MTBE as a Contaminant:

with Field Data on a Release of Unleaded Fuel in an Unconfined Fractured Aquifer

September 1993

R M Symington, University College London

Anglian Regional Operational Investigation 562

OI/562/1/A

NRA
National Rivers Authority

MTBE as a Contaminant: with Field Data on a Release of Unleaded Fuel in an Unconfined Fractured Aquifer

Anglian Region Operational Investigation 562

Project Leader: **Paul Waldron**
Contractor: **University College, London**

Dissemination Status:

Internal - **Limited Release to Anglian Region Staff only (Named Persons on Document Status and Use Note)**
External - **Restricted**

September 1993

Anglian Region
Kingfisher House
Goldhay Way
Orton Goldhay
Peterborough
PE2 5ZR

Tel: 0733 371811
Fax: 0733 231840

Further Information:

For further information on this project, please contact the Project Leader or the R&D Section at the address above.

MTBE as a Contaminant: with Field Data on a Release of Unleaded Fuel in an Unconfined Fractured Aquifer.

(Submitted in partial fulfilment
of an MSc. in Hydrogeology)

University College London
September 1993

Prepared by:
R.M. Symington, P.Geol.

Abstract

MTBE as a Contaminant: with Field Data on a Release of Unleaded Fuel in an Unconfined Fractured Aquifer.

MTBE is currently the fastest growing petrochemical in the world, and since its was introduction in as a fuel oxygenate in 1979, and can form up to 15% by volume of unleaded gasolines. Driven by environmental legislation the long term anticipated trend is to increased use of MTBE in unleaded fuels. MTBE is recalcitrant in the groundwater environment and, despite its relatively low toxicity, more work is needed on long term effects.

The chemical properties of MTBE differ from those of the BTEX components and have led to concerns about its behaviour in aquifers. MTBE is hydrophobic in a ternary system of MTBE, fuel, and water, and under aquifer conditions will concentrate approximately 80% in the free product phase. MTBE is an order of magnitude (27 times) more soluble than benzene and has been recorded to travel at the same rate as stable tracers (chlorides) in groundwater. Contrary to first indications, MTBE shows no cosolubility effects with the BTEX components. The weight of experimental evidence points to fact that MTBE is nonbiodegradable.

Aqueous phase MTBE contaminant plumes have been observed as a "halo" around the plume of aqueous phase BTEX and MTBE. MTBE is commonly the first of the fuel components to be detected and, due to its low toxicity in comparison to the aromatic, is a comparatively "good" indicator of fuel spill.

Field data on an MTBE fuel spill, and site conditions, are presented for an unconfined fractured chalk aquifer in south-eastern England. The data has been interpreted to provide a post mortem account of MTBE behaviour. The remediation efforts are documented and methods employed are evaluated with reference to a nearby public supply borehole.

Acknowledgement

I would like to thank the Anglian Region National Rivers Authority for their support and comments during the preparation of this thesis. In particular I would like to extend appreciation to the Brampton NRA Office for their help with the field sampling and in assembling the historical information, and the Research and Development Department, Anglian Region, NRA, for their contributions.

The cooperation of Anglian Waters and PSA (RAF Mildenhall) were greatly appreciated during the field sampling exercises.

Table of Contents

Table of Contents

Table of Contents

Appendix

List of Graphs

List of Figures

List of Tables

Introduction

UCL was contacted by the Anglian NRA in May, 1993, with a request to assign an MSc. Hydrogeology student to investigate MTBE as a contaminant, with reference to a release of unleaded fuel in an unconfined fractured aquifer. Four months were spent in the preparation of the thesis which involved a literature review on MTBE along with field sampling on the site of the contamination incident. The thesis is broken down into four sections.

Section 1)	MTBE as a Fuel Oxygenate: looks at current usage, driving forces behind current legislation, and the anticipated future of MTBE.
Section 2)	The Physical Properties of MTBE: reviews laboratory experiments conducted on MTBE, with interpretation of the physical properties as they apply to a groundwater contaminant.
Section 3)	MTBE as a Groundwater Contaminant: reviews one published incidence of MTBE unleaded fuel contamination and one experimental field data set on a planned release on MTBE unleaded fuel.
Section 4)	Field Study on the Beck Row MTBE Contamination: post-mortem analysis on a release on MTBE unleaded fuel with respect to contaminant migration, water remediation, site remediation techniques, and future investigation.

A summary and discussion is included at the start of each section. The raw data has been included in the Appendix.

1.1 MTBE as a Fuel Oxygenate

Summary and Discussion

Fuel oxygenates are defined as fuel additives which have a substantial molecular oxygen content, and can be sub-divided into two major categories, the alcohols and the ethers. Oxygenates were first introduced in the 1920's as octane boosters. During the 1970's leaded additives were phased out and oxygenates were looked at for increasing octane rating and overall fuel quality. During the 1980's and 1990's atmospheric legislation has driven the development of fuel oxygenates.

Currently ethanol based fuels account for 1% of fuel sales in the United States. Experiments with Methanol, with TBA as a cosolvent, were considered unsuccessful in the United States. MTBE is the only ether blended in U.S. fuels and is the only ether used extensively in the world.

The combustion of fuels containing oxygenates require less atmospheric oxygen and theoretical complete combustion of the fuel components. The result is a reduction of carbon monoxide (smog), nitrous oxides (ozone depletion), and unburnt hydrocarbons (deforestation). EEC atmospheric legislation has targeted vehicle emissions (25% of the total volatile organic emissions) in recent directives. Vapour pressure limits, controlling evaporative losses (10% of the total volatile organic emissions), have been left to member states. Current EEC directives on oxygenates as fuel additives have limits of 10% or 15% by volume of MTBE, with Britain conforming to 10% maximum by volume MTBE.

Refiner and automotive acceptance has driven the move towards MTBE from the alcohol additives. The corrosive nature and low water tolerance of the alcohols would require added expenditures in the areas of automotive construction and fuel distribution systems. The lower blended vapour pressure of MTBE when compared with methanol will also play a significant role pending British legislation on fuel volatility.

MTBE, since its introduction as a fuel oxygenate 1979, is the fastest growing petrochemical in the world and is manufactured in Britain at one refinery. Current British legislation allows up to 10% MTBE, although personal communication with industry representatives estimates current use to be less than 1% by volume. The long term trend is to increased use of MTBE in unleaded fuels in Britain.

1.2 Fuel Oxygenates

1.2.1 Definition of Fuel Oxygenates

Fuel Oxygenates can be divided into two major categories being the monoalcohols and the ethers. They are defined as fuel additives having a substantial molecular oxygen content.

The most important of the oxygenate additive groups are the alcohols and the ethers (Owen, 1990).

Table 1.2.1 Fuel Oxygenates (Owen, 1990)

Group	Substance	Oxygen Content (% wt mass)
Alcohols:	Methanol (MeOH)	49.9
	Ethanol (EtOH)	34.7
	Isopropanol (IPA)	26.6
	t-Butanol (TBA)	21.6
	Mixed C1 to C5 Alcohols	
Ethers:	Methyl tertiary Butyl Ether (MTBE)	18.2
	Tertiary amyl methyl ether (TAME)	15.7
	Ethyl tertiary butyl ether (ETBE)	
	Mixed ethers	

1.2.2 History of Fuel Oxygenates

Oxygenate compounds were first introduced in the 1920's as octane boosters in fuel, and consisted of blends of methanol or ethanol. With the advent of the energy crisis of the 1970's, and the introduction of environmental legislation phasing out the use of leaded compounds as anti-knock and octane enhancers, refiners began to look more closely at a variety of oxygenates as a means of extending the fuel supply. Oxygenates appeared to meet the demands of increasing the octane rating and overall fuel quality, and in part, by reducing the dependency on crude oil.

Through the 1980's and 1990's atmospheric emissions were targeted by the environmental community and were followed by introduction of catalytic converters and vehicle emission tests. A variety of oxygenate and oxygenate mixtures of ethers and alcohols are currently being laboratory and field tested for both automotive and environmental acceptance (Laing et al 1987).

1.2.3 Marketing of Oxygenates

During the 1980's the price of crude oil, and dependence on foreign supplies, led to the development of an ethanol program in the United States. Ethanol, produced from corn and feed grains, reached a plateau of 50,000 to 60,000 b/d, less than 1% of the overall market, prior to the collapse of oil prices in the mid 1980's (Unzelman 1991). Ethanol fuels are still available today and still account for less than 1% of the overall U.S. market share, predominantly in fleet vehicles (Owen 1990).

Methanol, with TBA as a cosolvent, was experiment with in the United States in the early 1980's but never gained large market acceptance, partly due to irresponsible downstream blending which resulted in a rash of stalled cars.

U.S. refiners have moved decisively in the direction of MTBE as the preferred oxygenate additive, and since the first MTBE plant came on line in 1979, production has increased dramatically. MTBE is currently the only ether blended in U.S. fuel (Unzelmen, 1991) and is the only ether used extensively in worldwide fuel blending.

1.2.4 Combustion of Oxygenates

Oxygenates require less atmospheric oxygen for complete hydrocarbon combustion as can be illustrated by the combustion of methanol and MTBE as compared with a n-heptane. Under ideal conditions the combustion of all hydrocarbons in the presence of oxygen will result in the production of carbon dioxide and water.

Table 1.2.4A Combustion of Oxygenates

Substance	**Combustion**
n-heptane	$C_7H_{16} + 11\ 0_2$ -> $7\ CO_2 + 8\ H_20$
methanol	$2\ CH_3OH + 3\ O_2$ -> $2\ CO_2 + 4\ H_2O$
MTBE	$2\ CH_3OC(CH_3)_3 + 15\ O_2$ -> $10\ CO_2 + 12\ H_20$

The ratio of oxygen to the hydrocarbon to give theoretically complete combustion is known as the stoichiometric ratio. Therefore as observed in the chart below that MTBE and methanol require less oxygen than a typical hydrocarbon fuel component.

Table 1.2.4B Stoichiometric Ratio of Oxygenate Combustion

Theoretical Oxygen Requirement for Complete Combustion

Per 100 grams	**grams Oxygen**
n-heptane	352
MTBE	273
Methanol	150

The addition of fuel oxygenates will therefore theoretically reduce the amount of nitrous oxides, carbon monoxide, and unburnt hydrocarbons. Purely from and oxygen content perspective methanol is seen to be the preferential additive over MTBE.

1.3 EEC Legislation

EEC regulations, both atmospheric and oxygenates as fuel additives, are the driving force behind the increased use of MTBE. Increasingly strict targets are being set by the EEC directorates and, subject to world oil price and fuel additive research, MTBE is the favoured choice.

1.3.1 EEC Regulations on Atmospheric Emissions

Fuel powered vehicles are the second largest source (after solvent evaporation) of volatile organic emissions in Europe. Fuel emissions are contributed from three sources in the following proportions:

Table 1.3.1 Volatile Atmospheric Emissions

Source	**% of Total Volatile Organic Emission**
1) Exhaust	25.0
2) Evaporative	10.0
3) Re-fuelling	1.8
4) Total	36.8

The EEC has adopted the emission regulations as laid down by the United Nations Economic Commission for Europe (UN-ECE), the main emission regulations being ECE 15. The result have been EEC directives 78/665 and 83/351 which have been signed by the member states. These regulations outline the target emissions for carbon monoxide, nitrous oxides, and hydrocarbons for fuel powered vehicles. These emissions have been identified as damaging to the environment with respect to smog, the ozone, and forests respectively.

The aim of the legislation has been to totally phase out leaded fuel sales, (West Germany and Luxembourg have already banned leaded gas). Tax incentives have been implemented by most countries to encourage unleaded use. In 1989 a 3.4% price differential in favour of unleaded over leaded fuels existed in the U.K. due to tax incentives (European 1989).

The atmospheric legislation lead directly to the EEC Directives on Oxygenates as Fuel Additives and will be the controlling factor on future developments on fuel oxygenates. One area not covered in the directives and left up to member states is the formulation of a policy on vapour pressure limits on fuel blends. This policy will play and important role in the choice of oxygenates. Strictly by volume MTBE could account for some 1.5% of the total volatile organic emissions.

1.3.2 EEC Directives on Oxygenates as Fuel Additives

The EEC Directive 85/536/EEC , sets allowable limits for the use of monoalcohols and ethers as oxygenate blending agents. Member states must permit fuels containing levels as laid down in column A of the table and may authorise proportions of oxygenates up to the levels of table B. Fuels containing in excess of column B must be clearly marked on dispensing pumps. The higher quantities of additives beyond column B may require changes to the carburettor/fuel-injection systems.

Table 1.3.2 EEC OXYGENATES LIMITS, DIRECTIVE 85/536/EEC

	A (% Volume)	B (% Volume)
Methanol[1]	3%	3%
Ethanol[2]	5%	5%
Isopropyl alcohol	5%	10%
TBA	7%	7%
Isobutyl alcohol	7%	10%
Ethers[3] (includes MTBE)	10%	15%
Other organic Oxygenates[4]	7%	10%
Mixture of any organic oxygenates[4]	2.5%[5]	2.5%[5]

1) Suitable stabilizing agents must be added in accordance with national or industry specifications.

2) Suitable stabilizing agents may be added in accordance with national or industry specifications.

3) Containing 5 or more carbon atoms per molecule.

4) Other organic oxygenates.

5) Oxygen weight, not exceeding the individual limits fixed for each of the above components.

The refining and marketing industry in the U.K. is currently conforming to the standards as laid out in column A.

1.4 Refiner and Automotive Acceptance

A comparison of oxygenates and especially MTBE verses Methanol has been extensively researched by the refiner and automotive industry from the aspects of storage, transport, drivability, and vapour pressure.

1.4.1 Materials Compatibility

Materials compatibility are concerned with the corrosive property of the oxygenate additives to automotive and storage facilities. The order of attack of some of the additives has been defined as (Laing 1987):

<---------increasing corrosion<--------

methanol > ethanol > TBA > MTBE

1.4.2 Distribution of Oxygenates

Methanol and ethanol both require cosolvents when used as fuel additives due to their shared problem of water tolerance. The alcohol additives will, in the presence of hydrocarbons, show a greater affinity for the water than for the hydrocarbons. If the distribution system is too wet the alcohols, and to a much lesser extent the ethers, will be leached out by free water and two distinct oxygenate-rich phases will form impairing the quality of the product (Lang 1987).

