

Major Findings

After seventeen months of funding, we have 5 publications that were either inspired by our CZO's overall goals (i.e. the 2 synthesis papers in *Frontiers in Ecology and the Environment*) or answered questions relevant to our CZO objectives with data obtained from our CZO watersheds. We have presented similar CZO-relevant findings on over 20 different occasions at scientific meetings (<http://www.udel.edu/czo/publications.html>).

The work of one student, Chunmei Chen, is worth highlighting below, because it has been completely funded by our CZO project, from its beginnings. Other research findings that have been completely funded by our CZO are still in stages that are too preliminary for presentation.

3.1 Nano-scale Organo-Mineral Interactions

One of our CZO doctoral graduate students, Chunmei Chen who is advised by PI Don Sparks, with input from other CZO participants, has been conducting studies at the Stanford Synchrotron Radiation Laboratory (SSRL) and the Canadian Light Source (CLS) to directly determine the distribution, speciation, and elemental associations of soil organic carbon under varying landscape topographic positions at the molecular scale. This research deals with Objective 1 of our proposal.

The role of organic matter-mineral interactions in the long-term protection of soil organic matter against decomposition is increasingly recognized as a key process for soil carbon (C) stabilization. In a preliminary study, we examined the structural composition of organic matter and its interaction with soil minerals along a pasture hillslope transect within the Christina River Basin Critical Zone Observatory (CRB-CZO). The CRB-CZO is underlain by metamorphosed sedimentary bedrock and is located in the Piedmont Region of southeastern Pennsylvania. Soil samples were collected from A and B horizons at the ridge and the base of a hillslope. Humic acids were extracted from the bulk samples as well as from the clay fractions and characterized by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR). Scanning transmission X-ray microscopy (STXM) and C-1s near-edge X-ray absorption fine structure (NEXAFS) spectroscopy at the Canadian Light Source were used to assess soil organic matter distribution, speciation and elemental associations at the nm scale. Based on the ATR-FTIR spectra, humic acids at the hillslope base, compared to those at the summit, have greater proportions of more recalcitrant aromatic-C and smaller proportions of more labile polysaccharides in the bulk soils and the clay fractions. The C NEXAFS analysis of the clay fractions from A horizons indicated that: (1) aromatic-C, O-alkyl-C and carbonyl-C were present at both the ridge and base of the hillslope; (2) the more labile aliphatic-C, which was present at the ridge of the hillslope, was not found at the base of the hillslope; (3) the more recalcitrant aromatic C was enriched at the base of the hillslope (compared to the ridge of the hillslope). These results suggest that the stability of soil organic matter is greater at the base of the hillslope than at the ridge of the hillslope and could be ascribed to the selective preservation of recalcitrant carbon forms by the soil mineral matrix. STXM- NEXAFS results demonstrated that organic matter (especially aromatic-C and aliphatic-C) associated with clay particles exhibited a larger variability at the ridge of the hillslope than at the base of the hillslope from the nm to the μm scale. In this work we were also able to determine the major mineral elemental (Si, Al, Ca, Fe, K) compositions simultaneously with C distribution and speciation. Future CZO research to constrain the physical and chemical weathering history of the hillslope will be integrated with this study to understand how such topography-dependent C-mineral interactions

have emerged, eventually helping efforts to scale up organic matter–mineral associations to landscapes and to land-atmosphere carbon exchange processes.

Posters and oral presentations, based on this research, has been presented at the National CZO meeting in Boulder, CO, and at the American Geophysical Union (AGU) and Soil Science Society of America (SSSA) meetings.

Research Related to Objectives 1 and 2

Iron speciation and mineralogy in soils along a redox gradient using X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD), respectively.

We are investigating changes in soil iron concentration, mineralogy, and speciation across pasture and forest hillslope transects as well as a floodplain soil profile subjected to redox gradients. Iron (II) mineral phases were found in only one sample which is the soil from the buried A horizon of the floodplain soil profile. This soil sample is in a water saturated zone and undergoes reductive dissolution of minerals, as indicated by the soil color. The crystallinity of the Fe^{III}-(oxy) hydroxides decreased with increasing anoxia, with the amorphous Fe^{III}-(oxy) hydroxides more prominent in the wetter sites. Approximately 50% of the total Fe was found in the phyllosilicates. The largest absolute amount of Fe loss, due to reductive dissolution in the wetter areas, occurred with the Fe-bearing phyllosilicates.

