2018 ESS PI Meeting Breakout Session Agenda

Impact of Natural Organic Matter on Water Quality and Biogeochemical Processes

Organized by J. Bargar and P. Santschi

1. Implications of Microbial Energetics for Carbon Fate in Floodplain Soils and Groundwater.
   Kristin Boye (SLAC)
2. Organic Carbon Speciation and Thermodynamics Regulate Hyporheic Zone Metabolism.
   Emily Graham (PNNL)
3. Pop-up Talk: Effects of NOM on Mercury Methylation and Contaminant Metal Transformation.
   Baohua Gu (ORNL)
4. Pop-up Talk: Microbial Pathways of Organic Carbon Utilization.
   Ted Flynn (ANL)
5. Radionuclide-Associated Moieties in Natural Organic Matter.
   Chen Xu (Texas A&M University Galveston)
6. Pop-up Talk: NOM Mineralization and Metal Cycling during Flood Plain Evolution.
   Hana Naughton (Stanford University)
7. Pop-up Talk: Colloidal Radionuclides in Wetlands.
   Dan Kaplan (SRNL)
8. Drought and Rewetting Effects on Soil Carbon Biogeochemistry.
   Vanessa Bailey (PNNL)

Group Discussion: Strategic Research Priorities, Science Challenges and Gaps that Need to be Addressed

Group discussions after presentations

Biogeochemistry Grand Challenge

from the 2018-2023 CESD Strategic Plan

Following the presentations, four Subgroups were convened to brainstorm challenges, opportunities, and research needs on questions four through six from the Biogeochemistry Grand Challenge within the 2018 CESD Strategic Plan: (https://science.energy.gov/~/media/ber/pdf/workshop%20reports/2018_CESD_Strategic_Plan.pdf).

1. How can biogeochemical pools and fluxes and their associated uncertainties be better constrained and represented in Earth and environmental system models? (global to local scales)
2. How can improved understanding of biogeochemical interactions and feedbacks within the current Earth system be used to improve projections of future environmental states?
3. How will compounding short-term perturbations and sustained change influence biogeochemical cycles and impact the functioning of Earth systems across relevant spatio-temporal scales? What are the associated critical thresholds?
4. How do natural and anthropogenic changes in land cover and land use affect biogeochemical processes and cycles, especially at critical land-water-atmosphere interfaces?
5. How do geochemical, genomic, and metabolic interactions influence environmental system dynamics from single measurement sites to watershed scales? How can improved understanding of these processes and interactions be effectively incorporated into environmental and Earth systems models?
6. What are the key environmental factors that create and sustain biogeochemical hot spots/moments in specific locations, and to what extent are these pheomena important at larger scales?

Instructions provided to subgroup facilitators: Each of the four subgroups was asked to define knowledge gaps, strategic research questions, and technical R&D needs.

Grand Challenge Question 3. *How will compounding short-term perturbations and sustained change influence biogeochemical cycles and impact the functioning of Earth and environmental systems across relevant spatio-temporal scales, and what are the associated critical thresholds of those systems?*

Notes from breakout group (Facilitator: S. Fendorf, Stanford):

- Duration of "short term" is important. 'Recovery' periods are required following short-term perturbations (hours, days) may be shorter than required following longer perturbations (weeks, months, years).
- The rates of processes (transport, chemical kinetics) occurring during perturbations as well as 'recovery' in between perturbations are important.
- We need to understand how the duration of perturbations and the intervening gaps influences processes that occur separately & in ensemble (ecosystem function).
- How does the rate of 'compounding' (accumulation of ecosystem disturbance) impact tipping points? Do higher overall rates of compounding/disturbance cause the system to be less resilient?
- How do space & time amplify compounding?
- We need to understand the thresholds beyond which short-term perturbation do not 'heal' and become sustained change. What are implications of crossing these thresholds?
- When does the tap run dry? / How quickly do you reach tipping points?

