

## Chemical Composition of Groundwater Hydrocarbon Mixtures Before and After Aerobic Biodegradation

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Changes in biodegradability and chemical composition of weathered hydrocarbons in groundwater were investigated through biodegradation experiments at the former Guadalupe Oil Field. Diesel-range-oil was used at this site as a diluent to facilitate pumping of crude oil, and leaks of this diluent caused contamination of soil and groundwater. Natural attenuation is being considered as a remediation option for some groundwater (GW) plumes and source zones and as a remediation polishing step for others. To ensure the diluent hydrocarbons in the GW will be reduced to acceptable levels through natural attenuation, it is important to demonstrate that the hydrocarbons continue to be biodegradable after partial biodegradation and weathering. Previous studies have shown rapid initial biodegradation is followed by much slower biodegradation. One hypothesis that may explain this observation is that more easily degraded hydrocarbons are biodegraded first, leaving the more recalcitrant hydrocarbons. To investigate this hypothesis, large-scale microcosms were operated on site to observe changes in biodegradability and chemical composition over the course of long-term biodegradation experiments. Five microcosms were constructed from 4-ft-cubed polypropylene boxes and filled with non-contaminated sand taken from the site. 100 gallons of GW containing dissolved-phase diluent hydrocarbons was collected from the site and recirculated through the saturated zone of the boxes. GW samples were periodically collected from each of the 5 boxes over the course of two 104-day biodegradation experiments. Biodegradability was measured using 20-day incubations of the GW samples and measuring initial and final total petroleum hydrocarbon (TPH) concentrations. Gas chromatography (GC) with simulated distillation (SIMDIS) integration was used to determine changes in equivalent carbon chain length of the hydrocarbons. IR spectroscopy was used to examine functional groups and silica gel column fractionation was used to determine changes in aliphatic, aromatic, and polar TPH fractions.

During the first experiment, the average TPH concentration decreased by 50% in the first 19 days, starting at  $3.57 \pm 0.43$  mg/L and biodegrading to  $1.65 \pm 0.39$  mg/L. Between 19 and 67 days biodegradation was slower, decreasing from  $1.65 \pm 0.39$  mg/L down to  $0.88 \pm 0.12$  mg/L. Between 67 and 104 days, little or no further biodegradation was observed, as the final TPH concentration was  $0.86 \pm 0.09$  mg/L. Trends in biodegradability were similar for a second experiment. GC/SIMDIS showed the preferential biodegradation of short-chained hydrocarbons. Column fractionation revealed that the dissolved petroleum material was entirely in the polar fraction at the start of the experiment and this material biodegraded over time. Infrared spectroscopy showed the polar character was due to carbonyl groups. Experiments with diluent source material showed that the polar compounds containing carbonyl groups are present in very

low concentrations in the non-aqueous phase, and that these compounds preferentially fractionate into water. During biodegradation the peak areas for the carbonyl groups decreased at a slightly faster rate than that of the alkyl groups. These results suggest that weathered hydrocarbons are polar and contain carbonyl groups, but that other characteristics are responsible for observed decreases in biodegradability during weathering.