Department of
Environmental Protection

Jeb Bush
Governor

Twin Towers Office Building
2600 Blair Stone Road
Tallahassee, Florida 32399-2400

David B. Struhs
Secretary

January 5, 2004

Mr. Robert Coburn, President
Coburn Construction
P.O. Box 14010
Bradenton, Florida 34280-4010

Re: **Humus/Surfactant Bioremediation Technology**

Dear Mr. Coburn:

The Bureau of Petroleum Storage Systems hereby accepts Humus/Surfactant Bioremediation Technology, a process that utilizes humus and a proprietary biodegradable surfactant, for the remediation of petroleum contaminants.

As indicated by Dr. Richard W. Popino of the environmental consulting firm Common Sense Solutions, there are also applications of this process that are beyond the jurisdiction of this bureau, which is the cleanup of petroleum pursuant to Chapter 62-770, Florida Administrative Code (F.A.C.). Other state agencies and other bureaus within the Florida Department of Environmental Protection may choose to recognize this acceptance for applications involving non-petroleum contaminants if their needs are similar. The Bureau of Petroleum Storage Systems, however, is not responsible for applications beyond its own jurisdiction.

This acceptance applies to ex situ applications of the process. It also applies to in situ remediation of soil, but only to the extent that leachate from the humus and surfactant will not affect the underlying groundwater. In situ application for the purpose of groundwater remediation may be possible in the future if a chemical analysis of the humus and surfactant is presented to the Bureau of Petroleum Storage Systems, for comparison to Florida's groundwater standards. Enclosure 1 contains regulatory advice in regard to applications, and enclosure 2 contains additional general information.

While the bureau does not endorse specific or brand name remediation products or processes, it does recognize the need to provide advice from an environmental regulatory standpoint with respect to applicable rules and regulations, and the interests of public health, safety and welfare. Vendors must then market the products and processes on their own merits regarding performance, cost and safety in comparison to competing alternatives in the marketplace. In no way, however, shall this regulatory acceptance letter be construed as a certification of performance.

Also, it is <u>not</u> 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 Remedial Action Plan. The plan, however, must contain

sufficient information about the product or process to show that it meets all applicable and appropriate rules and regulations.

The Bureau of Petroleum Storage Systems recommends, to those who prepare site-specific Remedial Action Plans proposing the humus/surfactant process, that a copy of this letter be included in the appendix of the plans they submit to the state and its contracted local county programs for technical review and approval. This may help to expedite the review and approval process of those plans by making sure that reviewers who may not yet be familiar with this new technology, or who may not yet have obtained a copy of this letter from the Bureau of Petroleum Storage Systems' web site, are provided some regulatory advice at the onset of their review. The web site address is www.dep.state.fl.us/waste/categories/pcp/pages/innovative.htm.

The bureau reserves the right to revoke its acceptance of a product or process if it has been falsely represented. Additionally, bureau acceptance of a 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 site-specific design details must be provided in Remedial Action Plans proposing the product or process. You may contact me at 850/877-1133, extension 29 or at the letterhead address, Mail Station 4590.

Sincerely,

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

Rebecca S. Lockenbach
FDEP Section Leader
Bureau of Petroleum Storage Systems
Petroleum Cleanup Section 6

c: Richard W. Popino, Ph.D.
Common Sense Solutions, LLC
9837 Faust Drive
Vienna, Virginia 22182

Tom Conrardy – FDEP/PCS3 - Tallahassee

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ENCLOSURE 1

REGULATORY ADVICE

1. Applicable and appropriate rules and regulations: The onus shall be on Coburn Construction and users of the Humus/Surfactant process to comply with all applicable and appropriate rules and regulations. At cleanup sites where the process is used, all soil and groundwater contaminant criteria (and surface water contaminant criteria when applicable) must be met for the following: the residual concentrations of the contaminants being remediated; the residual concentrations of constituents of the humus and surfactant; and the concentrations of any byproducts produced as a result of chemical or biochemical reactions involving the constituents of the humus, surfactant, and the contaminants being remediated. The following chapters of the Florida Administrative Code, either in part or in their entirety depending on the situation, that are most often applicable to cleanups include but are not necessarily limited to Chapter 62-550, for primary and secondary water quality standards; Chapter 62-520, for groundwater classes and standards, and minimum criteria; Chapter 62-522, for groundwater permitting and monitoring requirements; Chapter 62-528, for underground injection control; Chapter 62-770, for petroleum cleanup criteria; Chapter 62-777, for groundwater and soil cleanup criteria, and also for minimum groundwater criteria and surface water criteria; and Chapter 62-785, for brownfields cleanup criteria. These chapters of the Florida Administrative Code are often more simply referred to as "rules", and are currently available as such at web page www.dep.state.fl.us/legal/legaldocuments/rules/rulelistnum.htm.

