I computationally "build" the same clay that the experimentalists are using, then "add" an amount of organic solute that corresponds to [redacted] adsorption isotherms and "add" an amount of water that corresponds to the X-ray swelling measurements. Once all components of our simulated clay-water-organic systems correspond closely to our group's experimental data, we perform molecular dynamics on this system, which then yields a set of plausible structural interaction mechanisms, transition states between them, and also interaction energies. The mechanisms are directly comparable to [redacted]

spectroscopic results, and both simulation and experiment seem reasonably self-consistent so far. Of course a major difficulty with FTIR and Raman is how to assign the spectral peaks to particular molecular vibrations. The classical simulations help somewhat in this regard, but our other computational skills have been useful, too. Several times, we have effectively employed high-quality quantum calculations of organic-inorganic systems to help assign [redacted] spectral peaks and the shifts they make when the POP adsorbs to clays.

Simulated interaction energies (from the molecular dynamics described earlier) are comparable to experimental adsorption enthalpies, which we have measured for several cases. We have developed and published novel first-attempt methods for simulating adsorption energies for POP solutes interacting with clays. If such methods can be improved, they would be an important advance since quantitative prediction (on a fully mechanistic basis) for the extent of sorption should then be possible.

Our teams, combining the bulk, spectroscopic, X-ray, and simulation results, have built comprehensive cases describing how and why many neutral organics can form strongly bound complexes with swelling clays. Several sorption mechanisms have long been postulated, but never actually demonstrated until our recent joint papers. The like-minded scientists on our team have achieved a critical mass whereby we are arguably the leading group studying POP interactions with environmentally relevant minerals. Understanding POP binding mechanisms and the factors that promote them already allows us to hypothesize which organic-clay combinations ought to interact strongly, which geochemical variables should influence sorption/desorption, and hence new management strategies (one patent application in 2006) for controlling the release, transport, and fate of organic compounds in soils.

4. What are my future directions?

Accordingly, we have broadened our studies beyond "simple" sorption to pursue more nuanced topics such as the bioavailability and chemical transformations of sorbed chemicals. For example, we have three currently funded projects to study a) How the presence of clay minerals affects the potency of dioxins in mice and the availability of dioxins to bacteria in soils, b) How clay minerals affect the induction of antibiotic resistance in bacterial systems containing tetracycline, and c) How clay minerals may catalyze the creation of highly toxic dioxins from common chlorophenol pesticides in soils.

These two bioavailability grants (plus another from NSF during 2005-2007) have been important steps for me, since a key question about environmental chemicals is how "bioavailable" they are to humans and other species in receiving ecosystems. While working on these projects, I am building expertise in the area of fundamental chemistry that determines bioavailability, which will be a long-standing and important problem for human and ecosystem health.

The grant on antibiotic resistance is my first national project toward addressing the developing concern about bioactive pharmaceuticals that we routinely release into the environment. Many pharmaceuticals are pesticide-like molecules: Their binding to soils and sediments is critical to assessment of environmental risk. We can use our understanding of adsorption mechanisms to begin predicting which classes of pharmaceuticals have the potential to sorb strongly to clay minerals, and then use our team approach at both bulk and molecular scales to quantify sorption, understand the mechanisms that control it, and understand how sorption affects bioavailability and hence exposure of organisms to the chemicals.

My work on thermodynamics of cation adsorption has led to an interest in understanding

the role of nitrogenous organic compounds in both soils and in oilfield shales. For the latter case, in 2007 I submitted an MSU intramural proposal entitled "A new hypothesis for petroleum generation," which was "highly recommended" but was judged too basic to fit the more applied goals of the program. I plan to pursue external proposals of those ideas: My molecular simulation methods are ideally suited to the high temperatures and pressures characteristic of deep oil shales. This is an example of using my basic knowledge to test novel ideas in fields outside the traditional, which is a unique societal role of research university faculty.