1.4.3 Drivability

All oxygenates showed acceptable levels of vehicle performance and were comparable in tests of i) anti-knock, ii) drivability iii)fuel economy iv) and v)inlet system cleanliness. Ether spirits could cause icing problems in improperly mixed and in older vehicles not containing thermostatically controlled intake control (Laing 1987).

1.4.4 Vapour Pressure

The industry standard test for fuel volatility is the Reid Vapour Pressure (RVP) test. Member states of the EC are permitted to set their own standards in this area, with Britain having no current policy. A base fuel was observed to have a volatility of about 9psi. MTBE blended in proportions of up to 20% by volume with the base fuel showed only a slight increase, or no change, from the RVP of the base fuel. Methanol blended in proportions of up to 20% by volume with the base fuel, showed a dramatic increase in the RVP to approximately 12psi, even at lower blending ratios of 2.5% (Owen 1990).

1.4.4 Methanol verses MTBE, Refiner and Automotive Acceptance

The debate continues between methanol based and MTBE based fuels as both exhibit different but desirable qualities. MTBE appears to be the definite winner over methanol for general purpose fuel sales. A summary of the major differences are:

1) MTBE is compatible with other hydrocarbons and requires no cosolvents to increase its water tolerance in the presence of other fuel components.

2) MTBE has a lower blended vapour pressure when compared with methanol, and will probably be more compatible with pending legislation on fuel volatility, especially in the summer months.

3) No engine modifications are required with MTBE as compared with higher content methanol blends.

4) MTBE can be handled and stored like any fuel component and does not require any special adaptations to a dryer distribution network.

5) MTBE is far less corrosive than methanol.

While methanol has shown itself to be a suitable fuel for fleet operations, MTBE is far more suited to all purpose general sales. The immediate future would appear to belong to MTBE and its continued growth in the U.K. is anticipated (MTBE File).

1.5 Manufacture, Production, Uses, and Fuel Content

1.5.1 Manufacture of MTBE

MTBE is produced by a number of commercial process, each process relies on a final reaction step that consists of reacting methanol with isobutylene. The reaction is reversible and exothermic (Lang, BP Research).

$$(CH_3)_2C{=}CH_2 + CH_3OH \rightarrow (CH_3)_3COCH_3$$

1.5.2 MTBE Production

MTBE is the fastest growing petrochemical in the world, pulling ahead of methanol which will become number two (OGJ Special; 1993). MTBE is currently the favoured choice in the United States and U.S. Refiners have moved decisively in the direction of MTBE as the preferred oxygenate for fuel blending. Production in 1991 had reached 118,000 b/d in U.S. refineries and projections indicate the capacity could reach 200,000 b/d by 1995 (Unzelman, 1991).

MTBE is produced in the U.K. at the Lindsey Oil Refinery in Killingholme, a 50/50 joint venture between Petrofina (U.K.) Ltd. and Total Oil (G.B) Ltd., with an estimated production of 2325 b/d (MTBE File). There are plans for numerous plants worldwide in anticipation of increasing demand for this fuel oxygenate.

1.5.3 Uses of MTBE

MTBE has three commercial uses i)fuel additive, ii)dissolution of gallstones in humans, and iii)as a carrier fluid in liquid chromatography. Almost all MTBE production is directed towards fuel additives.

1.5.4 MTBE content in Fuels

The content of MTBE in motor fuels varies widely depending on the refining process, blending properties of the basic fuel (ie: aromatic contents, etc), and legislative requirements. Fuels in Canada and the United States may contain, and will in most cases, up to the limit of 15% by volume MTBE. Fuels in the U.K. can be blended to 10% by volume MTBE, but are currently thought to be blended to less than 1% (Private Communication). No exact figures are available. Refiners are unwilling, and are not required, to release the exact blending properties of their products as this is considered to be proprietary information. The MTBE content of U.K. fuels is anticipated to follow the trend as established in North America and a maximum level of 15% will probably be attained in the future.

2.1 Physical Properties of MTBE

Summary and Discussion

The physical properties of MTBE differ from those of the BTEX components of fuel and lead to concerns about its behaviour under aquifer conditions. MTBE shows a solubility of 48,000 mg/l in water, 27 times that of benzene the most soluble aromatic. The solubility of MTBE is a reflection of the dipolar nature of the molecule (ie a more positive and negative end) which lead to concerns about its cosolubility effects on other fuel components.

Results of experimental data have indicated that the solubility of MTBE increases with decreasing temperature and at aquifer conditions a solubility of greater than 48,000 mg/l may be expected. No cosolubility effects were noted with the other BTEX components, and in fact, one set of data points to a slight decrease of the BTEX solubilities in the presence of MTBE. MTBE can be described as hydrophobic in a ternary system of water, fuel, and MTBE, and under aquifer conditions will concentrate approximately 80% in the fuel phase.

MTBE is an order of magnitude less volatile than the BTEX components of fuel and is therefore less susceptible to volatilisation techniques. The weight of experimental evidence, (three of four published experiments) points to the fact that MTBE is nonbiodegradable under aquifer conditions. MTBE is indicated to have a low carbon adsorption factor, and will adsorb only slightly to aquifer organic carbon. MTBE has a lower taste and odour threshold than the BTEX components of fuel.

Health studies are ongoing, although MTBE is currently classified as having a low toxicity. MTBE has been banned in Alaska due to its atmospheric persistence under cold climate conditions. A more comprehensive health study is expected to be available in 1993, published by the U.S. EPA.

The experimental evidence points to a persistent contaminant which will be recalcitrant under aquifer conditions. Due to its assumed low toxicity and low taste and odour detection thresholds, MTBE may be a "good" indicator of a spill of unleaded fuel.

Additional work is required in the area of biodegradation and health.

2.2 Basic Organic Chemistry

The binary solubility of organic compounds in water is a function of the temperature of the water and the nature of the organic substance. MTBE has a relatively high water solubility when compared with the aromatic components of fuel (27 times that of benzene, the most soluble). Solubility, volatilization, and cosolubility effects are all related, and can be estimated from the polarity of the solutes and the water solvent.

Table 2.2.A Binary Solubility of Selected Fuel Components
Solubility of some major gasoline components
binary equilibrium solubility in water at 25 C

	mg/l	**%**	**relative to benzene**
Methanol	Miscible in all proportions		
MTBE	48,000	4.8	27
benzene	1,780	0.18	1
toluene	515	0.05	0.3
m-xylene	170	0.02	0.1

(Data form API, 1985, Table 2-1 for BTX)

The binary solubility of organic compounds in water is a reflection of the dipolar moment of the organic compound. Water is a dipolar molecule as its centres of positive and negative charge do not coincide. The magnitude of this dipole movement can be measured and is a product of the magnitude of the charge times the distance between the centres of the charge and is reported in debye units (1.84 for water).

Ionic bonds are those formed between elements of widely different negativities and involve transfer of electrons form one atom to another. Of more interest to the organic chemist are the covalent bonds which involve the sharing of electrons. In the case of hydrogen each of the atoms involved is identical in electronegativity and we speak of a pure covalent bond. Between the extremes of ionic and pure covalent bonds are the polar covalent bonds. Polar covalent bonds involve the unequal sharing of electrons between atoms of intermediate differences in electronegativity. Polar covalent bonds cause molecules to exhibit more positive and negative ends, sometimes described as the partial ionic character, and form the basis of organic chemical interactions. Polarity is related to two physical properties which are boiling point and solubility of the substance in a particular solute (Brown 1972).

Table 2.2.B Boiling Point and Solubility of Selected Fuel Components

	Boiling Point (Centigrade)	**Solubility in Water (mg/l)**
Methanol	65	100%
MTBE	55	43,000
Benzene	80.1	1,780

As can be observed in table 2.2.B, the relationship of solubility to boiling point is not the only variable (molecular weight is also important), but can be used as a good relative indicator of expected behaviour. The properties of polarity, boiling point, and solubility are related by the type of forces which bring the molecules together. The two types are the dipole-dipole reactions and the much weaker van der Waals forces. Key to the dipole-dipole reactions are a special attractive force of hydrogen bonding, which are about 5% as strong as the average C-C, C-N, or C-O bonds.

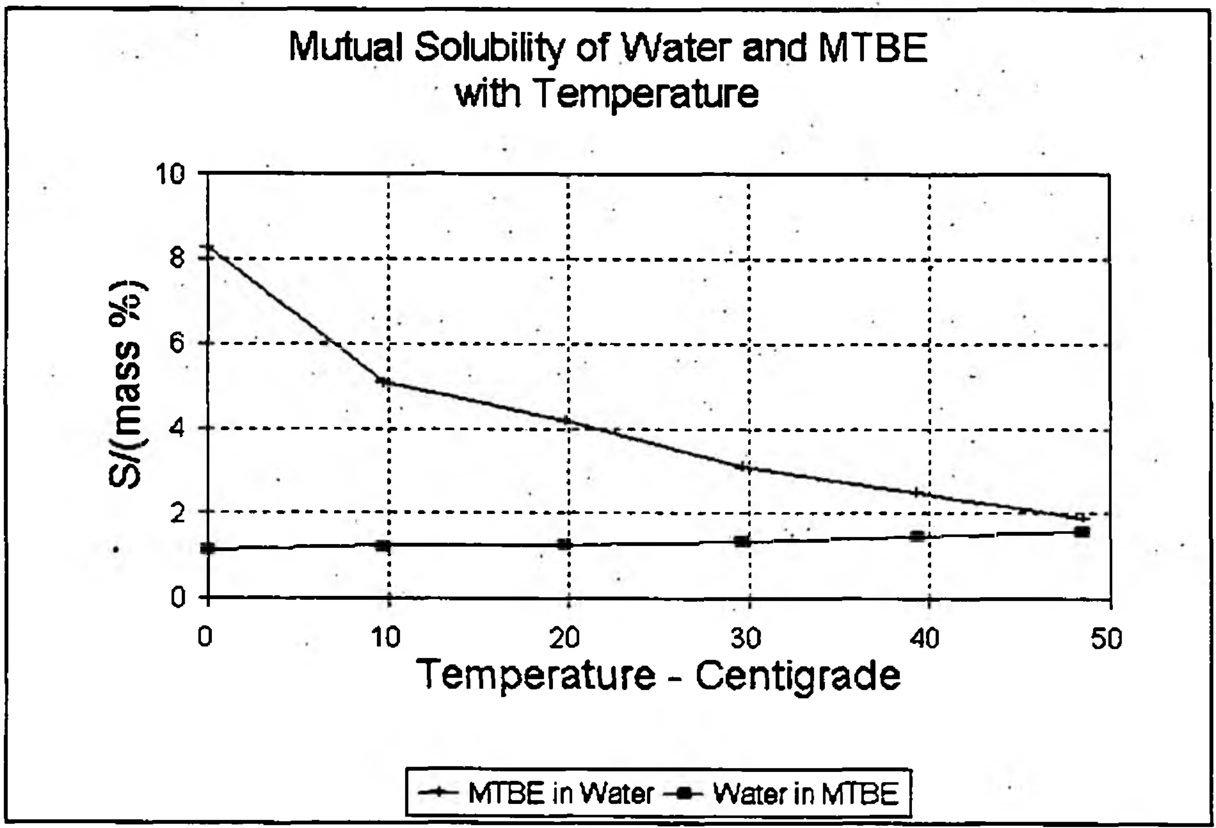
Strongly dipolar solutes, such as methanol, will dissolve completely in strongly dipolar solvents such as the mix of methanol and water. These two molecules are 100% soluble in each other in all proportions. MTBE is a less dipolar solute and is therefore only partly soluble in water, although far more than any of the aromatic components of fuel including benzene, the most soluble of the aromatic's.

No work on a dipolar measurement was discovered for MTBE.

2.2.1 Binary Solubility of MTBE and Water

The binary solubility of MTBE is often seen quoted in the text as 48,000 mg/l. This value has been calculated under laboratory conditions of standard temperature and pressure of 1 atmosphere and 20^0 centigrade (STP).

Aquifer conditions are never those of STP, and experimental data was found to exists for varying temperature, although no pressure experiments were documented. From graph 2.2.1 it is apparent that MTBE, like many compounds, exhibits increasing solubility with decreasing temperature. Thus under aquifer conditions we will expect to find increased solubility over the stated STP values. Graph 2.2.1 has been constructed from experimental data conducted under laboratory conditions (Stephenson 1992). The relationship of solubility to temperature appears to be exponential with solubility increasing dramatically toward the lower temperature ranges.



Graph 2.2.1 Binary Solubility of Water and MTBE with Temperature

2.2.2 Cosolubility of MTBE and Fuel Components

The binary relationships of solutes and solvents are relatively simple to determine from laboratory experiments. Due to the high binary solubility of MTBE with water it was postulated that the presence of this additive may increase the solubility of other components due to co-solvent effects (Garratt et al, 1986). As fuel is a complex mixture of over 200 organic compounds (Fetter 1992) the interrelationships of some, or all, of the components may result in unexpected changes in the solubility of an individual component. Analysis of fuel spills is often noted to be stated in terms of BTEX (benzene, toluene, ethylbenzene, and toluene) where in reality these components may only comprise 15% of the composition of the fuel.

Two experimental data sets were found for varying mixtures of MTBE and model fuels. The two data sets show a range of solubility of the components of mixtures of BTEX and MTBE. Both data sets show solubilities of the individual components to be with-in the binary solubility of the components. The difference may be attributable to the varying composition of the so called "model" fuels, including whether enough of each components was available to reach saturation. No cosolubility effects were identified.

