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07/29/2004 03:48 PM

To gwtf@emsus.com

cc

bcc

Subject Fw: Cleanup Goals for DNAPL Source Zones

Mr. Lovelace,

I have read with a great interest the documentation of your group on "Cleanup Goals Appropriate for DNAPL Source Zones". Our company has developed since few years an innovative sampling method for fluids in soil (gas in the vadose zone or groundwater in the saturated zone). This technology has been demonstrated in Canada for the vadose zone, and is named the "In Situ Flux method". Nevertheless, since almost all standards are actually set with concentrations (in groundwater or soil), flux measurements are not yet commercially attractive. I believe that the task force you lead should focus on flux methods and on their potential commercialization.

Some points of view expressed in the documentation of your group were particularly interesting :

"One of the alternative metrics for judging the performance of source-mass depletion technologies is contaminant mass discharge, defined as the summation at a point in time of point values of contaminant mass flux (mass per time per area)."

"It is important to estimate the downgradient contaminant mass discharge rate or flux distribution. There are three methods to estimate mass flux : 1) use water quality data from transect (multiple location and depths) combined with groundwater velocity, 2) use downgradient aquifer tests in a transect of wells, tracking mass pumped, and 3) use sorptive permeable media placed in downgradient wells to intercept contaminant groundwater and release resident tracers".

The purpose of this email is to bring to your attention a fourth method your group has not considered yet. We have sent last May to the EPA SBIR program a proposal to demonstrate the concept of our new sampling method in the saturated zone. Find attached a copy of this proposal. Our method is explained in the first 8 page. The main advantage of this method is relying on its capacity to measure directly flux beside DNAPL, rapidly, at low cost and with simplicity. This possibility opens doors to set standards in term of flux, instead of concentrations. Of course, this should be of interest

for your group, as you have indicated :

"Research is needed on : development, verification and comparison of alternative technologies for measuring mass flux and mass discharge from DNAPL source areas before and after source depletion", "to establish guidance for ... source-zone characterization".

Furthermore :

" A strategy for achieving benefits from partial source mass depletion would be to reduce contaminant mass discharge to a level less than the natural attenuation capacity within the dissolved plume". "The panel urges EPA to provide appropriate guidance for defining the conditions under which DNAPL source remediation would be a viable option for site clean up compared to a containment option."

This guidance would be straightforward and clear only if conditions to meet are expressed in terms of flux, instead of concentrations.

If you find it relevant, it would be a pleasure for me to meet your committee, to explain our innovative sampling technology and to answer questions. We may also proceed via a conference call and a Powerpoint file.

The most innovative aspect of the proposed method is its ability to collect groundwater samples, at an In Situ collection flowrate equal to zero (when injection flow rate of clean water is equal to the collection flow rate). (no draw down)

This technology will be presented on October 19, during the "AEHS Conference on Contaminated Soils, Sediments and Water" in Boston. If any member of your group may attend to my presentation, it will be a pleasure for me to meet afterwards for further discussion.

Innovation most of times comes from a mix of different sciences. This innovative technology comes from equations used in the industrial hygiene area. Please, feel free to contact me, if you have any comments or question.

Regards,

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U.S. Environmental Protection Agency
Small Business Innovation Research Program,
Solicitation No.PR-NC-04-10308
(SBIR – Phase 1)

PROJECT SUMMARY

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Site Characterization, Risk Assessment and Monitoring of Natural Attenuation via In-Situ Flux Measurements

Topic: F1. Hazardous Waste Monitoring,
Principal Investigator : Andre Tartre, R&D manager

The intent of this research proposal is to develop a device and to assist the U.S. Environmental Protection Agency in advancing the development of an innovative *In Situ* measurement technology for assessing the mobility of contaminants or daughter compounds in soil and groundwater.

The proposed sampling technique starts by purging the subsurface with a non-contaminated fluid (gas or liquid) for a few minutes. The same fluid is collected somewhat apart from the injection point, and concentrations are monitored. Stabilized concentrations reached during the purge are used to estimate the flux of compounds (analytes) immediately available for migration. We term this flux "*advective flux*". When concentrations reach equilibrium, the purge is stopped. Rebound concentrations are monitored over a short period of time to evaluate the migration of compounds induced by the presence of a "clean volume" of fluid. If there is no *advective flux*, rebounds are used to estimate migration due to hydrodynamic dispersion. We define this flux as a "*dispersive flux*". This new sampling technique may be used as an extension of conventional groundwater or soil-gas investigations. These *In Situ* flux measurements may, in turn, be used to estimate contaminant migration or biodegradation rates below the water table as well as in the vadose zone. The commercialization of a new sampling device designed to apply this technology will accelerate site characterization and risk assessment and will simplify the evaluation of natural attenuation processes and result in more efficient site monitoring.

In current practice, estimates of *In Situ* advection and the hydrodynamic dispersion of contaminants are inferred from hydrogeological parameters obtained via observed or induced processes (e.g., tracer tests, slug tests, pumping tests, etc.), from laboratory tests of disturbed samples, from numerical modeling based on *In Situ* tests of soil properties, or by using "typical values from the literature". The proposed technology is the only one so far that evaluates the *In Situ* potential for contaminant migration, using the contaminant of interest.

This innovative sampling technique is currently in the advanced development stage for application in the vadose zone. It is, however, only in the preliminary stages of development for application below the water table, where significant engineering challenges remain to be addressed. The primary focus of the proposed research is to develop a device and supporting software that will extend the applicability of the technique to the saturated zone. This research project includes the design and fabrication of a probe, the design and fabrication of a coaxial tube for existing wells, and performance testing of these systems at field sites.

1 INTRODUCTION

1.1 Statement of problem

Containment and remediation of subsurface contamination caused by the release of petroleum products and industrial solvents constitutes one of the major challenges facing the environmental industry. To efficiently meet these challenges, environmental engineers now recognize the importance of completing a comprehensive site characterization before beginning any remediation effort. Sampling activities must not only characterize contaminant concentrations in the subsurface, but must also provide an appropriate understanding of migration processes occurring in the subsurface.

Under ideal conditions, it must be demonstrated that the migration and/or biodegradation rates of contaminants must be such that unacceptable concentrations of the contaminants will not reach potential human and/or environmental receptors. To evaluate migration rates, conventional sampling methods rely on the measurement of contaminant concentrations in soil and/or in groundwater, along with physical geological and hydrogeological/hydrochemical characteristics of the pathways and the contaminants themselves. To evaluate biodegradation rates, practical and emerging methods assess mainly reactant consumption and/or daughter compound production rates, along with an historical portrayal of declining concentrations of contaminants with distance along the flowpath.

Results obtained using conventional sampling methods provide concentrations in soil and/or groundwater which are in (or near) chemical equilibrium with dissolved, sorbed, trapped or non-aqueous phases within the media. Spatial and temporal variations of these concentrations, along with groundwater flow estimates, are used to evaluate transport mechanisms with interpretations assisted by mathematical simulation. Most of the time, advection, hydrodynamic dispersion and retardation processes are estimated from hydrogeological parameters obtained via inference from observed or induced processes (e.g., tracer tests, slug tests, pumping tests, etc.). Other practices include testing of disturbed samples in the laboratory, numerical modeling based on *In Situ* tests of soil properties, or by using "typical values from the literature." Thus, modeling results are in most cases a rough simplification of reality. There is considerable uncertainty with these simulated results.

Nevertheless, these mathematical transport models are actually required in risk based assessment studies to understand processes affecting the transport and the transformation of contaminants in the subsurface. There is a well-recognized need for reliable field techniques designed to measure chemical migration and biodegradation rates directly on site⁽¹⁾. Moreover, the degree to which these techniques are rapid, inexpensive, *In Situ* and relatively simple to perform increases their value substantially. This proposal addresses the components of contaminant migration and of degradation pathways/rates via an innovative, *In Situ* measurement technology.

1.2 Theory of the technique

Development of the proposed innovative *In Situ* measurement technique was begun during two-years of research conducted in Canada. The research specifically investigated releases from underground storage tanks (USTs)⁽²⁾. This technique is built on the same theoretical foundation as well-established procedures for assessing the ventilation efficiency within buildings. The procedure involves locally ventilating the UST backfill with fresh atmospheric air over a range of flow rates, while concurrently measuring increases or decreases in gas or vapor concentrations which vary as a function of the flux from the surrounding environment. Fluctuations in concentrations under these imposed dynamic conditions permit an estimate of gas or vapor flux within the backfill. When a closed (or reasonably confined) space is ventilated, gas concentrations fluctuate depending on both the generation rate and the effective ventilation flow rate (extraction rate)⁽³⁾. If the generation rate is greater than the extraction rate, gas concentrations increase. Conversely, if the flow rate is greater than the generation rate, gas concentrations decrease.

