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Environmental Health

OCT 31 2005

Alameda County

Estate of Michael Dolan

3215 Deer Park Dr.

Walnut Creek, CA 94598

LETTER OF TRANSMITTAL

DATE	October 27, 2005	BEI Job No.	202016
ATTENTION:	Mr. Michael Fitzpatrick		
SUBJECT:	Dolan Property		
	Scarlett Ct.		
	Dublin, CA		
	ACEH Fuel Leak Case # RO0000210		

We are sending you

Invoice

Copy of letter

Report

Prints

Plans

Work Order

Change Order

Specifications

Copies	Date	Number	Description
1	10/26/05		Corrective Action Plan For Source Soil Excavation and Dewatering

These are transmitted as checked below:

For signature

For payment

As requested

For approval

FOR BIDS DUE

Approved as submitted

Approved as noted

Returned for Corrections

For review and comment

For your use

Resubmit ___ copies for approval

Submit ___ copies for distribution

Return ___ corrected prints

REMARKS: For your files. The CAP has been additionally transmitted as listed below.

COPY TO:

File

Mr. Barney Chan, Alameda County Environmental Health

Mr. Peter MacDonald, Esquire

Mr. John Steinbuch, Colliers International

SIGNED: Mark Dettelman

If enclosures are not as noted, kindly notify Blymyer Engineers, Inc. at once.

**Corrective Action Plan
For Source Soil Excavation and Dewatering**

Dolan Trust Property
6393 Scarlett Court
Dublin, California
ACEH Fuel Leak Case No. RO0000210

October 26, 2005
BEI Job No. 202016

Alameda County
OCT 31 2005
Environmental Health

Prepared for:

Estate of Michael Dolan
Mr. Michael Fitzpatrick, Trustee
3215 Deer Park Dr.
Walnut Creek, CA 94598

Prepared by:

Blymyer Engineers, Inc.
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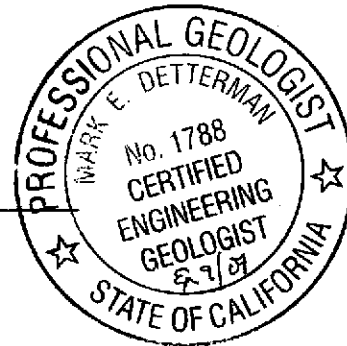
Limitations

Services performed by Blymyer Engineers, Inc. have been provided in accordance with generally accepted professional practices for the nature and conditions of similar work completed in the same or similar localities, at the time the work was performed. The scope of work for the project was conducted within the limitations prescribed by the client. This report is not meant to represent a legal opinion. No other warranty, expressed or implied, is made. This report was prepared for the sole use of the client, The Estate of Michael Dolan.

Blymyer Engineers, Inc.

By: Mark E. Determan

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6393 Scarlett Court, Dublin, CA**

The following corrective action plan (CAP) provides details to implement corrective actions in order to remove hydrocarbon-impacted unsaturated and saturated soil, and to capture and treat impacted-groundwater as recommended in the Remedial Investigation / Feasibility Study report dated October 7, 2005. Contaminants of concern at the site include Total Petroleum Hydrocarbons (TPH) as diesel, TPH as gasoline, and benzene, toluene, ethylbenzene, and total xylenes (BTEX), and methyl tert-butyl ether (MTBE) in groundwater. The implementation of the CAP should significantly reduce hydrocarbon impacts at the site. The CAP should provide both the fastest method and the most cost-effective approach to alleviate environmental conditions at the site (Figures 1 and 2).

1.0 Project Planning and Design

This task will involve the development of necessary plans, obtaining necessary permits, and generating project design calculations to implement the CAP.

1.1 Plans and Permits

1.1.1 Plans

Necessary plans include:

1. An excavation or grading plan and Best Management Practices (BMPs) for storm water pollution prevention are required by the City of Dublin (City) to permit the excavation. These plans will be generated and submitted to the City by the selected corrective action contractor (CAC).
2. A Health and Safety Plan (HASP) that lists contaminants of concern and details appropriate site-specific safety measures for the project-related work, including personal protective equipment, and monitoring to be implemented to protect workers. The CAC will be responsible for generation of this plan for all of its site workers and subcontractors. Blymyer Engineers will operate under a separate HASP, as it will not be a subcontractor to the CAC. The Blymyer Engineers HASP will incorporate an Air Monitoring Plan.

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3. A Dust Control Contingency Plan is not anticipated to be required due to the shallow condition of groundwater at the site and fall or winter conditions; however, a water hose shall be present at the site for suppression of dust with sprays of water should significant dust be generated. Additional dust suppression measures may include:
 - a. Haul trucks shall be covered, or shall maintain at least 2 feet of freeboard,
 - b. Restrict non-essential traffic to offsite pavement,
 - c. Limit vehicle speeds to 5 miles per hour on the unpaved site,
 - d. Minimize drop heights while loading trucks, and
 - e. Cover soil stockpiles.

1.1.2 Permits

Prior to the beginning of the project all necessary permits will be obtained.

Required permits will include:

1. A POTW permit for the discharge of treated groundwater to the sanitary sewer system. This permit will be obtained by the CAC.
2. An Alameda County Zone 7 Water Services Agency (Zone 7) well destruction permit for well MW-2, which is located inside the planned excavation area, a well construction permit for the vadose well to be installed in the corner of the resulting excavation, and a soil bore permit for the injection of oxygen releasing compound (ORC) will be obtained. Zone 7 has verbally approved destruction by excavation for well MW-2, and construction of the vadose well in the excavation by the CAC. Blymyer Engineers will obtain these permits.
3. A Bay Area Air Quality Management District (BAAQMD) permit will be obtained by the CAC for the off-gassing of volatile organic compounds (VOCs) from soil stockpiles and the open excavation.

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1.1.3 Excavation Design

The remedial excavation will have dimensions of 40 feet by 40 feet by 20 feet deep (Figure 2). To prevent soil cave-in and provide a safe working environment, the excavation will be supported by a slide-rail system or interlocking sheet piles and bracing, with the sheet piles installed to 30 feet bgs using the vibro-hammer method. If sheet piles are used, a starter trench will be installed that outlines the perimeter of the excavation, and reviewed by site engineer prior to driving sheetpiling. The shoring and bracing details will be reviewed by a qualified professional engineer to ensure the shoring will withstand earth pressures.