Grand Challenge Question 4. *How do natural and anthropogenic changes in land cover and land use affect biogeochemical processes and cycles, especially at critical land-water-atmosphere interfaces?*

Notes from breakout group (Facilitator: D. Kaplan, SRNL):

- Systems that are at steady state (energy/reactant inflows balanced by outflows) will experience rapid changes to energy/reactant inflows when perturbed. In that event, changes in system variables are expected to occur, and system energy utilization and outflows will change. Example: impact of bark beetle tree kill on export of toxic hydrocarbons from Rocky Mtn soils.
- Changes to hydrology in particular will alter Biogeochemical processes, rates
    - Draining/desiccation of sediments and soils is generally followed by oxygen intrusion and loss of sulfidic or reduced conditions. In some cases, oxidation of sulfide-rich sediments may create acidic sediments.
    - Inundation of sediments may lead to development reducing conditions, which affects pH, and causes dissolution of iron oxides and release of sequestered organic carbon and contaminants.
- Changes in organic carbon fluxes will alter the availability of electron donors and consequently microbiology and biogeochemical processes, rates
- How do the above dynamics help mediate ecosystem resilience? (impact of changing fluxes on resilience, system state shifts)

Grand Challenge Question 5. *What are the key environmental factors that create and sustain biogeochemical "hot spots and moments" in specific locations, and to what extent are these phenomena important at larger scales?*

Notes from breakout group (Facilitator: V. Bailey, PNNL):

- We felt that an understanding of what constitutes a "hotspot" is needed for different spatial scales. E.g., globally a small lake is a hotspot, but within that ecosystem a shoreline is a hotspot, and within that system, a particular pore with a root growing through it may be a hotspot. And then, how do we address hotspots through time, so that we understand the duration of a hotspot, and if it has a natural "pulse" of activity.

- There is room for a probabilistic accounting of hotspots. What is the likelihood for their occurrence and their activity? This could be connected to driving controls on the overall ecosystem. We definitely need new statistical tools and approaches to understand their occurrence. And we also need to understand i) how hotspots assemble, and if they grow, and ii) do they grow? If they grow, or if they persist as "hot spots" long enough, how do we determine if they become a "new norm?"

- Ideally, we want a GIS-type representation of a particular system, with layers for resources (to foster activities), layers for metabolites (to report activities), and a means to reflect these coincident events across space, time, and at an appropriate scale.

Grand Challenge Question 6. *How do geochemical, genomic and metabolic interactions influence environmental system dynamics from single measurement sites to watershed scales, and how can improved understanding of these processes and interactions be effectively incorporated into environmental and Earth system models?*

Notes from breakout group (Facilitator: E. Graham, PNNL):

- Interactive and open source platforms such as KBase, in which emerging model frameworks can be evaluated and compared to current gen models
- Investment in reduced order models and statistical approaches that collapse small scale data into tractable units at ecosystem and larger scales
- What are the scales of organization we should focus on? Is one scale more important than another? Sensitivity analyses can assist this
- Are there correlates for complex data that can be deciphered with remote sensing (bioindicators)
- We know comparatively little about spatial & temporal dynamics. We should invest in this while also evaluating the importance of variability for predictions at different scales

The following research needs were gathered from speakers prior to breakout and subsequently we have grouped them into the categories of:

i. **Drivers/needs that motivate science**
ii. **Process research needs**
iii. **System behavior research needs**

These categories are detailed in the following pages.

