



Department of Environmental Protection

Jeb Bush
Governor

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

David B. Struhs
Secretary

July 10, 2001

Ms. Helen Harrison
Novozymes Biologicals, Inc.
111 Kesler Mill Road
Salem, Virginia 24153

Re: BioBlend Rapid
BioBlend 3-1
BioBlend 5-1

Dear Ms. Harrison:

The Bureau of Petroleum Storage Systems hereby reaffirm its acceptance of BioBlend Rapid, BioBlend 3-1, and BioBlend 5-1 as innovative products for the bioremediation of petroleum contamination in groundwater and soil, both in situ and ex situ. This letter supersedes the original June 16, 1998 acceptance letter that was issued to Sybron Chemicals Incorporated for these products, in order to reflect that Sybron's biochemical division is now owned by Novozymes Biologicals Incorporated. All references to Sybron in the original letter have been replaced by references to Novozymes Biologicals Incorporated.

Per the list of ingredients in enclosure 1, each of these formulations is a source of nitrogen and phosphorus, both of which are essential nutrients for the growth of bacteria that destroy petroleum. All three BioBlend formulas are granules that the user dissolves in water prior to application. Either one BioBlend product at a time, or combinations which target a desired effect or nutrient concentration, may be applied.

For soil remediation, in locations where groundwater will not be affected by the use of these products, there are no special concerns beyond those which would normally need to

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be addressed in preparing a Remedial Action Plan and conducting a cleanup in accordance with the petroleum cleanup requirements of Chapter 62-770, Florida Administrative Code (F.A.C.). For ex situ groundwater treatment, where an aboveground treatment system produces effluent meeting the petroleum cleanup criteria of Chapter 62-770, F.A.C., and the drinking water standards of Chapter 62-550, F.A.C., for disposal via recharge gallery or NPDES permit, there are no special concerns. But for in situ groundwater remediation, via direct injection of BioBlend nutrient solutions into an aquifer, there are underground injection control (UIC) regulations that must be observed. Since in situ aquifer remediation via injection is likely to be a common application of these products, the bulk of the regulatory requirements discussed herein will be directed to that topic.

The bureau recognizes these three specific BioBlend formulations as viable products for the remediation of petroleum contaminated sites in Florida. There are no objections to their use provided: (a) the considerations of this letter are taken into account; (b) a Remedial Action Plan is approved by the Department; and (c) applicable and appropriate underground injection control regulations are observed when the product is used for in situ aquifer remediation via injection.

While the Department of Environmental Protection does not provide endorsement of 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. Vendor's 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 letter regarding regulatory acceptance (or the conditions of regulatory acceptance) be construed as certification of product or process performance. For the three specific BioBlend formulations,

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the major environmental and regulatory considerations are set forth in enclosure 2.

Preparers of Remedial Action Plans may include a copy of this letter in the appendix of plans they submit, and call attention to it in the text of their document. In this way, technical reviewers throughout the state will be informed that you have contacted the Department of Environmental Protection to inquire about the environmental acceptability of these products. To aid those reviewers, the Bureau of Petroleum Storage Systems provides supplemental information as enclosure 3.

The Department reserves the right to revoke its acceptance of a product if the nature or composition of either or any of its principal and proprietary ingredients, or its performance has been falsely represented. Additionally, Department 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 prescribing the product or process. You may contact me at 850/487-3299 if there are any questions.

Sincerely,

Rick Ruscito, P.E.
Bureau of Petroleum Storage

Systems

History:

inn_015.doc - 6/16/98
inn_015b.doc - 7/10/01

ENCLOSURE 1

BIOBLEND INGREDIENTS (Note 1)

BIOBLEND RAPID (granules)

<u>INGREDIENT</u>	<u>AMOUNT</u>	<u>UNITS</u>
Urea (Note 2)	72	% by weight
Monosodium Phosphate (Note 3)	26	% by weight
Dicyanodiamide (Note 4)	2	% by weight
pH	(Note 5)	
Total Dissolved Solids	(Note 6)	

BIOBLEND 3-1 (granules) (Note 7)

<u>INGREDIENT</u>	<u>AMOUNT</u>	<u>UNITS</u>
Urea (Note 2)	40	% by weight
Diammonium Phosphate (Note 3)	58	% by weight
Dicyanodiamide (Note 4)	2	% by weight
pH	(Note 5)	
Total Dissolved Solids	(Note 6)	

BIOBLEND 5-1 (granules) (Note 7)

