Natural Source Zone Depletion (NSZD) Investigation at a Paved Former Service Station Site in Spain

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Background/Objectives. An investigation is underway to determine whether NSZD is a viable remedial option for gasoline and diesel residues in unconsolidated sediments below a former service station in Spain. The unconsolidated material includes boulders, pebbles and gravels in a sandy to clayey matrix, underlain by shale and sandstone beds. A perched water table is present at the base of the permeable units about 30 feet below ground, with a thickness of <2 feet. The objectives of the project are to: 1) determine if NSZD of a diesel LNAPL (Light non-aqueous phase liquid) plume at a paved site (typical for retail stations) is a viable remedial option, 2) evaluate the rate of NSZD using the standard CO_2 flux trap method along with testing the effectiveness of two alternative NSZD rate measurement methods (temperature and O_2/CO_2 gradient), and 3) test a phased approach using the existing groundwater monitoring wells supplemented with shallow soil gas samples as the first step to optimize the NSZD investigation. Since NSZD is a new technology in Europe, this site has been chosen to demonstrate NSZD to Spanish regulators before proposing wider implementation in the country. This work is a collaboration involving BP and Concawe.

Approach/Activities. Phase 1 of the investigation, which has already been completed, included an initial assessment of the site using existing groundwater monitoring wells to collect soil gas samples at the base of the vadose zone, and vertical profiles of temperature through the vadose zone and into groundwater. Using a low- flow sampling technique, soil gas O_2 and CO_2 measurements were made in the field using a portable gas analyzer (infrared). Indirect LNAPL delineation was also attempted using shallow soil gas O_2 and CO_2 measurements below the cover. Phase 1 demonstrated patterns of temperature and soil gas O_2 and CO_2 concentrations in the subsurface consistent with in-situ biodegradation of fuel residues, confirming the viability of phase 2. Phase 2, which was initiated in June 2017 includes the installation of 7 new groundwater monitoring wells, 5 dedicated vapor probes, 5 CO_2 traps, 26 soil sample analyses, and deployment of continuous in-situ temperature sensors. The O_2 and CO_2 gradient and temperature measurements will be collected quarterly, and CO_2 flux measurements will be made twice a year. ^{14}C analysis will be performed on the CO_2 trap samples along with selected soil, soil gas and LNAPL samples. The intent of Phase 2 is to cover seasonal fluctuations over a full year, supporting better estimates of air and thermal diffusivities, and therefore NSZD rate.

Results/Lessons Learned. The Phase 1 monitoring well measurements of soil gas O_2 and CO_2 and temperature data resulted in estimated rates of non- aqueous phase liquid (NAPL) biodegradation of 500 to 5,000 and 600 to 1,800 gal/acre-year, respectively, indicative of NZSD being a viable remediation option for the site. Documenting that O_2 was available in the subsurface alleviated concerns that the pavement might impede the flow of oxygen into the subsurface. The shallow soil gas O_2 and CO_2 measurements below the asphalt cover resulted in the discovery of hydrocarbon-impacted surface fill material over a portion of the site. This finding meant that the location of any surface CO_2 flux chambers and background locations must be outside the influence of the impacted fill. Initial Phase 2 data is pending. The first

temperature recordings will be retrieved in October 2017. We expect to present 6-months of data at the conference. We will discuss the seasonal variability observed, the effectiveness of the three measurement methods tested and compare in-well and dedicated vapor probe measurements.