Enhanced in situ Bioremediation at a Former Refinery Site due to Recycling of Aerosol Sulfate in the Groundwater Fluctuation Zone

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Background/Objectives. The results from a 10 year monitored natural attenuation (MNA) study at a former refinery site in north-central US show that the input of aerosol sulfate is responsible for more hydrocarbon biodegradation in the saturated smear zone than occurs through methanogenesis. The MNA study was initiated in response to the fact that the residual hydrocarbon composition in the smear zone indicated a rate of BTEX loss at the site that was an order of magnitude greater than projected by the conventional MNA model. Two main natural attenuation processes not included in the MNA model were to be addressed in the MNA study: 1) addition of electron acceptors (EAs) through dispersion of underlying groundwater; and 2) loss of methane from the groundwater through gas transport to the vadose zone. As the site was located within the region of the US where coal burning occurs, aerosol sulfate addition to groundwater was included in the MNA model.

Approach/Activities. Vertical profile sampling of soil, soil gas and groundwater was carried out at 21 locations across the almost 1 mile long smear zone footprint. At locations downgradient from where EAs from groundwater are depleted, sulfate concentration near the top of groundwater (1 - 2 feet) seasonally ranged from greater than 100 mg/L at high groundwater level to < 5 mg/L at low groundwater level. At these locations, aerosols were the only potential source of sulfate. The reduced sulfur content in the saturate zone soil near the top of groundwater was generally > 100 ppm, compared to < 10 ppm at the background locations. The concept of 'recycling of aerosol sulfate' was developed to explain these field measurements. The model included: 1) sulfate reduction and formation of mineral sulfide in the saturated smear zone near the top of groundwater; 2) groundwater level drop and mineral sulfide oxidization to sulfate in the vadose zone; and 3) dissolution of sulfate in groundwater as groundwater level rises leading to another cycle of sulfate reduction and mineral sulfide formation. As a result, aerosol input of sulfate (estimated at 15 mg.L in percolation water) is primarily accumulated in the soil near the top of saturate zone, increasing with time the magnitude of anaerobic biodegradation in the saturate zone. This concept was tested in the bioventing area of the site to determine whether changes in the rate of anaerobic biodegradation would be increased due to engineered aeration of the soil. Separately, a pilot study was carried out in which heated Epsom salt ($MgSO_4$) solution was added to the vadose zone above the smear zone through a 40 foot perforated pipe placed perpendicular to the groundwater flow. Downgradient of the pipe, multi-depth groundwater sampling and continuous temperature monitoring were carried out for a 9 month period of time.

Results/Lessons Learned. Several years of semi-annual groundwater measurements were used to evaluate the relative importance of vertical dispersion, transport of methane to the vadose zone, and aerosol input. Based on groundwater chemistry, aerosol input was concluded to be the main process for hydrocarbon degradation. The input of sulfate at the top of the smear zone reduced the rate of methanogenesis in groundwater so that gas saturation only occurred seasonally over part of the site. Within the smear zone, benzene concentration decreased significantly during the time of monitoring. The highest sulfate concentrations and greatest decreases in benzene concentrations, in general, occurred in the bioventing area. The results from the pilot study will be discussed in terms of lessons-learned, and the benefit for

adding sulfate to the vadose zone, rather than directly to groundwater, as a potential long-term remediation option.