Drivers/needs that motivate science

- Understand maintenance of essential ecosystem services under increasing stress
- Anticipate ecosystem responses to increasing drought and resource utilization
- Sustain water and food security for a growing population
- Sustainable clean water for energy
- Repair/restore functionality of impacted soils
- Need for flexible and site/condition-specific technological solutions and management strategies for farming, water treatment & utilization
- Predict migration and fate of radionuclides
- Evaluate the feasibility and applicability of a remediation strategy in the DOE sites and other contaminated site (e.g., Fukushima prefecture), in the complex environment context (redox, speciation, the presence of NOM, etc.)
- Water and contaminant management in and around cities

Process Research Needs
NOM structure, reactivity & processes

- Molecular-scale understanding of the kinetics and dynamics of the reactions between individual DOM molecules and specific metal ions or minerals is critical
- DOM coupled reactions with minerals and microbes
- DOM formation of ternary and multi-phasic colloidal or dissolved complexes, affecting contaminant metal transformation, transport, and fate
- Identify the key processes of how specific and strongly radionuclide-binding bio- and geopolymers are embedded into particulate organic matter networks
- What is the relative importance of extrinsic (physical properties of the environment, nature of microbial activity) and intrinsic (chemistry of the NOM itself) properties to the transformation of NOM across different environments?
- How does setting impact above question? E.g., highly structured environment like grassland soil, with its variably-connected pore architecture and microaggregates, vs. fully-saturated sediment.
- Because NOM is constantly being reworked by microbial and other activity, it can be very difficult to understand process and mechanism from snap shots in the field.
- Lab experiments like incubations help, but those of course don't recapitulate all of the complexities of the field and can be prone to artifacts.
- High resolution characterization of in stream OM processing and resultant export from urban/suburban watersheds
- How does soil pore flow rate, or stream flow rate impact the quality of the OC with respect to its tendency to bind contaminants?

System Behavior Research Needs
Hydrologic – biogeochemical coupling

- Thresholds: Identify key processes, thresholding properties and conditions that trigger critical transformations in carbon, nutrient, and contaminant behavior.
  - Minimize prerequisites for measurements, model input, and predictions
- Optimize use of statistical tools for biogeochemical research.
- Impact of flow rate on water quality: Especially relevant at the watershed scale, does episodic high-flow rates dominate SOM transport, and by extension, water quality? How relevant is understanding steady state flow conditions?
- Effect of episodic rain events on wetland release of OC; wetlands dominate water quality in humid, and to a lesser extent arid conditions.
- Capillary fringe biogeochemistry: Transport and mixing, Coupling between hydrology and biogeochemistry, Controls over redox transition behavior, Temporal and spatial variability of microbial communities & metabolic potential, Nutrient mobilization processes, Contaminant mobilization processes, Impacts on under/overlying zones.

System Behavior Research Needs
Resilience & response

- How do soils (soil microbes, SOM, etc) buffer ecosystems from insults such as climate change, pollution, etc? - View against a backdrop of continuous change - whether it is climate change or land use. (soils not steady state!)
- Knowledge about how to intervene with and improve soils that have been impaired and may be at risk due to poor management, climate, etc.

System Behavior Research Needs

Generalizing across scales and regions

- Moving soil research from a site-specific finding to a generalizable principle is a significant gap - we don't have the investments we need to develop generalizable findings. Key needs are distributed networks of sites, and even moving to a 5-y funding cycle from a 3-year cycle. Environmental research needs a little more time to pursue and develop research.
- Good, biologically-informed mathematical approaches to moving across scales is a major gap.

System Behavior Research Needs
Urban streams

- How to reconcile field surveys with lab experiments.
- Influence of engineered structures on stream health (e.g., channel and streambed morphology, impervious surfaces, vegetation distribution).
- Interplay of management regimes and contaminant loads into urban streams.

System Behavior Research Needs

Heterogeneity

- Spatiotemporal dynamics of non-point biogeochemical inputs to urban/suburban streams.
- Land cover/use heterogeneity and biogeochemical function in mixed cover/use areas.

