Department of
Environmental Protection

Jeb Bush
Governor

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

David B. Struhs
Secretary

October 24, 2002

Mr. Sam Ward, President
dinoSoil Incorporated
2945 Parramore Shores Drive
Tallahassee, Florida 32310

Re: **dinoSoil**

Dear Mr. Ward:

The Bureau of Petroleum Storage Systems hereby reaffirms its original December 13, 2001 acceptance of dinoSoil, a humic substance, as a product for ex situ remediation of petroleum-contaminated soil. This reaffirmation supersedes the original December 13, 2001 dinoSoil acceptance letter, and is updated to cover in situ uses of dinoSoil for the remediation of soil and groundwater as well.

As the information you provided indicates, there are other uses for this product beyond the cleanup of petroleum pursuant to Chapter 62-770, Florida Administrative Code (F.A.C.), which is the jurisdiction of this bureau. Some of those other uses are the chelation of metals, cation exchange, neutralization of acid wastewater, removal of anions, and flocculation. Other state agencies and other bureaus within the Department of Environmental Protection may recognize this acceptance if their needs and regulations are similar to those of this bureau. This bureau, however, is not responsible for applications beyond its jurisdiction.

Also as indicated in the literature you provided, humus is a natural-occurring group of substances consisting of partial or completely decayed plant matter. The bureau, as a result of its own literature search, notes that humic substances account for some 70 to 80 percent of all the organic matter present in soils. Humic acids found in soil and groundwater are known to act like surfactants, so there may be a role for them to play as an alternative to artificial surfactants in the remediation of petroleum-contaminated soil.

Enclosure 1 contains a summary of dinoSoil's chemical and physical properties. Enclosure 2 identifies applicable regulations, and provides additional information about dinoSoil and humic substances in general. It is anticipated, however, that in the near future there will be changes to the soil and groundwater criteria for some chemical species listed in Chapter 62-777, F.A.C., especially arsenic. Users of dinoSoil are advised to keep a watch on "Rules" at web page www.dep.state.fl.us, for a revision of Chapter 62-777, F.A.C., that supersedes the current August 5, 1999 issue. Those users should note and observe any changes that apply to the chemical constituents of dinoSoil, and the site-specific contaminants of concern at remediation sites where dinoSoil is involved.

A copy of this letter should be provided in the appendix of site-specific Remedial Action Plans proposing the use of dinoSoil, so that technical reviewers throughout the state will be informed that the bureau has evaluated the acceptability of the product from a regulatory standpoint.

While the bureau does not endorse specific or brand name remediation products or processes, it does recognize the need to determine their acceptability from an environmental 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 certification of product performance.

The bureau reserves the right to revoke its acceptance of a product or process if any aspect of its nature, components, constituents, or performance has been falsely represented. Additionally, bureau 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 site-specific design details must be provided in Remedial Action Plans proposing the product or process. You may contact me at 850/245-8911 if there are any questions.

Sincerely,

Rick Ruscito, P.E.
Bureau of Petroleum Storage Systems

c: Mike Houghland
2257 Cayenne Lane
Shalimar, Florida 32579

Tom Conrardy, PCS3, Tallahassee

History:

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ENCLOSURE 1

CHEMICAL AND PHYSICAL PROPERTIES OF dinoSOIL

Analyte		Analytical Method	Result	Units	See Foot-note	*Florida Cleanup Standards* [1] *Soil* Direct Residential Exposure (mg/Kg) [2]	*Soil* Direct Commercial & Industrial Exposure (mg/Kg) [2]	*Soil* Leachability based on Groundwater Standards (mg/Kg) [2]	*Groundwater* Cleanup Criteria (milligrams per liter) (mg/L)
Arsenic	(in sediment)	3050/7061	**1.5**	mg/Kg	*3*	***0.8***	*3.7*	*29*	***0.05***
Arsenic	(in sediment)	3050/7061	**15.7**	mg/Kg	*4*	***0.8***	*3.7*	*29*	***0.05***
Arsenic	TCLP	1311/206.2	**<.005**	mg/Liter	*4*				
Cadmium	(in sediment)	3050/7130	**<1.0**	mg/Kg	*3*	*75*	*1,300*	*8*	*0.005*
Chlorine	(in solids)	EPA 325.3	**15.6**	mg/Kg	*3*	*7,800*	*200,000*	*SPLP or TCLP*	*250 (chloride)*
Chromium	(in sediment)	3050/7190	**11.4**	mg/Kg	*3*	*210*	*420*	*38*	*0.1*
Lead	(in sediment)	3050/7420	**22.6**	mg/Kg	*3*	*400*	*920*	*SPLP or TCLP*	*0.015*
Mercury	(in sediment)	7471	**.078**	mg/Kg	*3*	*3.4*	*26*	*2.1*	*0.002*
pH	(slurried)		**3.6**		*5&6*				***6.5 – 8.5***
Selenium		7740	**2.6**	mg/Kg	*3*	*390*	*10,000*	*5*	*0.05*
Sodium		3050/7770	**6,457**	mg/Kg	*3*				***160***
Percent Solids		SM 2540G	**92.38**	%	*3*				

Analysis of the Acid Soluble Fraction (expressed as a weight percent of the original "as received" sample)

Acid Insolubles		**71.53**	%	*5&7*
Aluminum	(as Al_2O_3)	**1.87**	%	*5*
Iron	(as Fe_2O_3)	**3.78**	%	*5*
Magnesium	(as MgO)	**0.48**	%	*5*
Phosphorus	(as P_2O_5)	**0.00**	%	*5*
Potassium	(as K_2O)	**0.19**	%	*5*
Sodium	(as Na_2O)	**0.68**	%	*5*

Notes:

1. Per the August 5, 1999 issue of Chapter 62-777, F.A.C., to which a revision is expected in the near future, including changes to cleanup criteria for arsenic in soil and groundwater. The applicable standard for a given soil contaminant or a constituent of dinoSoil itself is the lower of the direct exposure and the leachability criteria, otherwise institutional and/or engineering controls may apply. For more information about cleanup criteria for conditional and unconditional declarations of No Further Action (NFA) at petroleum-contaminated sites, and institutional and engineering controls, please see Section 62-770.680, F.A.C. Likewise, for information about conditional and non-conditional NFAs, and institutional and engineering controls for non-petroleum and brownfield sites, please see Section 62-785.680, F.A.C.
2. mg/Kg is an abbreviation for milligrams per killigram
3. From a dinoSoil Incorporated information sheet dated June 25, 2002 summarizing analytical results of a dinoSoil sample sent to a certified contract laboratory: Analytical Services Corporation, Niceville, Florida.
4. Analytical results of a dinoSoil sample sent to a certified contract laboratory and analyzed in July 2002: Analytical Services Corporation, Niceville, Florida. TCLP is an abbreviation for Toxicity Characteristic Leaching Procedure. SPLP stands for Synthetic Precipitation Leaching Procedure.
5. Analysis reported by the Florida Institute of Phosphate Research (FIPR), February 14, 2002.
6. pH after slurrying 30 grams of dinoSoil in an unspecified volume of deionized water.
7. The acid insoluble fraction is mostly quartz and swelling-Montmorillonite clay.

