An Empirical Ecological Risk Assessment at a Mature Bay Margin Petroleum Site Focused on Polar Degradation Metabolites

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Background/Objectives. Site-specific point-of-compliance (POC) levels for total petroleum hydrocarbons (TPH) as diesel, bunker fuel, and jet fuel were established in 2001 for groundwater discharging to San Francisco Bay ("the Bay") at a 400-acre former fuel storage facility. The POC levels were based on TPH analysis by EPA Method 8015B with silica-gel cleanup (SGC) and were established to be protective of the saltwater aquatic habitat in the hyporheic zone. In 2014, the Regional Water Quality Control Board (RWQCB) requested TPH analysis without SGC, to qualitatively evaluate the presence of polar petroleum degradation metabolites ("polar compounds") in groundwater. Until 2014, TPH concentrations in most shoreline wells met POC levels; however, results of TPH analysis in these wells without SGC exceeded POC levels due to the presence of polar compounds. The RWQCB then requested an evaluation of potential ecological receptor toxicity related to polar compounds. A regulatory screening level for polar compounds in groundwater has yet to be established, due to the difficulty in identifying and quantifying the complex mixture of polar compounds and a paucity of ecological toxicity data. Therefore, an empirical ecological risk assessment was implemented to evaluate such potential toxicity and to re-assess POC levels.

Approach/Activities. A laboratory test was developed to assess potential ecological risk from polar compounds. The test used the EPA method for estimating acute and chronic toxicity effects in marine and estuarine organisms. The test consisted of direct aquatic toxicity testing of representative saltwater species (benthic invertebrate, crustacean, and fish) using groundwater that contained polar compounds only. Groundwater salinity, temperature, and dissolved oxygen were adjusted to match estuarine conditions. A "persistence test" was initially conducted using the same protocol as the direct aquatic toxicity test, but without aquatic species, to assess the potential loss of transient polar compounds via volatilization and degradation during sample handling and storage. Subsequent testing included direct aquatic toxicity testing of the selected species using undiluted, adjusted groundwater, as well as serial dilution testing. Serial dilution testing was conducted to generate a dose-response curve that could yield an ecological receptor toxicity threshold value for polar compounds.

Results/Lessons Learned. The persistence test did not indicate significant losses of polar compounds during storage. Direct aquatic toxicity testing showed an effect (both acute and chronic growth) from undiluted, adjusted groundwater for the crustacean (mysid shrimp) receptor only. Toxic effects were not observed for the benthic invertebrate (mussel embryo) or the fish (inland silverside) species. Confounding factors were excluded by confirming that no toxicity resulted from background groundwater that had no polar compounds, as well as through use of reference toxicant tests. The serial dilution testing identified a threshold concentration of 581 to 763 micrograms per liter, quantified as TPH as diesel. The results of the test represent a preliminary assessment for the establishment of a regulatory threshold, with follow-up direct aquatic toxicity testing to be conducted to evaluate potential seasonal effects. This threshold applies to the broad class of polar compounds that can be detected by EPA Method 8015B. Study findings may result in a lowering of POC levels, with potential implications for site closure. Based on site-specific conditions, other near-Bay sites approaching regulatory closure, or even

having obtained regulatory closure, may have to adopt a similar site-specific risk-assessment approach in the interim, until regulatory screening levels for polar compounds are established.