1.3 Development of the technique

The proposed technique involves the purging of the vadose zone in the vicinity of a sampling probe with a non-contaminated gas during the soil-gas investigation. The equipment used to perform this task is presented in Figure 1a on page 4. Purging the soil gas with nitrogen or other inert gases affects the gas-liquid-soil equilibrium, causing compounds (analytes) that are present in sorbed or dissolved phases to partition into the gas phase. During the ventilation period, chemical equilibrium among soil phases is disrupted such that the rate at which vapor contaminants and biogenic gases are transferred to the soil gas may be estimated. We define this mass transfer as a generation rate. The mass transfer value (the flux of gas and vapors immediately available for migration) is derived through the division of the gas generation rate by the area of the exposed void. The void is created *In Situ* by the probe. We term this flux as an “*advective flux*”, since advection is the most probable transport process in such case.

After conditions begin to stabilize, the ventilation is significantly reduced or stopped altogether. Subsequent increases in analyte concentrations, as well as the length of the lag time between purge cessation and concentration rebounds, are used to identify analytes that disperse due to this instantaneous presence of “clean volume” of gas. We term this flux “*dispersive flux*”, since hydrodynamic dispersion is the most probable transport process during such event. This process is shown schematically as Figures 3a, 3b and 3c on page 5. More comprehensive explanations of the sampling procedure and on flux calculation are detailed in “Appendix 1”.

This new sampling concept has been applied more recently to estimate the migration of soluble compounds. *In Situ* flux measurements of soluble compounds are performed in the saturated zone by purging a known volume of medium with clean water for a brief period in order to reduce analyte concentrations in the targeted area. When the effective flow rate of the clean water used for purging approaches the generation rate, *advective flux* is estimated. When this equilibrium is reached, the purge is stopped. Rebound concentrations are measured over a short period of time to evaluate the migration of analytes into the design volume. If there is no *advective flux*, rebounds are used to estimate migration due to hydrodynamic dispersion induced by this instantaneous presence of “clean water” in the sampling area. We define this flux as a *dispersive flux*. The actual equipment used to perform this task is presented in Figure 1b. The method may be used to measure *In Situ* flux of soluble contaminants. Using the same sampling event, the *In Situ* flux of degradation products or daughter compounds in the saturated zone (e.g., those produced during the degradation of organic contaminants) may also be evaluated. When the *advective flux* of daughter compounds within “active” subsurface locations is superior to their *In Situ* flux at “inactive” locations, production rate is estimated. Basically, mapping of *advective and dispersive flux* are used to evaluate whether migration processes are primarily controlled by advection, hydrodynamic dispersion, or production. An experimental setting is shown on Figure 2a and 2b on page 4 in the application of the proposed sampling method to existing wells.

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 the direct and more relevant measure of mass transfer and mass production rates for a limited volume of soil, as small as few cubic feet when necessary.

Figure 1. Schematic of the *In Situ* flux method and associated equipment actually used.

1 a. Vadose Zone

1 b. Saturated Zone.

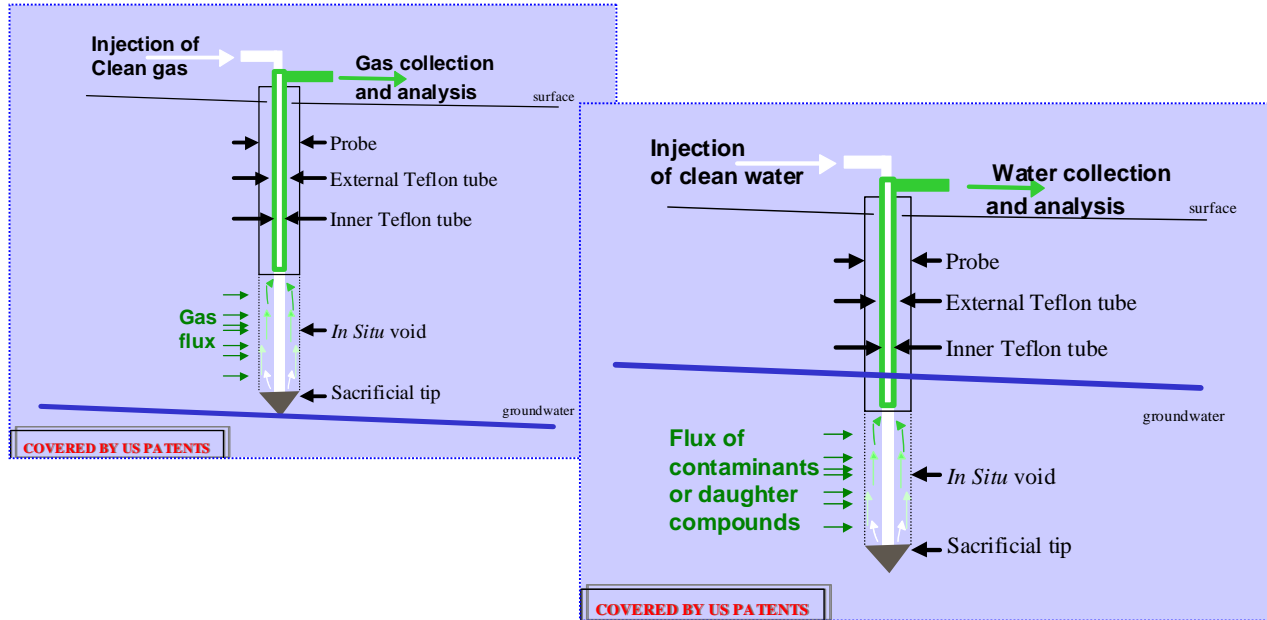


Figure 2. Schematic of the *In Situ* flux method for existing wells.

2 a. Vadose Zone.

2 b. Saturated Zone.

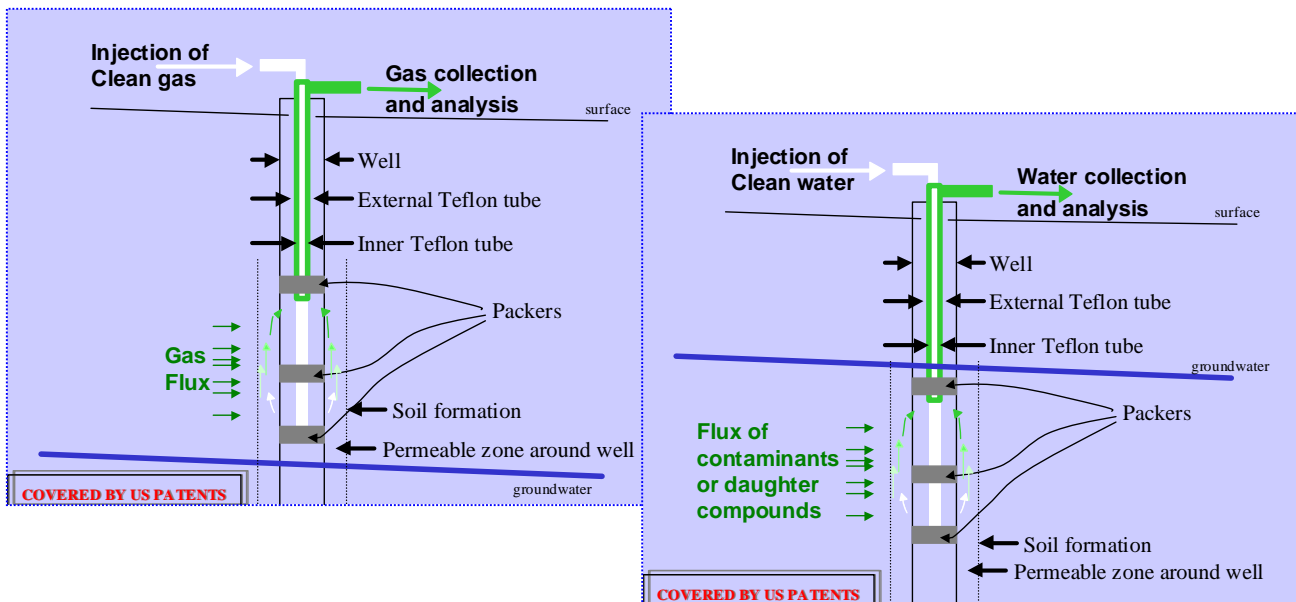
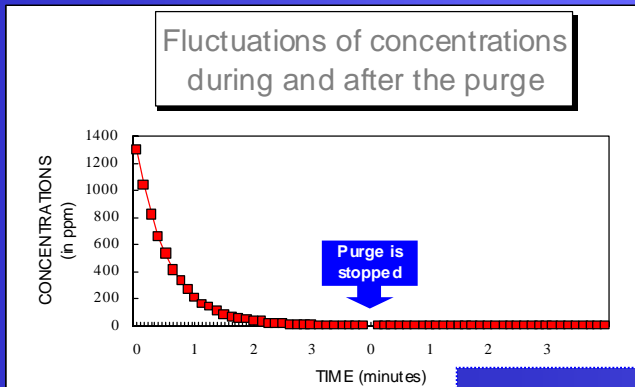


Figure 3. Typical results for three different flux conditions of organic vapors in the vadose zone for a volatile contaminant.