Summary of dinoSOIL Interactions with Various Solutes in Aqueous Solutions *

Pounds of Element (expressed as the oxide) Released into Water from a Tonne ** of dinoSoil

			Florida Groundwater Standard for the element
1.41 lbs.	**MgO**	into solution per tonne of dinoSoil	*Magnesium not regulated.*
2.85 lbs.	**CaO**	into solution per tonne of dinoSoil	*Calcium not regulated.*
0.38 lbs.	**Al_2O_3**	into solution per tonne of dinoSoil	*0.2 mg/L (milligrams/liter)* ***aluminum***
0.05 lbs.	**Fe_2O_3**	into solution per tonne of dinoSoil	*0.3 mg/L* ***iron***

Phosphorus Releated Compounds Adsorbed by dinoSoil

0.8 lbs. **P_2O_5** adsorbed from aqueous solution per tonne of dinoSoil

1.1 lbs. **PO_4** adsorbed from aqueous solution per tonne of dinoSoil

Grams of Heavy Metal Adsorbed from Solution by each Tonne of dinoSoil

3.3 grams **Cadmium** from aqueous solution per tonne of dinoSoil

8.6 grams **Arsenic** from aqueous solution per tone of dinoSoil

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* Analytical work performed by the Florida Institute of Phosphate Research, February 14, 2002

** Tonne is a metric ton (1,000 kilograms)

ENCLOSURE 2

ADDITIONAL TECHNICAL AND REGULATORY INFORMATION ABOUT dinoSOIL

The technical information below includes that which was compiled by the Bureau of Petroleum Storage System during its literature search, as well as information provided by dinoSoil Incorporated.

1. Applicable and appropriate rules and regulations: The onus shall be on users of dinoSoil, and dinoSoil Incorporated, to ensure that all applicable soil and groundwater criteria will be met at the time of project completion, for petroleum, other contaminants that may be present, any residuals associated with the constituents of dinoSoil, and any byproducts produced as a result of chemical or biochemical reactions involving those constituents. The chapters of the Florida Administrative Code that may apply to a given cleanup may include but are not necessarily limited to the following: 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 cleanup criteria and also for minimum groundwater criteria; and Chapter 62-785, for brownfields cleanup criteria.

   A noteworthy aspect of the minimum criteria set forth in Chapter 62-520, F.A.C., is that it requires groundwater to be free from substances which 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 regulated as a specific primary or secondary drinking water contaminant.

2. No Further Action Criteria: Soil and groundwater cleanup criteria for contaminants are set forth in Chapter 62-777, F.A.C. <u>These criteria also apply to any constituents of dinoSoil that happen to be listed as contaminants</u>. For a given contaminant in the soil, its applicable cleanup target is the <u>lower</u> of the direct exposure and leachability cleanup criteria set forth in Chapter 62-777, F.A.C.

   Users of dinoSoil 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 <u>unconditional</u> declaration of No Further Action (NFA) or a <u>conditional</u> NFA involving institutional and/or engineering controls. Likewise, for non-petroleum brownfield sites, Section 62-785.680, F.A.C., should be consulted for information about unconditional and conditional NFAs, and institutional and engineering controls.

   Additionally, it is anticipated that soil and groundwater cleanup criteria in the current August 5, 1999 issue of Chapter 62-777, F.A.C., will revised in the near future, including changes to the cleanup criteria for arsenic. Users of dinoSoil are advised to keep a watch on “Rules” at web page www.dep.state.fl.us for the revision. They should note and observe any changes that apply to the chemical constituents of

dinoSoil, and the site-specific contaminants of concern at remediation sites where dinoSoil is involved when the revision is issued.

3. Groundwater monitoring: If dinoSoil is used in a location or in such a way that there is a potential or concern that the underlying groundwater could be impacted by leachate, from either the contaminants of concern being remediated or the constituents of dinoSoil itself, then groundwater monitoring of appropriate chemical species and parameters should be addressed in a Department-approved Remedial Action Plan.

   Regardless of whether the dinoSoil is used in a topical, ex situ, in situ, or injection-type manner, if there is potential or concern for an impact on the underlying groundwater, then monitoring should be conducted. Groundwater monitoring should also be conducted if there is a situation where dinoSoil has been used as backfill, or as an amendment to the backfill dumped into an open excavation pit that has been allowed to fill with contaminated groundwater, for the purpose of remediating that water.

