

A Report Prepared for

Exxon Company, U.S.A.
P.O. Box 4032
Concord, California 94520

**BIOREMEDIATION TREATABILITY STUDY
EXXON STATION #7-0104
ALAMEDA, CALIFORNIA**

HLA Job No. 04167,326.02

by:

S Michelle Watson

S. Michelle Watson
Project Geologist

Donald R Smallbeck

Donald R. Smallbeck
Principal Environmental Scientist

Harding Lawson Associates
7655 Redwood Boulevard
P.O. Box 578
Novato, California 94948
415/892-0821

July 26, 1991

TABLE OF CONTENTS

LIST OF TABLES.....	iii
LIST OF ILLUSTRATIONS.....	iii
1.0 INTRODUCTION.....	1
SAMPLE ANALYSIS AND INTERPRETATION OF RESULTS.....	1
2.1 Sample Collection	1
2.2 Microbial Populations in Groundwater.....	2
2.3 Microenvironmental Factors in Groundwater	2
2.4 Biological Treatment Simulation	3
3.0 SUMMARY AND CONCLUSIONS.....	5

TABLES

ILLUSTRATIONS

DISTRIBUTION

LIST OF TABLES

Table 1	Enumeration of Total and Hydrocarbon-Utilizing Hydrocarbons in Groundwater
Table 2	Groundwater Chemistry Profile
Table 3	Bioreactor Process Summary

LIST OF ILLUSTRATIONS

Plate 1	Laboratory Bioreactor Treatment System
---------	--

1.0 INTRODUCTION

This report summarizes the findings of Harding Lawson Associates' (HLA) evaluation study to assess the feasibility of using biological treatment to remediate contaminated groundwater at Exxon Station #7-0104, 1725 Park Street, Alameda, California (site). The scope for this investigation was presented to Exxon Company, USA (Exxon) in a letter dated April 5, 1991. The work was authorized by Exxon Work Release No. 91064698 dated May 8, 1991.

The purpose of this study was to evaluate if inorganic chemistry and microbiological constituents in groundwater would require enhancement in order to optimize the biological degradation of total petroleum hydrocarbons (TPH) and benzene, toluene, ethylbenzene and xylenes (BTEX) present in groundwater at the site, and to perform a laboratory-scale study to evaluate the effectiveness of the biological treatment process. The evaluation study was designed to:

- o Evaluate the existing microbial populations capable of degrading petroleum hydrocarbons (gasoline).
- o Evaluate groundwater chemistry factors that could influence the rate of biological degradation of petroleum hydrocarbons.
- o Perform a laboratory-scale simulation of the biological treatment process to evaluate TPH and BTEX removal efficiencies for several combinations of residence time and influent concentrations of TPH and BTEX.

SAMPLE ANALYSIS AND INTERPRETATION OF RESULTS

2.1 Sample Collection

Three groundwater samples, each approximately 5 gallons in volume, were collected from monitoring wells MW-2 (1 sample) and MW-5 (2 samples) by HLA on

April 10, 1991. These samples were used in the microbial and groundwater chemistry evaluations and in the laboratory treatment simulation study.

2.2 Microbial Populations in Groundwater

Each groundwater sample was analyzed in HLA's bioremediation laboratory to estimate the total number of microorganisms per milliliter of sample and, of these, those microorganisms that have the metabolic capability to use petroleum hydrocarbons (gasoline) as a primary source of carbon and energy. Microorganisms capable of degrading hydrocarbons were present in each groundwater sample. The percentage of hydrocarbon-utilizers as a portion of the total population ranged from 0.2 percent to 2.2 percent. Results of the microbial evaluation of the groundwater samples are summarized in Table 1.

The results indicate that the existing microbial population in the groundwater contains a subpopulation of microorganisms capable of degrading hydrocarbons. Stimulation of the hydrocarbon-utilizing microorganisms with the proper nutrients should increase their percentage of the total microbial population and result in a significant decrease in the concentration of petroleum hydrocarbons in the groundwater.

2.3 Microenvironmental Factors in Groundwater

A groundwater chemistry profile, which included pH and concentrations of nitrogen as ammonia and nitrate, phosphorus as orthophosphate, sulfate and dissolved iron, manganese, magnesium, calcium, and potassium was obtained from a composite groundwater sample. The results of the groundwater chemistry analysis are summarized in Table 2.