1.1.4 Utility Location

An onsite utility survey will be performed to locate any possible unknown utility lines. Except a single overhead telephone line, all utilities at the site are reported to have been rendered dead by the demolition contractor. Underground Service Alert (USA), 1-800-227-2600, will be notified at least 48 hours prior to the start of construction activities.

2.0 Excavation Dewatering

Prior to digging the excavation, dewatering of the excavation area and surrounding saturated soil will be required. Groundwater will be lowered to below the planned 20-foot bgs depth of excavation. The CAC will be required to obtain a POTW permit prior to pumping, treating and discharging groundwater from the excavation. At a minimum, three 20,000-gallon storage tanks will be maintained onsite during excavation activities, unless otherwise demonstrated to be unnecessary. Appropriate water treatment equipment will include, at a minimum, a settling tank, particulate filters and liquid-phase activated carbon.

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3.0 Excavation and Stockpiling

3.1 Excavation

Excavation and removal of soil will be performed by a CAC, which will be a California-licensed contractor with a hazardous substance certification. The estimated volume of soil to be removed, based on excavation boundaries, is approximately 1,185 cubic yards in-place. All workers on site, and visitors to the site, will observe OSHA safety standards and follow an approved HASP that addresses safety issues for workers conducting or overseeing the work, including equipment operation, and sampling. Air monitoring will be performed by Blymyer Engineers during soil excavation activities in accordance with the Air Monitoring Plan.

3.1.1 Excavation Confirmation Soil Samples

Due to the use of sheet piles or a slide-rail system to retain the sidewalls, sidewall soil samples will not be able to be collected. Excavation bottom samples will be collected to document the extent of removal vertically. Four soil samples, each representing a 400-square-foot quadrant, will be collected from the base of the excavation, and analyzed for TPH as diesel and TPH as gasoline by Modified EPA Method 8015; BTEX, MTBE, other fuel oxygenates, and lead scavengers by EPA Method 8260; and total lead by Method SW 7010.

3.2 Stockpiling

Excavated soil should be stockpiled in an area adjacent to the excavation due to the need for dewatering. Stockpile size is planned to average approximately 200 cubic yards. Each soil stockpile will be field screened to test gross VOC content in soils. Available TPH as gasoline and BTEX soil results indicate that upper five¹ of soil is relatively clean, and this soil may be separated, profiled, and re-used for backfill or spread onsite, if approved by regulators; however, petroleum-impacted soil will not be reused onsite due to the high groundwater levels at the site. Waste characterization will observe standard industry protocols. Impacted soil will be stockpiled in a 10-mil Visqueen plastic lined, bermed staging area prior to disposal. The soil stockpiles will

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be covered at the end of each working period to minimize dust and odor that might be liberated from the stockpile. Water laden excavated soil will be stockpiled in an adjacent bermed area covered with a lining of 10-mil Visqueen plastic. A temporary ditch may be excavated for the stockpile water to drain back into the excavation. Alternatively a low point will be constructed in the bermed area, and a sump pump will be used to remove the stockpile water and will discharge to either the remedial excavation, or preferably to the aboveground storage and treatment tanks, depending on practicality.

4.0 Waste Characterization

4.1 Extracted Groundwater

After soil excavation activities are completed, or the aboveground storage tanks reach capacity, a confirmation grab groundwater sample will be collected after the treatment unit to confirm concentrations are within POTW-defined discharge limits. Analysis shall conform to the POTW-required analytical program, but will at a minimum include TPH as diesel and TPH as gasoline by Modified EPA Method 8015, and BTEX, and MTBE and the other fuel oxygenates and lead scavengers by EPA Method 8260.

4.2 Excavated Soil

After soil stockpiles are completed, discrete soil samples will be collected from each stockpile for laboratory compositing and analysis for the purpose of waste characterization.

1. Non-impacted near surface soil may be considered for reuse at the site. Characterization of soil stockpiles for reuse onsite will conform to the Draft *Characterization and Reuse of Petroleum Hydrocarbon Impacted Soil (PHIS)* issued by the RWQCB on June 6, 2003.
 - a. This document excludes reuse of PHIS within 5 feet of groundwater, 100 feet from a surface water body, requires protection

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against 100-year peak stream flows, requires a minimum 3-foot burial, and requires property owner acknowledgement. As a consequence, PHIS will not be reused at the site.

b. Soil suspected of being free of contamination will be sampled at an interval of one discrete soil sample for every 25 cubic yards of soil, and will be analyzed for TPH diesel and TPH as gasoline by Modified EPA Method 8015, BTEX and MTBE by EPA Method 8020, and total lead by Method SW 7010.

c. Soil documented to be free of contamination, as demonstrated in accordance with the draft PHIS document may be reused onsite.

2. Stockpiled PHIS will otherwise conform to landfill specifications for acceptance.

5.0 PHIS Removal and Disposal

Stockpiled soil will be profiled and profile data will be transmitted to the identified landfill for acceptance. Stockpiled soil will be loaded onto dump trucks and transported to the landfill for disposal. Dust control by wetting with water will be performed as necessary based on air monitoring measurements and physical conditions. Loaded trucks will move to a truck decontamination station, where soil will be removed from fenders and tires and the bed will be covered. Dump truck trays shall be lined with 10-mil Visqueen plastic and either burrito-wrapped or tarped, for transport to the selected landfill. A signed waste manifest or bill of lading must accompany impacted soil from the site to landfill.

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6.0 Excavation Backfill and Compaction

To provide suitable permeability for the Oxygen Releasing Compound (ORC) application, crushed rock, drain rock, or pea gravel is required for backfill to one-foot above the saturated zone of the excavation. Dimensions will not exceed 3/4" by 1-1/2". The rock backfill will be augmented with 1,000 pounds of ORC slurry and bio-nutrients. The rock will be wetted and compacted due to a higher potential for settlement related to the heavy traffic load on the adjacent freeway and city streets. A geotextile fabric, Mirafi 500 or equivalent, will be placed on top of the rock. Clean soil will be placed in six-inch lifts to surface grade. Imported soil will be compacted to at least 95% relative density.