<u>INGREDIENT</u>	<u>AMOUNT</u>	<u>UNITS</u>
Urea (Note 2)	69	% by weight
Diammonium Phosphate (Note 3)	29	% by weight
Dicyanodiamide (Note 4)	2	% by weight

pH	(Note 5)
Total Dissolved Solids	(Note 6)

Notes:

1. As reported on Material Safety Data Sheets by Novozymes Biologicals, Inc. Composition is expressed as percent by weight for granular BioBlend, which is dissolved in water by the user prior to application.
2. The urea component of BioBlend provides nitrogen from ammonium, not nitrate or nitrite.
3. In the case of BioBlend Rapid, phosphate is supplied in the form of monosodium phosphate. In the case of BioBlend 3-1 and BioBlend 5-1, it is supplied in the form of diammonium phosphate.
4. A small amount of dicyanodiamide is added to BioBlend to inhibit the nitrification of ammonium to nitrate.
5. Novozymes Biologicals, Inc., in a January 7, 1998 submittal of information to the Bureau of Petroleum Storage Systems, indicates that the optimum pH range for bioremediation using the products is 6.8 to 7.4, which is in keeping with the 6.5 to 8.5 range allowed in the secondary drinking water standards of Chapter 62-550, F.A.C. Additionally, a technical representative provided information about pH on June 10, 1998, indicating that a sufficient volume of water is used in preparing an aqueous solution of BioBlend prior to application, and that the dilution factor is large enough for the resulting solution to fall within the required pH range.
6. Novozymes Biologicals, Inc., in a January 7, 1998 submittal of information to the Bureau of Petroleum Storage Systems, indicates that the applied concentration of BioBlend, as an aqueous solution, is generally 500 parts per million [equivalent to 500 milligrams per liter (mg/L)]. This is in keeping with the secondary drinking water standards of Chapter 62-550, F.A.C., which sets the total dissolved solids (TDS) content at 500 mg/L, maximum. Chapter 62-550, F.A.C., also allows a TDS concentration greater than 500 mg/L, provided no other maximum contaminant level is exceeded, which is the case for the BioBlend products.
7. BioBlend 3-1 nomenclature denotes the weight ratio of total nitrogen to phosphorus (as ortho phosphate). Likewise, BioBlend 5-1 represents a 5 to 1 ratio.

ENCLOSURE 2

BIOBLEND: ENVIRONMENTAL AND REGULATORY INFORMATION

For BioBlend formulations, the major environmental and regulatory concerns are listed below.

- a. Groundwater cleanup standards: The onus shall be on users of BioBlend formulations to ensure that all applicable groundwater contaminant standards will be met at the time of project completion, for petroleum and any residuals associated with the ingredients, and any byproducts produced as a result of chemical or biochemical reactions. The following chapters of the Florida Administrative Code 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; and Chapter 62-770, F.A.C., for petroleum cleanup criteria.
- b. Groundwater injection standards: For in situ aquifer remediation, the composition of an injected fluid must meet the drinking water standards set forth in Chapter 62-550, F.A.C., pursuant to underground injection control Rule 62-528.600(2)(d), F.A.C. Enclosure 1 shows the ingredients of three particular BioBlend formulations, as sold by Novozymes Biologicals Incorporated, which meet this requirement.
- c. 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 the application of BioBlend. However, no "designated" monitoring well, dedicated to the tracking of remediation progress (by sampling), shall be used to apply BioBlend formulations. This will avoid premature conclusions that the entire site meets cleanup goals. By making sure that designated tracking wells are not also used for treatment, there will be more assurance that the treatment process has permeated the entire site and that it did not remain

localized to the area immediately surrounding each injection well.

- d. Bioaugmentation option: The three BioBlend formulations are bionutrient formulas which do not contain microorganisms. For projects in which bioaugmentation will accompany these nutrients, only microorganisms that are naturally occurring (not genetically engineered), non-pathogenic (do not cause disease), and non-opportunistic (will not cause disease in a compromised host) shall be used.
- e. Groundwater monitoring:
 - 1. Active remediation petroleum monitoring: During the period of active remediation, groundwater shall be monitored in accordance with the requirements set forth in Section 62-770.700, F.A.C. Two noteworthy rules within that section are 62-770.700(3)(i), F.A.C., for frequency of sampling, and 62-770.700(5)(f), F.A.C., which requires a sampling schedule for bioremediation.
 - 2. Post remediation petroleum monitoring: At least one (1) year of quarterly post remediation groundwater monitoring shall be conducted at a minimum of two (2) wells, one located in the area of maximum petroleum contamination, the other downgradient of the area of maximum petroleum contamination, pursuant to Section 62-770.750, F.A.C.
 - 3. Underground injection control monitoring: Since no ingredient in the BioBlend formulations exceeds a maximum contaminant level (MCL) allowed by the drinking water standards of Chapter 62-550, F.A.C., the Department has determined that tracking of any particular ingredient shall not be mandatory for underground injection monitoring purposes. However, as a matter of good bioremediation practice and thoroughness, it is suggested that a monitoring schedule for injected fluids, pursuant to Rule 62-528.615(2), F.A.C., include a quarterly sampling of selected key bioremediation parameters in at least two (2) wells, one located in the central region of the injection points, the other downgradient.

