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Interpreting Interactions between Ozone and Residual Petroleum Hydrocarbons in Soil

Tengfei Chen (tchen53@asu.edu), Anca G. Delgado (anca.delgado@asu.edu), Burcu M. Yavuz (Burcu.Yavuz@asu.edu), and Juan Maldonado Ortiz (Juan.Maldonadoortiz@asu.edu) (Arizona State University, Tempe, AZ, USA)
Yi Zuo (yizuo@chevron.com) (Chevron Energy Technology Company, San Ramon, CA, USA)
Roopa Kamath (rkamath@chevron.com) (Chevron Energy Technology Company, Houston, TX, USA)
Paul Westerhoff (p.westerhoff@asu.edu), Rosa Krajmalnik-Brown (Dr.Rosy@asu.edu) and Bruce E. Rittmann (rittmann@asu.edu) (Arizona State University, Tempe, AZ, USA)

Background/Objectives. Extensive anthropogenic activities related to the petroleum industry inevitably result in hydrocarbon contamination in terrestrial environments. Accidental release of petroleum to soil results in long-term contamination that has potential hazard to health and can harm the ecosystem and functionality. While natural attenuation can remove petroleum's lighter and simpler compounds, such as short-chain alkanes and single-ring aromatics, the heavier residuals (long-chain branched alkanes, cycloalkanes, polycyclic aromatic hydrocarbons, and asphaltenes) may remain even after decades of weathering and are resistant to biodegradation. Ozone gas is capable of transforming recalcitrant organic compounds to more biodegradable forms and can be used as pre-treatment to benefit the following bioremediation. We used ozone gas at the bench scale to determine the efficacy of pre-oxidation for making HH residuals in unsaturated soils more bioavailable.

Approach/Activities. We treated 300 grams of soil containing weathered petroleum hydrocarbons (18 g TPH/kg) with ozone gas (inlet concentration10,000 ppmv) for 1, 2, 3, and 4 hours. We measured soluble chemical oxygen demand (SCOD), 5-day biochemical oxygen demand (BOD_5), dissolved organic carbon (DOC), and total petroleum hydrocarbons (TPH) before and after ozone treatment. We also established a carbon balance to better understand the chemical processes occurred in soil.

Results/Lessons Learned. A dose of 3.4 kg O_3/kg initial TPH reduced nearly 5 gC/kg (40%) of TPH in air-dried soil, and this was accompanied by an increase of about 4 gC/kg in dissolved organic carbon (DOC) and a four-fold increase in 5-day biochemical oxygen demand (BOD_5). Ozonation also resulted in two measurable alterations of the composition of the organic carbon. First, part of DeOC was converted to DOC, 75% of which was no longer extractable by dichloromethane. Second, the DeOC containing saturates, aromatics, resins, and asphaltenes (SARA), was partially oxidized; this resulted in a decline in saturates and aromatics, but increases in resins and asphaltenes. The results illuminate the mechanisms by which ozone gas interacted with the weathered petroleum residuals in soil.