7.0 Application of ORC and Bio-Nutrients

7.1 Application of ORC

The contractor will purchase and apply the ORC material. REGENESIS software indicates that approximately 1,000 pounds of ORC should be introduced to the excavation. The ORC material will be mixed into the excavation backfill, at all depths, below the level of groundwater, according to REGENESIS excavation mixing specifications (Appendix A). Specifically, the ORC will be mixed as slurry (63% solids) into the selected backfill under the REGENESIS "Type 1" scenario. The resulting thick slurry allows the material to remain in place at depth once mixed into the backfill below groundwater in order to deliver oxygen to each of the impacted water-bearing zones. The ORC will be largely placed along the upgradient (northern) edge of the excavation so that groundwater will transport the released oxygen across the former excavation.

7.2 Application of Bio-Nutrient Package

If site conditions indicate that bio-nutrients are required by the subsurface microbes at the site, Blymyer Engineers will apply a nitrogen-phosphorous-potassium (NPK) bio-nutrient package. In order to determine if NPK are required, groundwater will be

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sampled and analyzed for background levels of NPK in groundwater at the site. If required, the NPK fertilizer will be mixed with the ORC slurry to provide bio-nutrient compounds to facilitate bacterial activity. The ratios of NPK will be determined by the method outlined in the April 2003 *Pollution Engineering* article entitled *Bionutrient Modeling for Design of In situ Bioremediation* (Appendix B). Full details will be included in the report documenting the corrective actions.

8.0 Installation of 4-Inch-Diameter Monitoring Well

The contractor will install a groundwater monitoring well in the southern area of the excavation in order to monitor residual impact to groundwater, and to monitor contaminant concentration trends. Blymyer will obtain the required well construction permit from the Zone 7. The well will be installed at the time of backfilling and will be 4 inches in diameter, 20 feet in depth, and the screened casing will contain 0.020-inch perforations from 5 to 20 feet bgs. A minimum 10-inch diameter double casing will be used to encase the upper 5 feet of the well to provide a surface seal as required by the state. The lower approximately 3.5 feet of that seal will be hydrated bentonite clay, and the upper approximately 1.5 feet will be cement surrounding a surface-completed well box. These construction details have been verbally approved by Zone 7.

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9.0 ORC Injection Bores

To stimulate bacterial activity outside the remedial excavation, a mixture of ORC, and may be NPK fertilizer, will be injected in a series of strategically placed boreholes (Figure 2). A drilling contractor will be retained by Blymyer Engineers to drill and pressure-inject the ORC / NPK mix into the boreholes. The ORC will be injected under pressure from 20 to 8 feet bgs. The remaining portion of the borehole to ground surface will be backfilled with neat cement grout. NPK fertilizer will be mixed with the ORC slurry to provide bio-nutrient compounds to facilitate bacterial activity.

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10.0 Reporting

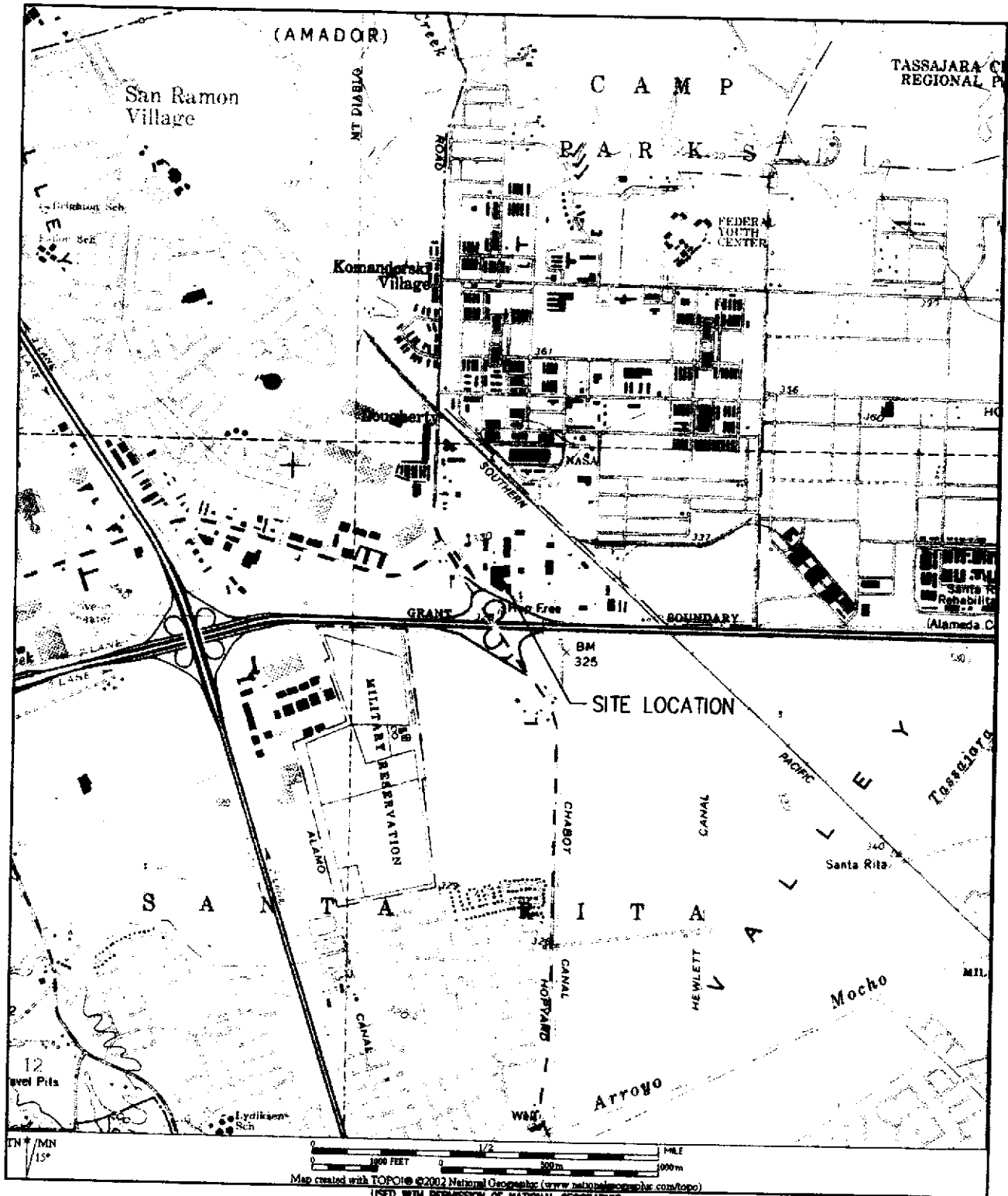
After completion of field activities, and receipt of final documentation for disposal of the excavated soil and other wastes, a report will be prepared for submission to ACEH. The report will include descriptions of field methods, observations, monitoring, and disposal documentation of excavated soil and other waste materials. Field and laboratory data will be tabulated as appropriate. Copies of appropriate documentation, including field and laboratory report data sheets, manifests or bills of lading, and permits, will be included.