For a given remediation site, costs may be kept to a minimum by installing only two monitoring wells, whose locations are such that they may serve as both the required petroleum remediation tracking wells, pursuant to Section 62-770.750, F.A.C., and the underground injection control tracking wells, pursuant to Rule 62-528.615(2), F.A.C. A partial list of bioremediation parameters, from which several, if any, may be tracked and compared to a site's naturally occurring background levels appears in enclosure 3, paragraph e.

- f. Background samples: Prior to commencement of in situ injection type aquifer remediation projects, the Department recommends the sampling of at least one (1) monitoring well located upgradient of the petroleum contamination plume, or at least one (1) non-upgradient monitoring well, located beyond the edge of the plume, for the background concentration of selected key bioremediation parameters. If more than one well is sampled, then the average value of each parameter can be used as the background value for the site.

Since no ingredient in BioBlend formulations exceeds an MCL set forth by the drinking water standards of Chapter 62-550, F.A.C., the measurement of background concentrations, for injection control purposes, shall not be mandatory. Such sampling, however, is recommended as a matter of good bioremediation practice.

- g. Underground injection control inventory: Remedial Action Plans prescribing in situ aquifer injection type remediation shall include information pursuant to Rule 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 Remedial Action Plan, provided the construction, operation, and monitoring requirements of Chapter 62-528, F.A.C., are met. A memorandum outlining the inventory information about injection type aquifer remediation plans to be transmitted by Department reviewers to the Underground Injection Control Section is provided as enclosure 4. Only reviewers within the

Department, including its district offices, may approve in situ injection type remediation plans in which the approval constitutes a Class V injection permit; local programs are not authorized to grant such approvals. See enclosure 3.

h. Operation:

1. Avoidance of migration: For in situ injection type aquifer remediation projects, injection of BioBlend formulations shall be performed in such a way, and at such a rate and volume, that no undesirable migration of either the product's ingredients or the petroleum contaminants in the aquifer results, pursuant to Rule 62-528.630(3), F.A.C.
2. Underground injection control operating permit: Although an operating permit is not required for aquifer remediation wells pursuant to Rule 62-528.640(1)(b), and 62-528.640(1)(c), F.A.C., since no movement of the petroleum contamination plume is expected to accompany the BioBlend formulations treatment process, the Department requests that the information items listed in Rule 62-528.640(1)(b), F.A.C., be considered and included in Remedial Action Plan proposals as a matter of good and thorough design practice. Briefly summarized, they are: quality of water in the aquifer; quality of the injected fluid; existing and potential uses of the affected aquifer; and well construction details. Additionally, each Remedial Action Plan should clearly indicate the total amount of BioBlend that will be injected.
3. Operating parameter measurements: Rule 62-770.700(9)(h), F.A.C., sets forth frequency requirements for the measurement of bioremediation operating parameters such as dissolved oxygen levels, rates of nutrient addition, temperature, etc. It also includes an option for reduction in the frequency or discontinuation of some measurements in situations when appropriate.

- i. Abandonment of wells: Upon issuance of a petroleum Site Rehabilitation Completion Order, or a

declaration of "No Further Action", 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 the injection wells can be removed from the inventory tracking list.

ENCLOSURE 3

BIOBLEND: SUPPLEMENTAL INFORMATION

The information below, compiled from several sources, may be helpful to reviewers of Remedial Action Plans prescribing bioremediation.

- a. Department of Environmental Protection reviewers of in situ injection type aquifer remediation plans, regardless of whether in Tallahassee or district offices, must fill in the blanks on the enclosure 4 memorandum, whose subject is "Proposed Injection Well(s) for In Situ Aquifer Remediation at a Petroleum Remedial Action Site". The completed form must be submitted to the Underground Injection Control Section at 2600 Blair Stone Road, Tallahassee, Florida 32399-2400.