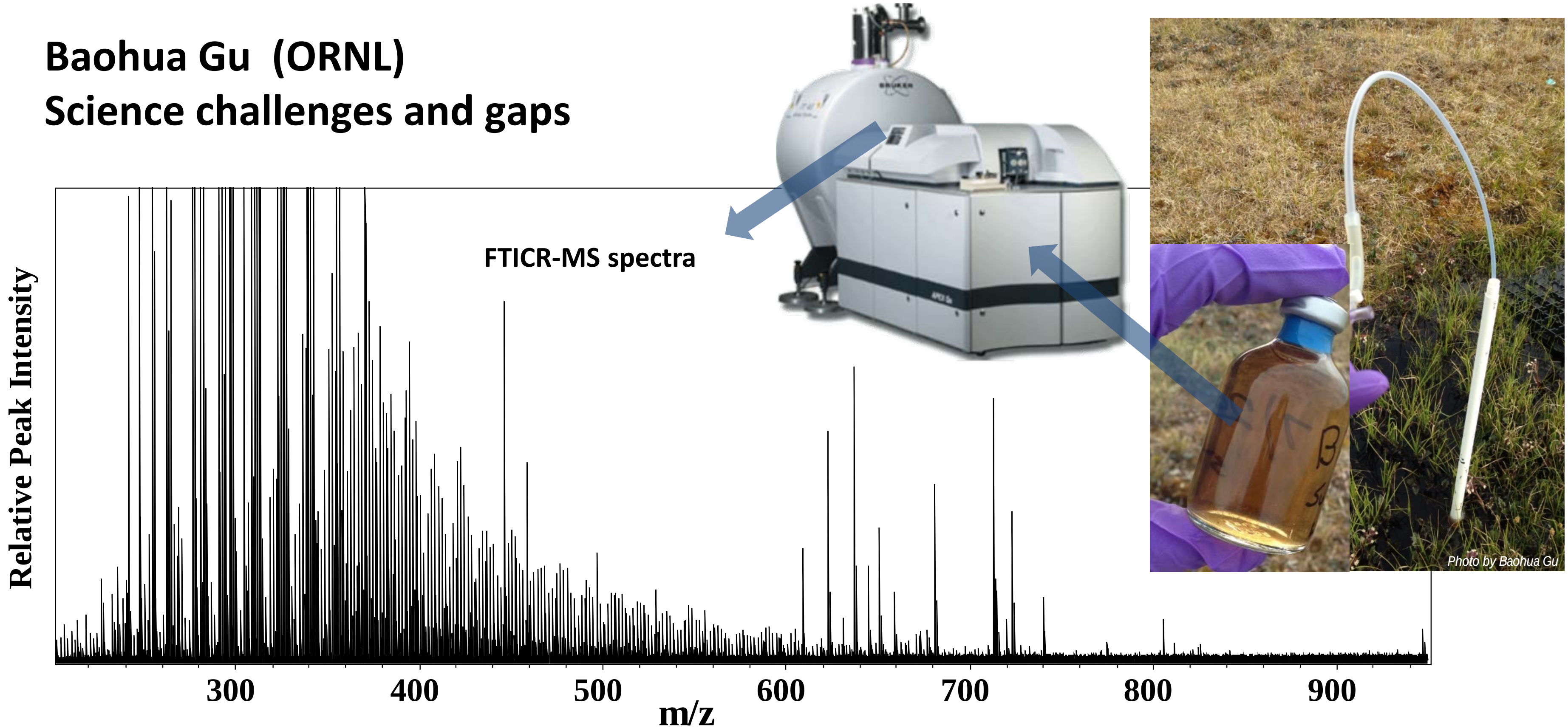
Technical R&D Needs

- Improved radionuclide-specific extraction and purification methods to obtain representative organic fractions from soil and aqueous systems.