11.0 Quarterly Groundwater Monitoring

Quarterly groundwater monitoring will continue uninterrupted through corrective action activities. To achieve final site closure, a period of groundwater monitoring, typically a minimum of four quarters after completion of remedial activities, will likely be required. Should contaminant concentrations be reduced below regulatory acceptable levels or show a declining trend, then site closure may be achieved through the risk-based corrective action (RBCA) approach.

Figures

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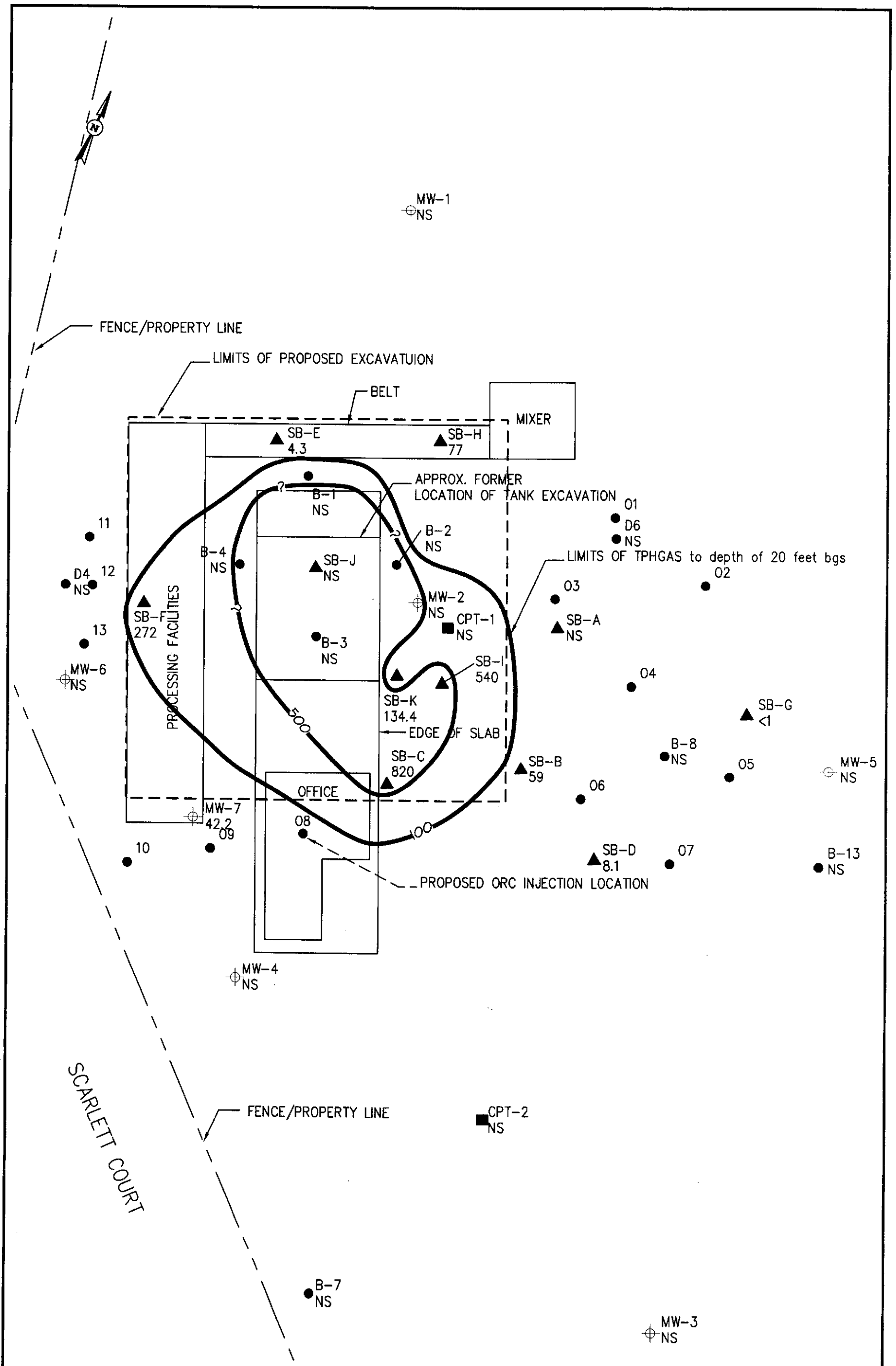
 BLYMYER ENGINEERS, INC.	
BEI JOB NO. 202016	DATE 6-27-02

LEGEND

SITE LOCATION MAP

FORMER DOLAN RENTAL
PROPERTY
6393 SCARLETT COURT
DUBLIN, CA

FIGURE
1



BASED ON SITE PLAN GENERATED BY AQUA SCIENCE ENGINEERS, INC.



BLYMYER ENGINEERS, INC.