2. Minimum criteria: A noteworthy aspect of the general minimum groundwater criteria set forth in Chapter 62-520, F.A.C., is that it 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. In effect, these "free from" requirements form a catchall. They close what would otherwise be a loophole in the regulations by preventing the introduction of a potentially harmful remediation product in the event that any of its ingredients or constituents is not specifically listed and regulated as a primary or secondary drinking water contaminant in Chapter 62-550, F.A.C., or specifically listed as a "minimum groundwater criteria" contaminant in Chapter 62-777, F.A.C.

   It would be advisable to take a similar approach in the case of surface water. For example, if a particular ingredient or constituent of the humus or surfactant is not specifically listed as a surface water contaminant in Chapter 62-777, F.A.C., along with a specific maximum allowable surface water concentration, then it should not be construed that the ingredient or constituent is of no environmental or toxicological concern. The reason is that there are numerous chemical species and compounds in existence, and it would be impractical for the state to attempt to develop criteria for each without first taking into account whether the chemical is even likely to be present in the Florida environment. Therefore, for any chemical species in the humus and surfactant that is not regulated by the state of Florida, consideration should be given to whether its presence in surface water will be harmful

to plants, animals, and organisms, and whether it is carcinogenic, mutagenic, teratogenic or toxic to human beings.

3. Surface waters: If humus and surfactant will be applied at a cleanup site where there is a potential for the humus and surfactant constituents to enter a nearby surface water body, then the concentration of each constituent in that surface water body must not exceed its maximum allowable surface water concentration set forth in Chapter 62-777, F.A.C. The maximum allowable surface water concentrations for contaminants listed in Chapter 62-777, F.A.C., are provided separately for fresh surface waters and marine surface waters.

   It should be noted that the bulk of petroleum cleanup sites in Florida within the jurisdiction of the Bureau of Petroleum Storage Systems are typically "subterranean" cleanups at gasoline service stations, where soil and groundwater have been contaminated by leakage from underground petroleum storage tanks. A nearby surface water body is sometimes impacted by the migration of the subterranean petroleum contaminants, so surface water criteria are set as cleanup target goals, but this is the occasional exception and not the usual cleanup site case.

   Also, in regard to surface water issues, it should be noted that the regulatory jurisdiction of the Bureau of Petroleum Storage Systems does not include surface water cleanups of petroleum that originates, for example, from ship spills and boat bilges, since these activities are not directly associated with the storage and dispensing of petroleum fuels.

4. No Further Action Criteria: Soil, groundwater, and surface water "No Further Action" cleanup criteria for the contaminants being remediated at a site are set forth in Chapter 62-777, F.A.C. The groundwater and surface water cleanup criteria are straightforward; they are expressed as maximum allowable concentrations. But for a given contaminant in the soil, however, its applicable cleanup target is the lower of the direct exposure and leachability cleanup criteria set forth in Chapter 62-777, F.A.C. In other words, the soil at the site has to be cleaned up to the point that it meets both the direct exposure and leachability cleanup criteria if an unconditional declaration of No Further Action is desired.

   The cleanup criteria in Chapter 62-777, F.A.C., also applies to any constituents of humus and surfactant that may themselves be classified by the State of Florida as contaminants, and therefore listed in that chapter, along with cleanup criteria. In other words, just because a chemical species is present as a constituent or an ingredient of a commercial remediation product, it does not necessarily mean that the chemical itself is not considered to be a groundwater, soil or surface water contaminant by the State of Florida. Therefore, before the State of Florida can issue a declaration of "No Further Action" for a site that is being cleaned up, both the contaminants originally at the site and the chemicals used to remediate them have to be at safe levels.

   Users of humus and surfactant for the remediation of petroleum-contaminated sites are advised to read Section 62-770.680, F.A.C., to determine whether a site qualifies for an unconditional declaration of No Further Action (NFA) or a conditional NFA involving institutional and/or engineering controls. Likewise, for non-petroleum sites, Section 62-785.680, F.A.C., should be consulted for information about

unconditional and conditional NFAs, and institutional and engineering controls.