Contributed slides

(Research needs listed in preceding slides were extracted from these contributed slides)

Baohua Gu (ORNL)
Science challenges and gaps



- DOM highly complex, polyfunctional, polyelectrolytic characteristics, with thousands of unknown molecular compositions
- Molecular-scale understanding of the kinetics and dynamics of the reactions between individual DOM molecules and specific metal ions or minerals is critical
- **DOM coupled reactions with minerals and microbes**
- **DOM formation of ternary and multi-phasic colloidal or dissolved complexes, affecting contaminant metal transformation, transport, and fate**

Kristin Boye (SLAC)

Societal and technological needs

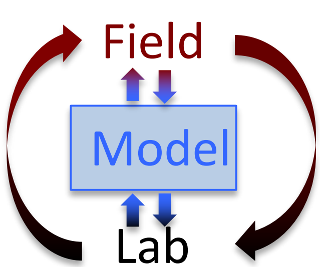
- Maintain essential ecosystem services while increasing pressure
- Predict ecosystem response to increasing drought and resource utilization
- Sustain water and food security for a growing population
- Develop flexible and site/condition-specific technological solutions and management strategies for farming, water treatment & utilization, remediation

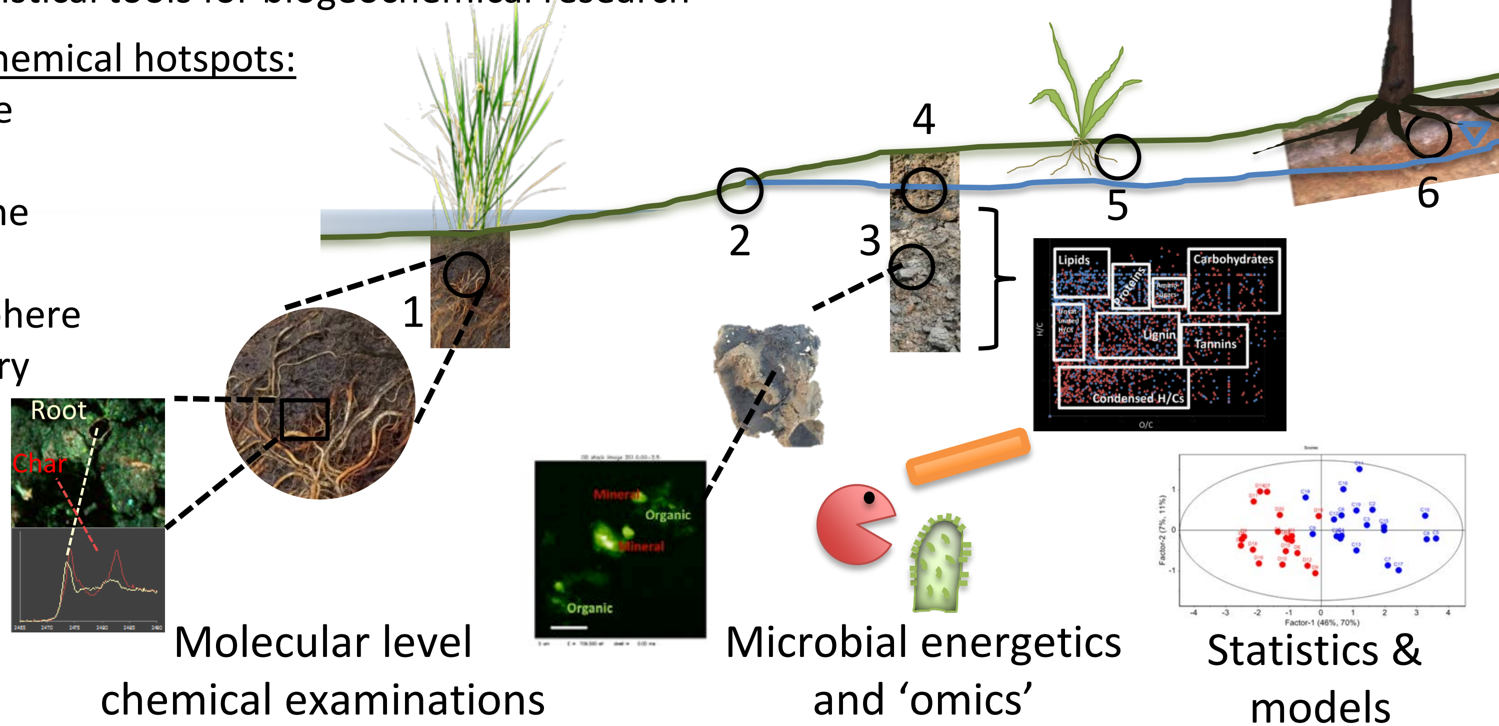
Priority research challenges and directions