Only reviewers within the Department and its district offices may approve in situ injection type remediation plans in which the approval constitutes the issuance of a Class V injection permit; local programs are not authorized to grant such approvals.

Reason: Although an arrangement between the Environmental Protection Agency and the Department delegates underground injection control authority to the Department, it does not allow the Department to delegate that authority any further. This includes delegation to the Department's contracted remediation review agencies such as those operated by the counties and other local governments.

- b. Pilot study: For bioremediation, per rule 62-770.700(2), F.A.C., a pilot study proposal shall be submitted for review, and a pilot test shall be performed prior to designing a treatment system. If conditions or the situation at a site do not warrant a pilot study, then a proposal explaining the rationale for the decision not to perform a pilot study shall be submitted for review. For state funded projects, reviewers are encouraged to use judgment in balancing cost and the need for technical information to be obtained from a pilot study. In some cases, it may be possible that a only a biotreatability test will suffice.

- c. Bacteria: It is generally reported (on a total weight basis) that bacteria are approximately 70 to 80 percent water. On a dry weight basis, approximately 95 percent of the composition is represented by 5 elements: carbon, oxygen, nitrogen, hydrogen, and phosphorus. At a petroleum remediation site, it is intended that the source of carbon for the growth of bacteria will come from the petroleum hydrocarbons themselves. Naturally occurring organic carbon at a site can also serve as a carbon source for bacteria. Depending on site's specific conditions, the remaining four elements must either be available naturally, or added as macronutrients in order to stimulate bioremediation. Micronutrients must also be present for bacteria to grow.
- d. Degradation products: Carbon dioxide and water are the ultimate products of aerobic and most anaerobic biodegradations of petroleum hydrocarbons. The intermediate products may include simple acids, alcohols, and fatty acids. Aerobic processes use oxygen as an electron acceptor to produce carbon dioxide and water. In the case of methanogenesis, an anaerobic process, carbon dioxide and methane are produced.

For some of the other major anaerobic hydrocarbon degradation processes, the byproducts (fate of chemical species involved) also include: the generation of nitrogen (N_2) when nitrate serves as the electron acceptor in nitrate reduction processes; the formation of ferrous (Fe^{+2}) forms of iron in ferric iron (Fe^{+3}) reduction processes; the formation of (S^{-2}) forms of sulfur when sulfate serves as the electron acceptor in sulfate reduction processes; and the formation of Mn^{-2} forms of manganese when manganese dioxide is reduced.

- e. Parameters: The following parameters may be useful in determining the potential for bioremediation at a site, or whether bioremediation is already occurring. They were selected from a list that appears in the publication "In Situ Treatment Technology" by E. Nyer et al., Lewis Publishers, 1996. The parameters are: dissolved oxygen; redox potential; pH; temperature; specific conductance; volatile organic compounds; nitrate; nitrite; ammonia nitrogen; manganese (total

and dissolved); iron (total, dissolved, and ferrous); sulfate; sulfide; and total organic carbon. Gaseous parameters include: carbon dioxide, oxygen, nitrogen, and methane. Other parameters that may be helpful are chemical oxygen demand, biochemical oxygen demand, and total organic carbon. Preparers of bioremediation plans and their reviewers should determine which parameters, if any, should be investigated on a site specific basis.

- f. Nitrogen source: The source of nitrogen in the BioBlend formulations is from urea ammonium, not nitrate or nitrite. Furthermore, a small amount of dicyanodiamide is added to prevent nitrification of the ammonium nitrogen to nitrate.
- g. Oxygen sources: The manufacturer indicates that oxygen for bioremediation using its products may be supplied by various sources such as hydrogen peroxide or oxygen releasing compounds. In addition to these methods, the Bureau of Petroleum Storage Systems has no objection to making use of in situ air sparging wells, which may already exist at some sites, for the delivery of oxygen.
- h. Dosage and application: The manufacturer indicates that BioBlend formulations are usually applied as aqueous solutions. Exact dosages will depend on site conditions, total organic carbon, and an assessment of nutrients already available for bioremediation. For in situ treatment, the formulations may be applied via injection wells, micro wells, quill, or direct push methods. For a soil farming applications, as a rough rule of thumb, approximately 3 to 6 pounds of BioBlend 5-1 and/or BioBlend 3-1 may be applied per cubic yard of soil.
- i. Operating parameters: The bioremediation parameters below were indicated by the manufacturer, along with their acceptable and optimum ranges. They are provided as guidance only, and should not be construed as absolute, or used as the sole criteria for approval or disapproval of proposed Remedial Action Plans or remediation status reports.

