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Nature of the Problem

Understanding the fate and transport of chemicals in subsurface systems is a fundamental issue when addressing environmental concerns related to safe drinking water and sustainability of ecosystem health.

Research Objectives

We propose to conduct a high resolution biogeochemical study of a wetland associated with a long-term research site (contaminated landfill-Norman, OK) in order to discriminate major microbial processes (e.g. denitrification, iron reduction, sulfate reduction, and/or methanogenesis) and their response to inputs from atmospheric deposition (rain) and/or subsurface flow (groundwater). To accomplish this we will sample mixing interfaces from the main components of the system namely, groundwater, porewater, surface water and sediments, in an effort to determine the main controls on redox conditions and contaminant transport at microscale resolution from one location in the wetland. Describing the redox conditions and microbial dynamics in the wetland and the processes by which organic matter can be solubilised and transported through the wetland (e.g. by rain events or groundwater) are imperative in assessing surface and groundwater quality. The innovation of this research is the quantification of hydrological, microbiological, and geochemical processes in a small-scale mixing interface, where most of the dynamics occur. The knowledge gained by the understanding of these processes could be readily transferred to both natural and contaminated wetlands in Texas, thereby improving the ability to protect and manage these fragile important ecosystems.

The toxicological endpoints of numerous chemical species, including nutrients and contaminants, are controlled by changes in the reduction-oxidation (redox) potential of a system. Of particular importance in subsurface systems are the metabolic activities of microorganisms, which mediate redox reactions through a series of terminal electron accepting processes (TEAPs) including aerobic respiration, denitrification, iron reduction, sulfate reduction, and methanogenesis. Safe drinking water and ecosystem health are thus controlled, in part, by TEAPs. Studies suggest that in highly anaerobic systems, shifts in TEAPs are controlled by the supply of terminal electron acceptors (TEAs) such as oxygen, nitrate, or sulfate at interfaces (mixing zones) between waters of differing redox potential. Recent models show that mixing at interface zones results in increased microbial activity; however, field investigations to quantify these processes have not been undertaken, presumably due to difficulties obtaining measurements at the scales needed to locate and characterize the small, highly transient nature of these zones. Without an understanding of the activity stimulated at interfaces, accurate prediction of the impact of environmental conditions on biogeochemical cycles cannot be made and consequently, the risk to human health and ecological sustainability cannot be assessed.

Water samples will be collected down a vertical profile that includes surface water and porewater from the slough and groundwater beneath the slough system. Groundwater from beneath the slough will be collected by pushing 2-cm PVC wells into slough sediments during sampling events. Slough porewater chemistry will be collected using passive-diffusion dialysis membrane "peeper" samplers. Peeper ports will be filled with deaerated, distilled, deionized water (DDDW) and inserted into the slough. A dialysis membrane will allow for diffusion of solutes between the DDDW and surrounding pore water until equilibrium is achieved, thus, samplers will be allowed to equilibrate for at least 2 weeks. These measurements will be taken in conjunction with redox microelectrode measurements collected by Dr. Michelle Lorah, funded by the U.S. Geological Survey Toxic Substances Program. She will make in-situ microelectrode measurements at various locations across the slough by pushing the microelectrodes into the sediment at centimeter increments until the top of the aquifer is reached.

Surface water, porewater, and groundwater samples from the slough will be analyzed in the field for temperature, pH, dissolved oxygen, and specific conductance using a water quality meter. Alkalinity, dissolved iron and sulfide will also be measured in the field using potentiometric titration and colorimetry respectively. Samples will be collected, preserved and analyzed in the laboratory using capillary electrophoresis (CE) for anions (Cl, Br, NO₃⁻, NO₂⁻, SO₄²⁻), cations (Ca, Mg, Na, K, Fe, and NH₄⁺), and low molecular weight fatty acids (LMWFA; formic, acetic, lactic and butanoic acids).

Upon completion, we expect to have mapped the distribution of TEAPs within the slough and identified the important processes initiated at the sediment-water interface. These data will provide new knowledge of the importance of microbiological, geochemical, and diagenetic processes on the fate and transport of chemicals through the slough system. These findings will provide the data necessary to identify the detailed distribution of TEAPs at a vertical transect at a single snapshot in time. However, preliminary bulk geochemical data within the slough suggests that TEAPs are highly variable both spatially and temporally. Therefore, we will use these preliminary data to design a full-scale spatial and temporal investigation of TEAP variability within the slough system. This knowledge is critical to assess the impact of mixing interfaces on the overall redox conditions of groundwater-slough system as well as other anaerobic systems and contributes directly to ongoing studies. We expect that by including increased TEAP dynamics at mixing interfaces (both those identified in the previous proposal and the sediment-water interface) into calculations of the overall rates of biodegradation and nutrient cycling cost effective remediation strategies such as monitored natural attenuation may become feasible at more locations.

The outcomes of this proposed research are expected to be of great value not only to scientists searching for improved ways to measure and interpret complex, interrelated, multidisciplinary processes, but also to members of industry, regulatory agencies, and environmental planners. We expect the new fundamental knowledge obtained from this work and the other related studies will significantly advance our understanding of the dynamics of coupled biotic and abiotic redox reactions in anaerobic environments and

thus enhance our ability to design and evaluate remediation and management plans for redox sensitive systems such as groundwater contaminant plumes and wetlands. This proposal will directly fund a graduate student (Susan Baez-Cazull) and hopefully lead to future work in this area. In addition, since the work will be performed at the USGS research site, the findings of this research will be summarized in a USGS "Fact Sheet" to ensure that results are widely distributed.

Intended Career Path Statement

My professional background includes a Bachelor of Science in Chemistry, a minor in Environmental Sciences, and a Teaching Certificate for High School Chemistry. Currently my research is the understanding of biogeochemical cycles, specifically the redox changes and the fate of chemicals in subsurface waters. The interdisciplinary emphasis of my research, integrating Chemistry, Environmental Sciences, Biology and Geology, will let me pursue a career in a competitive and interdisciplinary field. I envision myself working in a research related career (Academia/National Lab or Private Research) assessing water quality and the preservation of natural environments.