BEI JOB NO. 202016	DATE 8-30-05
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LEGEND	
	GROUNDWATER MONITORING WELL
	SOIL BORE (BY OTHERS)
	GEOPROBE SOIL BORE
	CPT BORE
	NOT SAMPLED
	MULTIPLE CONCENTRATIONS WITHIN DEPTH INTERVAL
	<1/42

LAYOUT for RECOMMENDED REMEDIAL ACTION PLAN

FORMER DOLAN RENTAL PROPERTY
6393 SCARLETT COURT
DUBLIN, CA

FIGURE
2

Appendix A

REGENESIS ORC Excavation Mixing Specifications



REGENESIS

Oxygen Release Compound (ORC[®])

Installation Instructions

(Excavation Applications)

SAFETY:

Pure ORC is shipped to you as a fine powder, which is rated at -325 mesh (passes through a 44 micron screen). It is considered to be a mild oxidizer and as such should be handled with care while in the field. Field personnel should take precautions while applying the pure ORC. Typically, the operator should work up wind of the product as well as use appropriate safety equipment. These would include eye, respiratory protection and gloves as deemed appropriate by exposure duration and field conditions.

Although two options are discussed, application of ORC should never be applied by personnel within the tank excavation, unless proper shoring or sidewall cutback is in place.

GENERAL GUIDELINES:

ORC can be applied in a dry powder form or as a slurry. Field conditions dictate which form of ORC can be used most effectively.

Installation of ORC should be within the tank excavation floor and/or in an adequate backfill section thickness to account for the anticipated groundwater "smear zone".

Maximum treatment effect is obtained when ORC is mixed as thoroughly as possible within the backfill material. The more dispersed the ORC slurry/powder within the excavation backfill, the more effective the treatment.

The quantity of ORC to be used is generally calculated prior to moving into the field for installation. Generally it is applied at a rate of between 0.1% and 1.0% by weight of the soil matrix. The following illustrates a dilute application rate calculation:

Use a weight/weight percent of ORC/backfill material to ensure distribution of the ORC into the desired aquifer section. For example: a 0.15% weight of ORC to weight of backfill for the standard ORC weight (30 pounds) per container calculates as follows: $30 \text{ lb. ORC} / 0.15\% = 20,000 \text{ lbs. of soil matrix}$. Thus, to achieve a 0.15% mixture of ORC in the backfill material, 30 lb. of pure ORC should be mixed into 10 tons ($20,000 \text{ lbs.} \div 2,000 \text{ lbs./ton}$) of backfill, or approximately 7 - 10 cubic yards of soil depending on field conditions. Professional judgment should be used to select the appropriate soil mass per cubic yard for designing each site treatment.

CHOOSING THE FORM OF INSTALLATION:

Pure ORC is shipped to you in a powder form. Weather conditions (especially wind) may have a direct effect on the application of ORC as a tank backfill amendment.

Application of the dry powder may be difficult in windy conditions. To counter the effects of wind (and the subsequent potential loss of ORC), Regensis recommends that a water source or a spray tank be on-site to wet down the ORC and the backfill material as ORC is applied.

Application of ORC in a slurry format is a very effective method and eliminates the wind issue.

Four somewhat different installation conditions can be encountered in the field:

- ORC in a pea gravel back-fill. ("Type 1")
- ORC in a soil back-fill. ("Type 2")
- ORC mixed in native soil in the bottom of a tank pit. ("Type 3")
- ORC installed in soil under standing water in the bottom of a tank pit. ("Type 4")

A single tank pit excavation can include more than one of these conditions, depending on the site and extent of treatment. Instructions for each condition are discussed separately in the following sections. After the installation instructions are detailed instructions for mixing the slurry, if that is the option chosen.

INSTALLATION INSTRUCTIONS:

"Type 1," ORC in a Pea Gravel Back-fill

The easiest method for installing ORC in pea gravel back-fill is to mix the ORC in the material in a backhoe or skid loader bucket before placing it in the excavation.

- **Dry Powder method**

Into each scoop of back-fill material add the appropriate portion of ORC being installed. Generally, it is advisable to moisten the material in the bucket to reduce wind blown ORC loss. Excessive winds make this method not feasible.

After mixing the dry powder in the bucket, it is dumped into the bottom of the excavation. The backhoe bucket can be used for further mixing in the excavation.

- **Slurry method**

Mix a 63% solids slurry of ORC and water (see "Steps to make ORC slurry). This relatively thick slurry is used to help keep the ORC dispersed through the pea gravel, even when it contacts water in the bottom of the excavation during installation. It is generally desirable to avoid having the ORC run down through the pea gravel and collect in the bottom of the excavation. The thick slurry addresses this issue.

In each scoop of back-fill material, add the appropriate amount of ORC slurry. Pre-mix the materials in the backhoe bucket. After mixing, dump the slurry and back-fill into the bottom of the excavation. The backhoe bucket can be used for further mixing in the

excavation.

If the slurry method is being used, observe the physical behavior of the ORC in the fill material. If the ORC collects at the bottom of the back-fill material, increase the percent solids content by reducing the amount of water being used to make the slurry.

"Type 2," ORC in a Soil Back-fill

Follow the instructions for the pea gravel back-fill method, except:

If the slurry method is being used, the solids content should be reduced. Typically a 50% solids is appropriate, although soil conditions sometimes dictate lower solids contents (see "Steps to make ORC slurry").

"Type 3," ORC Mixed in Native Soil in the Bottom of the Tank Pit

When ORC is added to the bottom of a tank pit it may be done by backhoe or injection.

CAUTION: Personnel should never work within the tank excavation, unless proper shoring or sidewall cutback is in place.

• Backhoe method

A skilled backhoe operator can distribute the ORC around the bottom of the tank excavation and, using the bucket, mix it thoroughly. If there are no winds, it may be possible to:

1. Put the dry ORC powder in the backhoe bucket,
2. Lower it to the bottom of the pit,
3. Gently deposit the ORC evenly on the remaining soil,
4. Use the bucket to mix the powder into the soil,
5. To mitigate dusting, if necessary, spray water into the excavation during the process.

An alternative backhoe method is to use a 50% (or less) solids ORC slurry (see "Steps to make ORC slurry") in place of the dry powder. This eliminates the dusting problem, and in some cases enhances the even distribution of ORC into the soil. Observe the slurry mixing behavior in the bottom of the excavation, and adjust the water content of the slurry to optimize mixing, if necessary.

