# Approaches to Evaluate Ecological Risk from Polar Petroleum Degradation Metabolites in Groundwater at Mature Petroleum Sites

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**Background/Objectives.** Polar petroleum degradation metabolites ("polar compounds") are a group of thousands of compounds that are generated from the degradation of diesel, bunker fuel, and other fuel products. The vast majority of polar compounds cannot be quantified using commercially available analytical methods, and have no regulatory screening levels. The San Francisco Bay Regional Water Quality Control Board (RWQCB) has required the analysis of total petroleum hydrocarbons (TPH) in groundwater at mature petroleum sites to be performed by EPA Method 8015B without silica gel cleanup (SGC) to provide a qualitative measurement of polar compounds, which can be detected, but not quantified, using this method. The RWQCB has also required screening of results against TPH screening criteria, even though risk-based TPH groundwater screening levels are developed using fresh (undegraded) fuels. TPH analytical methods and screening levels were not designed to measure or screen polar compounds. Concentrations of polar compounds can often vastly exceed TPH concentrations in groundwater because of differences in solubility. Consequently, previously established point-of-compliance (POC) levels can be exceeded because analysis of TPH in groundwater by EPA Method 8015B without SGC will yield elevated concentrations due to the presence of polar compounds. Responsible parties are faced with a dilemma of re-assessing POC levels for TPH in groundwater discharging to estuarine waters. Benefits and challenges of approaches to evaluate site-specific risk from polar compounds in groundwater were explored.

**Approach/Activities.** Currently, responsible parties have the following options for evaluating site-specific risk from polar compounds: (1) screen TPH concentrations measured without SGC (i.e., "TPH+polars") against previously established site-specific POC levels or current state and local TPH screening levels; (2) conduct a fate-and-transport evaluation of polar compounds; (3) conduct a near-shore hydrogeologic investigation to identify groundwater discharge zones and test sediment porewater in proximity to these locations; and (4) conduct site-specific toxicity testing to assess acute and chronic toxicity effects on ecological receptors. An evaluation of these alternatives was performed for a near-Bay site.

**Results/Lessons Learned.** (1) Screening of TPH+polars concentrations against established TPH site-specific POC levels and/or standard regulatory TPH screening levels is not technically sound and may set an unachievable goal. Polar compounds can be generated at mature petroleum sites for decades in the presence of slowly degrading fuels. (2) A fate-and-transport evaluation is difficult due to the sparse physical and chemical properties available for polar compounds. (3) Identifying groundwater discharge zones in dynamic tidal environments requires a rigorous, and likely expensive, hydrogeologic study, the results of which may be inconclusive. Collecting pore water from the right location in the hyporheic zone is a challenge. Interpretation of sediment porewater data collected along a transect where groundwater is discharging is complicated by potential comingling of polar compounds from other sources and the certain presence of naturally-occurring organic matter in the hyporheic zone. (4) A site-specific ecological toxicity assessment may be the most favorable option. Groundwater from near-shore wells can be used for direct aquatic toxicity testing of select saltwater species, provided that salinity, temperature, and dissolved oxygen in groundwater are adjusted to match saltwater conditions. Furthermore, serial dilution testing can be used to establish a threshold for chronic effects that can then be used to establish polar-compound-specific POC levels for the site.