Comparing Natural Source Zone Depletion in the Vadose and Saturated Zones at a Fuel Release Site

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Background/Objectives. Natural source zone depletion (NSZD) refers to processes within the vadose and saturated zones impacted by chemical releases that reduce the mass of contaminants remaining in a defined source control volume (SCV). There are only a few studies of large petroleum hydrocarbon (PHC) release sites that have compared vadose zone NSZD rates to saturated zone NSZD rates. These studies show that the depletion rate by vapor phase migration of degradation products (DPs) from the SCV through the vadose zone (V-NSZD) is often considerably higher than the rate of depletion from the SCV by groundwater flow carrying dissolved PHCs arising from dissolution, desorption or back diffusion, and DPs arising from biodegradation (GW-NSZD). In this study, we quantified V-NSZD and GW-NSZD at a small fuel release site in California typical of those in low permeability media at which natural attenuation of groundwater contaminants has been progressing at a slow rate. During operation from approximately 1930 to 1993, multiple releases of unknown volume and composition impacted soil and groundwater. In March 1993, the service station ceased operations and all above- and below-ground facilities were removed. Various investigative and remedial efforts were employed to delineate and remove or degrade PHCs at the site. Engineered remediation ceased in October 2006 and an MNA strategy was employed through August 2015, at which time a new in situ remediation approach was initiated. This study evaluates NSZD during the MNA period, i.e. from October 2006 through August 2015.

Approach/Activities. We estimated V-NSZD using a dense network of efflux monitoring locations around the unpaved site in four sampling events over two years; our method could monitor efflux of both CO_2 and CH_4. We estimated GW-NSZD using groundwater monitoring data from pre-existing wells downgradient of the SCV in three depth intervals spanning up to 9 years. Species included in GW-NSZD were contaminants, represented by TPH_g and $TPH_{d\text{-}sgc}$ (i.e., TPH_d determined after silica gel cleanup), and the following DPs: dissolved inorganic carbon (DIC), nonvolatile dissolved organic carbon (NVDOC), and CH_4.

Results/Lessons Learned. V-NSZD (on average, 1741 ± 74 g/d as C) was >15 times greater than GW-NSZD (on average, 107 ± 53 g/d as C) during the time interval of comparison. If octane is taken as representative of the fuel released at the site, V-NSZD is equivalent to a depletion rate of approximately **75**0 gallons per acre per year, in the range of estimates made at one former refinery, but lower than estimated for a second former refinery or for a crude oil spill in Minnesota. Uncertainty in both V-NSZD and GW-NSZD arose from spatial and temporal variations in measured parameters. CH_4 was not detectable in the efflux. DIC was by far the most important component of GW-NSZD. The order for the rest of the species was $NVDOC>CH_4>TPH_g>>TPH_{d\text{-}sgc}$. V-NSZD and GW-NSZD rates measured prior to vadose zone or groundwater remediation can serve as a baseline and measurements can be repeated during and following remediation to assess changes**.** Although not tested specifically in our work, our data suggest that achievement of remediation goals for groundwater may not be strongly related to V-NSZD at sites where the smear zone for released fuel extends deep into the saturated zone due to historical GW level fluctuations.