- Identify key processes, thresholding properties and conditions that trigger critical transformations in carbon, nutrient, and contaminant behavior
  - ➢ Minimize prerequisites for measurements, model input, and predictions
- Link molecular-scale reactions to field-regional-global scale responses
- Optimize use of statistical tools for biogeochemical research

<u>Interfaces are biogeochemical hotspots:</u>

1. Wetland rhizosphere
2. Hyporheic zone
3. Diffusion limited zone
4. Groundwater table
5. Unsaturated rhizosphere
6. Soil horizon boundary





Chen Xu (TAMUG)

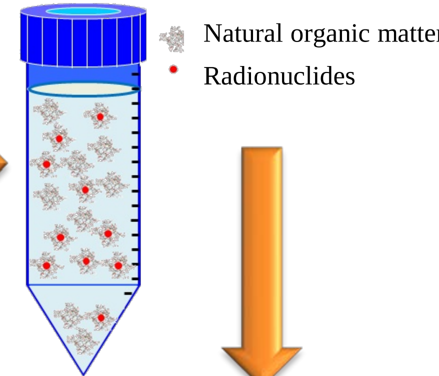
Strategic Research Driver: Coupled Effect of dynamic flow and soil OM on water quality

We know:

- OM binding properties are dynamic and change in response to many natural parameters.
- Extreme rainfall patterns are expected to be more common as a result of climate change, including more frequent high-flow conditions and more frequent dry periods.
- Antecedent moisture conditions influence OC release from soils.
- [OC] greatly increases in soil porewater and in stream water with increased flow rate.
- Dissolved OC, Colloidal OC, or fulvic acid fractions (small molecular weight & hydrophilic) are especially reactive fractions for binding metals and anions

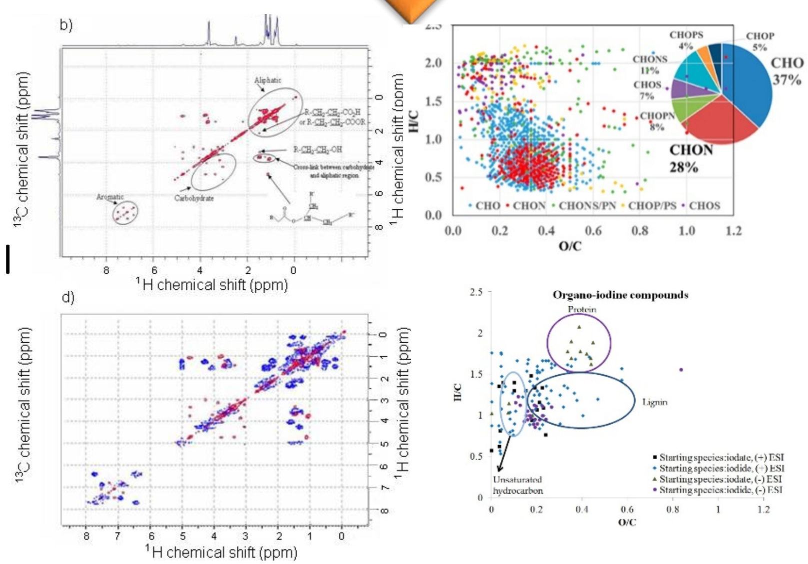
Strategic research:

- Especially relevant at the watershed scale, does episodic high-flow rates dominate SOM transport, and by extension, water quality? How relevant is understanding steady state flow conditions?
- Effect of episodic rain events on wetland release of OC; wetlands dominate water quality in humid, and to a lesser extent arid conditions.
- How does soil pore flow rate, or stream flow rate impact the quality of the OC with respect to its tendency to bind contaminants?



