

## ARE ETHYLENE AND PROPYLENE DERIVED FROM ETHANE AND PROPANE IN SOIL GASES AND CONTAMINATED GROUNDWATER?

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### ABSTRACT

Ethylene and propylene found in shallow soil gases have been suggested to be biological degradation products generated in the shallow vadose zone from their saturated counterparts, ethane and propane under low oxygen conditions (Telegina, 1971). ETI has an extensive data base from both exploration and environmental surveys that confirms their presence in association with essentially all shallow soil gas surveys conducted over the past 40 years. A case study conducted over a very large Petrochemical complex (PCC) that included an old (inactive) and an active refinery, fuel storage tanks, service stations and even leakage from deep production wells, provided a wide and complex variety of examples where ethylene and propylene occurred in large anomalous concentrations in both the soil gas and in the groundwater in contact with free products. Although their magnitudes are scattered by unknown biological factors, this data clearly shows that these two olefins occur in all areas surveyed where anomalous ethane and propane are present. This was true in all contaminated areas on the PCC site, whether from shallow petroleum leakage, or deep production casing leakage.

This PCC environmental case study was conducted using a phased assessment approach, starting with measuring the soil gas hydrocarbon vapors derived from the lost products to accurately define the lateral extent of subsurface petroleum contamination and the complex subsurface geological pathways that control the migration and distribution of these petroleum products in the earth. The more volatile components (methane, ethane, propane, butanes and C5+) contained within the lost product provided guidance for drilling monitor wells. In this case, over 5000 soil gas samples were placed on a 50 ft. (15m) regional grid, with final infill (1109 sites) varying down to as close as 10 ft. (3m) in order to properly place and design recovery trenches during the remediation phase.

Using the soil gas component maps as a guide, 104 borings/monitor wells were installed and sampled on 2 foot intervals to determine the vertical contaminant distribution in the subsurface. Eighty-two (82) of these monitor wells had significant concentrations of contaminants, with 63 having up to 2 feet of liquid hydrocarbons on the ground water. Sediment core samples were analyzed on two foot intervals using multiple analysis techniques (synchronous fluorescence, in addition to BTEX and TPH), for mapping vertically distributed products. Geological coring logs were used to generate detailed geological cross-sections, and to confirm geological migration pathways, initially defined by the soil gas data. A seven-foot deep soil gas data set was used to more accurately determine pathways where interceptor/recovery trenches would be most effective. Using approximately 1109 seven-foot deep samples for control, interceptor/recovery trenches, totaling 1600 feet in length, were installed and recovered over 1,300 barrels of hydrocarbon products in less than one year.

Free product and groundwater samples were collected and analyzed from the monitor wells on a periodic basis as the free product was purged from the wells. Product thicknesses and groundwater levels were recorded and mapped. All purged free product samples and the impacted groundwater underlying the free product were analyzed for all components, including

both C1-C4 soil gases and benzene/BTEX components in groundwater, illustrating the compositional coherence between the near-surface soil gases, the subsurface free product and the groundwater, validating and confirming the direct association and accuracy of the soil gas plumes for mapping the offsite migration avenues.

It was striking to find very large magnitude olefins 100 to 300 ppm range (ethylene and propylene) in the groundwater within the more contaminated areas, and in the overlying soil gases. The close fit of the contours for ethane and propane with respect to these two olefins suggests some sort of genetic relationship between these saturated and olefin components. The presence of these olefins in both the soil gas above, and the groundwater below product contaminated areas suggests they are likely generated independently within the vadose zone and the underlying groundwater. Since the olefins do not occur in the background uncontaminated areas, they are clearly related to the presence of the free product contamination.

"Variations in component magnitude show no obvious relationship to variations in product type or thickness in any of these wells. With the exception of two wells (MW-102 and MW-175), similar variations are noted for all the wells, with ethane and propane always being larger than ethylene and propylene, again suggesting that these olefins are likely generated from their respective saturate components. The scatter between the saturated and olefin ratios suggests a microbiological relationship that strongly depends on the local environmental conditions, which would be affected by purging the wells of water and free product. Oxygen levels would likely be increased by this process, interrupting the biological community.

It is significant to note that these two olefins do not occur at such large concentrations in any of the background sites, but only where there are large magnitude ethane and propane present. In spite of their magnitudes being scattered by unknown biological factors, this data clearly shows that these two olefins occur in all areas surveyed where anomalous ethane and propane soil gases are present on this site. This is true in all contaminated areas, whether from refined products, or from deep production casing leakage, both of which are dominated by ethane and propane. To our knowledge, this is the first and only time that these olefins have ever been collected and measured in contaminated groundwater under free product.