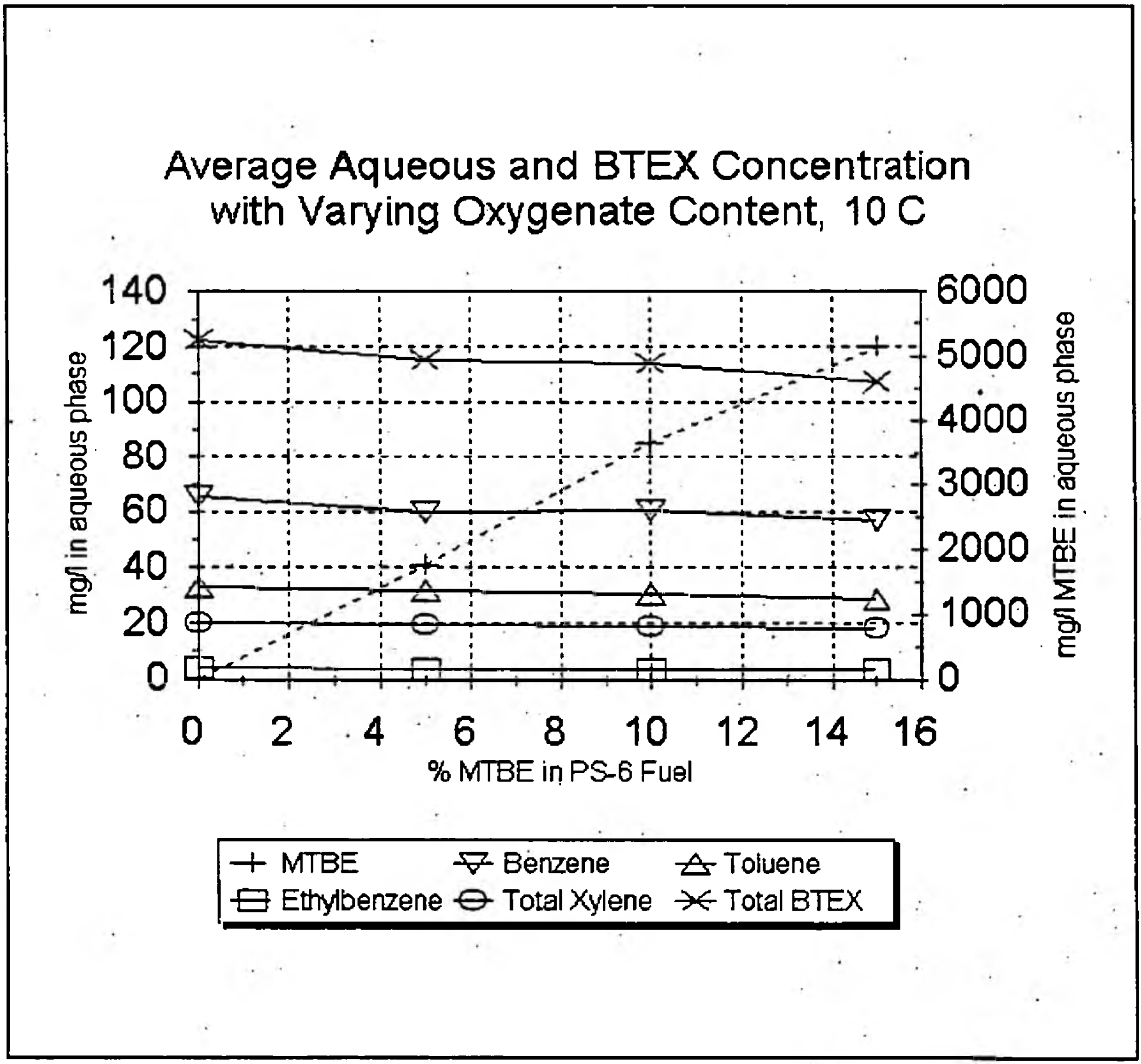
The reported decreased solubility of the BTEX components is most likely due to the strong polar nature of the MTBE over the BTEX components. The MTBE molecules, with their strong dipolar movement, will form dipolar bonds with the water molecules preferentially over the BTEX components forcing the BTEX components into the fuel phase (assuming both a water and aqueous phase are present).

2.2.3 Cosolubility Laboratory Experiments

Laboratory experiments have been conducted to determine the cosolubility effects of oxygenates on individual components and their mutual solubility in water. Several articles are available on the cosolubility effects of oxygenates, the most comprehensive being API Document 4531 on the Chemical Fate and Impact of Oxygenates in Groundwater: Solubility of BTEX from Gasoline-Oxygenate Compounds. Three separate lab experiments indicated that the presence of MTBE had either no effect, or actually decreased, the solubility of the components of gasoline (API Document 4531 1990, Groves 1988, and Cline et al 1991).

Graph 2.2.3 has been constructed for experimental data from the API Document 4531, 1991. The water:fuel ratio was 10:1 in all cases and the experiments were conducted several times and the results averaged. PS-6 is a standard reference unleaded gasoline with an average 15.139% by volume BTEX.

The analysis for all the BTEX components shows decreasing solubility with increasing MTBE content in the PS-6. For an initial MTBE concentration of 15% the aqueous solubility of the BTEX components was found to be 121.5 mg/l or 121,500 ppb.



Graph 2.2.3 Cosolubility of BTEX and MTBE Components at 10 C

Suflita et al 1993, conducted experiments with a model gasoline spiked with MTBE and brought into equilibrium with distilled water at 20° centigrade.The experimental data was matched against calculated data from the formula

$S = S_p * X_{eq}$ where

S = solubility of compound in equilibrium

S_p = solubility of pure compound in water

X_{eq}= molar fraction of gasoline phase at equilibrium

Table 2.2.3 Experimental and Calculated Aqueous Cosolubility of Fuel Components

Compound	Solubility Pure Compound (mg/l)	Calculated Solubility (mg/l)	Experimental Solubility (mg/l)	Percent of Model Fuel
Benzene	1780	175	146	8.6
Toluene	515	190	140	34.8
Ethylbenzene	152	25	26	17.4
o/m - xylene	186	61	61	34.8
naphthalene	31	1.2	3.8	4.4
Total		452.2	376.8	
MTBE	48000	766	867	

The solution was prepared from 920 ml distilled water, 0.89grams MTBE, 13.25 grams model gasoline.

Cline et al 1991, experimented in the lab with regular unleaded gasoline containing no oxygenated components which was then spiked up to concentrations of 11% by weight with MTBE. The concentrations of benzene and toluene measured in the aqueous phase showed typical analytical variations in concentration and were not enhanced by the higher percentage of additives. Cline postulates that MTBE is not expected to show co-solvent effects even at high fuel to water ratios.

Groves 1988, experimented in the lab with the aqueous solubility of benzene and n-hexane in the presence of MTBE. Experimental results showed that MTBE preferentially concentrates in the hydrocarbon phase and had little effect on the solubility of the hydrocarbons in water. The alcohols ethanol and methanol were also tested and were shown to dramatically increase the solubility of the aromatic.

2.3 Volatilization

Volatilization is a measure of the rate of evaporation of a liquid and plays an important role in the fate of fuel components in aqueous systems and in their remediation. Volatilization is usually stated in terms of HENRYS GAS CONSTANT, but may also be expressed in aqueous systems (measured at 1m below the water surface) as the half-life.

Table 2.3 Volatilization Constants of Selected Fuel Components

	Half Life in Aqueous Systems (minutes)	**Henrys Gas Constant (atm m3 * mol-1)**
MTBE	540[2]	4.5 * 10-4[2] to 8.9 * 10-4
Benzene	37.3[1]	
Toluene	30.6[1]	
O-xylene	38.8[1]	

[1] API, 1985
[2] Canadian 1986

Laboratory expressions of volatilization are difficult to apply to environmental conditions and may be affected by any of temperature, complex molecular associations, water agitation, etc. Treated as environmental indicators only we can draw the conclusions that MTBE is far less susceptible to volatilization, by an order of magnitude, than the aromatic or alcohol portions of gasoline.

2.3.1 Atmospheric Chemistry

MTBE emitted into the atmosphere will react slowly. Reported reaction rates are 4 days for MTBE in a typical summertime conditions (see Alaska in 2.8 Health). It is anticipated that the MTBE will disperse by dilution before it contributes to a spike in the ozone layer. The intermediate reaction product of MTBE is tertiary butyl formate which also has a low atmospheric reactivity.

Table 2.3.1 Reaction Rates of Selected Fuel Components in the Atmosphere

Compound	**Atmospheric Reactivity (OH) (10^{-12}cm^{3} molecule^{-1}second^{-1})**	**Estimated Atmospheric Half Life (Days)**
MTBE	2.8	4
Benzene	1.3	

(Bott et al 1992)

2.4 Biodegradation

Biodegradation in the ground is a result of a consortium of bacteria acting in unison under anaerobic or aerobic conditions. The normal products of anaerobic degradation will include carbon dioxide and methane, while the products of aerobic degradation will include carbon dioxide. The type of bacteria is normally not identified as the interrelationships are often too complex to be analyzed independently (West, 1993). In unconfined and confined aquifers the aromatic hydrocarbons (benzene, ethylbenzene, etc.) are readily biodegradable with studies are available identifying the types of microbes. Key to the statement on MTBE biodegradability is the understanding that different microbes will attack certain organic compounds while ignoring others (API 1985).

Ether compounds in general are reported to be difficult to degrade and MTBE appears to be recalcitrant under aerobic and anaerobic conditions. Of the four references to the biodegradation of MTBE, one unpublished report referenced by Bott et al 1992, would indicate it to be degradable. The weight of evidence supports the fact that MTBE is nonbiodegradable although additional research in this area is needed to identify the microbes in the test mediums.

2.4.1 Aerobic Biodegradation

Jenson et al 1990, experimented in the laboratory with MTBE in a solution containing aromatic with four types of inoculation material. (top soil, a sandy aquifer material, and two types of activated sludge). A comparison was made under aerobic conditions at 20 degrees centigrade with a solution of MTBE with water in equilibrium with a model gasoline PS-6 (see Appendix 1). No biodegradation of a solution of 10 mg/l MTBE and 3.5 mg/l aromatic was observed for the sandy aquifer or top soil/activated sludge was noted over 40 and 60 days respectively. Tests were done on solutions of 0, 4, 40, and 200 mg/l MTBE, with the latter solution exhibiting signs of weak inhibitory effect on the bacteria.

Experimental field data compiled by Barker et al 1990, involved the injection of gasoline-contacted water along with i) 85% methanol, ii) 15 % MTBE, and iii) no additives. The MTBE was found to be recalcitrant after 476 days, with no inhibitive effect on the rate of disappearance of the aromatic fractions.

Bott et al 1992, has indicated that MTBE is biodegradable in a well climated system. Bott's reference is an unpublished study by The Petroleum Environment Research Forum, Project 90-10, 1992, in which MTBE solutions were added to a base containing bacteria and organic food under laboratory conditions. The samples ranged from 0% to 100% MTBE, with the 0% used as control, the decreased dissolved oxygen measured is used as an indicator of increased biodegradation of the test material in addition to the base organic food. The samples were held at 20 degrees centigrade for 3 days prior to measurement. Graphs of the tests show decreasing dissolved oxygen indicating that biodegradation has occurred. At 1700 ppm, or about 35 % of the solution, the oxygen intake diminished and bacterial inhibition would appear to have occurred (see Figure 1 and 2). No measurement of the MTBE remaining in solution appears to have been attempted nor have the types of bacteria been identified.

2.4.2 Anaerobic Biodegradation

Suflita et al 1993, tested MTBE and other oxygenates as to their biodegradation using sediment and groundwater from an anoxic aquifer polluted with municipal landfill leachate. Slurries of 50 gm of sediment along with 75 ml of groundwater were prepared and each oxygenate added to a concentration of 50mg/l. The solutions were incubated in the dark at room temperature in 160 ml serum bottles. The bottles were sealed with teflon lined stoppers and resultant pressure, from the formation of biogas (methane and carbon dioxide) were measured by transducer. The containers were incubated until the pressure stabilized (see Table 2). MTBE showed no biodegradation after an acclimation period 182 days testifying to its persistence under anaerobic conditions.

2.5 Detection Threshold

2.5.1 Chemical Analysis

Analysis for MTBE can be performed by head space gas chromatography or high pressure liquid chromatography. Detection limits by the latter method have been identified at the NRA Peterborough as <.*ug*/l (<.1ppb).

2.5.2 Odour Threshold

MTBE has been described as foul smelling and malodorous with an odour threshold of 680 ppb (Angle, 1991). The author, and MSc. Hydrogeology classmates (UCL, 1993), nasally challenged a 99.9% solution of MTBE and defined the odour as "medicinal and ether-like" and, although strong smelling, not a particularly unpleasant aroma. Other descriptions found included pleasant hydrocarbon odour, slight terpene-like, and mint-like (IWD, 1991). Odour is a subjective sense, although it is agreed that the usual first indicator of MTBE contamination will come from odour or taste tests. Due to the low toxic properties of MTBE verses the aromatic portions of gasoline, the aroma of the MTBE will be a good first indicator of groundwater contamination by fuels, a side benefit of this contaminant.

2.5.3 Taste Threshold

No research data on taste threshold was found in the literature. David Tester (NRA) reported in correspondence that MTBE is detectable in concentrations of 2 - 3 *u*g/l and personal communication indicated a threshold of 6 *ug*/l.,

2.6 Partition Coefficient

2.6.1 Octanol-Water Partition Coefficient (Kow)

The Octanol-Water Partition Coefficient (Kow) is a measure of how hydrophobic a compound is and is determined from experimental data. A compound is added to a mixture of n-octanol and water and shaken, the proportion of the compound which dissolves into each phase is measured. The co-efficient is taken to be the ratio of $C_{octanol}/C_{water}$ and is usually expressed as a log value in reference books (Fetter, 1993).