• Injection method

If available, a pump and root feeder may be used to inject an ORC slurry into the excavation floor. This may require a more dilute slurry mix, and care should be taken to assure that the solids do not settle out of the slurry prior to injection.

"Type 4," ORC installed in standing water in the bottom of a tank pit

Application of ORC into tank excavations with standing water requires the operator apply ORC in a slurry form. ORC powder application in this scenario is not advised because a portion of the ORC particle fraction is not likely to pass through the surface tension of the standing water. **Caution:** Personnel should never work within the tank excavation, unless proper shoring or sidewall cutback is in place.

- **Backhoe method**

A skilled backhoe operator can distribute the ORC slurry within the excavation, and mix it into the soil underlying the standing water with the bucket. Steps for installation:

1. Mix a high solids content ORC slurry (63% solids). See ("Steps to make ORC slurry").
2. Pour slurry into the backhoe bucket.
3. Lower the bucket to the standing water level in the excavation, and deposit the slurry as evenly as possible across the excavation floor. The dense slurry (63% solids is 1.6 grams per ml) will tend to make the majority of the slurry sink quickly to the bottom of the water layer.
4. Use the bucket to mix the slurry into the soil.
5. Water in the vicinity of the ORC slurry will often turn white and milky, since some of the ORC is dispersed within the standing water. This provides additional dispersion within the standing water and back-fill material as it is added to the excavation.

- **Injection method**

If available, a pump and root feeder may be used to inject an ORC slurry into the soil in an excavation. This may require a more dilute slurry mix, and care should be taken to assure that the solids do not settle out of the slurry prior to injection.

MIXING ORC SLURRY:

ORC powder is shipped to you in pre-measured batches. Each batch is contained in a plastic bag which is shipped in a 5-gallon bucket.

Remove the pre-measured ORC bag from the 5-gallon bucket and open. Measure and pour the appropriate amount of water from the following table into the 5 gallon bucket

Slurry Solids Content (%)	Pounds of ORC	Gallons of Water
63%	30 lbs.	2.1 gal. (2 gal. + 2 cups)
50%	30 lbs.	3.6 gal. (3 gal + 2 1/2 qts.)

Add the entire ORC pre-measured bag to the water (30 pounds). If the slurry solids contents of less than 50% are desired, the quantity of ORC per batch mixed in the bucket must be reduced. For example, a bucket containing four gallons of water would require 22.4 pounds of ORC to make a 40% solids slurry, and 16.6 pounds of ORC to make a 33% slurry.

Use an appropriate mixing device to thoroughly mix ORC and water. Regensis

recommends use of a 0.5 Horsepower (minimum) hand held drill with a "jiffy mixer" or stucco mixer. A common paint paddle can be used to scrape the bottom and sides of the container to ensure thorough mixing. Standard environmental slurry mixers may also be used.

After mixing, small amounts of water can be added to adjust the consistency of the slurry.

When slurries are used, the early batches should be observed in the process of mixing with the soil. Each site can vary, due to soil type and moisture content. Based on professional judgment, additional water can be added to subsequent slurry batches.

ORC slurry should be used ASAP; if the ORC slurry has been standing more than 15 minutes, it should be remixed immediately before using. Do not let stand more than 30 minutes without stirring. Otherwise, the slurry will begin to harden into a weak cement.

For direct assistance or answers to any questions you may have regarding these instructions, contact Regenesi s Technical Services at 949-366-8000.

**REGENESIS, 2002
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Appendix B

*Bionutrient Modeling for Design of In situ Bioremediation,
Pollution Engineering, April 2003*



BIONUTRIENT MODELING

for Design of In situ Bioremediation

by Warren B. Chamberlain, R.G., C.H.G., P.E.

Enhanced bioremediation is a remediation technology that involves the stimulation of natural microbial activity to address specific environmental contamination. In the "natural" state, microbial activity that is capable of degrading organic compounds can stall for lack of one or more of the elements necessary to promote bacterial activity — most often oxygen or hydrogen depending on the need for oxic or anoxic subsurface conditions. It is also commonly found that macronutrient compounds of nitrogen and/or phosphorous are also depleted. In biological terms, the missing or depleted nutrients are known as the Limiting Factor to microbial growth.

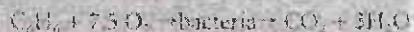
This article presents an anabolic design approach to quantifying macronutrient additions for in situ bioremediation projects.

Background

With the exception of methane, most organic solutes encountered in natural waters are not in thermodynamic equilibrium with their environment (Strumm and Morgan, 1981). Nonphotosynthetic organisms such as heterotrophic bacteria tend to restore thermodynamic equilibrium by decomposing "unstable" organic compounds through energy yielding oxidation-reduction reactions; in so doing, the bacteria obtain a source of energy for their metabolic needs. As such, bacteria play an active role in the breakdown process of complex organic compounds

to more environmentally inert chemical compounds such as carbon dioxide, ethane, or methane.

However, the traditional design approach for the degradation of say, benzene, is viewed as a simple redox reaction, with the following stoichiometric relationship for the breakdown of benzene (C₆H₆):



In this design approach, only the addition of oxygen (as a terminal electron acceptor) is deemed necessary, and the bacteria are viewed as mere catalysts.

Essentially, the traditional bioremediation design considers only those paths of the bacteria's metabolic process that are catabolic (reaction processes that liberate free energy due to the breakdown of complex molecules to simpler molecules). While this design approach is valid, it presents only a partial picture of the bacteria's role and the processes involved in contaminant degradation. While designers of the catabolic (or terminal electron acceptor) approach often state the need to consider macro and micronutrients, a method or procedure to quantify the macro and micronutrient requirements has not been established. Collectively termed bionutrients, macronutrients are usually nitrogen, sulfur, phosphorous, and potassium compounds, and micronutrients are usually trace metal compounds.

The addition of macronutrient compounds to groundwater is of particular

concern to regulators, as the fate of added bionutrients is not usually well described in the bioremediation design. Because of this, regulators will typically permit the addition of (non-toxic) oxygen and hydrogen releasing compounds to groundwater but will not allow bionutrient compounds (for example, NPK fertilizers). This restriction can lead to less than optimum conditions for promoting bacterial metabolic activity and colony growth. However, when regulators are presented with more explicit quantification of the fate of macronutrients that will be added, they can be less restrictive.

