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# Field Demonstration of Citrate Amendments for Hydrocarbon Degradation in Cold Region Soils

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**Background/Objectives.** Phosphorus (P) bioavailability often limits gasoline biodegradation in calcareous cold region soils. One method to increase P bioavailability in such soils may be the addition of citrate. Citrate addition at the field scale may increase hydrocarbon degradation by: (i) enhancing inorganic/organic P dissolution and desorption, (ii) increasing hydrocarbon bioavailability, and/or (iii) stimulating microbial activity. Alternatively, citrate addition may inhibit activity due to competitive effects on carbon metabolism. Using a field-scale in situ biostimulation study, we evaluated if citrate stimulated gasoline degradation and the dominant mechanism of this stimulation.

**Approach/Activities.** Two large bore injectors were constructed at a site contaminated with gasoline, and a biostimulation solution of 11 mM $MgSO_4$, 1 mM $H_3PO_4$, and 0.08 mM $HNO_3$ at pH 6.5 in municipal potable water was injected at approximately 5000 L $day^{-1}$ for six months. Following this, 10 mM citric acid was incorporated into the existing biostimulation solution and the site continued to be stimulated for nine months. We tracked basic properties, common cation/ anions, petroleum hydrocarbon fractions for eight groundwater monitoring wells from three areas (Background Area, Area 1 and Area 2) in the site. Soil P fractions, petroleum hydrocarbon fractions were also determined before and after two different amendment deliveries for unsaturated/saturated zones from nine soil boreholes in three areas. Soil resin extracted inorganic P, $NaHCO_3$ extracted P and NaOH extracted P were analyzed by chemical sequential extraction method. Soil petroleum hydrocarbon fractions were collected and analyzed mainly based on CCME protocol.

**Results/Lessons Learned.** The citrate addition increased phosphate amendment efficiency for anaerobic gasoline bioremediation in calcareous soil. After citrate addition, the bioavailable P fraction in groundwater and soil increased. For example, dissolved phosphorus in Area 1 was undetectable before September 2015 to 0.2 mg $L^{-1}$ after citrate addition, increased from 0.2 to 0.6 mg $L^{-1}$ in Area 2 before and after citrate addition. Iron(II) groundwater concentrations increased and corresponded to decreases for BTEX (benzene, toluene, ethylbenzene, xylenes) in groundwater as well as decrease for $F1_{-BTEX}$ in the soil saturated zone. Overall, citrate addition increased P bioavailability and stimulated microbial activity, resulting in accelerated anaerobic gasoline bioremediation in cold region calcareous soils.