Table 2.6.1 Octanol-Water Coefficient for MTBE

Kow Values MTBE	**Source**
1.30	Veith et al 1983a
1.24	Fujiwara et al 1984
1.06	Veith et al 1983b
0.94	Funasaki, 1985
1.135	Mean Value
0.94 - 1.30	Range

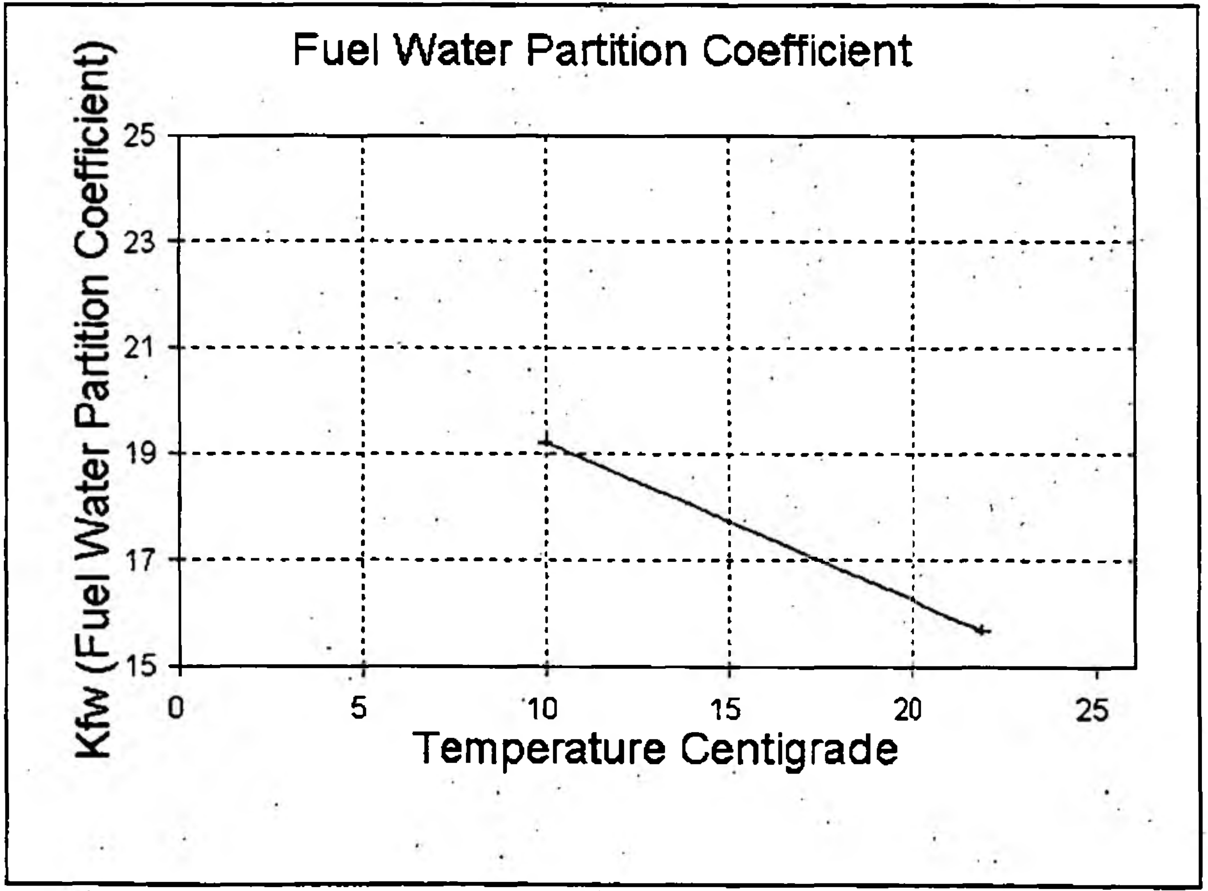
Koc (Organic Carbon) may be mathematically derived from the Kow values.

2.6.2 Fuel-Water Partition Coefficient

MTBE preferentially concentrates in the fuel component over the aqueous phase. This relationship has been quantified in the laboratory and is shown to be temperature dependant. The lower the temperature, the more the MTBE will preferentially partition into the fuel phase. Graph 2.6.2 illustrates this relationship. Although only two data points are plotted, an inferred trend exists. The data has been taken from separate experiments conducted at different temperatures.

The demonstrated relationship shows agreement with data on solubility of binary phase water and MTBE solutions. Thus, at aquifer temperatures, we will expect approximately 80% of the MTBE to remain in the fuel phase.

1)Kfw 15.5 at 22 C, Fuel Water Ratio 20:1 (Cline et al, 1991)
2)Kfw 19.2 at 10 C, Fuel Water Ratio 10:1 (API 4531, 1991)*
*Note: Assumes saturation in aqueous phase.



Graph 2.6.2 Fuel Water Partition Coefficient

2.7 Adsorption by Activated Carbon

Two references concerning laboratory experiments were found relating to activated charcoal adsorption.

Illet et al, 1990, investigated the adsorption of MTBE to activated charcoal in research directed toward the medical community. This study indicated that maximum adsorption occurred, approximately 96%, at a Charcoal:MTBE ratio of between 6:1 and 8:1. Maximum desorption, by washing with distilled water, was estimated at 3.2%,

The API document 4497, 1991, quotes a figure of maximum absorbtion capacity for MTBE of 0.004 grams organic/ 1.0 gram carbon compared with a BTX adsorption capacity of 0.03 grams organic/ 1.0 gram carbon, a difference of an order of magnitude.

2.8 Human Health

The initial effects of a case of acute exposure to MTBE vapours would be anaesthetic with some respiratory irritation (26,300 to 33,000ppm). Initial experiments have concluded that MTBE has a low toxicity with adverse effects only occurring at very high levels, beyond what might be expected from refuelling of vehicles (public exposure).

Experiments conducted with laboratory animals show no mutagenic properties or permanent neural damage. Exposure may result in moderate reddening of the skin (liquid) and transient eye irritation (vapour). Experiments are ongoing in the areas of birth defects and oncogenicity (cancer).

MTBE is readily absorbed by inhalation, oral, dermal, and intravenous routes and is rapidly eliminated in the exhaled air or metabolized to TBA (tertiary butyl alcohol). The TBA breaks down into 2-methyl-1,2-propanediol and a-hydroxyisobutyric acid and is excreted in urine. The complete breakdown of MTBE is not identified (Duffy et al 1992).

MTBE has been banned in Alaska as of December, 1992, because of reported headaches, nausea, and breathing difficulties, after driving or refuelling their cars (Crow 1993). The effects of MTBE exposure will first be observed to effect the Central Nervous System with the above symptoms.

Table 2.8.A Acute Toxicity Data Summary

Toxicity Assay	Data	Toxicity Ranking
Oral LD50	3.0-3.8 g/kg body weight	Low
Dermal LD50	>10g/kg body weight	Very Low
Inhalation LC50	23,630 - 33,000 ppm	Very Low
Skin Irritation	Moderate Reddening	Not a Primary Irritant
Eye Irritation	Transient Effects	No Irreversible Effects
Skin Sensitization	Response	Not a Skin Sensitizer

(Duffy et al 1992)

2.8.1 Drinking Water Standards

No official drinking water standards were discovered for MTBE in British, EC, or United Sates legislation.

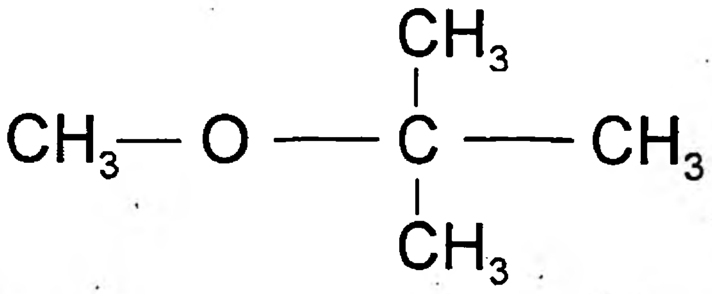
Table 2.8.1 Recomended Drinking Water Standards MTBE

MTBE(*ug/l*)	Authority
200	Hardly et al 1990, Tulsa University Medical Centre
50	Garratt et al 1986, State Toxicologist for Maine, U.S.A
5	Anglian Water Authority

2.9 Common Names and Chemical Struture

MTBE	Methyl tertiary Butyl Ether
TBME	tertiary Butyl Methyl Ether

2-Methoxy-2-methylpropane



$$CH_3 - O - \underset{CH_3}{\overset{CH_3}{C}} - CH_3$$

2.10 Summary of Physical Properties

Physical State:	Liquid	(The Merck Index 1989)
Colour:	Colourless	(The Merck Index 1989)
Odour Threshold:	680*ug*/l, 680ppb	(Angle C.R., 1991)
Taste Threshold:	2 - 3 *ug*/l	
Water Solubility:	48 g/100g 20 C	(The Merck Index, 1989)
Cosolubility Effect	Non cosolubility effect.	(Stephenson R.M., 1992).
Density:	0.7404 g/ml @20 C	(The Merck Index, 1989)
Vapour Pressure:	32.66 kpa @ 25 C	(The Merck Index, 1989)
Aqueous Half Life:	540 minutes	
Adsorbtion:	0.004 grams organic per 1.0 gram activated carbon	(API 1991)
Henrys Law Constant:	4.5 E10-4(atm*m3*mol-1)	(USA EPA 1986)
Molecular Mass:	88.15	(The Merck Index, 1989)
Melting Point:	-110 C	(The Merck Index, 1989)
Boiling Point:	55C	(The Merck Index, 1989)
Log Octanol/Water Partition Co-efficient (Kow):	0.94 - 1.30	
Log Fuel Water Partition Co-efficient (Kfw):	15.5 at 22 C	(Cline et al 1991)
Drinking Water Standards:		
EEC, WHO, EPA:	None	
Recommendations:	200 ppb	(Hartly et al 1992)
	50 ppb	(Garrett et al 1986)
	5 ppb	(Anglian Water)
Biodegradation		
Aerobic:	Weight of evidence points to Nonbiodegradable	
Anaerobic:	Nonbiodegradable	
Atmospheric		
Half Life:	4 days under summer conditions	
Reactivity (OH):	$2.8 * 10^{-12} cm^3 molecule^{-1} second^{-1}$	

3.1 MTBE as a Groundwater Contaminant

Summary and Discussion

Field data on an MTBE contamination incident shows a "halo" of MTBE is observed developing around the plume of the MTBE and BTEX components which result from the release of unleaded fuel. Field experimental data using conservative tracers has shown that MTBE is recalcitrant in the environment over 476 days and that MTBE travels in groundwater at the same rate as conservative tracers.

The development of the contaminant "halo" testifies to the mobility and persistence of MTBE in the environment. MTBE will most likely be the first of the fuel components to be detected, due to its higher mobility when compared with the other fuel components and its low taste and odour detection threshold. MTBE will then be a comparatively "good" early warning indicator of an unleaded fuel spill due to its low toxicity in comparison to the BTEX components.

As MTBE concentrates 80% in the fuel phase the effectiveness of remediation of MTBE contaminated sites will be controlled by the ability of the remediation system to recover the free product phase. Pump and Treat remediation of MTBE will be limited by the recovery of the floating free product phase and will not recover the MTBE partitioned in the fuel phase "bound" or "held" in the aquifer. Some form of Volatilization Extraction Techniques will prove more successful in remediation of the "bound" and "held" fuel phase components, and therefore the MTBE. The best remediation effort will probably involve a combination of the two systems, relying on the Pump and Treat to contain the contaminants and Volatilization Extraction to remove the remaining fuel phase

Remediation of the contaminated water is best undertaken by volatilization techniques, such as air sparging. Due to the early breakthrough of the MTBE verses the fuel components, activated carbon treatment, is an expensive option.

3.2 MTBE in a Contaminant Plume

3.2.1 Field Data on MTBE in a Contaminant Plume

Field data presented by Garrett et al 1986, shows the development of a contaminant plume in an unconfined sand aquifer (see figure 3.2.1). The plume has been subdivided into three phases, MTBE only, MTBE and Fuel Components, and Free Product phase. The MTBE plume has travelled the greatest distance and can be observed as a halo around the MTBE and Fuel Component plume. Given the mobility of MTBE in the environment this type of plume is considered to be typical of MTBE unleaded fuel spills. The first indicator of these spills will probably be the detection of MTBE, by smell, odour, or chemical analysis. Given the low toxicity of MTBE over the aromatic portions of the fuel, this effect will be of benefit in early detection of fuel spills.

3.2.2 Cosolubility in Field Data on MTBE in a Contaminant Plume

MTBE can be the largest single component of any fuel spill with up to 15% by volume. Only limited field data was found on actual contamination sites, and has created some confusion as to the cosolubility. Garrett et al 1986 indicated that the solubility of the aromatic constituents was increased by an order of magnitude in his study of a contaminated site in Maine.

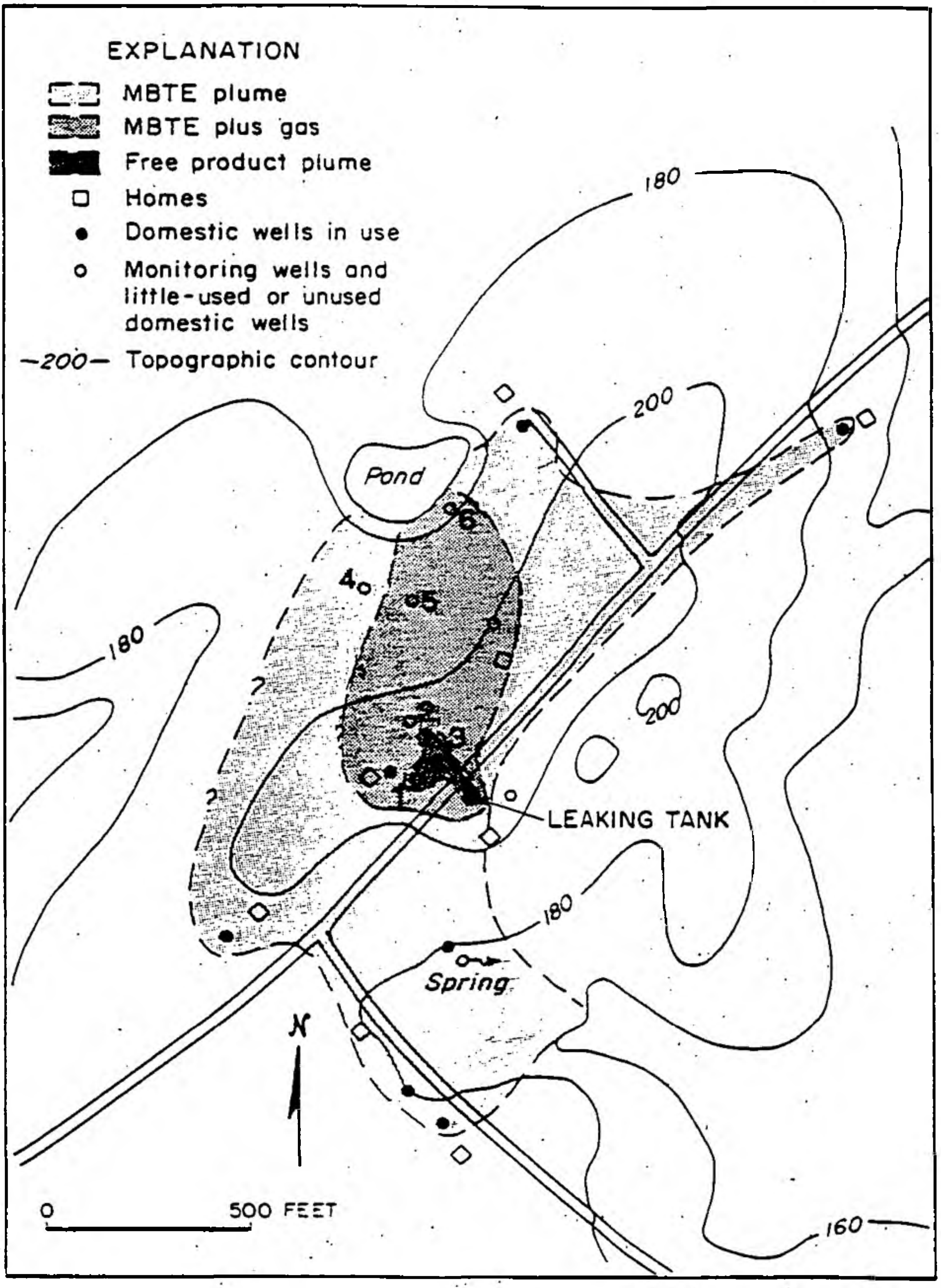
Field data collected from a variety of contaminated sites in Maine, USA, Garrett et al 1986, cited incidence of total gasoline contamination exceeding 600,000 ppb compared to a usual maximin contamination level of 10,000 to 30,000 ppb. One "hot spot" of contamination was described as a water table sample taken from a shallow dug well in a sand aquifer which had a floating free product layer. No breakdown of the fuel components were given in the analysis, nor was an aquifer temperature given. The MTBE to be included in the reported fuel analysis. Analysis of up to 236,000 ppb MTBE and 304,069 ppb Gasoline (with or with-out MTBE?) were also reported at a separate site.

