Florida Department of
Environmental Protection
Bob Martinez Center
2600 Blair Stone Road
Tallahassee, Florida 32399-2400

Charlie Crist
Governor

Jeff Kottkamp
Lt. Governor

Michael W. Sole
Secretary

August 13, 2008

John Archibald
inVentures Technologies, Inc.
670 Wilsey Road
Fredericton, New Brunswick E3B 5C8, Canada

Re: **groundwater Pressurized Remediation Optimizer (gPRO®)**

Dear Mr. Archibald:

The Division of Waste Management (the Division) hereby accepts the groundwater Pressurized Remediation Optimizer-Low Pressure (gPRO® LP) and the groundwater Pressurized Remediation Optimizer-High Pressure (gPRO® HP) as devices for the dissolution of gases into water for the purpose of groundwater remediation. It is anticipated that gPRO® LP will most often be used as an in-situ, in-the-well device, but it can be adapted to ex-situ applications. The gPRO® HP unit, however, is an aboveground device that dissolves gases into groundwater for in-situ remediation via direct injection, re-injection or re-infiltration. The underlying scientific principles for dissolution of gases into water, under pressure, are the same for both the gPRO® LP and the gPRO® HP. The gPRO® systems, depending on the type of gas infused, can be used for biological, chemical, or physical treatment processes.

The Division recognizes the gPRO® systems as methods for remediation of contaminated sites in Florida. The Division has no objections to their use provided a site-specific Remedial Action Plan (RAP) is approved by the Department. Regulatory information is provided in Enclosures 1.

The Department of Environmental Protection does not provide endorsement of specific or brand name remediation products or processes; however, it does recognize the need to determine their acceptability in the context of environmental regulations and protection of public health and safety. In no way shall this regulatory acceptance letter be construed as Department certification of performance. Additionally, the Department emphasizes a distinction between its regulatory "acceptance" letter and an approval. Products and processes are accepted but they are not approved. Vendors and consultants must market the products and processes on their own merits regarding performance, cost, and safety in comparison to competing alternatives in the marketplace.

RAPs that include use of an "accepted" product should include a copy of the acceptance letter in the RAP's appendix and reference it in the text of the document. To aid regulatory agency

reviewers, supplemental information is provided as Enclosure 2. It is not a requirement that a particular remediation product or process have an official acceptance letter in order for it to be proposed in a site-specific RAP. The RAP, however, must contain sufficient information about the product or process to show that it meets all applicable rules and regulations.

The Division reserves the right to revoke its acceptance of a product or process if it has been misrepresented. Additionally, Division acceptance of any product or process does not imply it has been deemed applicable for all cleanup situations, or that it is preferred over other treatment or cleanup techniques in any particular case. A site-specific evaluation of applicability and cost effectiveness must be considered for any product or process, whether conventional or innovative, and adequate design details must be provided in a site-specific RAP submitted for Department review and approval. You may contact me at (850) 877-1133, extension 3722, or Gary Millington at (850) 245-7502, if there are any questions.

Sincerely,

Rick Ruscito

Rick Ruscito, P.E.
Ecology and Environment, Inc.
Bureau of Petroleum Storage Systems
Petroleum Cleanup Section 6

Gary Millington

Gary Millington, P.E.
Florida DEP
Bureau of Waste Cleanup
Program & Technical Support Section

c: Don Ray
Performance Technologies, Inc.
337 Hunters Crossing
Tallahassee, Florida 32312

T. Conrardy - FDEP/Tallahassee
R. Cowdery - FDEP/Tallahassee

# ENCLOSURE 1

## REGULATORY INFORMATION

1. Regulations: Users of gPRO® LP and gPRO® HP devices shall ensure that all applicable groundwater contaminant standards are met at the time of project completion for the contaminants of concern, any residuals associated with the gases dissolved into the groundwater, and any byproducts of concern produced as a result of chemical or biochemical reactions involving those gases. The following chapters of the Florida Administrative Code (F.A.C.) are cited: Chapter 62-550, F.A.C., for primary and secondary water quality standards; Chapter 62-520, F.A.C. for groundwater classes and standards; Chapter 62-522, F.A.C., for groundwater permitting and monitoring requirements; Chapter 62-528, F.A.C., for underground injection control, particularly Part V, for Class V, Group 4 aquifer remediation projects; Chapters 62-770, 62-780, 62-782, and 62-785, F.A.C., for cleanup criteria; and Chapter 62-777, F.A.C., for cleanup target levels.