Generally, acceptable concentrations of key inorganic nutrients necessary to sustain microbial metabolism are as follows:

- Nitrogen as nitrate or ammonia - 20 milligrams (mg) per 100 mg hydrocarbon
- Phosphorus as orthophosphate - 5 mg per 100 mg hydrocarbon.

Comparison of the analytical results to microbial growth requirements indicates that the low concentrations of nitrogen as nitrate or ammonia, and phosphorus as orthophosphate are probably limiting the potential for microbial degradation of the petroleum hydrocarbons. Therefore, stimulation of the indigenous microbial population capable of degrading petroleum hydrocarbons will require the addition of nitrate or ammonia and phosphorus in a form readily available to the microorganisms.

Additionally, the groundwater is unbalanced towards the cation side with some peculiarities such as magnesium in excess of calcium and high levels of dissolved iron and manganese. While these imbalances should not affect biodegradation in the reactor, they may cause precipitation and/or scaling in ancillary equipment (pumps, piping, and filters) and should be accounted for in design of the treatment system. If the treated water is to be injected into the subsurface to stimulate microbial degradation, the iron and manganese imbalances must be considered when developing injection strategies for nutrients and oxygen.

2.4 Biological Treatment Simulation

A laboratory scale treatment system was constructed to simulate conditions under which the bioremediation process would be operated in the field. The treatment system (Plate 1) consisted of a bench-scale bioreactor equipped with appurtenances for oxygen and nutrient additions. Initially, a microbial seed was developed in the bioreactor.

Groundwater containing petroleum hydrocarbon and indigenous microorganism was pumped into the reactor. A predetermined amount of inorganic nutrients was added to support microbial growth and the bioreactor contents aerated for 72 hours. During the 72-hour incubation period, the hydrocarbon utilizing population in the reactor increased three orders of magnitude (1.5×10^3 to 3.7×10^6). Additionally, the TPH and BTEX concentrations in the groundwater were reduced 99.5 percent and 99.98 percent, respectively.

Following biological stabilization of the reactor, a series of flow-through tests were performed. A composite groundwater sample containing petroleum hydrocarbons was pumped to the bioreactor at several specified rates over the three-week treatment period to determine the flow rate for optimum biological degradation of the petroleum hydrocarbons.

Daily influent samples to the bioreactor and effluent samples following biological treatment were collected and analyzed for TPH as gasoline and BTEX to assess the degradation efficiency of the bioreactor under specific operating conditions. Additionally, the bioreactor contents were sampled daily and analyzed for microbial populations. The results of the bioreactor study are summarized in Table 3.

Chemical analyses of the effluent quality from the bioreactor at a liquid retention time of 18 hours indicated a TPH and total BTEX removal efficiency of greater than 99 percent. A twelve hour liquid retention time resulted in TPH and total BTEX removal efficiency ranging from 84 to 98.4 percent and 88.7 to greater than 99.9 percent, respectively. Effluent quality monitoring from the bioreactor at an 8-hour liquid retention time indicated TPH and total BTEX removal efficiencies ranging from 65 to 96 percent and 26 to 98.7 percent, respectively.

These results indicate that biological treatment of petroleum hydrocarbons in groundwater at the Exxon Alameda site is technically feasible and effective.

3.0 SUMMARY AND CONCLUSIONS

The microbial evaluation indicates that the existing microbial population in groundwater at the Exxon Alameda site contains a subpopulation of petroleum hydrocarbon-utilizing microorganisms.

The groundwater chemistry results indicate that low concentrations of the inorganic nutrients nitrogen and phosphorus could be limiting the metabolism of the existing microorganisms capable of degrading hydrocarbons in the groundwater environment. The addition of these limiting nutrients in conjunction with aeration should stimulate the growth of the hydrocarbon-utilizing microorganisms, resulting in a reduction in the concentration of hydrocarbons in the groundwater.

The laboratory simulation results indicate biological treatment of the groundwater resulted in a decrease in TPH and total BTEX concentration of approximately 99 percent at a liquid retention time of 18 hours. Influent groundwater having a dissolved TPH concentration ranging between 10 and 50 parts per million (ppm) may require post-treatment in a carbon adsorption system before the treated water may be discharged. Based on the bioreactor studies it is anticipated that at a liquid retention time between 12 and 18 hours, the maximum total BTEX loading from the treated effluent into the carbon adsorption system will not exceed 5 parts per billion (ppb). Continued groundwater extraction and operation of a full scale system should result in a decrease of influent TPH and BTEX concentrations; thus, a reduced hydrocarbon loading rate for the carbon adsorption system would be anticipated over the duration of the project.

