

Mobility of a Highly Weathered Mixed Bunker Fuel and Diesel NAPL

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Background/Objectives. Targeted soil excavation at a former fuel depot was identified as a key component of a remedial strategy to prevent petroleum hydrocarbon sheens from forming on the adjacent estuary. The sheens were potentially caused by mobile non-aqueous phase liquid (NAPL) migrating from soil within approximately 300 feet of the shoreline. The NAPL consists of a mixture of varying proportions of highly weathered bunker fuel and diesel. The NAPL is present in discontinuous pockets in highly variable soil types, ranging from low-permeability silts and clays, to loose sand and gravel. Laboratory methods were used to develop a range of total petroleum hydrocarbon (TPH) concentrations in soil above which mobile NAPL was present, and which could be used as an action level to screen soil during excavation, thereby limiting the excavation extent to areas where the NAPL was potentially mobile. In addition, a correlation between laboratory and field TPH analysis methods was developed to facilitate real-time field screening of soils during excavation.

Approach/Activities. An initial study was conducted to estimate residual NAPL saturation (C_{res}) for representative NAPL bunker-fuel/diesel compositions and soil types. NAPL mobility was tested in 16 soil samples using the ASTM D425 centrifuge method. Bunker fuel and diesel concentrations were measured in immediately adjacent soil samples from 1-foot-long cores using three methods: gas chromatography (GC; EPA Method 8015B), ultraviolet fluorescence (UVF; Sitelab UVF-3100A analyzer), and the Dean-Stark (DS) extraction method.

In a follow-up study, free product mobility and TPH concentrations were evaluated in 26 soil cores. Intact, post-centrifugation soil cores were homogenized and analyzed for TPH using GC to quantify immobile TPH concentrations. Adjacent soil samples for GC and UVF analysis were split from a homogenized sample to reduce sample-scale heterogeneity and improve reproducibility. Site-specific calibration standards for two typical bunker-fuel/diesel compositions were used for GC and UVF analysis.

Results/Lessons Learned. Mobile NAPL was detected in 12 out of 42 soil samples, predominantly in sandy/gravelly alluvial soil. The initial study identified several challenges associated with establishing C_{res} values based on a comparison of laboratory data on adjacent soil samples. The correlation between the DS extraction results and TPH measured using GC and UVF methods was poor. Substantial heterogeneity on the scale of a 6-to-12-inch soil core was observed, likely due to the presence of pore-scale ganglia, indicating the need for thorough sample homogenization prior to analysis. The wide range of bunker fuel-diesel proportions observed in the NAPL required the use of representative custom calibration standards for GC and UVF analysis, to be representative of site-specific NAPL composition.

The GC-UVF and GC-DS correlations improved substantially in the follow-up study due to the use of homogenized post-centrifugation soil for TPH measurement and the use of site-specific calibration standards. The C_{res} for bunker-fuel-dominated NAPL ranged from approximately 20,000 to >140,000 mg/kg. The C_{res} for diesel-dominated NAPL was approximately 15,000 mg/kg. These C_{res} values are generally consistent with literature data. A soil screening approach was developed based on these data. However, due to the large variability in C_{res} , the screening approach is highly conservative and requires laboratory confirmation of TPH concentrations as well as laboratory mobility testing of samples containing TPH above the minimum C_{res} concentrations. This study illustrates challenges associated with evaluating the mobility of a complex, highly weathered NAPL present in soils of varying permeability.