   Chapter 62-520, F.A.C., requires groundwater to be free from substances that are harmful to plants, animals, and organisms, and free from substances that are carcinogenic, mutagenic, teratogenic or toxic to human beings. These "free from" requirements prohibit injection of a potentially harmful product in the event that any of its ingredients are not regulated as specific primary or secondary drinking water contaminants.

2. Gases covered by this acceptance: Since the gPRO® LP and gPRO® HP delivery devices are capable of infusing a wide range of gases into water, an attempt to cover every conceivable application in this acceptance would be impractical. Therefore, the scope of this acceptance is limited to the following ten (10) gases: the gaseous alkanes (methane, ethane, propane and butane); ammonia; carbon dioxide; ethylene; hydrogen; hydrogen sulfide; and oxygen.

   Gases other than those listed above may be used, provided all applicable and appropriate rules and regulations are addressed in a site-specific RAP approved by the Department. Additionally, regardless of whether or not a gas proposed for use is covered by this acceptance or regulated by rule, it will be incumbent on the submitter of a site-specific RAP to take into account the gas flammability, reactivity, toxicity, and any other safety considerations that are necessary. The residual concentration of the gas and any degradation byproducts of concern that remain in the groundwater upon completion of a remediation project must meet the minimum groundwater criteria of Chapter 62-520, F.A.C.

3. Groundwater criteria for gases covered by this acceptance: For the ten gases covered by this acceptance, the table below provides minimum groundwater criteria that serve as the groundwater cleanup target levels (GCTLs). For ammonia, butane, and hydrogen sulfide, the GCTLs are specified in Table 1 of Chapter 62-777, F.A.C. For the other gases listed in the table below, GCTLs were calculated using the method provided in Chapter 62-777, F.A.C., for non-carcinogens. For these calculations, it is assumed that an oral reference dose is equivalent to the inhalation reference dose in a route-to-route exposure conversion. No GCTL was calculated for oxygen.

   Hydrogen sulfide deserves the most attention because of its toxicity. By the time a remediation project involving this gas is completed, its residual groundwater concentration cannot exceed 21 micrograms per liter (µg/L). For ammonia, the minimum criteria set forth in Chapter 62-777, F.A.C., is 2,800 µg/L. With a relatively high solubility of 34%,

prospective users of this gas may need to take into account its potential to remain in the groundwater at high residual concentrations after the contaminants of concern at a cleanup site have been remediated. To avoid a lengthy waiting period during which the ammonia concentration attenuates to the acceptable level, it may be advisable to use no more than the necessary amount to accomplish remediation objectives. Butane is a gaseous alkane for which the Department has developed a minimum groundwater criterion of 9,100 µg/L.

For hydrogen at 20 degrees C and 1 atmosphere, the calculated 6,700 µg/L GCTL is greater than its 1,600 µg/L solubility limit. Therefore, the solubility limit will be the maximum allowable (possible) residual concentration for hydrogen applications until a depth is reached at which the pressure and temperature are such that the solubility is no longer less than or equal to 6,700 µg/L. Below that depth, the maximum allowable residual guidance concentration shall be 6,700 µg/L.

| Gas | Groundwater Cleanup Target Lev per Chapter 62-777, F.A.C. (micrograms per liter, µg/L) ♦ |
|---|---|
| Methane | 3,100 ■ † |
| Ethane | 5,900 ■ † |
| Propane | 8,700 ■ † |
| Butane | 9,100 |
| Ammonia | 2,800 |
| Carbon Dioxide | 43,600 ● † |
| Ethylene | 1,100 ▲ † |
| Hydrogen | 6,700 ‡ |
| Hydrogen Sulfide | 21 |
| Oxygen | Not calculated. Relatively benign |

♦ The criteria for ammonia, butane, and hydrogen sulfide are specified in Table 1 of Chapter 62-777, F.A.C. The other criteria listed here are calculated in accordance with the method provided in Chapter 62-777, F.A.C., for non-carcinogens.

■ When calculating the 3,100 µg/L for methane, the 5,900 µg/L for ethane and the 8,700 µg/L for propane, the 1,000 parts per million by volume (ppm/v) 8-hour, 5-day Time-Weighted Average (TWA) Threshold Limit Value (TLV) exposure recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) for each of these alkanes was mathematically adjusted to a 24-hour, 7-day basis.