Table 3.2.2 Experimental and Field Values for Solubility and Cosolubility

	Highest Values	**Experimental Value**	
	Garrett et al 1986	Suflita et al 1993	API Document 4531
Total Fuel	600.00 mg/l	1243.8 mg/l	1870.9 mg/l
MTBE	236.25 mg/l	867.0 mg/l	1755.5 mg/l

The field data fits with-in the experimental range for MTBE and MTBE unleaded fuels. The reporting method of Garret et al 1986, total fuel rather than by component, is confusing. No evidence of cosolubility effects could be derived from this paper.

Figure 3.2.1 MTBE in an Unleaded Fuel Contaminant Plume (Garrett et al 1986)

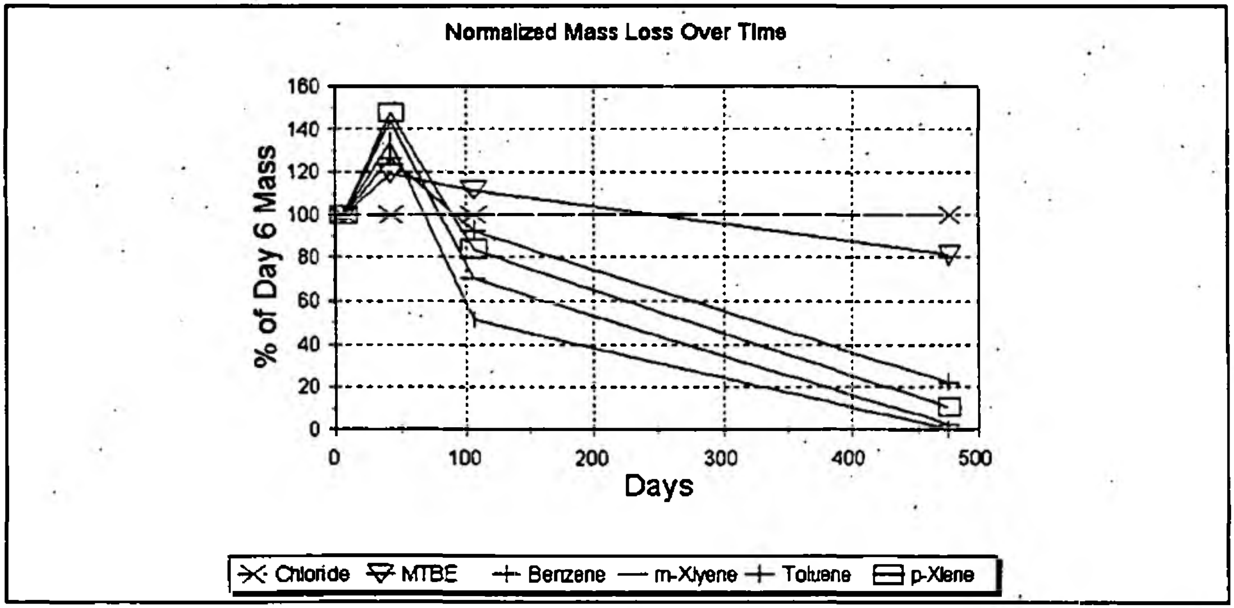


3.2.3 Experimental Data on Contaminant Plumes

Barker et al 1990, conducted plume experiments at Camp Borden, Ontario, Canada with PS-6 Fuel (see Appendix D) and PS-6 Fuel spiked with Methanol (85%) and MTBE (15%) in an aqueous phase solution of 10:1 water to fuel. The sample slugs were injected into a line of three parallel boreholes at right angles to the groundwater flow direction into an unconfined aerobic sand aquifer. Chlorides were injected into each of the plumes as a conservative tracer. Samples were taken periodically from a dense network (0.5m) of multilevel piezometers.

Figure 3.2.2 shows a series of cross sectional values for MTBE, Chlorides, Benzene, and p-Xylene, along a flowline. The flow direction is from right to left across the site, with scaling ticks every 10m. The vertical scale is from 0 - 6 m depth, with scaling ticks every 1 m. The scaling of the contours Is mg/l for the MTBE and Chlorides and ug/l for the Benzene and p-Xylene. The snapshot was taken at a time of 476 days form injection of the sample slugs.

Mass balance on the MTBE were derived form the contours of the MTBE verses the Chlorides (conservative tracer). The MTBE mass decline was noted to be only slightly less (50% for Chlorides verses 37% for MTBE) than the Chlorides testifying to its recalcitrance under unconfined aquifer conditions.



Graph 3.2.3 Barker et al 1990

Figure 3.2.3 Distribution of MTBE and Selected Components along a Flowline (Barker et al 1990)

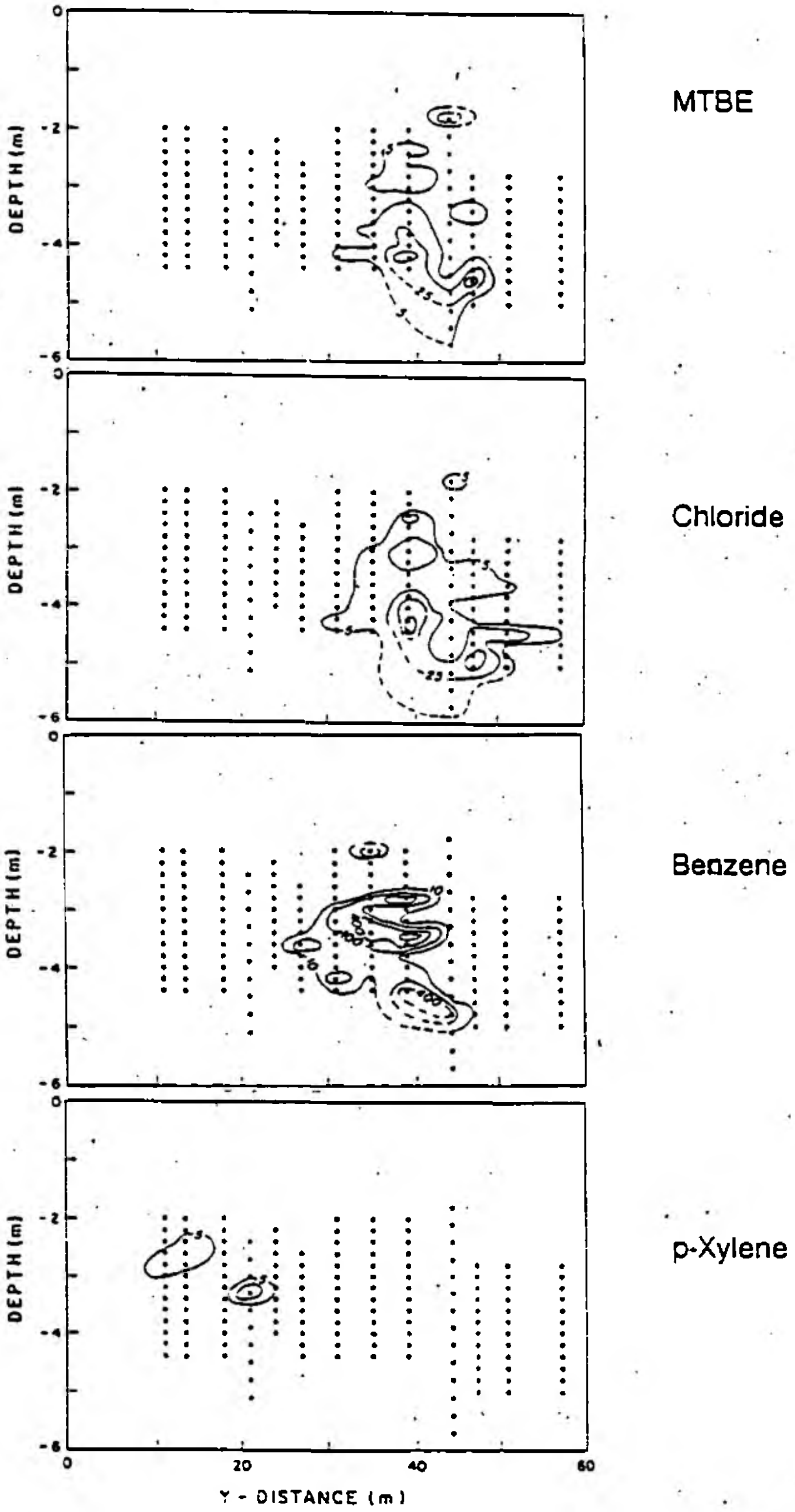


Figure 6. The distribution of selected solutes in the MTBE plume, shown in cross-section. Contours for MTBE and chloride are in mg/L; for monoaromatics: ug/L. The cross-section is indicated as AA' in Figure 3.

3.3 In-Situ Remediation of MTBE Contamination

3.3.1 Pump and Treat

Pump and Treat methods rely on the development of a negative hydraulic gradient towards a pumping well or trench to contain contaminant migration The pumped contaminated water is retrieved and treated in a conventional manner. The free product phase, in any, will migrate towards the well or trench, and can be recovered with skimming pumps or similar technology.

MTBE is hydrophillic in a binary phase (water-MTBE) and is hydrophobic in a ternary system (fuel-water-MTBE) and will preferentially concentrate in the fuel phase. The MTBE will remain, approximately 80%, in the fuel phase and its remediation will be closely tied to the recovery of the free product phase of the fuel spill. The fuel phase will exist in the aquifer and overburden in intergranular pore space, caught in fractures, pooled on lenses of impermeable material, and as free product on the water table. The recovery of MTBE will then be dependant on the recovery of the free product phase. Pump and treat is limited to recovering free product on the water table and aqueous phase contaminants.

The Pump and Treat remediation is a slow process and may take tens of years before site cleanup has been achieved (Mackay et al 1989). This type of technology is limited by aquifer properties including transmissivity. No data on pump and treat remediation of MTBE contamination was found.

3.3.2 Volatilization Extraction Techniques

The process of volatilization comprises the basis of several common techniques of remediation. These include vapour extraction in the unsaturated zone, combined vapour extraction and air injection in the unsaturated zone, and combined vapour extraction and air injection in the saturated zone. These techniques do not restrict contaminant migration but are extremely effective in the remediation of fuel phase components unavailable to pump and treat methods. The vapours phase recovered are collected and can either be emitted to the atmosphere or passed through an air scrubber to remove the volatile components. Sites with volatalization techniques show a faster rate of remediation of the fuel phase contaminants held in the aquifer and unavailable to pump and treat methods, and have been applied successfully in the release of fuels in aquifers (Domenico et al 1990).

The effectiveness of this technique is limited by hydrogeologic characteristics and the rate of volatilization of the contaminant. MTBE is less volatile by an order of magnitude than the aromatic portions of gasoline and will be less susceptible to olatilization. No field data on volatilization remediation was available for MTBE.

3.3.3 Bioremediation

The weight of experimental evidence indicates that MTBE is nonbiodegradable, thus any bioremediation methods are inferred to be ineffective.

3.4 Remediation of MTBE Contaminated Water

3.4.1 Activated Carbon Filtering

The API Document 4497 quotes a figure of maximum absorbtion capacity of 0.004 grams organic/ 1.0 gram carbon verses 0.03 grams organic/ 1.0 gram carbon. The only documented case of activated carbon treatment was found in API Document 4525 with a reported MTBE removal of 87.2%.

