Measuring In Situ Degradation by Tracer Stable Isotope-Labeled RDX Groundwater Release

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Background/Objectives. Munitions-derived chemical contamination represents a significant environmental hazard at military range sites and a challenging financial consideration for managing liability. Managing impacted sites requires understanding contaminant attenuation rates - either pre-, during- or post-remediation efforts. Methods which measure contaminant mineralization under natural or engineered conditions are particularly desirable. Natural abundance compound-specific stable isotope analysis (CSIA) has been used to track contaminant biodegradation in discreet plumes. Often, sites like military ranges are contaminated over long time periods with multiple source end-members making natural abundance isotope Raleigh distillation modeling problematic for calculating contaminant mineralization rates. Alternatively, because minor carbon (^{13}C) and nitrogen (^{15}N) isotope natural abundances are relatively low (carbon-13 ~ 1%, nitrogen-15 ~ 0.4%), adding small quantities of isotopically-labeled substrates into the environment may allow tracking biodegradation into intermediates or final degradation products. Isotopically-labeled compound analysis is highly sensitive so tracer levels of labeled substrates may be added to the environment at concentrations allowing regulatory approval. Tracking the label into degradation products (*e.g.* CO_2, CH_4, N_2O, N_2, NO_{2+3}, NH_4^+, etc) allows determining in situ contaminant degradation rates.

Approach/Activities. We identified several range sites at the Naval Base Kitsap (Bangor, Washington) having elevated RDX concentrations above regulatory levels (0.8 µg L^{-1}) - requiring active remediation (pump and treat). In an effort to determine natural RDX degradation rates and rates associated with biostimulation (fructose addition) and bioaugmentation (*Gordonia* sp. KTR and *Psuedomonas* Strain I-C addition), push-pull tests (PPTs) using conservative tracers (Cl^{-1}) and dual ^{13}C-, ^{15}N-labeled RDX (uniform ring label) were performed in April - May 2018 at "Site F." Groundwater was sampled for 30 days (14 time-points) subsequent to the push (~ 400 gallons containing 1 mg L^{-1} ^{13}C-, ^{15}N-labeled RDX) at 6 wells (1 bioaug and 1 bioaug downgradient (3 m), two biostim (fructose) and two native). Groundwater was assayed for RDX concentration, Cl^{-1} concentration, dissolved CO_2 (DIC), dissolved CH_4, $\delta^{13}CO_2$, $\delta^{13}CH_4$, $\delta^{15}N_2O$, $\delta^{15}N_2$, $\delta^{15}NO_{2+3}$, and $\delta^{15}NH_4^+$. Concentrations and isotope ratios were used to determine enrichment factors representing labeled RDX *in situ* degradation. First order degradation kinetics were determined from starting and time-point RDX concentrations for comparison. Longer-term CO_2 traps (NaOH) were suspended in the well headspaces to assess long-term labeled RDX fate. A zone of influence (ZOI) model is developed to determine the spatial sampling volume for in-well traps.

Results/Lessons Learned. We observed relatively rapid RDX degradation rates calculated from ^{13}C- and ^{15}N-labeled RDX. Isotopically-enriched CO_2, CH_4 and N_2O, N_2, NH_4^+, and NO_{2+3} was observed at each well during the PPTs. Former bioaug wells (F-DW03 and F-MW59 (downgradient)) showed relatively high RDX turnover (conversation to $^{13}CO_2$ and $^{13}CH_4$ and ^{15}N-DIN endrpoducts) to over mg quantities per L within 1 week of injection. Biostim wells (F-MW35 and F-MW39) had ^{13}C- and ^{15}N-enriched CO_2, CH_4 and N_2O as well indicating

biodegradation. A control well (F-MW58) showed degradation but at levels lower than bioaug or biostim wells. Data are still being analyzed at present, so full reporting will be available by the meeting.