● When calculating the 43,600 µg/L for carbon dioxide, the 5,000 ppm/v, 8-hour, 5-day TWA TLV exposure recommended by the ACGIH was mathematically adjusted to a 24-hour, 7-day basis.

▲ When calculating the 1,100 µg/L for ethylene, the 200 ppm/v, 8-hour, 5-day TWA TLV exposure recommended by the ACGIH was mathematically adjusted to a 24-hour, 7-day basis.

† Conversion of TLV ppm/v to milligrams per cubic meter ($mg/m^3$) was calculated at 21.1 degrees Centigrade. The 8-hour, 5-day TWA TLV in $mg/m^3$ was mathematically adjusted to a 24-hour, 7-day Inhalation Reference Dose (RfDi). This RfDi is assumed equivalent to an Oral Reference Dose (RfDo) for extrapolation of route-to-route exposure, a reasonable assumption in this case if bioavailability by the inhalation and oral routes are both assumed to be 100%. A safety factor (SF) of 100 is used. The amount of air breathed by a human in one day is 20 $m^3$, and the average adult body weight is 70 kilograms (kg). 2 liters per day (L/d) is the amount of water consumed by an adult human. The Relative Source Contribution (RSC) factor for other sources of exposure is 0.2, and the 1,000 µg/mg is a conversion factor. Equations used to determine the calculated values of Groundwater Cleanup Target Levels (GCTL) in micrograms per liter (µg/L) are shown below.

‡ ACGIH TWA TLV information is not available for hydrogen. However, NASA, for spacecraft, and the U.S. Navy, for submarines, occupied for lengthy periods of time, both consider 4,100 ppm/v hydrogen (or 10% of its 41,000 ppm/v lower explosive limit) a reasonable 90-day Continuous Exposure Guidance Level (CEGL). Since 4,100 ppm/v is already a continuous exposure concentration, it was not adjusted to a 24-hour, 7-day exposure basis in the equations below. That is, the (8/24) and (5/7) adjustment terms in the equation below were omitted when calculating the residual groundwater concentration of 6,700 µg/L.

RfDi (as milligrams per kilogram per day) = [ (TLV $mg/m^3$) x (8hr/24hr) x (5days/7days) x (20 $m^3$) ] / [ (100 sf) x (70 kg) ]

RfDi = RfDo (assumption)

GCTL (in µg/L) = [(RfDo) x (0.2 RSC) x (70 kg) x (1,000 µg/mg) ] / [ 2 L/d ]

By the time a cleanup project is completed, the residual concentration of each gas injected during the course of remedial action must not exceed the GCTL listed above, or its natural-occurring groundwater concentration at the cleanup site, whichever is less stringent.

4. Temporary injection zone of discharge: Rule 62-522.300(2)(c), F.A.C., applies to both gPRO® LP and gPRO® HP when they are used for injection-type aquifer remediation. The type of injection can be either direct injection or closed-loop re-injection/re-infiltration. It is anticipated that gPRO® HP will most often be used for the closed-loop method but the gPRO® LP can be adapted for such use too. Rule 62-522.300(2)(c), F.A.C., allows a temporary injection zone of discharge (ZOD) for the primary groundwater standards that apply to the contaminants of concern, the prime constituents of the reagents used to remediate a site's contaminants, and for the secondary groundwater standards. In order for users of gPRO® to comply with this rule, a Department-approved RAP must address the duration and size of the ZOD, and provide for groundwater monitoring of the gas (i.e., the remediation agent) and any site contaminants in the injected or re-injected/re-infiltrated fluid that do not meet their respective primary or secondary drinking water standard, or their respective groundwater cleanup target level.

   For most gases that will be used by gPRO®, the Department anticipates that the temporary injection ZOD --- when such a zone is needed --- will be permitted most often by Rule 62-522.300(2)(c), F.A.C., not by variance. A variance granting permission for a temporary injection ZOD will be necessary in cases where a chemical species classified as a primary groundwater contaminant is present as an impurity in the remediation agent to be injected (a gas in this case) if the impurity plays no role in the remediation process, and the concentration of the impurity in the fluid to be injected or re-injected/re-infiltrated is in excess of its primary groundwater standard.