Elucidating the mechanisms of the interactions between organic matter and mineral components and characterizing C speciation along hillslope transects and a floodplain soil profile.

Investigations were conducted on pasture and forest hillslope and floodplain soil profiles to determine soil mineral-organic matter complexation mechanisms using synchrotron-based scanning transmission X-ray microscopy and carbon near edge X-ray absorption fine structure spectroscopy (STXM-CNEAFS) at the Canadian Light Source (CLS). Additionally, synthesized organic matter-ferrihydrite-kaolinite coprecipitates are being studied as model organo-mineral complexes. Our specific goals are: (1) to identify distinctive binding mechanisms of OM and specific mineral components; (2) to determine the major mineral species for OM-mineral complexation formation; and (3) to characterize solid-phase carbon speciation along hillslope transects. Clay samples from the top and base of a pasture hillslope and the buried A-horizon of a floodplain soil profile were analyzed at the CLS. Maps from these samples show a broadly dispersed and locally concentrated distribution of C within the soil clay particles. Calcium is positively well correlated with C. The spectroscopic data rules out CaCO₃ as an explanation for C–Ca correlations in these samples. The good correlation between Ca and C may suggest Ca plays an important role in organo-mineral formation via “cation bridging”. The data shows a general negative correlation between C and K, indicating carbon is depleted in K-enriched minerals such as illite. The absence of aliphatic carbon in the soils at the base of the hillslope might suggest that OM has undergone a greater degree of humification. Cluster analysis yielded chemically distinct regions. Interestingly, the carboxyl-C rich region also contains aluminosilicates with high Al and Si concentration. This may suggest that OM associates with aluminosilicates predominantly via “van der Waals forces” and/or “H bonding”, since ligand exchange should weaken/diminish the peak for carboxyl C. We can equally argue that OM bounds to the

minerals depleted in Al and Si (i.e. Fe and Al oxides) largely through ligand exchange. These experiments are being continued.

We are evaluating the in-situ sensitivity of the mineral surface area of soils with to changes in redox conditions (reducing versus oxidizing) across a wide range of landscape positions and uses, such as floodplain forest, upland forest, and agriculture areas within a transect A of the White Clay Creek Watershed. The proposed research questions include the following: (1) How do redox conditions in soils affect the transport of mineral surface area via the dissolved phase? (2) How deep and fast does oxygen penetrate through the soil under dynamic landscape changes and positions? (3) What happens during oxygen diffusion back into riparian soil/sediments e.g., precipitated Fe and Mn oxides recomplex with organic carbon that was present in the pore water, reduced Fe and Mn and OC both advect out of the system and to the stream, reduced Fe and Mn both advect away but the OC content might be preserved on the aluminosilicate clays? (4) How do soil properties, such as composition, mineralogy, mineral surface area, as well as redox state, vary depending on different types of land use and topographic position? and (5) How do microbial communities within soils and water change depending on redox fluctuations, seasons, landscape positions and uses?

Plans are in place during the next few months to construct and install extensive field instrumentation, conduct field sampling and analyze a combination of soil cores, soil pore waters and gases along the floodplain forest, upland forest, agriculture, as well as stream water, and groundwater. We will install redox sensors, pressure transducers (stream/groundwater), soil moisture/temperature/EC monitors, gas probes (O_2 , CO_2), and DO/temperature sensors. Groundwater, stream water, soil pore water will be analyzed for pH, temperature, DO, Fe^{2+} , conductivity, turbidity, TDS, DOC, TOC, NO_3 , C, N and metals. Selected samples will be analyzed by XRD, SEM, XAS and Mossbauer Spectroscopy. Bench-scale leaching experiments with in-tact soil cores coupled with the X-ray computed tomography are also planned along with geochemical reactive transport modeling using the field and laboratory data.