

Plume Delineation and Monitoring of Natural Attenuation Processes Via *In Situ* flux measurement

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Abstract : During the mid 1990s, a research has been conducted in Canada over a two-year period to develop an innovative sampling technique for petroleum contaminated sites. This method quantifies the rate at which vapors or gases are "produced" during a particular period of time under specific conditions of ventilation. Traditional soil-gas surveys evaluate concentrations of specific vapors that are in chemical equilibrium with dissolved, sorbed or free products in the media. The new proposed sampling technique involves to purge the soil with a non-contaminated gas in the vicinity of a sample probe for few minutes. The soil-gas purge affects the gas-liquid-soil equilibrium causing sorbed and dissolved vapors to transfer to the gas phase. During a period when the static equilibrium is unbalanced, the rate at which vapor contaminants are transferred to the soil gas phase is estimated. After this stabilization period, the purge is reduced or stopped altogether. Rebounds after the purging period indicate if petroleum products are present beside the sampling point. This method constitutes a major improvement for plume delineation at low cost. It delivers results on site within 10 minutes and investigated wastes are almost eliminated. More recently, this sampling approach has been further developed for the saturated zone. Rebounds are used to estimate *In Situ* flux rates of oxygen and biogenic gases. The primary advantages to evaluate biodegradation processes with this method include : [i] better estimates of reactant availability and daughter compounds production rate across a plume, [ii] less interference from temporal and spatial differences in hydrologic and geochemical conditions, [iii] data that are produced on a real-time basis, and [iiii] reducing overall monitoring cost of the natural attenuation option.

Containment and remediation of subsurface contamination caused by the release of petroleum products and industrial solvents constitute one of the major challenges facing the environmental industry. It is now recognized that much of the remediation occurs, not from engineered or invasive technologies, but through natural processes such as sorption, dispersion and biodegradation⁽¹⁾. Regulators require for most sites an accurate description of contaminant concentration, migration and dispersion, as well as an evaluation of degradation pathways and rates⁽²⁾. There is a well-recognized need for reliable field techniques that measure or estimate these essential components of the natural attenuation option⁽³⁾. Moreover, the degree to which these techniques are rapid, inexpensive, *in-situ* and relatively simple to perform increases their value substantially.

During the mid 1990s, a research was conducted to develop an innovative sampling technique for investigating releases from underground storage tanks (USTs)⁽⁴⁾. The development of this technique was initially based on procedures used in assessing the ventilation efficiency within buildings. The procedure included ventilating the UST backfill

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with clean nitrogen over a range of flow rates, while concurrently measuring increases or decreases in vapors concentrations. Fluctuations in concentrations under these imposed dynamic conditions permitted an estimate of generation rates within the backfill. When a closed (or reasonably confined) space is ventilated, analyte concentrations fluctuate depending on both the generation rate and the applied ventilation flow rate (extraction rate)⁽⁵⁾. The equipment used to perform this task in the subsurface is presented in the Figure below.

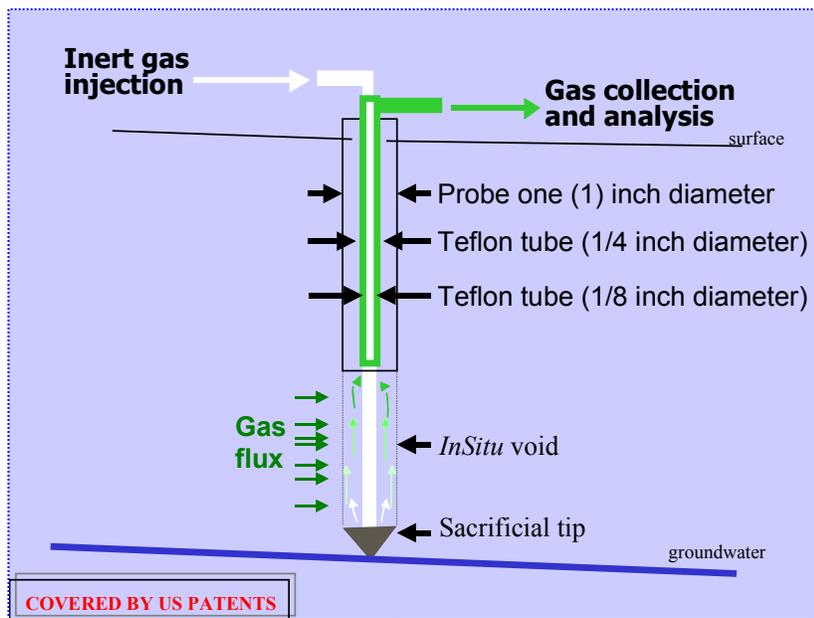


Figure 1 : Schematic of the *in Situ* flux method and associated equipment in the vadose zone