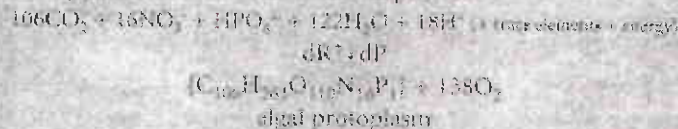
In the bionutrient design approach, an additional element is considered in the design: the anabolic process, that is, the nutritional requirements for growing bacterial cells. The bacteria's nutritional/reproductive needs are estimated based on the stoichiometric make-up of a microbial cell. The bionutrient approach considers the quantity of the contaminant as a carbon source, and what macronutrients (and trace elements) are essential to grow new cells and increase the bacterial colony. As such, the bionutrient approach represents an extension of traditional catabolic bioremediation design; it presents a method to quantify the amount of macronutrients needed to facilitate bioremediation.

Stoichiometric design for bioremediation

Microbial organisms are the product of inorganic matter and have a relatively constant stoichiometric composition of

$C_{106}H_{263}O_{110}N_{16}P_1$, plus species-specific trace elements. For contaminants to increase and promote bacterial growth, organisms also require a supply of inorganic chemicals to support the growth of new cellular structures and produce life-functioning proteins and enzymes (nitrogen based amino acids, and phosphorus based phospholipids and nucleic acids) for the expanding colony.

From a purely stoichiometric view, Strumm and Morgan (1981) provide the following reaction equation for the make-up of algal protoplasm (noting that the composition of simple organisms such as bacteria, yeast and algae are very similar) as an example of microbial elemental composition:



where:

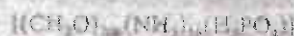
C = Carbon, O = Oxygen, H = Hydrogen, N = Nitrogen, and P = Phosphorus.

dP = rate of production of cellular organic matter (for bioremediation projects this means an increase in the microbial population while consuming contaminants).

dR = rate of destruction of cellular organic matter.

For comparison with the above example, Metcalf and Eddy (1991), in the design of anaerobic digesters, use the stoichiometric relationship of $C_{60}H_{87}O_{23}N_{12}P_1$, to represent the cellular composition of anaerobic bacteria.

Furthermore, the composition of the algal protoplasm may be conveniently expressed in terms of a basic carbon unit and inorganic compounds, ammonia (NH_3) and orthophosphate (H_3PO_4) as:



where:

(CH_2O) represents the carbohydrate unit (as basic sugar)

(NH_3) represents the base nitrogen unit (as ammonia)

(H_3PO_4) represents the base phosphorus unit (as orthophosphate)

These macronutrient molecules are readily soluble and electrochemically active, and therefore readily dispersed in the natural environment for uptake by microorganisms.

For a biological system as indicated above, biomass will continue to form as long as there exists a continuous supply of carbon (organic or inorganic) and bionutrient compounds. Only when one or more nutrients become a limiting factor will the production of biomass cease. However, the reverse destruction of biomass is typically very slow compared to the rate of production, as the biomass produced is predominantly composed of large macromolecules (that is, proteins, etc.).

Application of the stoichiometric design approach

Using the preceding formulation to represent bacterial cells, it can be seen that there exists a molar ratio of carbon to nitrogen to phosphorus (C: N: P) of (106: 16: 1). On this premise, the bionutrient design approach seeks to create a subsurface condi-

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tion where macronutrient chemical elements are present and available for microbial uptake at ratios similar to the compositional make-up of the bacterial cell, with the contaminant of concern being the design limiting factor nutrient.

The mass ratio of the macronutrients (nitrogen and phosphorus) with respect to carbon can be found by multiplying the molecular weight of each element by its respective molar ratio to get equivalent mass. To express nutrient mass requirements in terms of per gram of carbon, divide the mass of each element by the total mass of carbon. These calculation steps are summarized in Table 1.

Thus, for every gram of carbon used to grow new cells, 0.176 grams of nitrogen, and 0.024 grams of phosphorus are required, that is (C: N: P) = (1: 0.176: 0.024). The above design procedure can be readily expanded to consider other essential macronutrients and trace metals as needed based on the knowledge of a specific bacteria's nutrient requirements.

Example application

The following is an (applied) example of how the stoichiometric-bionutrient design approach is evaluated to determine macronutrient requirements for the aerobic degradation of a hydrocarbon plume:

Consider a (dissolved) gasoline plume with an average mass

concentration of six milligrams per liter (mg/L). Assume that the gasoline consists primarily of hydrocarbon molecules, with the carbon to hydrogen ratio consistent with a mid-range gasoline compound such as toluene (C₇H₈). For aerobic degradation to occur, a source of dissolved oxygen (DO) will typically be required, and DO concentrations should be maintained at two

Table 1 - Equivalent Mass Calculation of Microorganism Stoichiometry

Element	Carbon	Nitrogen	Phosphorus
Molar ratio (moles)	1	1	1
Molecular Weight (grams per mole)	12	14	31
Mass ratio (grams)	12	14	31
Per gram of carbon	1	0.176	0.024

mg/L to preserve aerobic conditions within the plume. Typically, the total DO requirements are taken as three to four times the average hydrocarbon concentration (see Suthersan, 1997) based on performing a mass balance of the hydrocarbon constituent

redox reactions similar to the one presented for benzene.

Now to determine the quantity of macronutrients required:

- Step 1: Determine the carbon mass concentration within the plume; in this example carbon (represented as toluene) accounts for 90 percent of the contaminant mass or 5.4 mg/L.
- Step 2: Determine the mass ratio of the macronutrients (nitrogen and phosphorus) with respect to carbon. That is, 5.4 times (1: 0.176: 0.024).
- Step 3: Suppose groundwater analyses determined that dissolved nitrogen and phosphorus were present in the aquifer at concentrations of 0.2 and 0.03 mg/L, respectively.
- Step 4: Perform a mass balance of the gas-line plume zone to determine the quantity of macronutrients required to utilize all the contaminant mass to grow new cells.

These steps are summarized in Table 2.