5. Safeguarding the underlying groundwater: In cases where Humus/Surfactant Bioremediation Technology is used for shallow in situ remediation of soil contaminants located well above the water table, the regulatory concerns regarding the potential for humus and the augmenting surfactant to have a negative impact on the underlying groundwater at a site are likely to be minimal. However, the Bureau of Petroleum Storage Systems believes it would be appropriate for the state's technical reviewers to take into consideration the possibility that humic acid and surfactant could leach into underlying groundwater at sites where Humus/Surfactant Bioremediation Technology is proposed for use close to the water table. For those applications that are closer to the water table, it would be advisable not to proceed until Coburn Construction provides a chemical analysis of the materials used in its process, so that regulators may compare the chemical species present in those materials with the groundwater standards for the State of Florida.

   There may be other situations in which technical reviewers may want to take into consideration the potential for an impact on groundwater when using Humus/Surfactant Bioremediation Technology. For example, shallow soil remediation using Humus/Surfactant Bioremediation Technology at sites where the water table is deep but the soil has a high permeability, thereby creating a situation in which leachate may easily reach the depth of the groundwater. Another example may be the backfilling of the deepest part of an excavation pit (either at or below the water table) with soil that was mixed or treated ex situ by the Humus/Surfactant Bioremediation Technology, thereby creating a potential for contact with the groundwater. The bureau suggests that technical reviewers throughout the state make decisions and use judgment regarding this matter on a case-by-case basis.

6. Restriction on use: The Bureau of Petroleum Storage Systems presently recommends that the use of Humus/Surfactant Bioremediation Technology be restricted to only those situations in which its leachate will not enter the underlying groundwater.

   In the future, if a chemical analysis of the humus and surfactant becomes available, then the bureau will reconsider the restriction. It is incumbent on Coburn Construction to provide a chemical analysis that completely and accurately describes both the humus and surfactant materials used in its process. The bureau anticipates that the chemical analysis of the humus portion of the humus and surfactant materials would include but not necessarily be limited to the chemical elements present in commercially available humic acids, as discussed in enclosure 2. Additionally, in order for a chemical analysis to suffice for regulatory purposes, it may also have to include chemical species and parameters such as sulfate, nitrate, ammonia nitrogen, pH, total dissolved solids, etc. The chemical analysis of the humus (presumably humic acid) and the surfactant should be for the composition that will actually be injected or introduced to the groundwater. If the analysis is for a concentrate that is diluted with fresh water by the user prior to injection, then the dilution ratio should also be provided, in order for the Bureau of Petroleum Storage Systems to perform a dilution calculation.

Any chemical species present in the humus and surfactant that could be of environmental or toxicological concern, and for which groundwater standards or minimum groundwater criteria do not yet exist in Florida, may require the development of groundwater criteria before this process can be used in situations where its chemical constituents could come into contact with groundwater. The reason for such concern about the groundwater is that it is the main source of Florida's potable water.

In the case of the proprietary biodegradable surfactant, the bureau can accept a confidential disclosure of the ingredients and its chemical properties. In return for the disclosure, the bureau, pursuant to Florida Statutes regarding trade secrets, will safeguard and not make the information available to the public. If the proprietary aspects of the surfactant are such that all Florida groundwater and underground injection control requirements are met, then the bureau will vouch for the disclosure. In the event that one or more groundwater standards will not be met, or groundwater criteria must be developed for ingredients that could be of environmental or toxicological concern, then the bureau will determine which regulations are applicable, and indicate which chemical species, ingredients, and intermediate degradation products of concern will require groundwater sampling.

For any parameters that may require groundwater monitoring when the humus and surfactant are directly introduced into the groundwater for remediation, or may come into contact with groundwater as a result of leaching when surficial soil is remediated, Coburn Construction will have to publicly make known the identity of at least those chemical species that exceed groundwater standards, in order for users of the process to monitor them for regulatory reasons. The State of Florida will not force Coburn Construction to disclose the names of any chemical species, ingredients or intermediate degradation products that may exceed groundwater standards, but it must be understood, in the absence of such a disclosure, that applications of the Humus/Surfactant process will remain restricted to situations where its chemical constituents will not come into contact with the groundwater.