Purging the soil gas with nitrogen or other inert compounds affects the gas-liquid-soil equilibrium, causing volatile compounds that are present in sorbed or dissolved phases to partition into the gas phase. During the ventilation period, chemical equilibrium among soil phase is disrupted such that the rate at which vapors are transferred to the soil gas may be estimated. After conditions begin to stabilize, the ventilation is significantly reduced or stopped altogether. Subsequent increases in concentrations, as well as the length of the lag time between purge cessation and concentration increases, are used to identify volatile compounds that have partitioned into the soil gas. Rebound permits a direct estimate of migration in soil under an artificial chemical gradient. Using the same sampling event, the method has been further developed to measure *in situ* flux of biogenic gases in groundwater (e.g., those produced during the degradation of organic contaminants). Basically, rebound concentrations in fluids are used to evaluate whether the process is primarily controlled by advection, diffusion or production. Furthermore, this new sampling concept will be developed to estimate migration of soluble compounds in groundwater.

Natural Attenuation (NA) should be confirmed either by demonstrating the immobilization of recalcitrant contaminants or by the occurrence of specific biodegradation processes.

The measurement of *in-situ* flux rates for reactants (e.g., contaminants or nutrients) and products (e.g., daughter compounds or biogenic gases) represents such a method.

Typical results for two different flux conditions for gases in the vadose zone are presented below.

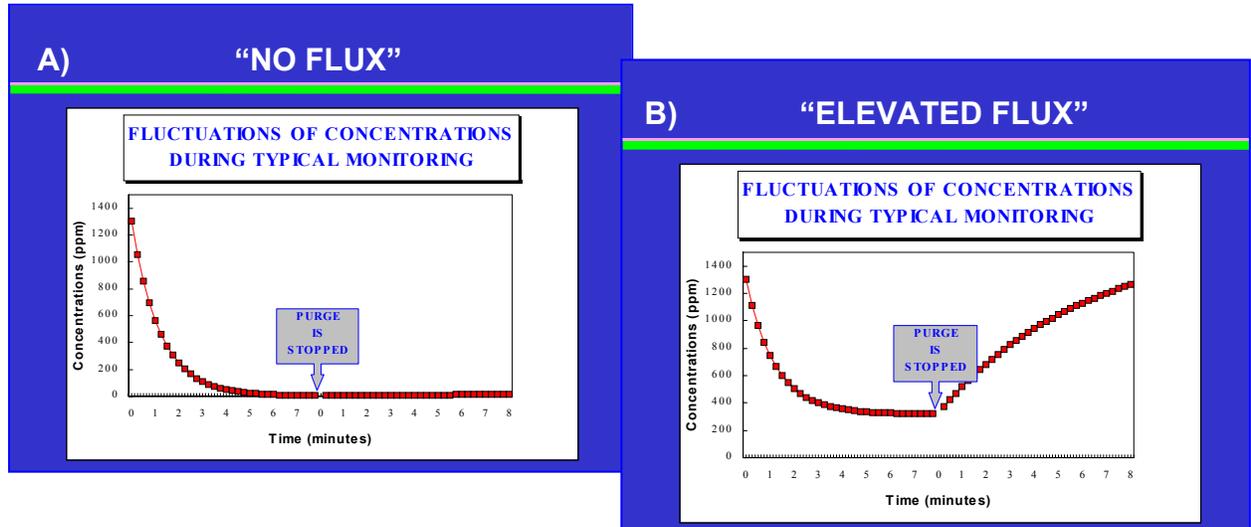


Figure 2 : Typical results for two different flux conditions in the vadose zone, [A] where no sorbed, solubilized or free contaminants are near sampling location, [B] near the source of the plume, where free contaminants are adjacent sampling area.

In essence, this new technique incorporates a dynamic approach into traditional “static concentration” approach, expanding the interpretation of results and their application. Whereas traditional methods rely on contaminant concentrations and hydrogeological parameters to estimate chemical fate, this technique focuses on rates of mass transfer and mass production for a limited volume of soil, as small as few cubic feet.

This technology is covered by US patents

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