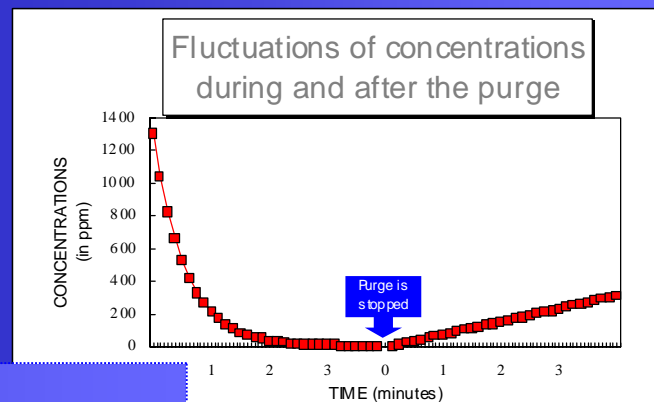
INTERPRETATION : NO FLUX



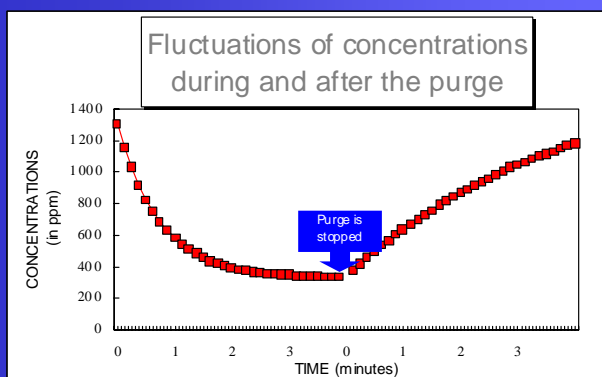
[A] Example :
At the plume edge, where no sorbed, solubilized or free phase contaminants are near sampling location.

[B] Example :
In the plume, where hydrodynamic dispersion is the dominant migration process.

INTERPRETATION : LOW FLUX



INTERPRETATION : HIGH FLUX



[C] Example :
In the source of the plume, where advection is the dominant migration process.

2 APPLICATION OF THE TECHNIQUE

2.1 Evaluation of advective flux

The proposed sampling technology is the only one so far that evaluates the potential for migration directly, *In Situ*, using the contaminant of interest. This new technology offers an interesting alternative method to existing sampling practices.

During the purging period, *advective* flux from free phase products or from sorbed contaminants on the soil matrix is quantified. This is done when stable concentrations are reached. In the vadose zone, *advective* flux of volatile contaminants correlates with concentrations of specific compounds in the surrounding soil ⁽²⁾ (eg. : $r = 0,88$ for BTEX). The proposed *In Situ* flux method may then be used in the vadose zone for most of volatile compounds (petroleum and chlorinated) to identify sources and plume extent. This method is particularly cost effective compared to standard gas and vapor sampling methods.

In the saturated zone, a rapid mobilization of a soluble compound occurs when a known volume of aquifer solids is purged with clean water. Clean water may be injected, along with a tracer, directly into the aquifer under positive pressure so that *advective* flux through porous material may be evaluated. Alternatively, water may be injected into a controlled aquifer volume at an inflow rate equal to the outflow rate of a more impervious material. This method is used to evaluate *advective* migration via preferential flow paths (i.e. fractures).

The steady state concentration reached during the purging period (concentration **(A)** in figure 4B) is multiplied to the effective flow rate of the clean water in order to evaluate the rate at which contaminants are partitioning into the aqueous phases (from non-aqueous or sorbed phases). This rate divided by the volume or the exposed surface of the soil void provides the *In Situ* flux of compounds immediately available for migration. This is identified as the *advective* flux and is due to a sudden recharge of clean water.

Figure 4 a : Steady state concentrations reached during the purging period as an estimate of the advective flux of compounds from the surrounding soil void.

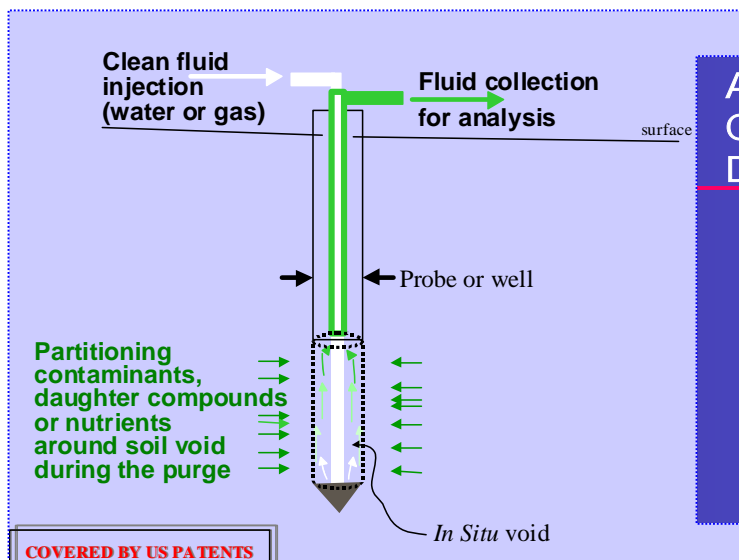
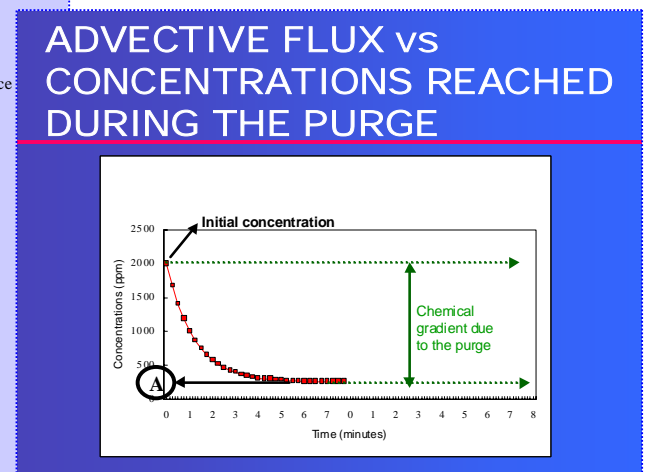


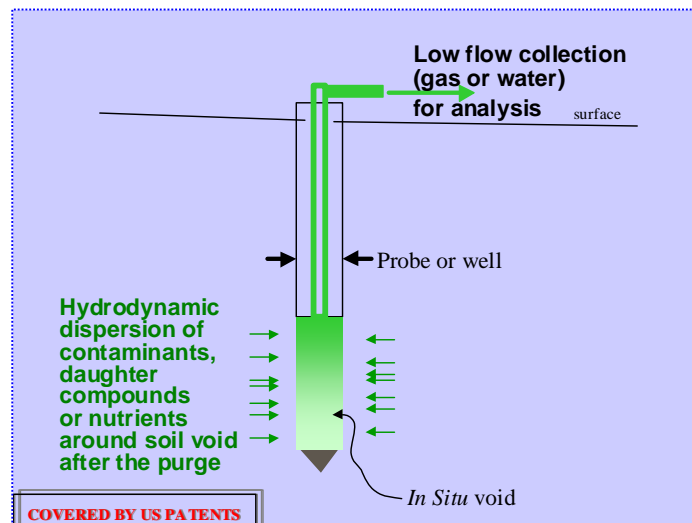
Figure 4 b : Example of results obtained during the purge



2.2 Evaluation of dispersive flux

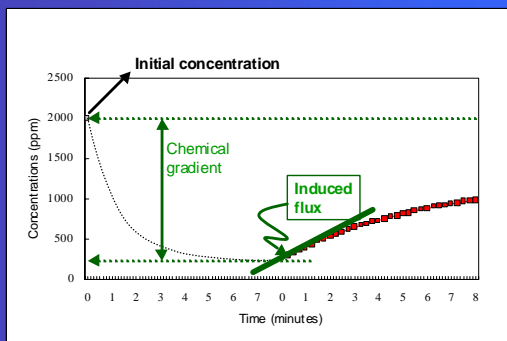
The proposed sampling technique can also be used to directly evaluate *dispersive* flux. When the effective flow rate of the purging fluid approaches the generation rate of analytes, the purge is halted. Rebound concentrations are monitored within the first few minutes. This monitoring permits a direct estimate of analytes migrating in soil gas or groundwater into the “clean fluid volume” at the sampling location. This provides a direct evaluation of dispersion and of molecular diffusion for a specific subsurface location. The proposed method estimates the *In Situ* flux with the slope of the curve when no “clean fluids” are injected.