Based on the above calculations, nitrogen and phosphorus should be added to the system until the plume volume contains a concentration of nitrogen and phosphorus of at least 0.95 mg/L and 0.13 mg/L, respectively. That is, a sufficient volume of nitrogen and phosphorous compounds should be added to the aquifer to amend the lacking nitrogen (0.75 mg/L) and phosphorus (0.10 mg/L) within the area of contamination. If indicated by site characterization testing, consideration should also be given to non-contaminant sources of carbon in determining nutrient requirements.

The molecular ratios presented in Table 1 may be used to determine nutrient requirements for the bacteria. The author has found that the use of the molecular formula for algal protoplasm to determine macronutrient requirements in conjunction with the addition of oxygen release compounds has worked well for the design of in situ biodegradation of petroleum hydrocarbon plumes. In cases where anaerobic conditions prevail and halo-respirators, nitrogen, sulfate, or methane reducing bacteria are the active remediating organisms, these bacteria will have cellular composition similar to that stated above.

The ability of these bacteria to degrade contaminants is a function of their active (degrading) enzymes, and the bacteria are best able to

Table 2 - Sample Mass Balance Calculation to Determine Nutritional Needs

Calculation Step	Carbon	Nitrogen	Phosphorus
(1) Mass of carbon present	5.4		
(2) Mass of carbon present to biotransform (mg/L)	5.4	0.95	0.13
(3) Nutrients present (mg/L)	0.2	0.03	0.03
(4) Nutrient deficiency (mg/L) Step (2)-(3)		0.75	0.10

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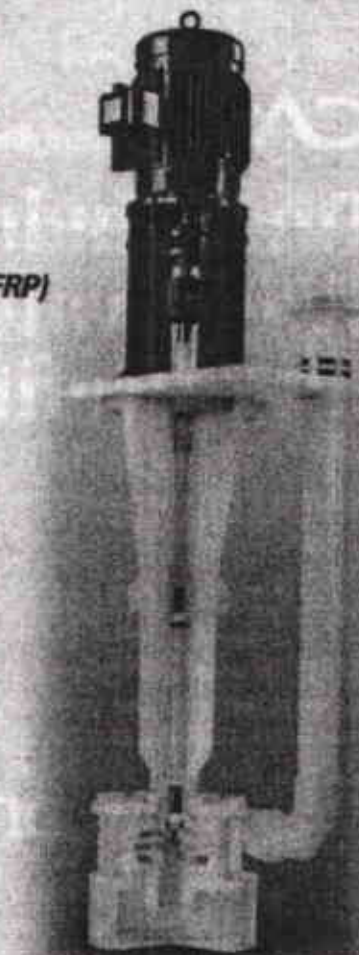
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Fate of added nutrient compounds

For sites where contaminated groundwater has the potential for use as a drinking water source, regulatory standards require the specific conductance of the

groundwater to be less than 900 micromhos per centimeter. The addition of macronutrients (nitrate, sulfate, or orthophosphate) will increase the specific conductance of the groundwater due to their ionic nature (that is, macronutrient compounds are generally composed of soluble cations and anions). As such, a drinking water aquifer could be affected

by the addition of excessive quantities of macronutrient compounds.

The federal government has determined Maximum Contaminant Levels (MCLs) for specific compounds in drinking water; if any one of the listed compounds exceeds its MCL in potable groundwater, consumption of the groundwater is considered to be potentially toxic. Nitrogen compounds have listed MCLs. However, the MCLs for the macronutrient compounds are usually 1,000 times higher than those established for organic or metal contaminants, as indicated in Table 3.

Table 3 - Comparison of typical MCL values for Pollutant Types


Contaminant	Pollutant	MCL
Benzene	Organic	5 mg/l
PCB	Organic	1 mg/l
Mercury	Inorganic	0.1 mg/l
DDT	Organic	0.1 mg/l
Nitrate	Nitrogen	10 mg/l

As shown in the example application presented above, the amount of macronutrient additions required to foster optimal contaminant biodegradation is significantly less than the mass of the contaminant of concern, and significantly less than the nitrate MCL. Therefore, if found to be lacking, macronutrients should be added only in amounts that do not exceed respective MCLs.

Furthermore, if the bioremediation is observed to be progressing, it may be reasonably assumed that the macronutrients are being assimilated by the bacteria and transformed into biomass (that is, used to synthesize complex biomolecules). The breakdown of biomass (organic proteins, etc.) to more fundamental compounds will take a significant amount of time.

Concluding remarks

The bionutrient (or anabolic) design approach focuses on how to expand a bacterial colony while considering the contaminant of concern as a limiting factor nutrient. The design approach provides a means

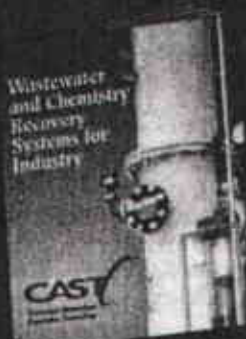


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 $10 \text{ mg/l} / 0.2 \text{ NO}_3^- = 45 \text{ mg/l}$

to quantify macronutrient (nitrogen and phosphorous compounds) additions to groundwater, making the addition of bionutrients justifiable to regulators. When used in combination with the traditional terminal electron acceptor (or catabolic) bioremediation design approach, the bionutrient design approach completes the microorganism metabolic cycle. Considering both metabolic pathways in bioremediation design leads to procedures that optimize subsurface conditions, fosters bacterial activity, and achieves remedial goals at the site. **PE**

For more information regarding this article, contact Warren Chamberlain, R.G., CHG, P.E., at 925-462-2665 or by e-mail at wchamberlain@claytongrp.com.

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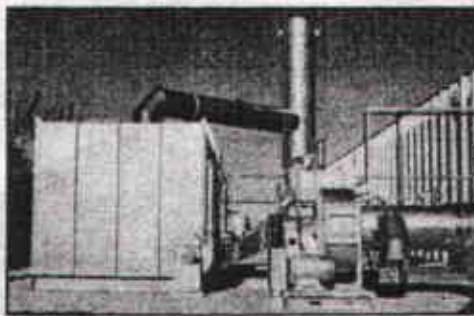
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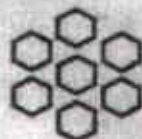
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