5. What are my areas of special achievement?

MSU would like each of its Professors to be "an expert of national stature" who has influenced and led their respective disciplines. I believe I have achieved this status through my work on developing and applying molecular simulation methods to soil minerals. Evidence is that I am often invited to speak at international symposia on these topics, and one of my papers on simulation method development has been cited more than 100 times. As a corollary of my simulations and a result of our work at MSU, I am an expert on the molecular mechanisms of adsorption to clays, which was my initial reason for creating simulations. Secondly, I have worked to understand the thermodynamics (that is, the energy balance) governing adsorption to swelling clay minerals. I published a short critical review of the thermodynamics of inorganic cation exchange, in which I attempted to revise the key paradigm for explaining this important soil process. Furthermore, I have applied similar analyses to organic cation exchange (one paper) and also to the thermodynamics of neutral organic solute adsorption (two papers). In sum, I have consistently striven to articulate clay mineral structure, swelling properties, and energy relations to explain how clays work in sorbing organic solutes.

I integrate these mechanistic and thermodynamic approaches into my teaching at both the graduate and undergraduate levels. My expertise with visualization of molecular simulations lends itself to teaching, in which I strive to help students see the structural and energetic reasons (again, mechanisms) for bulk soil chemical processes. Furthermore, I introduce my undergraduates to thermodynamic modeling ("chemical speciation") software and then use it extensively in graduate-level teaching to help the students develop their intuitions for the responses of soil processes to changes in soil chemical management variables such as pH, redox potential, and fertilization.

6. What has been my role within collaborative groups?

I am proud that [redacted] and I have created a highly functioning team in soil chemistry. We work together, each providing energy and expertise but without a lot of ego, and we have been successful. The basis of our work is experimental. However, a key factor that makes our proposals competitive is our combination of several types of experimental work along with my simulation work to create and test mechanistic hypotheses for the underlying physical causes of the experimental results. Reviewers clearly like this combination, since our last four collaborative USDA-NRI soil chemistry proposals have been funded, despite proposal success rates of just 5-10% in our program area. I was lead PI on the largest of these highly competitive grants.

As the molecular modeler on this team, my niche is to provide structural and energetic arguments that help integrate our diverse pool of experimental data. My simulation work strengthens the interpretation of both our bulk and spectroscopic experimental work, and the real-world data feed back to provide quality control for the simulations and to provide a

springboard for the development of new simulation methods. This synergy is attractive in proposals, but it is unusual for purely modeling work to attract much funding alone. In the 1990s, we were lucky enough to be supported by USDA for development of pure simulation tools: We proposed the vision that molecular simulations could contribute to our understanding of clay-organic interactions, and that vision has come to fruition with our current team. My applied simulation and thermodynamic work gains its significance from interplay with real data, so all of my current modeling projects are multi-investigator collaborations with experimentalists. The expertise and talents of our team members complement each other particularly well, as validated by the reviewers of our proposals and papers.

7. Graduate student advising

It is difficult to find graduate students in my area of expertise, since the work requires strength in both computational chemistry and soil science. Such students are extremely rare and I must therefore start with a student who knows one discipline and also has the talent and interest to learn most of the other discipline. In addition, the student must learn the art of integrating simulation results with many different types of soil chemical data, using miniscule, momentary simulations to represent complex, heterogeneous soil systems at many different temporal and spatial scales. I have been fortunate to have three good students. I am proud that our team has obtained grants to support some 12 grad students and 8 postdocs during my tenure at MSU, plus several in the laboratories of our Purdue and Iowa State collaborators. I have been a central "functional" advisor to most of these students, though not typically the formal major advisor, again because few of the students want to pursue computational chemistry.

8. Transition to an academic-year appointment

I am in many ways thankful for the change to a nine-month appointment about five years ago. This change has allowed me to enrich my family life and to rejuvenate my creativity. Furthermore, my transition to a nine-month appointment has been reasonable for MSU, since I have heretofore secured eight months of summer salary from nationally competitive grants.

In closing, I feel extremely privileged to be an Associate Professor at MSU. Tenure is a rare thing, and to have it coupled with independent, curiosity-driven research in a context of synergistic collaboration is a very satisfying combination.

Figure: Citations of refereed papers by [redacted] in the ISI Scientific Citations database.