Figure 5 : Steady state concentrations reached after the purging period as an estimate of migrating compounds due to hydrodynamic dispersion surrounding soil void

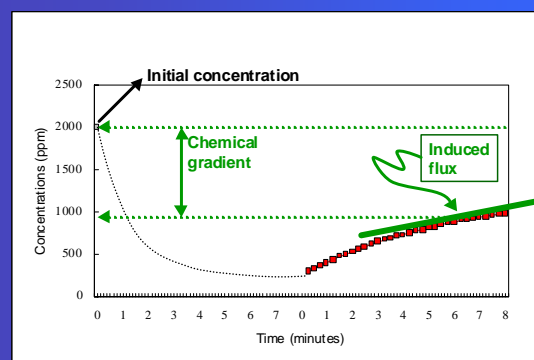


[B] Example of results obtained :

DISPERSIVE FLUX INDUCED BY a STRONG CHEMICAL GRADIENT AFTER THE PURGE



DISPERSIVE FLUX INDUCED BY a SMALLER CHEMICAL GRADIENT AFTER THE PURGE



2.3 Evaluation of biodegradation processes

The success of the natural attenuation application depends on both hydrogeological and hydrochemical parameters. Documented decreased contaminant concentration over time is not sufficient to demonstrate that natural attenuation processes are occurring⁽¹⁾. An observed reduction in contaminant concentration at any given location may result from spatial heterogeneities in the soil or hydrogeological conditions. Natural attenuation processes may fluctuate as a function of season or of changing geochemical conditions.

Monitored Natural Attenuation (MNA) is demonstrated to be effective in most cases through identification of specific biodegradation processes. Conventional monitoring techniques assess biodegradation processes via the comparison of parent and daughter product concentrations in up- and down-gradient locations within the plume. Relative concentrations of these analytes are used to identify which natural attenuation processes are actually occurring⁽⁴⁾. A common problem with using such a mass balance approach is that advection may not represent the dominant transport mechanism.

The effectiveness of biodegradation processes should be evaluated with respect to reactant (parent product) consumption or daughter product generation. The best measure of these processes is a method that is able to generate data on a small-scale basis. The method should compare the analyte concentrations in up gradient and down gradient plume areas and be minimally influenced by spatial and temporal variations in hydrology or geochemistry. The measurement of *In Situ* flux rates for reactants (e.g., contaminants or nutrients) and products (e.g., soluble daughter compounds or biogenic gases) represents such a method.

The traditional method for calculating field biodegradation rates requires integration of conservative tracer results, an estimate of retarded solute migration in the saturated zone, and hydrogeological calculations⁽⁵⁾. An alternative method proposes calculation of biodegradation rates using direct monitoring data⁽⁶⁾. With either method, the retarded solute velocity is generally overestimated to account for the uncertainty in model parameters. To our knowledge, there is no commercial method that directly measures either destruction rates of contaminants or consumption rates of reactants^(7,8,9,10).

The proposed innovative sampling technique provides a different approach to the assessment of the production of daughter compounds. For instance, generation rates of biogenic gas from petroleum products (e.g., carbon dioxide and methane) or soluble daughter compounds (e.g., ferrous ion, organic acids) are evaluated from *In Situ* flux measurement to predict biodegradation rates across a site. These production rates are estimated from advective flux from active subsurface locations (e.g., a subsurface zone where daughter compounds accumulate due to their generation rate exceeding their dispersive dissipation rate) compared to dispersive flux at inactive locations. *In Situ* flux measurements are relatively inexpensive to obtain especially for daughter products that partition into the gas phase from either the groundwater or in the vadose zone.

For chlorinated solvents, *In Situ* flux measurement will improve the accuracy and the cost effectiveness of the methodology to evaluate the "Time of Stabilization" of the plume and the "Time of Nonaqueous Phase Liquid Dissolution". These two (2) parameters are crucial to the estimation of the time required for Natural Attenuation processes to lower contaminant concentrations to levels protective of human health and the environment⁽¹¹⁾.

2.4 Optimization of extraction processes

The proposed innovative sampling technique may also be used as an indicator tool to optimize extraction processes during remediation efforts. Often the effectiveness of extraction processes are limited after a short period of operations to the rate of diffusion of the contaminant from a less permeable zone to more permeable zone. Knowledge on the exact locations of zones of high *advective* flux for extraction will be helpful. The proposed equipment for existing wells may be used to define clearly the subsurface zone with highest *advective* flux.

3 PROJECT DESCRIPTION

3.1 Main objective of the project

The objective of this project is to develop a device that extends the proven unsaturated zone methodology to the saturated zone. This device will create a local “clean volume” of fluid in the groundwater system in a short time period by purging the saturated zone with distilled or dionized water. The device will be used to evaluate the available contaminant flux in the subsurface for the purposes of: identifying sources of contamination, optimizing extractive or destructive remediation processes, the assessment of advective and dispersive migration processes during groundwater recharge, and the improvement of the accuracy of MNA. The project also targets the development of a field applicable software tool to calculate *In Situ* flux at the time of measurement.

3.2 Hypothesis

May we evaluate *In Situ* advective and dispersive processes by creating an instantaneous “clean volume” of fluid in the sampling area with a brief period of subsurface purging?

3.3 Work plan

3.3.1 Targeted contaminants

The project will evaluate at least three (3) sites contaminated with methyl-tertiary-butyl-ether (MTBE) and at least three (3) other sites contaminated with chlorinated compounds. These contaminants have been chosen for the project both for technical considerations and due to their respective potential market. Many examples of the spatial distribution of MTBE in groundwater, delineated from concentration data are not easily explained by our current understanding of the contaminant transport. The ability to evaluate flux for this contaminant will bring a greater level of understanding of these distributions during site investigations. This tool will effectively determine sources and migration pathways. Additionally, attempts to locate persistent DNAPL source areas driving many chlorinated solvent plumes are confounded by the influence of hydrogeologic heterogeneities in the flow regime. Again, the ability to evaluate flux for these contaminants will improve the discovery and delineation of source zones.

3.3.2 Collaborations

The project will be performed in collaboration with the New Hampshire Department of Environmental Services (NHDES), the New Jersey Department of Environmental Protection (NJDEP) and the “Savannah River Technology Center (SRTC) at the Department of Energy’s Savannah River Site (SRS) in South Carolina.

3.3.3 Parameters to consider in hypothesis verification

3.3.3.1 Considerations from previous demonstration (*In Situ* gas flux sampling)

For gas, we start the proposed sampling method by collecting the fluid at a low flow rate to verify if adequate soil permeability is present. When geological conditions allow the collection of about 60 to 80 ml of gas per minute without incurring a pressure loss of greater than 25 inches of water (0.9 psi), we consider the investigated subsurface permeable enough. In these situations, we verify the concentrations obtained on site, and determine if an *In Situ* flux measurement would be feasible. The following parameters are considered in this determination:

- a presence of sufficiently high concentrations of the contaminant to be conclusive;
- the likelihood that we are investigating near enough to a contaminant source or in an active biodegradation zone to observe discernable induced flux ;
- whether or not the flux investigation must consider the geological heterogeneity of the site.

If the soil is impervious to gas at the sampling location, we open the injection inlet of the soil void to the atmosphere or to a nitrogen bag at atmospheric pressure. We then allow the non-contaminated gas to enter the soil void. After a brief period, we close the clean gas inlet and allow conditions in the soil void to equilibrate. Following a few minutes of equilibration, we resume collection with the clean gas inlet open again. We calculate concentrations obtained in the soil void at the beginning of the second collection period and evaluate induced flux directly with concentrations obtained in equilibrium after a few minutes. This mathematical treatment is referenced in Appendix "1".

3.3.3.2 Parameters affecting the method for the saturated zone compared to the gas sampling in the vadose zone

A- Viscosity and density

The difference between the gas and the water sampling for the *In Situ* flux is linked to the difference in the viscosity and the density of the fluid sampled. The major impact of this difference will be the pressure differential created between the collection and the injection point immediately at the beginning of the purge. The pressure will be positive at the injection point and negative at the collection point. The fluid will have to move before the pressure will start to equilibrate. Since a laminar flow is an important parameter during the purge, we first need to determine the optimal distance between the injection and the collection point for specific sampling conditions.