pH:	6.0-8.5
	6.8-7.4, optimum
Ammonium nitrogen:	> 1.0 mg/L

Ortho phosphate:	> 0.5 mg/L
Temperature:	40-100 deg. F
	68-85 deg. F, optimum
Dissolved oxygen:	> 2 mg/L
	1 mg/L, minimum

Florida Department of Memorandum **Environmental Protection**

TO: Richard Deuerling, Mail Station 3530
 Division of Water Facilities
 Underground Injection Control Section
 Florida Department of Environmental Protection
 2600 Blair Stone Road, Tallahassee, FL 32399-2400

FROM: _____ (Note 1.)

DATE: _____

SUBJ: **Proposed Injection Well(s) for In Situ Aquifer
 Remediation at a Petroleum Remedial Action Site**

Pursuant to Rule 62-528.630(2)(c), F.A.C, inventory information is hereby provided regarding the proposed construction of temporary injection well(s) for the purpose of in situ aquifer remediation at a petroleum-contaminated site.

Site name: _____

Site address: _____

City/County: _____

Latitude/Longitude: _____

FDEP Facility Number: _____

Site owner's name: _____

Site owner's address: _____

Well contractor's name: _____ (Note
 2.)

Well contractor's address: _____

Brief description of the in situ injection-type aquifer remediation project:

Summary of major design considerations and features of the project:

Areal extent of contamination (square feet): _____

Number of injection wells: _____

Composition of injected fluid (Note 3)
 (ingredient, wt. %): _____

Injection volume per well (gallons): _____

Single or multiple injection events: _____

Injection volume total (all wells, all
 events): _____

A site map showing the areal extent of the groundwater contamination plume, and the location and spacing of injection wells and associated monitoring wells is attached.

The following is a summary description of the affected aquifer:

Name of aquifer: _____
Depth to groundwater (feet): _____
Aquifer thickness (feet): _____

The injection well(s) features are summarized below, and/or a schematic of the injection well(s) is attached.

Direct-push or Conventional (*circle the appropriate well type*)

Diameter of well(s) (i.e., riser pipe & screen)(inches): ____
Total depth of well(s) (feet): _____
Screened interval: _____ to _____ feet below surface
Grouted interval: _____ to _____ feet below surface
Casing diameter, if applicable (inches): _____
Cased depth, if applic.: _____ to _____ feet below surface
Casing material, if applic.: _____

The in situ injection-type aquifer remediation plan for this petroleum contaminated site is intended to meet the groundwater petroleum cleanup criteria set forth in Chapter 62-770, F.A.C. Additionally, all other groundwater standards will be met at the time of project completion for any residuals associated with the ingredients of the injected remediation products, and any by-products or intermediates produced as a result of the chemical or biochemical transformation of those ingredients or the contaminating petroleum during their use. Applicable primary and secondary drinking water standards are set forth in Chapter 62-550, F.A.C., and additional groundwater quality criteria are set forth in Chapter 62-520, F.A.C.

The remediation plan estimates that site remediation will take _____ months. We will notify you if there are any modifications to the remediation strategy that will affect the injection well design or the chemical composition and volume of the injected remediation product(s).

The proposed remediation plan was approved on _____ by an enforceable approval order. A copy is attached. The remediation system installation is expected to commence within 60 days. Please call me at _____ if you require additional information.

Note 1. Local programs are not authorized to approve underground injections into aquifers. Reason: Per agreement with EPA, the FDEP cannot delegate this authority. Local programs, after reviewing a Remedial Action Plan or an injection proposal document, should follow the instructions in a March 16, 2000 memorandum to arrange for Department headquarters' execution of an approval order, and then complete this form. This form is primarily for use by state and local program technical reviewers, but petroleum remediation contractors may fill in all blanks except those labeled "FROM", "DATE", and "approval date", and "telephone number" blanks in the last paragraph. Only a state or local program reviewer should complete those blanks.

Note 2. If an injection well installation contractor has not yet been selected, then indicate the name and address of the project's general remediation contractor/consultant.

Note 3. Chapter 62-528, Florida Administrative Code, requires complete chemical analysis of injected fluid. Proprietary formulations shall make confidential disclosure. Injected fluids must meet drinking water standards of Chapter 62-550, F.A.C., unless an exemption or variance has been granted