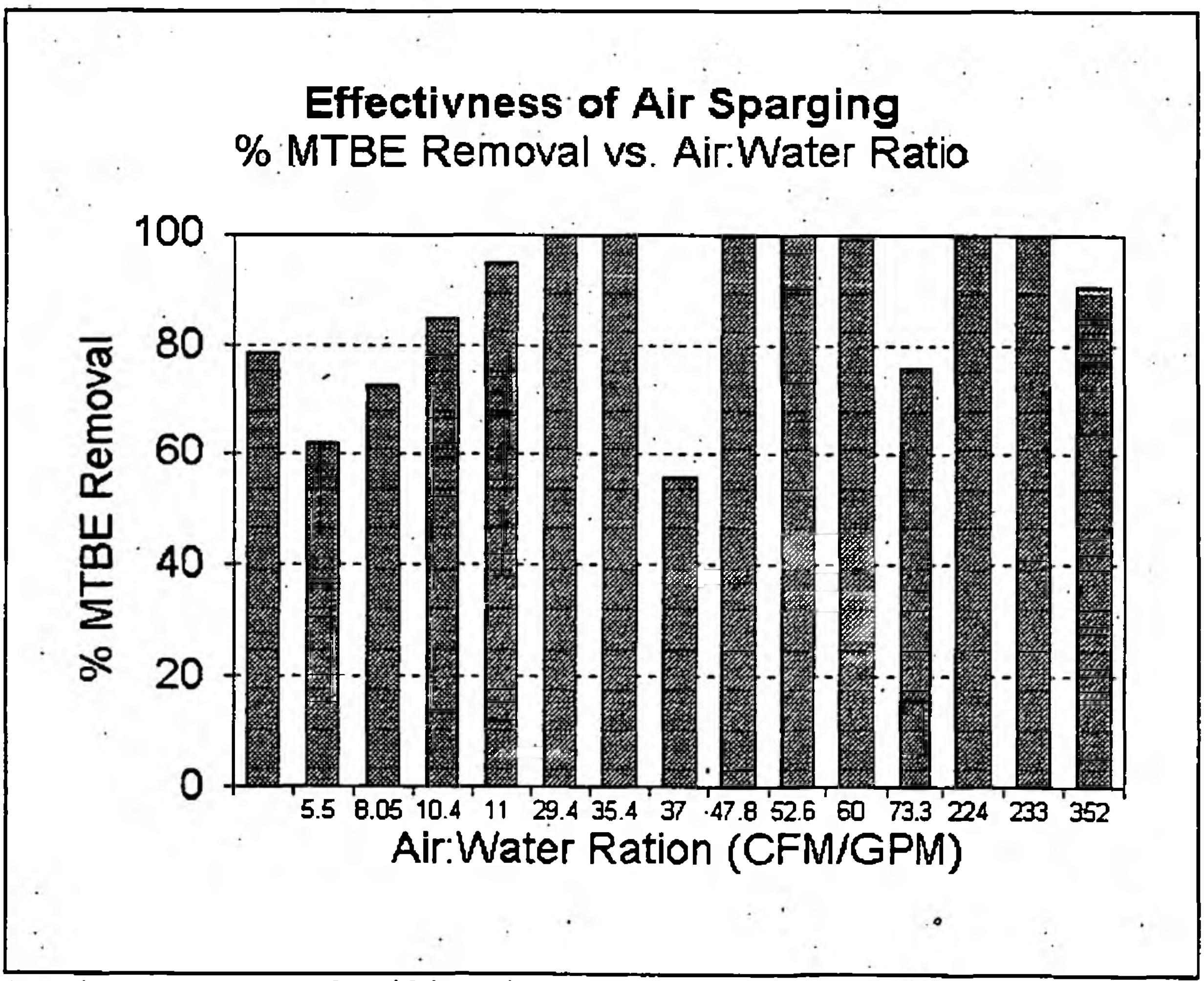
Because of the low absorption properties of MTBE and ,subsequent early break through when compared with the other fuel components, activated carbon filtering is considered an expensive option over volatilization techniques.

3.4.2 Volatilization

MTBE removal by air stripping systems have been well documented in the API Document 4525, November 1990. This document is a compilation of data from fifty seven anonymous sites in the United States. The graph 3.4.2 is a plot of air/water flow rates to percentage MTBE removal. MTBE removal varied in these systems from 55.6% to 99.9% with a median value of 91% averaged from the fifteen sites. Almost all systems achieved a high degree of removal of dissolved VOC's, with benzene removal normally at 99% or more.

Because of multiple factors including system design, flow rates, fouling, water temperature, and others no clear trend could be established of air:water ratios.

Volatalization remediation methods have been established to be the most cost effective form of contaminated water remediation (API 4525 1990).



Graph 3.4.2 Volatilization of MTBE by Air Sparging

4.1 Field Study on the Beck Row MTBE Contamination

Summary and Discussion

The Beck Row Site was contaminated in 1988 by a release of MTBE unleaded fuel from an underground storage tank. The release was detected at public supply boreholes in 1989. Remediation efforts included the installation of a Pump and Treat system in 1991 (to contain the contaminant migration) and expansion of Air Sparging facilities at the public supply borehole (to treat the contaminated water). Additional observation boreholes, in addition to pre-existing observation boreholes, were drilled in 1992 for the purposes of an investigation into MTBE.

The Beck Row Abstraction Borehole is a high efficiency well producing at rates of between 3,500 and 9,500 m^3/d from the unconfined Lower Chalk aquifer. The aquifer exhibits extremely high transmissivities in the range of 5000 to 25000 m^2/d from a well developed fissure system. The regional flow directions are from SE to NW, with site flow directions controlled by pumping practices at the Beck Row Site

The results of chemical analysis from field sampling conducted from 1988 to 1993, were combined with analysis from three sampling runs undertaken for this study Post-mortem analysis was conducted on fuel phase migration, aqueous phase migration, and remediation efforts with emphasis on MTBE. Time slices of the contaminant migration were prepared and mass balance calculated for remediated contaminants. The location of the remaining contaminants is inferred from site geology and analysis of contaminant levels.

The results of the study have been examined to produce recommendations on the Beck Row Site with respect to the remediation of the site and effectiveness of the remediation methods with regards to MTBE. The recommendations reflect the understanding of the behaviour of MTBE gained from research into the physical properties of MTBE and experimental and field data on MTBE migration. The recommendations include future work which could be conducted at the Beck Row site to better understand MTBE as a groundwater contaminant.

Figures relating to section 4 are contained in Appendix A, regression analysis results are contained in Appendix B.

4.1.1 Site Remediation Efforts at Beck Row

i) the remediation boreholes were only partially effective in containing the aqueous phase contaminants, including MTBE.

ii) the remediation boreholes were unsuccessful in attracting the floating product phase for several reasons (see text).

iii) the effectiveness of pump and treat systems regarding MTBE is limited by the ability of the system to recover the fuel phase "bound" or "held" in the aquifer and overburden.

iv) pumping from the Remediation Boreholes should be continued as regression analysis indicates that endpoint of MTBE remediation has not been reached.

v) a scavenger pump should be installed at Remediation Borehole 101.

vi) sampling should continue at regular intervals.

4.1.2 Remediation of Contaminated Water

i) the air sparging systems are the most cost effective method of MTBE contaminated water.

ii) activated carbon systems are an expensive option for MTBE due to its low adsorption factor.

4.1.3 Future of Contaminants at Beck Row

i) almost half the estimated released fuel is thought to be "held" or "bound" in the aquifer or overburden and will release slowly over time.

ii) levels of MTBE in the Beck Row raw water are inferred to remain at their current levels, and will rise slightly during periods of high water table (spring).

4.1.4 MTBE as a Contaminant

i) MTBE exhibits a persistent nature in comparison to the BTEX components.

ii) the MTBE plume exhibits little retardation comparison to the BTEX components and is consistent with the "halo" effect observed in field and experimental plumes of MTBE unleaded fuels.

4.1.5 Remediation of MTBE

i) the remediation of MTBE by Pump and Treat is limited by the ability of the system to remediate the fuel phase.

ii) volatilization extraction techniques are more effective in remediation the fuel phase "held" in the aquifer, and therefore the MTBE.

iii) the remediation of MTBE unleaded fuel contamination will best be approached by a combination of Pump and Treat (to contain the contaminants) and Volatilization Extraction Techniques (to remediate the fuel phase "held" in the aquifer).

4.1.6 Future Investigations of MTBE as a Contaminant

i) the Beck Row Site is a good location for continued investigation of MTBE as a contaminant due the shallow depth of investigation, number of observation boreholes, and amount of historic information.

ii) a shallow coring program is recommended to investigate the diffusion of MTBE into the chalk matrix, adsorption sites, and biodegredation.

iii) a second gas survey would aid in confirmation of the location of the free product phase and siting of core boreholes.

4.2 Beck Row Site History

	Date	Event
1)	1981	Anglian Water ceases abstraction at Beck Row due to prior contamination incidence.
2)	1988	Unleaded fuel containing MTBE first sold at aafes from one of the three 5000 gallon storage tanks (specific tank not identified).
3)	April/May 1989	New fuel pumps installed at aafes site. Fibreglass "boxes" installed over fuel storage tanks. New remote delivery point installed and buried delivery pipes installed for all three tanks. Two of three tanks now used for unleaded fuel storage.
4)	May 25/ 1989	Anglian Water resumes abstraction from Beck Row at approximately 9,500 m^3/d. Air stripping and carbon adsorption systems installed.
5)	March 31/ 1990	Anglian Water reduces abstraction rate at Beck Row from 9,500 to 3,500 m^3/d due inability of treatment systems to handle contaminant levels.
6)	April 2/90	PSA notified of MTBE in water by NRA. 10-15 *ug/l* raw water and 8-10 *ug/l* treated water.
7)	April 3/1990	DWO receives letter from AW confirming MTBE in water.
8)	April 9/1990	AW and PSA take groundwater samples.
9)	April 9-17/ 1990	NRA samples Anglian Waters Auger Holes for MTBE.
10)	April 9/1990	AW notifies DOE Water Quality Inspectorate.
11)	April 11-17, 1990	Scavenger pump installed at AH 4A, No details given pumping practices. Discharge to sewage works.
11)	April 30/1990	PSA take additional samples.
12)	April 30/1990	PSA receives LGC results.

	Date	Event
13)	May 21/ 1990	Dames and Moore conduct soil vapour survey. Eight hand augured soil vapour boreholes installed. Highest concentrations detected close to pipe trench between fuel storage tanks and fuel pumps (free product inferred). High concentrations also detected north and east of storage tanks. Moderate levels of contamination associated with soils and groundwater beneath concrete surrounding filling station. Concentration of volatile's increases with depth, the highest concentrations observed close to the water table. No MTBE contamination observed up groundwater gradient from the site.
14)	June 11/ 1990	Fuel storage tanks and delivery system at aafes station examined for leaks. Fuel storage tanks passed pressure test. Pressure testing of delivery and feeder lines identifies leakage in system from piping connecting tanks to fuel dispensers. Visual examination shows free product around all tanks and deterioration of seal at entrance of delivery pipes to fibreglass "box" around centre tank.
15)	1991	Pilot high capacity air stripping plant installed at Anglian Water Beck Row.
16)	Oct. 25/ 1991	Dames and Moore installs remediation boreholes to remove free product from water table. Total pumping rate from 4 wells of 500 m^3/day.
17)	June 1992	Second high capacity air stripping plant installed at Anglian Water Beck Row.
18)	May, 1992	NRA contracts for drilling of 9 auger holes on Beck Row Compound.
19)	June 10-15, 1992	Sampling of Anglian Water, PSA, and NRA observation holes and remediation wells.
20)	June-August, 1993	UCL undertakes field study and sampling at Beck Row.

4.3 Beck Row Geology

The Beck Row Abstraction Borehole (TL 6799 7727) fully penetrates the Lower Chalk and was drilled to a total depth of 30.5m in the Gault Clay in 1964. The Beck Row site is situated with-in 4km of the north easterly outcrop edge of the Lower Chalk. The Lower Chalk, at this point, is covered by a thin, 1 to 3 metre layer of quaternary deposits.

4.3.1 Quaternary Deposits

Regionally the quaternary deposits are described as consisting of unconsolidated sands, silts, and gravels of glacio-fluvial origin (1990, Geology of the country around Bury St. Edmonds). Locally (from observation and abstraction boreholes) the drift is described as unconsolidated reddish sands interbedded with clayey lenses. The sands are sub-mature and are composed of fine to medium grained, well sorted, and sub-angular grains. Sieve analysis of the sands gave an median d_{10} value of .075mm. Application of Hazens Rule

$K = C * d_{10}$ (K in cm/sec, d_{10} in cm, C = 100)

gives a hydraulic conductivity of 8m/d for the saturated sands. Porosity is estimated at 30 %, and specific yield at 15 percent.

For the purpose of this paper the drift will be treated as a homogeneous layer although site descriptions of the deposits would suggest a more complex geology.

4.3.2 Lower Chalk

The Lower Chalk at the Beck Row Site lies below the implied outcrop of the Totternhoe Stone and is known as the Chalk Marls (Geology of the country around Bury St. Edmonds, 1990). Broadly the section consists of a succession of fossiliferous marls, coarse bioclastic shell-detrital chalks, and fine grained chalks.

The Lower Chalk, for the purposes of this discussion, has been subdivided into three divisions.

The upper 1.7m consists of hard dry dirty chalk which lies above the highest normal water levels. The chalk is unsaturated and is expected to be a typical section of well jointed chalk with typical high porosity low permeability matrix. Some solution enhancement of the joints in the chalk is expected with vertical enhancement dominating due to infiltration

The middle 9.3 m consists of greyish white chalk, lying in the saturated zone, with a well developed fissure system and typical high porosity, low permeability matrix. The fissure development will be controlled by the regional lineaments within the chalk and the groundwater flow regime. The lineaments within the chalk are inferred to be perpendicular to the outcrop edge of the Lower Chalk, trending NW-SE. The horizontal fissures are thought to predominate and probably will have benefited from solution enhancement preferentially over the vertical fissures due to groundwater flow.

The lower 14.6 m consists of hard and soft dirty white putty chalk, lying in the saturated zone, with typical high porosity and low permeability matrix. No fissure development is thought to exist within this zone.

4.3.3 Gault Clay

The Gault Clay is described as hard grey clay. The Gault exhibits high porosity but will have extremely limited permeability and will be treated as an aquitard.

4.3.4 Beck Row Abstraction Borehole

Elevation (mAOD)	Depth (mBGL)	Interval (m)	Lithology	Interpreted Geology
4.7 - 4.1	0 - 0.6	0.6	Sandy Soil	Drift
4.1 - 3.1	0.6 - 1.6	1.0	Soft Yellow Sand	
3.1 - 1.5	0.6 - 3.3	1.5	Hard Dirty Chalk	Lower Chalk
1.5 - -7.8	3.3 - 12.6	9.3	Greyish White Fissured Chalk	
-7.8 - -17.8	12.6 - 22.6	10.0	Hard and Soft Grey Putty Chalk	Chalk Marl
-17.8 - -22.2	22.6 - 27.2	4.6	Hard and Soft Dirty White Putty Chalk	
-22.2 - -26.0	27.2 - 30.8	3.6	Hard Grey Clay	Gault Clay
-26.0 - -30.2	30.8 - 35.0	4.2	NO DESCRIPTION	

4.3.5 Schematic Geologic Cross Section - Beck Row

Schematic cross section cutting east-west across site from Anglian Water Borehole to fuel station. Fractures, as identified from Beck Row conductivity logs, and water levels are plotted approximately to scale.