   Another situation in which groundwater monitoring may be necessary would be one in which the dinoSoil is applied topically for the purpose of soil remediation at a site where there is a shallow water table. Regardless of whether or not the dinoSoil is plowed, disked, or watered, if there is a potential or concern for leaching, then groundwater monitoring should be addressed in the Department-approved Remedial Action Plan.

   Based on the chemical and physical properties of dinoSoil, as indicated in enclosure 1, groundwater monitoring would, at the least, be necessary for pH, sodium, aluminum and iron. And even though the TCLP result shown in enclosure 1 suggests that the arsenic level in dinoSoil does not render it a toxic waste, or likely to leach arsenic, it may be prudent to take groundwater samples, before, during, and after application of the dinoSoil, for analysis of arsenic. At non-petroleum cleanup sites, where the dinoSoil is actually being used to adsorb heavy metal contaminants such as arsenic, cadmium and the like, it may be prudent to monitor the underlying groundwater for these contaminants of concern before, during, and after the use of dinoSoil. This will help to make sure that watering and/or precipitation is not flushing the metal contaminants through the dinoSoil faster than the dinoSoil can adsorb them.

4. Other considerations: Those who prepare Remedial Action Plans proposing the use of dinoSoil should take into account and address the following in the plan when they apply to the situation. If spent dinoSoil will be removed from the site, then an appropriate and proper method of disposal must be identified in the plan. If spent dinoSoil will remain at the site, especially those sites at which heavy metals are contaminants of concern, then the Remedial Action Plan should address the verification of dinoSoil’s ability to adsorb and immobilize heavy metals in the long-term. Institutional and engineering controls may be necessary, and so may long-term verification sampling, albeit at sample intervals less frequent than those during the active remediation phase of the cleanup.

5. 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 accounts for approximately 70 to 80 percent of all the organic matter present in soils. Its approximate general chemical

composition can be described as 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.

6. 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.

7. 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."*

8. 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).

9. 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.

10. Decision regarding humic and fulvic acids: The Bureau of Petroleum Storage Systems notes the natural-occurring abundance of humus in the environment, accounting for some 70 to 80 percent of all the organic matter present in soils, and that humic and fulvic acid, and humins are known to degrade to fatty acids. With this in mind, and knowing that groundwater in the environment is already in contact, naturally, and to a great extent with soil containing humus, the bureau reasons that groundwater monitoring of humic and fulvic acid constituents should <u>not</u> be mandatory when dinoSoil is used.

    There are also elements of practicality and economics factored into this decision. If humic and fulvic acid were simple chemical compounds that

lend themselves to quick, easy and inexpensive analysis, then it would be expedient to simply require their monitoring. But they are not, and it would be cumbersome to track their presence by sampling and analyzing for their various constituent chemical species described in paragraph 8, or the disappearance of them by sampling and analyzing for the appearance of the various degradation products described in paragraph 9.

Ultimately, however, the final decision regarding whether or not to monitor the groundwater for humic and fulvic acids should be made by the state's technical reviewer of a Remedial Action Plan, on a case-by-case basis, with the input from the party that prepares the plan.

11. 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.

12. Material Safety Data Sheet (MSDS): The Material Safety Data Sheet for dinoSoil describes it as reddish-brown solid particles of inert organic soil/humate, having a specific gravity of 1.35 and being 90% soluble in water.

13. Application procedure and dosage: Procedural information provided to the Bureau of Petroleum Storage Systems for the use of dinoSoil was for a topical application. A 2-inch thick layer of dry dinoSoil is spread on top of the petroleum to be remediated. This is equivalent to a dosage of approximately 10 pounds of dinoSoil per square foot of petroleum-contaminated area to be remediated. Water is then applied until the dinoSoil is completely wet. Subsequent watering is generally on a weekly basis. Remediation time is approximately 1 to 1-1/2 months. For procedures, dosages and moisture levels required for other methods of remediation (i.e. ex situ soil piles, land farming, and in situ soil cleanup) the bureau suggests that users contact the manufacturer.