B- Turbidity of samples

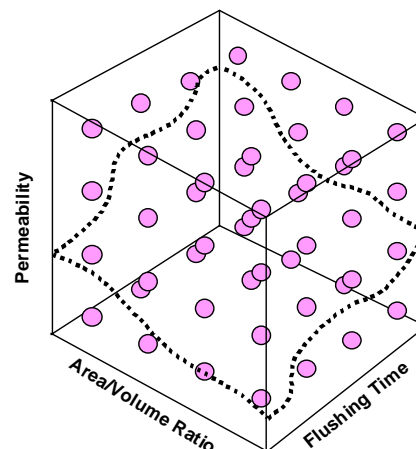
There is another obvious major difference between gas and water applications. The movement and collection of gas rarely generates particulate displacement, whereas groundwater collection often may. Therefore, the turbidity of a groundwater sample must be considered. To resolve these potential difficulties, we suggest that the collection should start with a standard groundwater "low flow sampling" method, with commercially available sampling equipment. During sampling, drawdown (e.g., local pressure) is verified and at least one chemical parameter is monitored. The collection flow rate must be sufficiently low to minimize turbidity, but sufficiently high to assure the collection of a representative sample of the saturated zone in a reasonable period of time.

3.3.3.3 Theoretical perspective of efficient purging of the saturated zone and anticipated results

In a more theoretical treatment of the purging period, this research will investigate the "configuration space" for the sampling device and method. The physical dimensions of the equipment, the applicable flow rates and geological conditions around the investigated area will be examined. We will configure the method to consider three (3) different metrics :

- the physical dimension of the void and the net purging-sampling flow rate, as a ratio of void volume to net flow (flushing time) ;
- the physical aspect of the void, as a ratio of length to diameter (measure of surface area to volume) ;
- the formation permeability.

Figure 6 : Visualization of the theoretical aspect for the purging period and metrics which would be investigated with anticipated results. The surface defined with dashed lines represents a response surface in the configuration space.



The Peclet number is a dimensionless parameter used to compare the relative dominance of advection versus diffusive transport processes in a given situation. We believe that the optimal combination of physical dimensions and operational parameters must be sensitive to the relative influence of advection versus diffusive mechanisms, to minimize induced advection during collection so that diffusive flux may be readily discerned. This proof of concept will begin with an examination of Peclet numbers for typical ranges of natural advection of groundwater in the subsurface and hypothetical device dimensions and flow rates. This sensitivity analysis will provide valuable insight into the dimensional impacts of device design, on the device performance and ultimately in the interpretation of the *In Situ* flux monitoring results. We are expecting to develop a range of Peclet numbers for which the device and methodology will be technically applicable. (e.g. : will have acceptable signal fidelity and signal-to-noise ratio). There will be also a region of the space which will be better disposed to the manufacture and operation of a commercial device. The intersection of these regions will define the region of the "configuration space" within which a successful device and methodology will lie. This space was already defined by trial-and-error in the development of the vadose zone methodology for gas, and is expressed in the existing commercial product and methodology. In essence, we are expecting a subset of Peclet number ranges, where the new product will be both commercially and technically feasible.

3.3.3.4 Other considerations

As with gas sampling in the vadose zone, we will collect and analyze a groundwater sample prior the purging period. With the same considerations as for gas sampling, an *In Situ* flux measurement would be then conducted when there exists:

- a presence of sufficiently high concentrations to perform the method;
- proximity to a contaminant source or an active biodegradation zone;
- geological heterogeneity and the need to investigate different soil strata.

This work will also examine the possibility of setting the equipment to collect samples prior, during and after the purge and to apply the proposed method with *on site* analyzers or by sending samples to a laboratory. In order to minimize the cost of sending samples in a fix laboratory, only samples collected prior the purge will be sent to the laboratory in a first step. After these standard results are obtained, *In Situ* flux measurements will be decided depending with the same considerations than with *on site* analyzers. Samples collected during and after the purge for some specific sampling locations will be sent to the laboratory for analysis to calculate *In Situ* flux. This strategy may even be applied in a tiered approach, where by flux measurements will be made as the budget of the project allows. The equipment will be set to minimize the time frame required for the *In Situ* flux method and to optimize the cost efficiency of the characterization effort. Cost efficiency will be a component of the comparative analysis.

This research will examine the injection flow rate in terms of purge sample turbidity and turbulence around the probe and will determine optimal rates. When the *In Situ* flux method is applied, the equipment will be set to increase the injection and the collection flow rate in parallel. By taking into account the Reynolds number, the clean fluid purge will be set low enough to avoid turbulence in the subsurface void.

3.3.4 Preliminary testing to develop two (2) sampling configurations

The project will develop two (2) sampling configurations to apply the *In Situ* flux sampling concept to the saturated zone. The two (2) types of equipment are:

1. a direct push probe capable of creating and purging a void *In Situ*, and
2. a dual tubing system to apply the method in existing wells.

The initial field work of this project will be used to determine the required settings for the two applications. Each of the sampling apparatus will be designed to maximize the efficiency of the groundwater purge yet maintaining laminar flow.

3.3.4.1 Direct push probe

The method is already commercially available for gas monitoring in the vadose zone. The “Geoprobe™ with PRT system” is specified. Under the proposed project, the *In Situ* flux method will be deployed on a few sites to investigate the saturated zone by injecting clean water, as shown in figure 1B. To optimize the cost of this effort, sites with a shallow groundwater table will be investigated first and the probe will be driven manually. This preliminary work will define the best “configuration space” after considering all possible combinations of the device’s physical dimensions and the operational parameters, via a combination of calculation and experimentation. We will also develop the injection and the automatic collection system for groundwater during this phase.

To further maximize the cost efficiency of this preliminary effort, we will develop and adjust the method by monitoring the temperature. We will inject clean water about 25 degrees Fahrenheit higher than the actual groundwater temperature. An increasing temperature will demonstrate the effectiveness of the purging process. The decreasing temperature after the purge will be an indication of the migration of the groundwater towards the sampling location. The following adaptations during the preliminary tests will be used to adjust the *In Situ* flux methodology for the saturated zone:

- applying the method with four (4) different flushing time ;
- applying the method with three (3) different ratios of area / volume of the soil void ;
- applying the method for three (3) different types of soil :
 - sandy ; more organic ; clay.

On few occasions in coarse sandy soil, we will experiment with the method without a screen around soil void to verify the impact of the turbidity of samples collected. The lack of necessity to have a screened soil void may substantially reduce the cost of the proposed method. The preliminary effort will evaluate the efficiency of the purge with clean water, since the method requires immediate and complete mixing of the injected water with the actual groundwater in the void. The device will then evaluate the temperature fluctuations in 36 different configurations in order to determine the best “configuration space”.

3.3.4.2 Existing wells

When the first effort with the directed push probe is complete, the method will be adapted to use in existing wells. The system will be modified and fitted with a set of three (3) packers, as shown in Figure 2. A similar methodology will be used to verify the best “configuration space” in existing wells. The following adaptations during the preliminary tests will adjust the *In Situ* flux methodology for already completed wells in the saturated zone:

- applying the method with four (4) different flushing times ;
- applying the method with three (3) different ratios of area / volume for each type of well (Geoprobe™ prepacked, 2 and 6 inches diameter);
- applying the method in three (3) different soil strata:
 - sandy; more organic; clay.

The device design for existing wells will be defined after the evaluation of temperature fluctuations through 36 variations of configuration.

3.3.4.3 Collection equipment

As shown in Appendix “1”, the technology will collect three (3) samples during the purging period, and three (3) other samples after the purge, during the stabilization. These samples are necessary to calculate induced flux during the purging period, and the induced flux from specific chemical gradients after the purge. Furthermore, each sample for both periods must be collected at one (1) minute of intervals. To improve the field accuracy of the method, a new automatic collection device will be set to collect groundwater samples during one (1) minute intervals during the purge, and during one (1) minute intervals after the purge.

3.3.5 **Field testing with chemical analysis**

When the two sets of sampling apparatus are set for the method, the second phase of the project will be initiated and will demonstrate the efficiency of the method. We will use a direct reading analyzer. Analytical methods used for the second phase of the project will follow standard EPA methods and part of the second phase will have the capability to identify and to quantify each compound of interest on site.