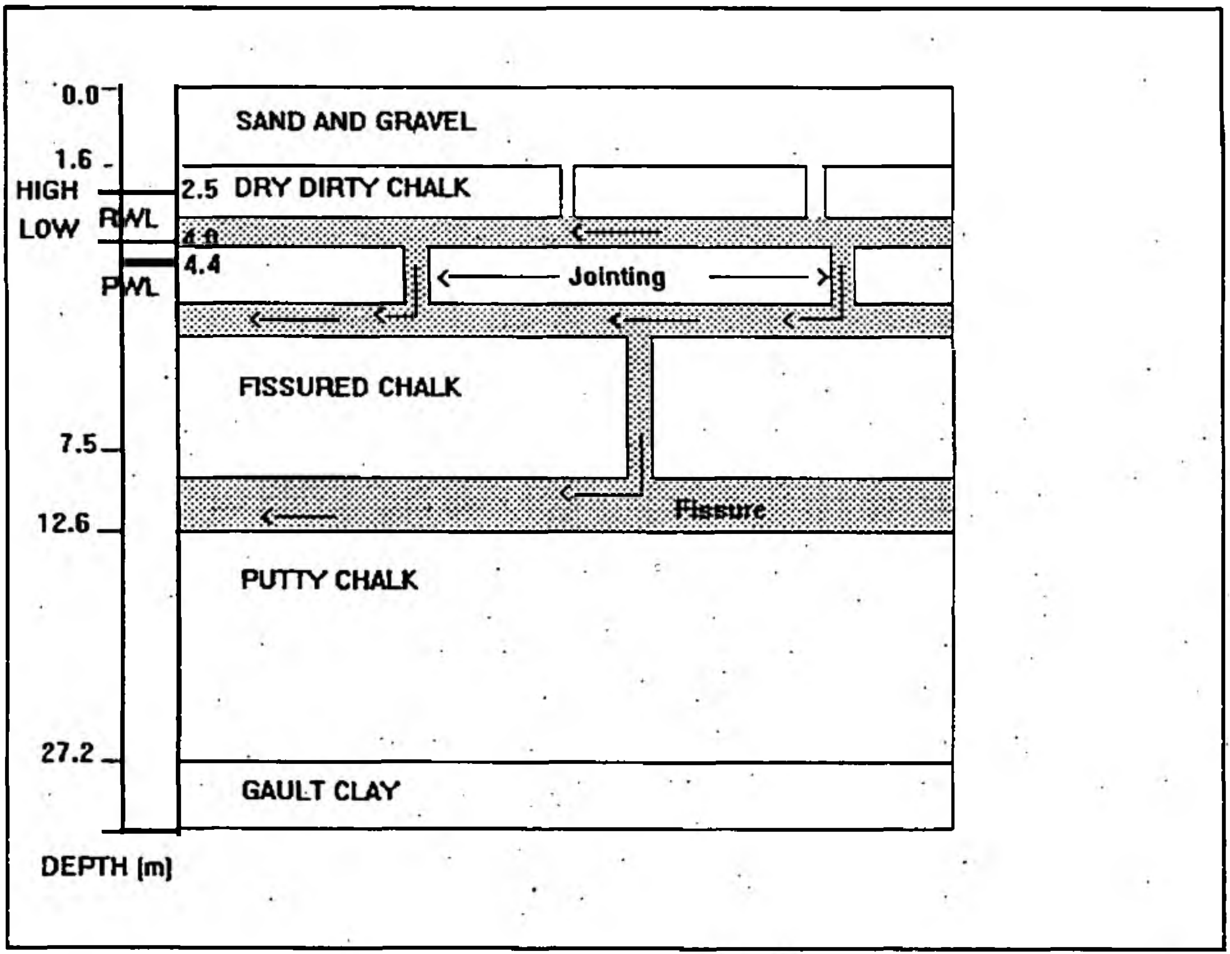


Figure 4.3.5: Schematic Geologic Cross Section - Beck Row

4.4 Hydrogeology

4.4.1 Regional Hydrogeology

The dominant influences at the site are the outcrop edge of the chalk, approximately 4km to the north east. and the drainage ditches associated with the spring line of the lower chalk. Approximate regional flow directions trend south-east to north-west. The regional flow gradients, from the observation borehole network, have been taken from the published maps on the Great Ouse River Diversion.

4.4.2 Hydrogeology of Beck Row Site

The hydrogeology of the Beck Site has been studied several times in reference to investigations on the abstraction borehole and in previous contamination incidence. The aquifer unit at the abstraction borehole has been identified as the fissured chalk which is dominated by a two phase flow regime (fissure and matrix porosity). The chalk is an unconfined, or water table aquifer, and demonstrates a small fluctuation of rest water levels between average spring lows and autumn highs of 1.55 m. As the aquifer is unconfined, the water levels in the aquifer will be a direct reflection of rainfall. During the sampling period between mid June and early August 1993 the levels in the aquifer varied by 15 cm.

The Beck Row Abstraction Borehole is pumped at rates varying form 3500 to 10,000 m^3/d. Measurements of water levels in the observation boreholes was complicated by the high aquifer transmissivity (5000 to 25000 m^2/d) with small observed drawdowns (0.5m at 5000 m^3/d). No direct measurement of the flow directions could be determined from the observed water levels. Due to the high transmissivity of the aquifer the observed drawdowns were outside the anticipated tolerances of the ground survey and dip technique, see figure Dip Level, Aug. 3-4, 1991, Appendix A. The flow system has been inferred from the contaminant migration of the plume of aqueous MTBE (assumes MTBE to be a conservative tracer).

The chalk is a two phase flow system with flow gradients predominantly controlled by the well developed fissure systems. Depending on the tortuosity of the fracture system the hydraulic gradients may, or may not, reflect in a true picture of actual groundwater movement.

Table 4.4.2.1 Aquifer Properties

Interval	Lithology	Transmissivity	Specific Storage
0 - 1.6m	Sand and Clay[1]	$12m^2/d$	0.2
1.6 - 7.5m	Fissured Chalk[2]	$350m^2/d$	0.03
1.6 - 12.6m	Fissured Chalk[3]	$5000 - 25000\ m^2/d$	0.03
12.6 - 27.2m	Putty Chalk[4]	$20m^2/d$	0.01

1) Calculated From Sieve Analysis
2) Dames and Moore
3) Anglian Water
4) Downing et al 1990

Table 4.4.2.2 Fissure Flow at Beck Row Anglian Water Borehole

Fissure	Depth (m)	Elevation (mAOD)	Interval (m)
Upper	4.0-4.2	0.2-0.4	0.2
Middle	6.0-6.2	4.0-4.2	0.2
Lower	9.4-12.6	4.6-7.8	3.2

Table 4.4.2.3 Water Levels at Beck Row Anglian Water Borehole

Type	Season	Depth (m)	Elevation (mAOD)
RWL	Spring	2.5	2.4
	Autumn	4.0	1.0
PWL		4.4	0.6

4.4.3 Schematic Hydrogeologic Cross Section - Beck Row

Schematic cross section of Beck Row Site Hydrogeology, east-west from Anglian Water Abstraction Borehole to fuel station. Indicated hydraulic conductivities taken from various sources.

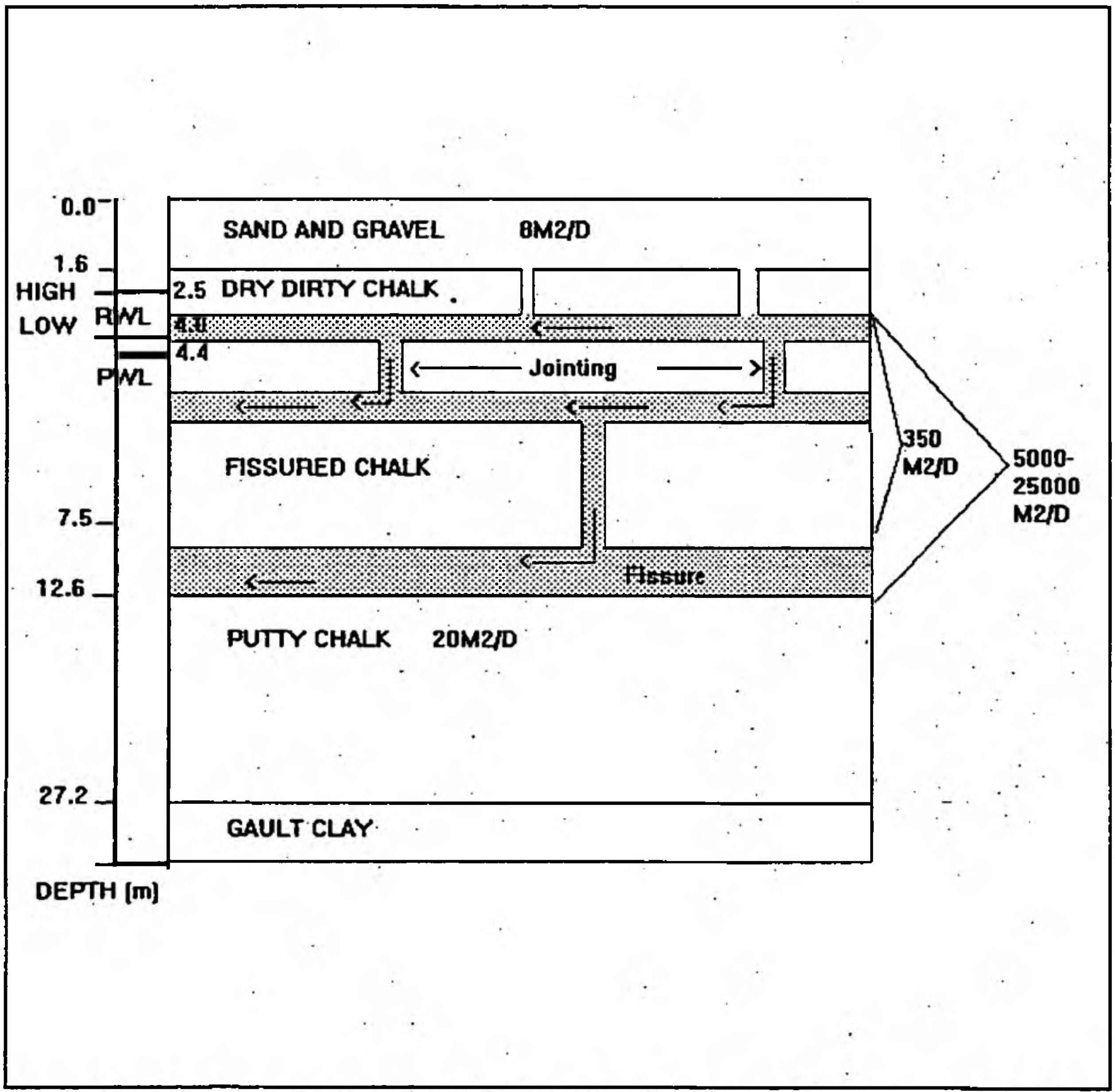


Figure 4.4.3: Schematic Hydrogeologic Cross Section - Beck Row

4.4.4 Flow Direction

4.4.4.1 Static Flow Direction

Regional flow directions across Beck Row Site taken from Average Groundwater Levels in the Chalk, prepared by the Anglian Water Authority for the

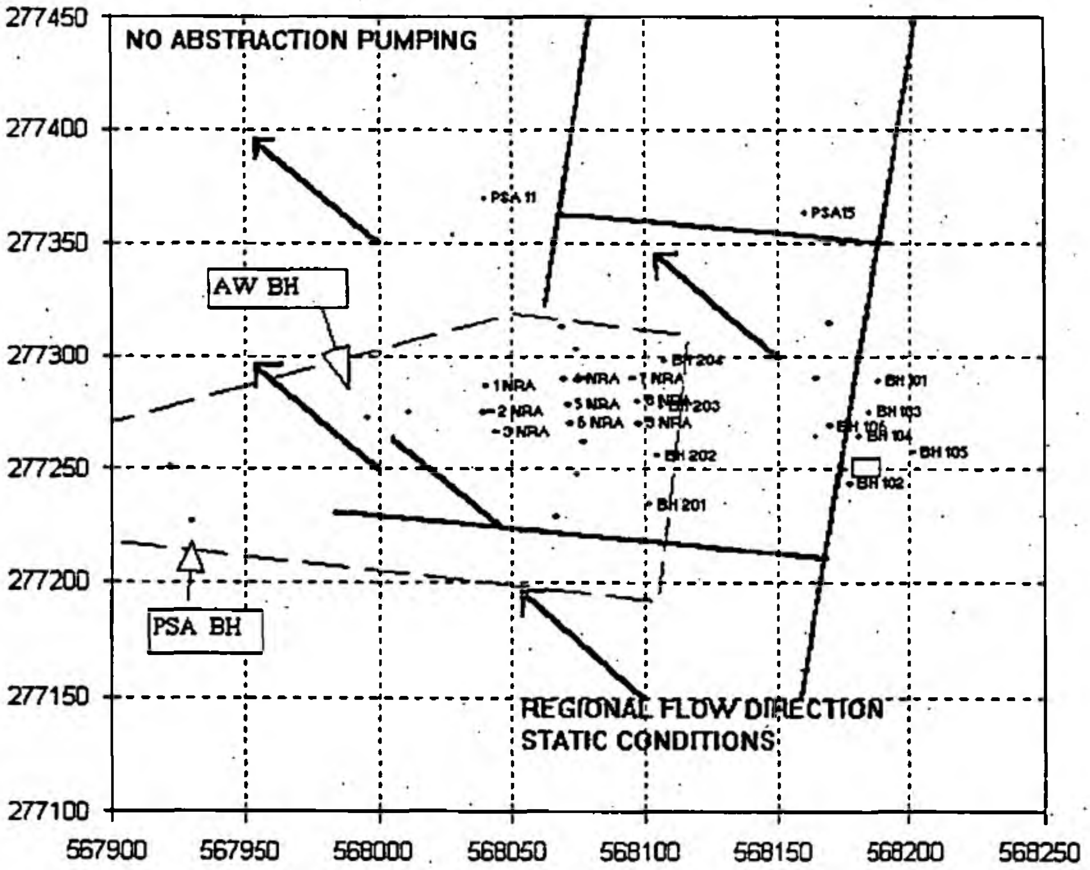


Figure 4.4.4.1: Static Flow Direction

Great Ouse Water Division, Cambridge (August , 1978).

4.4.4.2 Anglian Water and PSA Boreholes Pumping

Flow directions calculated from contaminant movement. Includes only flow directions from contaminant side of abstraction boreholes.

