

## Historical Trend Testing of a Mass-Balance Method for LNAPL Body Stability at Bemidji, Minnesota

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**Background/Objectives.** Site investigators often evaluate LNAPL body stability with a mass balance between rates of LNAPL lateral migration against rates of LNAPL mass depletion based on production of CO<sub>2</sub> over an LNAPL footprint area. These represent a “snapshot in late time.” Our objectives were to: 1) quantify historical trends in mass loss rates inferred from compositional changes in archived to recent LNAPL samples, with comparison to historical CO<sub>2</sub> efflux rates reported for the same project site, and 2) to model historical LNAPL transmissivities with estimated matrix properties, the history of fluid property changes, and mean water-table gradient to estimate historical inflow into a downgradient LNAPL area. The mass balance approach would be tested during: 1) a historical period when the leading edge was known to be advancing, and 2) a recent period when advancement was becoming asymptotic. Our approach included a probabilistic analysis to be consistent with the inherent uncertainty of reaching stability.

**Approach/Activities.** To test our hypothesis, we chose the North Pool oil body at the 1979 crude oil pipeline release site near Bemidji, MN. We obtained 30 years of monitoring well data from the USGS and mapped the average water-table configuration, plotted and quantified declining unconfined in-well LNAPL thickness trends, and mapped decelerating advancement of the North Pool leading edge. We analyzed 8 archived and 19 recent LNAPL samples with GC and GC/MS methods and estimated mass losses in each relative to a 1984 reference pipeline sample. We quantified historical trends in physical property changes reducing LNAPL mobility. We found significant oil saturation reductions in core samples collected 1991-92 and 2010-11, consistent with oil spreading, mass depletion by biodegradation, and mass removal efforts (1999-2003). Mass loss was based on changes in moles of 56 hydrocarbons normalized to one mole of Pristane, and minor additional mass losses for PAHs and biomarkers identified with GC/MS analyses.

**Results/Lessons Learned.** During 1979-89, the North Pool geochemical environment changed from aerobic to methanogenic. Mass losses were large, but changes in LNAPL physical properties were small. During 1990-2012, densities increased slightly but viscosities increased exponentially. The best-fit historical trend for LNAPL mass losses was re-arranged to represent the LNAPL mass remaining with a first-order exponential decay rate. Given a 1991-92 USGS LNAPL volume estimate based on ten core locations and 142 oil-saturations, the original mass that reached the water table was back-calculated. The derivative of the mass loss function provided historical daily rates of mass loss for the entire LNAPL body, and generally agreed with four historical CO<sub>2</sub> efflux estimates, supporting the CO<sub>2</sub> mass-loss approach. Historical LNAPL inflow rates exceeded mass loss rates in the 1980s-2000s. Future mass gain-loss trends ( $\pm$  95% C.I.) define a “window of stabilization” from 2019 to 2031. At older release sites, the remaining time needed to reach mass-balance stability is considered probable, rather than certain. Regulatory policies might consider incorporating this reality with multiple-lines-of-evidence approaches for demonstrating LNAPL stability.