For both the vadose and the saturated zone, we propose to delineate plumes and identify sources of MTBE or chlorinated compounds by applying EPA method 8265 with a "Direct Sampling Ion Trap Mass Spectrometry (DSITMS)" to the proposed sampling method. During the vadose zone investigation, methane, carbon dioxide and oxygen will be sampled in parallel with the "LFG 20". During the saturated zone investigation, the temperature of the groundwater will be monitored in parallel. Special care will be taken at sample sites where numerical modeling has been already performed and where the predicted contaminant migration processes have been already assessed. Advection, diffusion and hydrodynamic dispersion processes estimated with standard methods will then be compared with results obtained from the proposed sampling method. Biodegradation rates already estimated by standard methods will also be compared with results obtained from the proposed method. Finally, we plan to apply the proposed method to optimize vapor extraction on existing wells when this remedial process is applied. The success of this proposed SBIR "phase 1" project will be evaluated when results of traditional studies on migration and biodegradation rates can be compared with our "on site" results. We plan at least 30 *In Situ* flux measurements per targeted sampling configuration to statistically compare the results of our innovative sampling technology with the results obtained from traditional methods. For each site, the following comparisons are planned:

- define sources of contamination and compare transport process estimation obtained with standard methods (from concentration data and hydrogeological parameters) with results of the proposed *In Situ* flux method ;
- define active biodegradation zone and compare our results with zones delineated with more standard methods (Wiedemeier or Buscheck) ;
- compare migration rates in the dilute zone obtained with standard methods (as with tracer tests) with results obtained from the proposed *In Situ* flux method.

3.4 **Work plan and budget**

Proposed work plan and budget are presented in "Appendix 3".

4 **EXPECTED BENEFITS**

According to the EPA 2003-2008 Strategic Plan ⁽¹²⁾, the country will need by 2008, 88,000 health and environmentally based site assessments. By 2008, EPA targets to control 84 – 95 % of identified unacceptable human exposures from site contamination and 65 - 80 % of contaminated groundwater through engineered remedies or natural processes. EPA wants to select final remedies at about 514 RCRA facilities and 1,223 Superfund sites. EPA also has targeted by 2008 the clean up of approximately 70,000 leaking UST sites. To reach these goals, the optimal strategy will consist of maximizing the effectiveness of characterization and cleanup efforts by providing sound science and smarter technical solutions that enhance our ability to protect human health and the environment.

With standard sampling methods, extensive and expensive characterization works will be required through the country. This is especially true for sites that have been slated for remediation based on natural attenuation processes (MNA). Major contributors to the cost of these investigations include: extensive sample and data collection activities; mobilization (and re-mobilization) of drilling equipment and crews; installation of numerous permanent monitoring wells; chemical analysis; and Investigative Derived Waste (IDW). Sites aiming the use of natural processes for remediation are generally subjected to extensive long-term monitoring requirements and comprehensive modeling as a condition of their approval. Similarly, works rely on significant engineered intervention are subject to high costs associated with crew re-

mobilization, sampling, chemical analysis, and IDW disposal. Without diminishing the importance of previous cost contributors, we have to underline the astonishing tendency for many project managers or site owners to limit the budget and the quality of the characterization works to emphasize the “remediation effort”. This “working strategy” is still prevalent even though it is well recognized that an effective “remediation effort” is only possible when characterization work has clearly delineated all the source areas and has provided an accurate understanding of contaminant pathways and transport processes.

The costs of current sampling practices can be significantly reduced by adapting the proposed innovative technology for the measurement of chemical migration processes and biological degradation rates. Costs and schedules will be positively impacted during the first site investigations, especially by applying soil gas sampling in the vadoze zone for petroleum contaminated sites. During saturated zone investigations, MTBE migration paths (and other more soluble hydrocarbons) will be more clearly identified. The proposed technology will also locate with a greater efficiency DNAPLs, either in the vadose or saturated zone, thereby enhancing the remediation effort by more accurately defining subsurface locations for the focus of extraction or *in situ* destruction activities. Evaluations of *In situ* flux of DNAPL daughter compounds will permit a better identification and delineation of biodegradation processes. By using this innovative sampling approach, the consultant will have a better tool to develop a more cost effective and comprehensive site characterization. It will be more obvious to a site owner to spend a little more money during the characterization especially to evaluate contaminant mobility around the subsurface locations chosen for an extraction or destruction prior any remediation effort. Furthermore, since the proposed project will develop a device for *In Situ* flux measurement in existing wells and monitoring networks, the results of this work will provide an excellent opportunity to reduce the costs of site monitoring, especially for risk based corrective action, the tracking of natural attenuation processes (i.e., physical, chemical, biological), remediation process optimization, reverse modeling and to clearly identify source removal needs.

5 PERFORMERS

EcoRemediation inc. will be the project manager and the lead technical organization for this effort. Mr. Andre Tartre, the current holder of Patents for this sampling method, and the principle researcher, will provide technical expertise in development of the protocol and equipment design and optimization. He will also manage and collaborate on the fieldwork. This project will involve three (3) other collaborators. Dr. Joe Rossabi will review the experimental protocol and will participate in the determination of appropriate sites for the project. NHDES and NJDEP will also provide sites. Mr. Stephen Farrington from Applied Research Associates, Inc. will assist in the design and fabrication of prototype devices (for clean water injection and automation of sample collections) and for the development of software to collect and process data. Finally, Dr. William Davis from Tri-Corders, Inc. will help integrate the proposed device and method with the DSITMS (EPA method 8265). Brief resumes of principal contributors are shown in Appendix 2.

6 QUALITY ASSURANCE

6.1 For analytical equipment

All on site analytical equipment will be checked, calibrated and adjusted daily to obtain the accuracy specified by the manufacturers. Furthermore, performance evaluation standards (PES) suggested by manufacturers will be strictly applied for gas monitors and the DSITMS. During analysis in the field, equipment blanks will be run before and after PES, before samples are analyzed and periodically each four (4) hours. Triplicate samples will be analyzed periodically each four hours before the purging period, when concentrations are stable. Two (2) samples will be analyzed with the direct reading equipment and will be considered duplicates. The third sample will be sent to a traditional laboratory, in accordance with applicable sample identification, preservation, transportation, storage and chain of custody procedures. The sampling equipment will not allow atmospheric contact with collected samples.

All data will be subjected to strict data quality review (DQR) procedures. If the variation of each triplicate of the same day is less than 10%, analytical results from direct reading instrument for

the entire day will be considered acceptable. All data sheets and quality control data will be maintained for reference or inspection. This research effort will target a minimum use of tubing (to lower the quantity of equipment requiring decommissioning and IDW) and to minimize samples handling.

6.2 For sampling equipment

The flow meter for gas or water will be checked, calibrated and adjusted at a minimum, daily and as required. The automatic collection device developed during this project will be subjected to daily inspection. Automation of sample collection will minimize error due to variation of collection intervals.

7 RELATIONSHIP WITH FUTURE RESEARCH

Demonstration of the *In Situ* flux method during an SBIR phase 2 will be essential for rapid acceptance of this innovative sampling technology by both the engineering and regulatory communities. This acceptance, coupled with the broad applicability of the technology and the proven methodology will facilitate a rapid transition from the current development state to widespread use. Furthermore, during the second phase effort, we will continue to modify the method for improvement.

We will modify the *In Situ* flux method to fully exploit the potential to apply different purge flow rates in order to obtain different chemical gradients in equilibrium. If similar advective fluxes of contaminants are obtained with different chemical gradients, we believe that the source area can and will be better delineated. By applying this concept to parent and daughter compounds, the active biodegradation area will be delineated more accurately. For more permeable subsurface locations, we want the flexibility to adapt the method to higher injection rates than collection flow rates to partly purge the formation with a clean fluid and a tracer to evaluate *In Situ* flux surrounding the sampling location. These improvement will be used notably to address the following hypothesis :

- 1- May we define a sampling area as a source when we obtain an advective flux of contaminant during the presence of an instantaneous "clean volume" of fluid ?
- 2- May we define a sampling area as an active biodegradation zone when we obtain an advective flux of daughter compounds during the presence of an instantaneous "clean volume" of fluid ?
- 3- May we evaluate the migration flux rate of a contaminant during a water recharge at a specific sampling location when we obtain a dispersive rate during a stabilization to "normal" after the presence of an instantaneous "clean volume" of fluid ? May we use these induced fluxes to validate models used to predict plume behavior ?
- 4- May we estimate the migration flux rate of a contaminant between two (2) distinct sampling locations of different concentrations in a dilute zone of a specific groundwater system, when we obtain a dispersive rate during a stabilization to "normal" after the instantaneous introduction of a "clean volume" of fluid at the sampling location with a higher concentration, if the flux is calculated for an equivalent chemical gradient between the two (2) sampling locations ?
- 5- By mapping various advective flux in the source area and dispersive flux in the dispersed plume of a site for a specific contaminant, may we predict more accurately the migration rate and path of this contaminant if the source function and therefore the associated concentration gradients are modified, as after a source removal, extraction or destruction ?

We want also to use the SBIR phase 2 to expand the applicability of the method to reach different and larger markets. We will develop this sampling method to apply to:

- other types of soluble contaminants, namely for metals and radioactive compounds ;
- in conjunction with the "Hydrosparge" module (bubbling of helium in the groundwater) to decrease analysis cost for volatile compounds in the saturated zone ;
- predict desorption rates over a relative long period of time by purging the saturated zone with warm water or with slightly acidic liquids ;
- to mimic water recharge in the vadose zone during fluctuations in hydrogeological conditions by applying the method in the unsaturated zone with water.