ENCLOSURE 2

ADDITIONAL INFORMATION

The Bureau of Petroleum Storage Systems has surveyed the literature for the purpose of compiling and presenting some general information about humus. Readers who have not yet had an opportunity to become familiar with humus may be able to use this enclosure as a primer on the topic. It should be kept in mind that the information below is general information from the literature. It is not specific information about the Humus/Surfactant Bioremediation Technology.

Humus is a natural-occurring group of substances consisting of partially or completely decayed plant matter. To some degree, humus itself is considered to have a natural surface-active agent capability, but in the case of the Humus/Surfactant Bioremediation process, this natural capability is enhanced by the use of additional surfactant. Humic substances also have the ability to chelate metals, perform cation exchange, neutralize acidic wastewaters, and remove anions, all of which can serve a purpose in the cleanup of environmental contaminants.

The large amount of chemical jargon in this enclosure is not provided for the sake of making decayed plant matter into a more complex technical matter than necessary, although it is indeed a complex mix of substances. Rather, it is provided for the purpose of making users and technical reviewers of Humus/Surfactant Bioremediation Technology more knowledgeable, and therefore more comfortable with the process and the materials involved. At the least, the reader may find it handy to have at the ready some information that helps to keep track of a number of similar sounding words, like humus, humic, humate and humin, all of which appear under the topic of organic soil matter.

1. Humus: This is the term used to describe the group of natural-occurring organic soil colloids consisting of partial or completely decayed plant matter. Humus is rather ubiquitous, accounting for approximately 70 to 80 percent of all the organic matter present in soil. Its approximate general chemical composition is 30% lignin (the chief noncarbohydrate constituent of wood); 30% protein (nitrogenous organic compounds whose molecular structures contain amino acids); and polyuronides (a mix of complex sugars and uronic acid). An example of a uronic acid is glucuronic acid, a carboxylic acid having the molecular formula $C_6H_{10}O_7$. Glucuronic acid is widely distributed in the animal and plant kingdoms.

2. Humic substances: These substances are a mix of complex organic compounds, typically described as polymeric polyhydroxy acids, or as a complex mixture of large molecules of polymeric phenolic structure.

3. Chemical behavior of humus: Generally, the main fraction of humus is the humic acids and their salts, the humates. The remaining fractions contain fulvic acids and humins. The most concise description of the chemical behavior of humus found by the Bureau of Petroleum Storage Systems was in the McGraw-Hill Encyclopedia of Science and Technology.

> *"Based on their solubility in alkali and acid, humic substances are partitioned into three main fractions: humic acid,*

which is soluble in dilute alkali but is coagulated by acidification of the alkaline extract; fulvic acid, which is the humic fraction that remains in solution when the alkaline extract is acidified, that is, it is soluble in both dilute alkali and dilute acid; and humin, which is the humic fraction that cannot be extracted from the soil by dilute base or acid."

4. Chemical composition of the soluble fraction: The humic and fulvic acids that are extractable from humus are a mix of chemical species. Both of them contain essentially the same species but some of them are present in differing amounts depending on whether the acid is humic or fulvic. The following functional groups are present in these acids: carboxyls (COOH); hydroxyls (OH) of phenolic and alcoholic associations; carbonyls (C=O) that are either ketonic or quinonoid in nature; and methoxy groups (OCH_3).

5. Degradation products: Humic and fulvic acid, and humins are degradable by oxidative processes, producing straight chain (aliphatic) fatty acids, aromatic carboxylic acids, and phenolic acids that bear hydroxyl (OH) and carboxyl (COOH) groups.

6. Commercial humic acids: For information and comparative purposes only, the bureau notes that humic acids are available commercially under various trade names and synonyms such as Soil Organic Matter, Agro-Lig, and the like. The chemical composition of these commercial products is similar to that of the naturally occurring humic and fulvic acids.

   Sigma-Aldrich Chemical Company produces humic acid in granular and crystal forms having a major elemental composition as follows: carbon 39-40%; hydrogen 4.4%; and nitrogen, approximately 0.7%. The trace element analysis for the sodium salt technical grade is as follows: sodium, 7,670 parts per million (ppm); sulfur, 2,500 ppm; iron, 1,300 ppm; calcium, 1,200 ppm; magnesium, 1,091 ppm; phosphorus, 215 ppm; and lithium, 3 ppm.