5. Construction/Clearance Permit: Per Rule 62-528.630(2)(c), F.A.C., Class V injection-type aquifer remediation wells are exempt from the permitting requirements of Rule 62-528.635, F.A.C., provided they are authorized under the provisions of a RAP or other enforceable mechanism, and the requirements of the rules governing the remediation project, as well as the construction, operation, and monitoring requirements of Chapter 62-528, F.A.C., are met. In other words, the issuance of an enforceable, site-specific RAP Approval Order by the Department for injection-type aquifer remediation constitutes the granting of a Class V injection well construction/clearance permit.

6. Utilization of wells: If a remediation site happens to have an abundance of monitoring wells, then the Department has no objection to the use of some wells for injection. However, no "designated" monitoring well, dedicated to the tracking of remediation progress (by sampling) shall be used as an injection well. This will avoid a premature conclusion that the entire site meets cleanup goals. Not using designated tracking wells for injection will ensure that the remediation agents have permeated the entire site, and do not remain localized to the immediate area surrounding each injection well.

7. Groundwater monitoring: A distinction can be made between two categories of groundwater monitoring that are conducted during the course of aquifer remediation. The first category is that which is always conducted, regardless of the cleanup method employed, to monitor the concentration of the contaminants being cleaned up (i.e. the contaminants of concern). The second category is that which is conducted to monitor the concentration of chemical

remediation agents (gases in this case) when the cleanup method involves the injection or re-injection/re-infiltration of such agents into the groundwater. Chapter 62-528, F.A.C., Underground Injection Control, and Chapter 62-522, F.A.C., Groundwater Permitting and Monitoring Requirements, are the major regulations that apply to the latter type of monitoring.

For injection-type aquifer remediation, monitoring for Underground Injection Control purposes must be addressed in a RAP approved by the Department for any chemical species and parameters in the injected or re-injected/re-infiltrated fluid that do not the meet their primary, secondary or minimum groundwater criteria. As indicated in paragraph 4 above, upon expiration of the time permitted for a temporary injection ZOD, either by Rule 62-522.300(2)(c), F.A.C., or by variance, each chemical species and parameter for which the temporary ZOD was established must meet its respective groundwater water standard, or be no worse than its natural-occurring background level at the cleanup site, whichever is less stringent. In most cases, the Department anticipates that monitoring on a quarterly basis for underground injection control purposes will suffice.

8. Underground injection control inventory: RAPs proposing injection-type aquifer remediation shall include information pursuant to Rules 62-528.630(2)(c)1 through 6, F.A.C., for the inventory purposes of underground injection control. Per Rule 62-528.630(2)(c), F.A.C., aquifer remediation projects involving injection wells may be authorized under the provisions of a RAP, provided the construction, operation, and monitoring requirements of Chapter 62-528, F.A.C., are met.

9. Avoidance of migration: Per Rule 62-528.630(3), F.A.C., injection-type aquifer remediation projects shall be conducted in such a way that there is no undesirable migration of either the remediation agents or the contaminants of concern.

10. Abandonment of wells: Upon issuance of a Site Rehabilitation Completion Order, injection wells shall be abandoned pursuant to Section 62-528.645, F.A.C. The Underground Injection Control Section of the Department shall be notified so that injection-type treatment wells can be removed from the inventory tracking list.

SUPPLEMENTAL INFORMATION

1. Nature of the device: The gPRO® module contains hydrophobic, microporous, hollow fibers that provide interface area for mass transfer of gas into the cross-flowing groundwater. This method for the dissolution of gas into groundwater does not create bubbles. The underlying scientific principle for the gPRO® is the equilibrium that exists between a gas dissolved in a liquid and the partial pressure of that gas above the liquid. The proportionality constant that relates the partial pressure to the concentration of the dissolved phase is the Henry's Constant, for which additional information is readily available in textbooks.

2. Equipment description:

   a. The gPRO® LP unit is an in-situ, in-the-well gas infusion device consisting of a ½-horsepower, 115-volt water pump and gas transfer fiber module in a sturdy plastic housing. It is approximately 4 feet long and available in two overall diameter sizes: 4 inches and 6.25 inches. The unitary pump and fiber module is lowered into a well, but it can also be placed into an aboveground tank and used as an ex-situ treatment device. For in-situ applications, a hose delivers gas from an aboveground supply tank or gas generator to the microporous fiber module in the treatment well, where the gas is dissolved into the groundwater that is circulated by the pump.

   b. The gPRO® HP unit is an aboveground gas infusion system consisting of a water pump, control panel and gPRO® HP gas transfer modules. The standard number of modules is four, on model gPRO® 4 HP. The largest system listed in the manufacturer's bulletin is gPRO® 12 HP, which has 12 modules. Even though the equipment is located aboveground, it can be used for either ex-situ or in-situ remediation of groundwater.