8 COMMERCIALIZATION PLAN

Contaminated sites are a legacy of both cold war weapons production and robust manufacturing activity in an era when environmental matters and sustainable development were not fully understood. The estimated number of contaminated sites in the country vary between 130,000 and 450,000 sites with an accepted estimated cost of more than \$ 650 billion to clean up.

8.1 Potential markets

8.1.1 Underground Storage Tank (UST) sites

A total of 263,000 facilities own approximate 698,000 active UST⁽¹²⁾. The EPA estimates that about 60% are in operational compliance with release detection and prevention requirements. While these active USTs have the equipment required under the regulations, significant enforcement work remains to ensure that owners and operators maintain and operate their systems properly. Between FY 1999 and FY 2002, confirmed releases averaged 13,980. The target for 2008 is to minimize confirmed releases at UST facilities to 10,000 or fewer. While the frequency and severity of releases from UST have been reduced, they are still occurring. In the near future, it is possible that factors such as greater field presence and discovery of older releases during site closures will increase the number of confirmed releases. Furthermore, since many petroleum releases contain MTBE, remediation efforts are often more complicated and take longer to address.

8.1.2 Brownfields

This issue is one of the Bush administrations environmental priorities. In his 2003 budget, President Bush allowed \$ 73,1 million in Brownfields funds for a variety of different grants, for communities located in 37 states and seven (7) tribes. Of this funding, \$ 30,7 million has been used for 117 assessments. Since the beginning of the Brownfields program, EPA has awarded 436 assessment grants totaling over \$120 million, and 143 loans totaling over \$ 115 million. EPA's Brownfield assistance has leveraged more than \$ 4.6 billion in private investment, helped create more than 20,000 jobs and resulted in the assessment of more than 4,000 properties. The Brownfields program targets to encourage the redevelopment of 450,000 abandoned and contaminated waste sites through the country. Every acre of reclaimed Brownfields saves 4.5 acres of greenspace, and every green space created in an urban area, on average, has doubled the value of surrounding properties.

8.1.3 DNAPLs

Sampling technologies to detect, locate and monitor DNAPLs need to be improved ⁽¹³⁾. This need remains a high priority of the EPA - SBIR program. The program is designed to improve the scientific tools need to assess, predict, communicate risks associated with DNAPL and to evaluate innovative remediation options, develop risk management strategies and identify the fate and the impact of these contaminants in the subsurface.

8.2 Market Trends

Financial and technical limitations have started to substantially impact the remediation market in the past few years. Changes in baseline cleanup standards for groundwater and soil and in the overall process of site cleanup have become increasingly common. These changes include increases in the number of waivers to baseline cleanup standards and to original site remedies. There is an increasing use of natural attenuation in place of engineered remedies, emergence of brownfields programs with less stringent cleanup standards, and of new risk-based methods for priority setting. Furthermore, the remediation market is now mature and highly competitive. Mergers and consolidation of consulting business has taken place in the past few years.

8.3 Uniqueness of the method

The *In Situ* flux method is a patented technology used for the characterization of soil and groundwater with volatile organic compounds (chlorinated solvents, hydrocarbons, or more

specifically benzene, toluene, ethylbenzene, xylene, methyl terbutyl ether (MTBE), etc.). The development of the method for other types of contaminants is also a targeted objective and includes metals, radioactive compounds and even salt intrusion estimation in groundwater systems.

Each year, EPA personnel, consultants and other professionals assess, respond to, mitigate and clean up thousands of releases, whether accidental, deliberate or naturally occurring. These incidents range from small spills at a chemical facility to national disasters, such as during hurricanes, earthquakes or terrorist events. Leaching contaminants can foul drinking water in aquifers or surface waters used by public water intakes. EPA's Office of Research and Development (ORD) is working on leaching issues. The proposed *In Situ* flux method represents a major development in the area of site characterization, since it may be considered as an innovative *In Situ* leaching method for groundwater systems.

Some more standard and new site characterization technologies are close in principle to the proposed technology, but none of them are measuring the flux for the compound of interest. For the field screening market, the technology of EcoRemediation is in direct competition with the "Membrane Interface Probe", patented by "Geoprobe System inc." Some advantages of the EcoRemediation technology are the low cost, avoidance of membrane perforation and a more "user friendly" technology. Nevertheless, the main benefit of the *In Situ* flux method to the preliminary investigation or the monitoring market will be the importance of accessing information related to migration or degradation processes as apposed to just comparing the method to a characterization effort based on concentrations data alone.

We have to emphasize that the cost of this technology will be about the same as that for traditional sampling methods. The proposed method may be applied with direct push tools, standard augers or within existing wells. When equipment and crew are on site, the application of the proposed technology takes about eight (8) more minutes per sampling location (e.g. : the time required for the purging period and the rebound). This longer period of collection is about the only difference which will impact on the cost of the method. Analysis cost will increase as a function of the requirement for flux measurement. However, if a direct reading analyzer is on site, the cost of analysis remains about the same with the optimization tools available. If samples obtained during and after the purge are sent to a fixed laboratory, the number of additional analyzed samples will be in a direct relation with the quality of the estimation wanted for migration processes. Since this information generally makes a considerable difference in the ultimate performance of the subsequent remediation effort, the value of these additional analysis will be marginal in comparison to the value of the information obtained and the efficiency of remediation.

8.4 Strategy

EPA and its partners follow four (4) key steps to undertake clean up and to control risks : assessment, stabilization, selection of appropriate remedies and implementation. Following implementation, EPA encourages the monitoring of the site to ensure protective conditions to human health and the environment. To be totally effective, site assessment will need to be further optimized in the near future. This means that these steps will have to be supported by a better delineation of contaminant sources and a better understanding of transport processes in groundwater regimes. Furthermore, past experience has shown that better monitoring of sites results in lower total clean-up costs.

Targeted applications for Ecoremediation are:

- Field screening during first investigation, spills extent assessment and occurrence or absence of biodegradation processes for a site ;
- Site monitoring during risk-based assessment, source removal needs, seasonal behavior of biodegradation processes, the evaluation of the accuracy of predictive models.

For field screening, EcoRemediation inc. will introduce this innovative sampling tool in two (2) markets :

- Sales of sampling equipment through licensing agreements (with probe and / or bladder pump manufacturers) ;
- sales of software to calculate *In Situ* flux, and training.

For site monitoring, a third market will be added to these first two (2). EcoRemediation inc. will sell professional support for site characterization of highly heterogenic and complex hydrogeological systems.

This commercialization strategy for the *In Situ* flux method is based on market research and contact with industry and government performed over the past few years. EcoRemediation inc. wants to lead the market of the site characterization business, locally and internationally. For the field screening market, the technology will be offered nationally when the method will be demonstrated for volatile organic compounds in the saturated zone. Prospective agreements and market development work in Japan has already been undertaken. Steps have been taken to introduce our technology as a field screening tool for the unsaturated zone in this market. Commercial developments are also planned for Europe in this area.

For the site monitoring market and more specifically for the support of the characterization of complex hydrogeological systems, EcoRemediation inc. will introduce this innovative technology mainly in collaboration with site remediation consultants. Even though end customers will be landowners of underground petroleum storage tank field sites, dry cleaner sites, Federal States and urban owners of *brownfields*, consultants are the most important group involved in terms of market acceptance. They are directly linked with most of the property owners and with the regulatory bodies (governments). Generally, the site owners prefer to discuss investigation and remediation issues with one supplier, in this case the consultant, who has or will assume responsibility for the entire characterization and remediation program. Banks and insurance companies are also relying on the consulting community for their expertise. Some consultants involved in contaminated sites management invest in new technologies and knowledge to conquer new markets. Progressive and innovative consultants who attempt to decrease the characterization costs for their clients are attractive targets for EcoRemediation inc. These consultants are also active in training and conference activities, which further spread advanced information and techniques. Technical conferences are also used to identify new market trends. In order to promote its technology, EcoRemediation will partner aggressively appropriately disposed consultant businesses to capture a significant part of the contaminated site characterization support market, without competing directly on the engineered remediation market.

In order to increase the probability of success, EcoRemediation will follow the following path, chronologically :

1. Identify validation projects with partners, as the one planned for this SBIR proposal; Demonstrate the usefulness and accuracy of the flux method to evaluate natural attenuation processes (by comparison with microcosms test, modeling prediction or others);
2. Discuss agreements with equipment manufacturers ;obtain fixed license fees and progressive fees related to the number of cases where it is used by consultants ; obtain permission to work on different cases in order to verify the way the technology is used and to continue to collect data for a large number of cases.
3. Continue to promote the technology in conferences and training programs; continue to develop different applications for natural attenuation option and for enhanced *In Situ* treatment optimization.