These results indicate that biological treatment of TPH and BTEX in groundwater at the site is technically feasible and effective. The process data generated from this study will serve as the basis for design of the full scale treatment system.

**Table 1. Enumeration of Total and Hydrocarbon-Utilizing
Microorganisms in Groundwater
Exxon Alameda**

HLA Lab Number	Sample Designation	Total Microorganisms	Hydrocarbon-Utilizing Microorganisms (% of total)
90-2477	MW-02	1×10^6 cfu/milliliter*	2.2×10^4 cfu/milliliter* (2.2)
90-2478	MW-05	6.9×10^5 cfu/milliliter	1.3×10^3 cfu/milliliter (0.2)
90-2479	MW-05	5.2×10^5 cfu/milliliter	9.5×10^3 cfu/milliliter (1.8)

* cfu/milliliter. Colony forming units per milliliter.

Table 2. Groundwater Chemistry Profile
Exxon Alameda

Parameter	Sample Designation Groundwater Composite ⁽¹⁾
pH	6.9
Ammonia-N (mg/l) ⁽²⁾	0.09
Nitrate-N (mg/l)	ND (0.1)
Orthophosphate (mg/l)	0.1
Sulfate (mg/l)	22
Dissolved Iron (mg/l)	8.68
Dissolved Manganese (mg/l)	2.81
Dissolved Magnesium (mg/l)	56.3
Dissolved Potassium (mg/l)	1.7
Dissolved Calcium (mg/l)	54.4

ND Not detected at state detection limit in ().

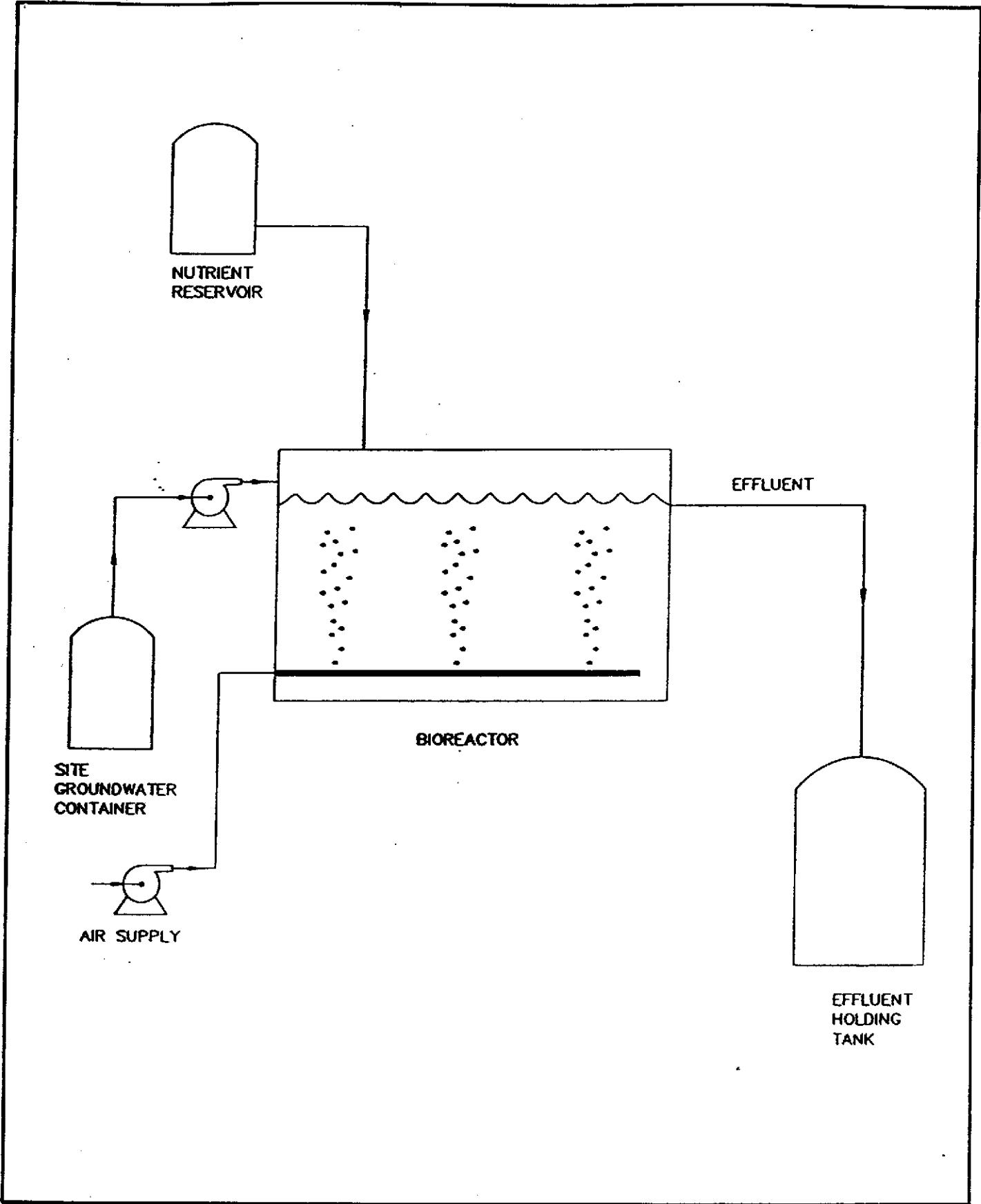
(1) Samples taken by HLA and analyzed by ETS Laboratories, Petaluma, California.