NMR

FTICR-MS



Societal and technological needs (Chen Xu, TAMUG)

- Predict the migration and fate of radionuclides under the influence of NOM.
- Evaluate the feasibility and applicability of a remediation strategy in the DOE sites and other contaminated site (e.g., Fukushima prefecture), in the complex environment context (redox, speciation, the presence of NOM, etc.)

Priority research challenges and directions

- Radionuclide-specific moieties in the bulk NOM pool are at trace levels and require a combination of classic with state-of-the art organic chemical approaches.
- Improve radionuclide-specific extraction and purification methods to obtain representative organic fractions from soil and aqueous systems ready for molecular-level characterization.
- Identify the key processes of how specific and strongly radionuclide-binding bio- and geopolymers are embedded into particulate organic matter networks.
- Connect molecular-scale features to remediation strategies.

Vanessa Bailey (PNNL):

Strategic research priorities

- how do soils (soil microbes, SOM, etc) buffer ecosystems from insults such as climate change, pollution, etc remains a challenge. But I think we need to prioritize studying these buffering properties against a backdrop of continuous change - whether it is climate change or land use. Soils and ecosystems are not at steady-state, yet we study them as though they are.

-also need to develop knowledge that helps us better intervene with and improve soils that have been impaired and may be at risk due to poor management, climate, etc.

Science challenges

- HETEROGENEITY. Soils and ecosystems are heterogeneous at all scales, but differently heterogeneous at each scale. It makes translating knowledge and research from site to site difficult. It makes translating knowledge across scales nearly impossible.

Gaps

- good, biologically-informed mathematical approaches to moving across scales is a major gap

- moving soil research from a site-specific finding to a generalizable principle is a significant gap - we don't have the investments we need to develop generalizable findings. Key needs are distributed networks of sites, and even moving to a 5-y funding cycle from a 3-year cycle. Environmental research needs a little more time to pursue and develop research.

Ted Flynn (ANL)

Strategic research priorities

To build off what Vanessa said:

- Discussion of the relative importance of extrinsic (physical properties of the environment, nature of microbial activity) and intrinsic (chemistry of the NOM itself) properties to the transformation of NOM across different environments would be valuable.
- Need to better understand how the relative contribution of these aspects vary between, say, a highly structured environment like grassland soil, with its variably-connected pore architecture and microaggregates, and fully-saturated sediment.
- I agree that heterogeneity (spatial, temporal) is a massive issue. I think this particularly becomes an issue when reconciling field surveys with lab experiments.
- Because NOM is constantly being reworked by microbial and other activity, it can be very difficult to understand process and mechanism from snap shots taken in the field.
- Lab experiments like incubations help, but those of course don't recapitulate all of the complexities of the field and can be prone to artifacts.

Emily Graham (PNNL)

Societal and technological needs:

- Biogeochemical impacts of urban and suburban development
- Sustainable food, water, and energy supplies under population growth
- Water and contaminant management in and around cities

Priority research directions

- Spatiotemporal dynamics of non-point biogeochemical inputs to urban/suburban streams
- High resolution characterization of in stream OM processing and resultant export from urban/suburban watersheds
- Land cover/use heterogeneity and biogeochemical function in mixed cover/use areas
- Influence of engineered structures on stream health (e.g., channel and streambed morphology, impervious surfaces, vegetation distribution)
- Interplay of management regimes and contaminant loads into urban streams

John Bargar (SLAC)

Societal and technological needs:

- Sustained availability of drinking water under intensified wet-dry cycling
- Sustainable clean water for energy
- Contaminant plume management
- Fit-for-purpose water treatment

Priority research directions

- Capillary fringe processes:
- Transport and mixing
- Coupling between hydrology and biogeochemistry
- Controls over redox transition behavior
- Temporal and spatial variability of microbial communities & metabolic potential
- Nutrient mobilization processes
- Contaminant mobilization processes
- Impact on under/overlying zones