Even though the market for a technology such as EcoRemediation's is quite restricted, it is a niche worth pursuing. The technology has a definite advantage over the tools currently available on the market. Furthermore, these advantages bring added value to the business of assessing natural attenuation (MNA), one of the fastest growing remedial strategies. By forging strategic alliances with consultants that thrive on technology pioneering, EcoRemediation will establish its technology in the marketplace, using the SBIR program as a springboard for a widened acceptance. By pursuing its own promotion efforts through technical conferences and demonstration projects, EcoRemediation will also add more consulting fees from work related to the characterization of complex subsurface systems and training activities.

7 CONCLUSION

This project includes the design and fabrication of a probe, the design and fabrication of a coaxial tube for existing wells, the development of a software and performance testing of these apparatus at field sites. The object of this work is to prove the concept of an innovative sampling method that will modify standard collection procedures during a site characterization effort. This new approach to soil gas and groundwater sampling is inexpensive, rapid and often provides a direct measurement of contaminant fate during site investigation. The use of this sampling technology will translate into more accurate assessment of contaminant migration rates and a better handle on the monitoring of natural attenuation processes (MNA), particularly by assessing biodegradation through the measurement of generation rates of daughter compounds.

Furthermore, the proposed sampling technique may enhance the acceptability of the MNA option by non-technical individuals, particularly if direct measurements of consumption and production rates due to biodegradation processes are available.

Usable land is a valuable resource. However, where contamination presents a real or perceived threat to human health and the environment, options for future land use may be limited. The National goal in EPA strategic planning related to contaminated sites is to return these land to long term, sustainable, and productive use. This goal provides impetus to the selection and implementation of remedies that, in addition to providing clear environmental benefits, will support reasonably anticipated future land use options and provide greater economic and social benefits.

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Appendix 1 : Sampling procedures and calculations for *In Situ* flux measurement

THEORY

The development of the proposed technique was initially based on procedures used in assessing the ventilation efficiency within buildings. For a defined volume, the concentration of a contaminant in a fluid at any time can be expressed by a differential material balance, which provides a rational basis for relating the generation and the removal rates of a contaminant. ⁽³⁾

Let $C =$ concentration of a contaminant in a fluid at time " t ";
 $G =$ rate of generation of contaminant;
 $Q =$ rate of purging;
 $K =$ design distribution constant, allowing for incomplete mixing;
 $Q' = Q/K =$ effective rate of purging, corrected for incomplete mixing;
 $V =$ volume of room or enclosure.

Starting with a fundamental material balance, assuming no contaminant is in the supply fluid,

« rate of accumulation » = « rate of generation » - « rate of removal »

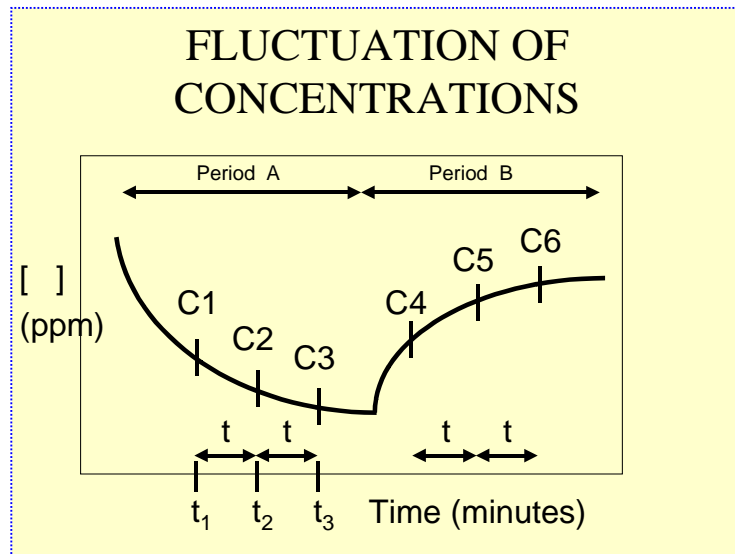
$$V dC = G dt - Q'C dt \quad (1)$$

With mathematical simplification, we arrive at:

$$G = \frac{Q' (C_2 - C_1 e^{-Q't/V})}{(1 - e^{-Q't/V})} \quad (2)$$

FLUX CALCULATION

For the proposed sampling technique, the following typical graphic is obtained during the purging period (period A) and after the purge is stopped (period B):



If we assume a constant rate of generation during the purging period (period A),
 So G_1 (between t_1 and t_2) = G_2 (between t_2 and t_3)

If $e^{-Q't/V} = H$, [then, $-\ln H = Q't/V$];

And if $t_3 - t_2 = t_2 - t_1 = t$

Then,

$$\frac{Q_1' (C_2 - C_1 e^{-Q't/V})}{(1 - e^{-Q't/V})} = \frac{Q_2' (C_3 - C_2 e^{-Q't/V})}{(1 - e^{-Q't/V})} \quad (3)$$

so

$$Q_1' (C_2 - C_1 H) = Q_2' (C_3 - C_2 H) \quad (4)$$

If we assume during the purging period that $Q_1' = Q_2'$, then

$$(C_2 - C_1) H = (C_3 - C_2) H \quad (5)$$

so

$$H = \frac{C_3 - C_2}{C_2 - C_1} \quad (6)$$

G is then obtained with H, as

$$G = \frac{Q' (C_2 - C_1) H}{(1 - H)} \quad (2)$$

As shown in figure « 1 », or « 2 », the first step is to create a soil void in the subsurface. With a direct push probe, the void is formed by the probe removal on an established distance. Within existing wells, three (3) packers are used to isolate a precise zone around the well. As a second step, this soil void is purged with a non-contaminated fluid. If the method applied to the vadose zone, the fluid is an inert gas. If the method applied to the groundwater, the fluid is clean water. The soil void is cylindrical and its approximate volume is estimated. We assume this soil void as a relative closed space, since extraction flow rate during the purge is similar to injection flow rate. When the purging flow is laminar in the soil void, the incoming fluids mix well with the soil fluid. With this condition, the constant « K » for incomplete mixing is considered near 1 and the effective flow rate is estimated similar to the applied flow rate of the purging fluid. « H » is obtained with equation « 6 » with « C_1 », « C_2 » and « C_3 » from samples collected at equal period of time. « G » is estimated with « H » and the applied flow rate. « G » expressed as a mass per unit of time is multiplied with the volume of or the exposed surface of the soil void to calculate *In Situ* flux (mass per volume per unit of time or mass per surface per unit of time).

Appendix 2 : Resume (principal investigator and main collaborator)

Mr. Andre Tartre, of EcoRemediation Inc. is the principal investigator of this innovative soil sampling approach. Mr. Tartre is the inventor of this technology and holds current U.S. patents for the process. Mr. Tartre has been responsible for the initial research and development of the technology in Canada and was the lead researcher during the prototype trials that were conducted at 27 gasoline service stations. Mr. Tartre received a Master Degree in Engineering (Occupational Health and Safety) from "Trois-Rivières" University in 1984. He received a Bachelor degree in Biology in 1982 from "Sherbrooke" University. After five years with the "Occupational Health and Safety Administration" in Quebec, he received his certification from the American Board of Industrial Hygiene (as a Certified Industrial Hygienist) in 1989. In 1990-91, he was responsible for the "Health, Safety and Environment" for "Hoesch-Celanese Canada inc." for five (5) plants in eastern Canada. In 1992, he started a consulting business in Montreal with other associates. In 1993, the company began in the "Environmental Audit Phase 1 and 2" market for financial companies. The company received a governmental grant of 175,000 \$ (can.) in 1994 to develop and to demonstrate an innovative technology to assess the tightness of Underground Storage Tanks (UST). The method evaluated the flux of vapors in UST backfills. After the demonstration project in 1996, the control of the company shifted to an investor. Mr. Tartre left the company and turned his attention to the start up of another business offering services in environmental site characterization and remediation. In 1998, Mr. Tartre received his first US patent for the proposed development. "EcoRemediation inc." was incorporated in Delaware in August 2001.

Mr. Stephen P. Farrington is a Senior Engineer for the New England Division of Applied Research Associates, inc. (ARA). Mr. Farrington has 15 years of experience in environmental engineering, contaminant fate and transport studies, site characterization and remediation technologies. Mr. Farrington's research and development efforts within ARA have focused on subsurface characterization and monitoring, including the development of real-time chemical sensor technology such as High Speed GC/CPT, the highly effective *Wireline CPT* (patent pending) and the implementation of long term monitoring sensor networks. He received an M.S. in Civil Engineering from the Environmental and Water Resources at Stanford University. He is a Professional Engineer registered in the State of Vermont