      When used in-situ, in a closed-loop, re-injection configuration, contaminated groundwater is extracted and pumped through the aboveground gas transfer fiber modules at high pressure (because higher concentrations of gas can be infused at higher pressures). The treated water is then re-injected into the aquifer.

3. Applications: gPRO® has a wide range of biological, chemical and physical applications. The list below, including the type of gas, was provided by inVentures Technologies Incorporated. Information added by the Department is shown in brackets.

   <u>Biological treatment</u>

   - Aerobic oxidation using oxygen

   - Co-metabolic oxidation using oxygen and alkane gas. [Co-metabolism is the metabolism of two compounds, in which the degradation of the second (the secondary substrate) depends on the presence of the first (the primary substrate). An example is the remediation of chlorinated solvents, in which bacteria, as they degrade methane, the primary substrate, release enzymes that degrade the chlorinated solvents, the secondary substrate. A substrate is a compound that is altered by an enzyme.]

   - Co-substrate oxidation using oxygen and ethylene gas or other co-substrates. [Co-substrates, also known as coenzymes, are small organic, non-protein molecules that carry

chemical groups between enzymes. They are substrates for enzymes and usually do not form a permanent part of the enzymes' structure.]

- Anaerobic degradation using hydrogen gas. For example, reductive dechlorination and treatment of perchlorate.

Chemical treatment

- pH adjustment using carbon dioxide (lower pH) or ammonia gas (raise pH)
- Geochemical fixation of metals using hydrogen or hydrogen sulfide
- Oxidation of metals using oxygen gas

Physical treatment

- LNAPL and DNAPL recovery can be enhanced by using carbon dioxide in combination with a dual-phase extraction system. [This application is listed only for the gPRO® HP.]

4. Safety: For gPRO® LP and gPRO® HP, like any other equipment items used for the remediation of contaminated sites, the Department requires all appropriate safety practices to be observed. Not every item in the list that follows may be applicable to every location where a gPRO® is installed, and the list is not intended to be exhaustive. Rather, it is intended as a starting point for safety considerations that designers of gPRO® installations may need to take into account.

   - The handling and use of high pressure gas cylinders;
   - Whether the site-specific location where the gPRO®, its gas cylinder or gas generator and associated tubing, valves, and fittings will be installed is a non-hazardous area or, for example, a Class 1, Group D, Division 1 or 2 hazardous area as defined by the National Electrical Code;
   - Whether the gas being used is heavier or lighter than air;
   - The toxicity and flammability, and reactivity of the gas with any other chemicals that may be present at a specific remediation site;
   - Static electricity and other potential ignition sources in the event of a flammable gas leak;
   - The lower explosive level (LEL) of the gas being used, if it is flammable; and
   - Fail-safe features for the gPRO® system itself.

5. Design considerations: For injection-type remediation strategies, the spacing of treatment points depends on the site-specific radius of influence. The distance to which the dissolved gas travels from the gPRO® well will be greatest in the downgradient direction, and it will depend on the concentration of gas infused at the well, the velocity of the groundwater and the site's chemical and biochemical demand for the gas. inVentures suggests that measurement of dissolved gas concentrations at various distances from the infusion well should not be the only means by which to determine a radius of influence. Measurement of other biological and/or chemical indicators should be made as well.

6. Dissolved gas measurements: Users of gPRO® shall ensure that there is a means by which to sample and measure the groundwater concentration of infused gas at the depth desired during a remediation project. Field and hand-held instruments are commercially available for the measurement of some dissolved gases in water. If no instrument or analytical method is available for the gas of interest for a gPRO® remediation project, the user shall develop a method.

   Users of the gPRO® are advised to discuss their specific groundwater analytical needs with their laboratory, in order to identify the field instrument or sample collection and analytical method that is most appropriate for the gas being used for a particular remediation project.

7. Limitation: gPRO® is not intended for use with ozone.