(2) Milligrams per liter - equivalent to parts per million.

Table 3. Bioreactor Process Summary
Exxon Alameda

Day	Influent Concentration		Effluent Concentration		TPH Removal Efficiency	BTEX Removal Efficiency	Liquid Retention Time (hours)
	TPH (mg/l)	Total BTEX (ug/l)	TPH (mg/l)	Total BTEX (ug/l)			
1	12	5,050	ND (0.05)	ND (0.5)	>99.6	>99.9	18
2	15	5,060	ND (0.05)	4.9	>99.7	99.9	18
3	14	4,730	ND (0.05)	4.0	>99.7	99.9	18
4	7.6	2,770	0.05	4.2	99.4	99.9	18
5	7.2	2,710	ND (0.05)	ND (0.5)	>99.4	>99.9	18
1	7.3	2,500	0.12	2.2	98.4	99.9	12
2	5.4	1,940	0.14	2.7	97.5	99.9	12
3	6.1	2,160	0.12	1.8	98.1	99.9	12
4	1.3	15	0.10	1.7	92.4	88.7	12
5	0.6	18	ND (0.05)	ND (0.5)	>91.7	>97.3	12
6	0.54	36.5	ND (0.05)	ND (0.5)	>90.8	>98.6	12
7	0.31	32	ND (0.05)	ND (0.5)	>84.0	>98.5	12
1	0.44	8.3	0.08	1.1	81.8	86.8	8
2	0.27	4.9	0.08	1.3	70.4	73.5	8
3	0.18	1.9	0.08	1.4	65.6	26.4	8
4	1.7	37	0.07	ND (0.5)	95.9	>98.7	8
5	0.87	23	ND (0.05)	ND (0.5)	>94.3	>97.9	8
6	0.72	52	ND (0.05)	0.8	>95.1	98.5	8

ND Not detected at stated detection limit in ().



Harding Lawson Associates
Engineering and
Environmental Services

LABORATORY BIOREACTOR TREATMENT SYSTEM^{PLATE}
EXXON ALAMEDA
ALAMEDA, CALIFORNIA

1

DRAWN
SS

JOB NUMBER
04167,326.02

APPROVED
JRS

DATE
7/91

REVISED DATE

DISTRIBUTION

BIOREMEDIATION TREATABILITY STUDY
EXXON STATION #7-0104
ALAMEDA, CALIFORNIA
July 26, 1991

Copy No. 1

Copy No.

5 copies: Exxon Company, USA
P.O. Box 4032
2300 Clayton Road
Concord, California 94520

1 - 5

5 copies: Harding Lawson Associates

6 - 10

SMW/DRS/lid/DRS1449-R

QUALITY CONTROL REVIEWER



Michael L. Siembieda
Associate Geologist - RG 4007