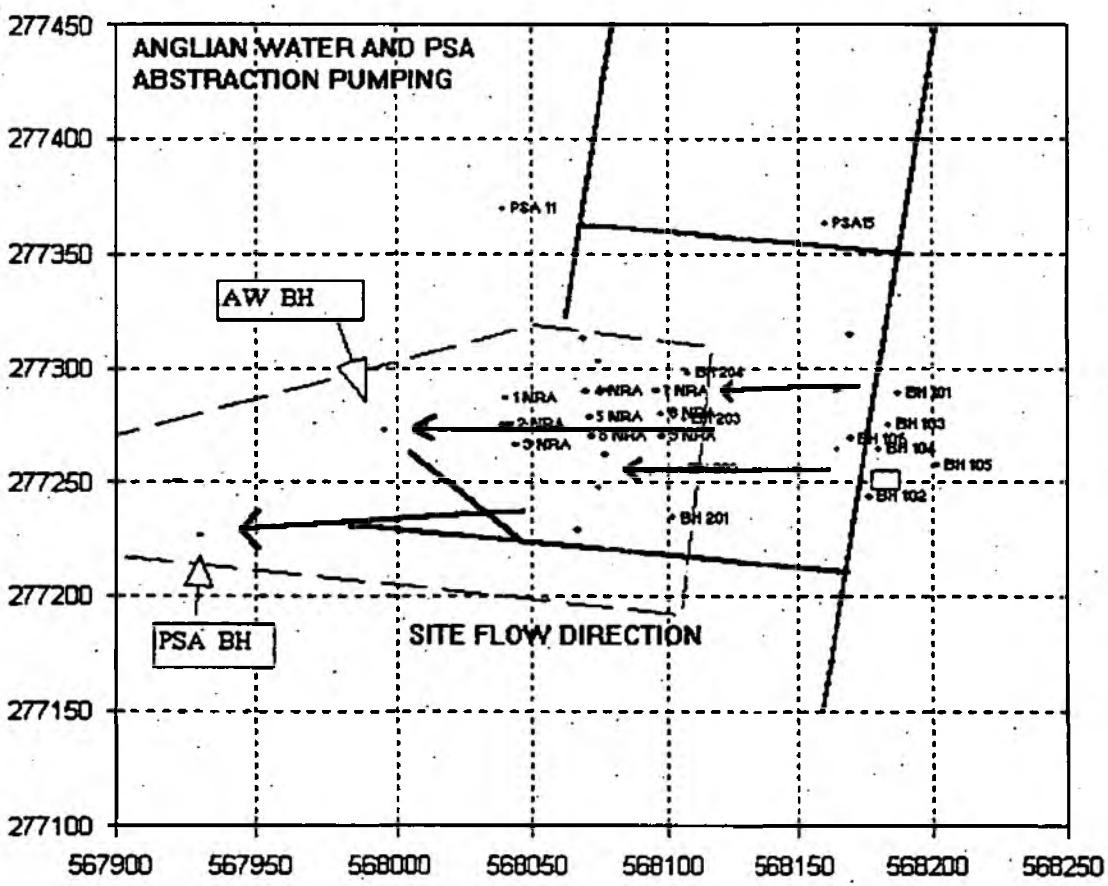


Figure 4.4.4.2: Anglian Water and PSA Boreholes Pumping

4.4.4.3 Anglian Water Borehole Pumping

Flow directions calculated from contaminant movement. Includes only flow directions from contaminant side of abstraction borehole.

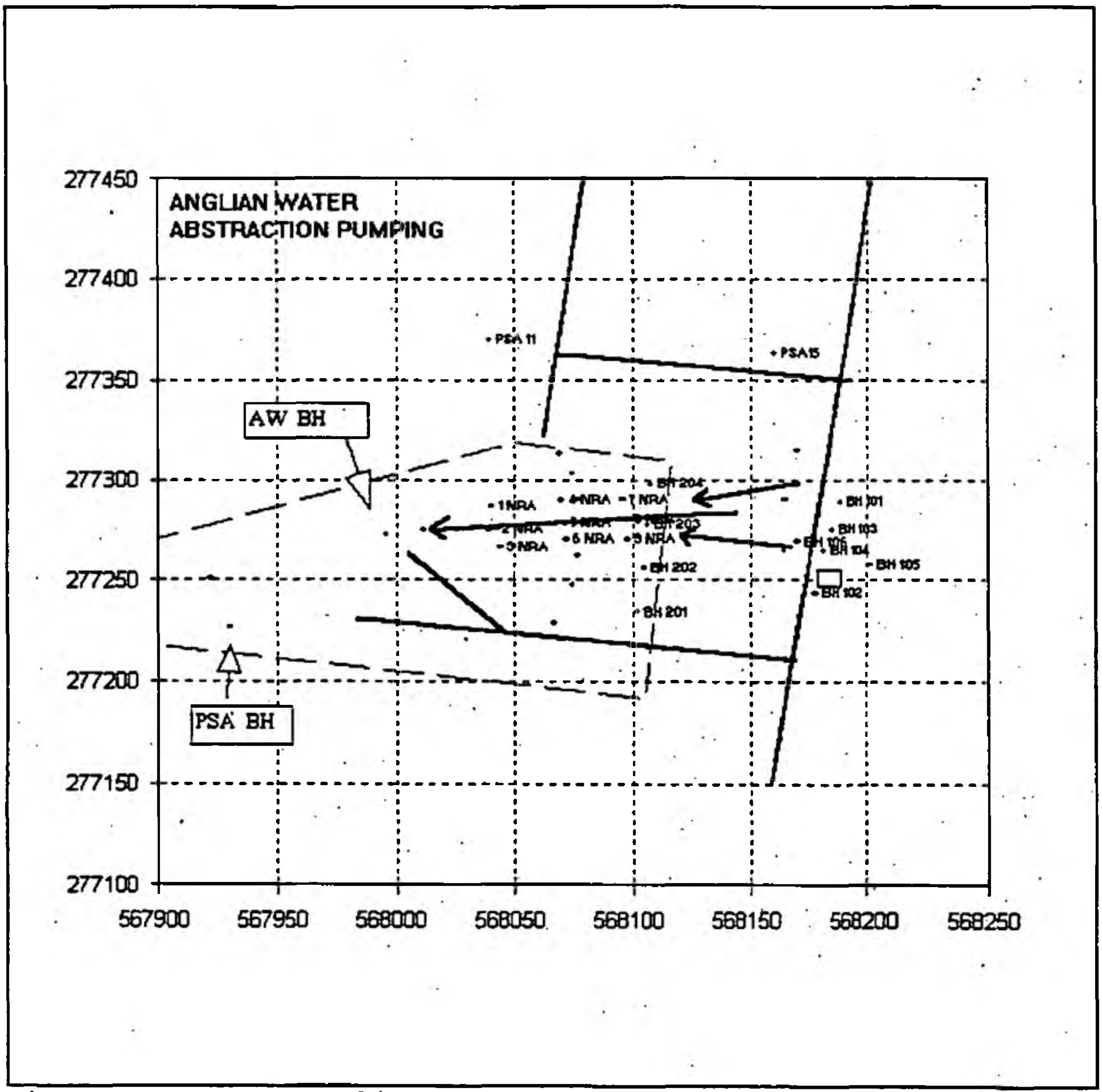


Figure 4.4.4.3: Anglian Water Borehole Pumping

4.5 Chalk Microbiology

Recent studies in the chalk have shown that aerobic and anaerobic bacteria exist with-in the chalk in significant numbers to a depth of 40 metres. The bacteria are present on the fissure walls but are absent in the chalk matrix (Downing et al, 1990). When considered in relationship to diffusion of contaminants into the chalk matrix it becomes apparent that although biodegradation of the contaminants will occur in the fissure system, no biodegradation will occur in the matrix of the chalk. This plays a major role in the persistence of contaminants in the chalk and will result in long term (possibly tens of years) persistence of low levels of contaminants in the chalk aquifer as the contaminants diffuse from the matrix back into the fissure system (Chilton et al 1990).

Certain microbe species have been proven to attack the Benzene compound while not attacking the Toluene compound (API 1985). Future work is needed at the Beck Row site to determine microbes present in the fissure and matrix system, and their impact on MTBE and BTEX biodegradation.

4.6 Contaminant Sampling

4.6.1 Equipment

Sampling was undertaken using a downhole submersible pump with varying discharge rate. Power was supplied by a portable generator run through a power box which allowed for adjustment of the power cycles controlling the pump rate.

Purging Rate:	200 cycles = 10 litres per minute
Sampling Rate:	80 cycles (slow trickle from discharge pipe)

4.6.2 Sampling Procedure

Boreholes were dipped for water levels and total depth of the boreholes. Casing inside diameter was measured and a hole volume calculated. Boreholes were then purged for approximately four times their hole volume.

Boreholes were purged at a rate of 10 litres per minute and then sampled at a reduced flow rate to avoid aeration while filling the vials. Sample containers were glass with teflon liners under screw caps. The sample vials were filled to capacity and checked for air bubbles.

Downhole equipment was washed with distilled water while lifting and dried as best as possible with paper towelling between sampling runs.

4.6.3 Sample Vials

Sample vials were filled to capacity, with no visible air bubbles evident. The vials were kept as cool as possible in the field in a light resistant container and transferred to Ely NRA office sample fridges at the end of each day. Samples were collected each day from Ely and transferred to the NRA Peterborough Labs for analysis.

4.6.4 Chemical Analysis

Samples were analyzed at the NRA Peterborough Laboratory and were analyzed using High Pressure Liquid Chromatographic techniques.

4.7 Source of Unleaded Fuel Release

The AGHAST (fuel station) facility has three underground storage tanks which each contain 5000 gallons of fuel. The storage tanks are connected by underground pipes to the fuel delivery point and to the fuel dispensers. The three underground storage tanks are sited in concrete containment structures which are excavated down to an approximate depth of three metres into the top of the chalk. The three tanks were pressure tested after the leak was discovered and were found to be competent. The leaking fuel has been attributed, by the PSA, to the underground piping connecting the tanks to fuel dispenser points.

No estimate could be made from station records as to the amount of fuel which has been lost. The only hard indication as to the size of the free product spill comes form free product observed in 1991 from teflon bailer samples. This information lead to the conclusion that site would not remediate naturally and that a free product recovery system would be required.

4.7.1 Location of Free Product

Figure Free Product, April 1991, Appendix A, is a contour map of the free product plume constructed from the 1991 teflon bail samples. The 1991 teflon bail samples were the only recorded indication of the free product plume. The leak source is directly north of the fuel station building (small square on figure) and the free product plume appears to have migrated north-easterly, probably due to the static regional flow.

4.7.2 Contaminant Plume Migration

The contaminant plume migration was used to construct the local flow directions at the Beck Row Site. The contoured plume migration indicates that the migration of the contaminants is a direct result of pumping practices at the Beck Row Site. The plume migration can be observed in a series of time slices in the appendices of figures. The time slices cover the period form 1990 through 1993.

The earliest of the contaminant plots, see figure MTBE April 1990, Appendix A, is under conditions of abstraction form the PSA and Anglian Water Abstraction Boreholes. The contoured plume shows contaminant migration towards both the abstraction boreholes. Abstraction from the PSA Abstraction Borehole was ceased in 1990 and the effect on the plume migration is evident in the later time slices (eg. MTBE January 1992, Appendix A.

The contaminant plots from 1991 to 1993 show only the effects of abstraction form the Anglian Water Boreholes. The contaminant contours during this period are observed as a plume extending from a site slightly north of the fuel station building and extending towards the Anglian Water Abstraction Borehole. The plume narrows towards the well bore. The Anglian Water Abstraction Borehole is pumped at values of 3500 to 10000 m^3/d and has a well developed zone of influence.

The chalk aquifer is known for its high porosity, due to lithology, and high transmissivity due to development of fissure flow along lineaments and fractures. The simplified cross section exhibits a likely scenario for the Beck Row site. The implications of a fissure flow dominated system cannot be underestimated. The lineament of the fractures may be aligned along the flow gradient, or may, in some cases be at some angle to the local gradient. This non-alignment may be reflected in localised fluid flow at some angle to the flow gradient. The implications of fissure orientation will be a direct reflection of spread of the contaminants plume.

With-in the aquifer three fissure zones have been identified. The basal fissure is identified as the major flow zone in the Anglian Water Borehole. It is expected the contaminants will be drawn down into this zone to some extent, and that a contaminant survey by depth would show decreasing contaminant levels with depth.

4.7.3 Plume Migration - MTBE verses Benzene

The figures of Benzene and MTBE January 1992, Appendix A, are a good indicator as to the relative migration of MTBE verses Benzene along a flowline in the unconfined chalk aquifer chalk aquifer.

Table 4.7.3 Plume Migration - MTBE verses Benzene

Fuel Component	BH101 (ug/l)	BH203 (ug/l)	Remaining Contaminant
MTBE	180	73	60%
Benzene	5700	13	0.2%

The MTBE proves itself to be recalcitrant when compared to Benzene under the conditions of the unconfined chalk aquifer. The most likely process contributing to this effect is Biodegradation. The Benzene has been mostly biodegraded while the MTBE shows no such effect. This effect is observed at the Anglian Water Abstraction Borehole as the MTBE is still evident in chemical analysis of the raw water while the Benzene is no longer detectable.

4.7.4 Site Remediation of Contaminants

4.7.4.1 Recovery of Free Product

The pumping and treatment of contaminated water, commonly known as pump and treat, is the most common form of remediation of VOC's. The pump and treat method relies upon development of a cone of depression to capture the contaminant and prevent its spread. Pump and treat is better described as a method of containment rather than a contamination remediation method. One or more pumping wells can be utilized in this type of remediation method depending on local conditions.

The Beck Row pump and treat system involved the drilling of ten wells, see figure Borehole Locations, Appendix A, with two lines of four wells, BH 101 - 104 and BH 201 - 204, perpendicular to the mapped contaminant plume. Two additional wells were located areas of highest contamination, BH 105 and 106. Pump and treat systems were installed in four of the ten wells, BH 103, 104, 106, and 203, with the long term plan of rotating the pumps as dictated by free product recovery. The system consisted of a dual pumping system, with a lower or depression pump and an upper or free product recovery pump. The depression pump was fixed and the recovery pump was on a hand crank system to be raised and lowered into the free product layer (see figure 4.7.4.1.A).

Figure 4.7.4.1.A Pump and Treat Systems

The Beck Row pump and treat system depended on the operator to raise and lower the pump with changes in groundwater levels. The rapid changes in groundwater levels associated with the unconfined aquifer required monitoring and a floating skimmer pump may have been recomended.

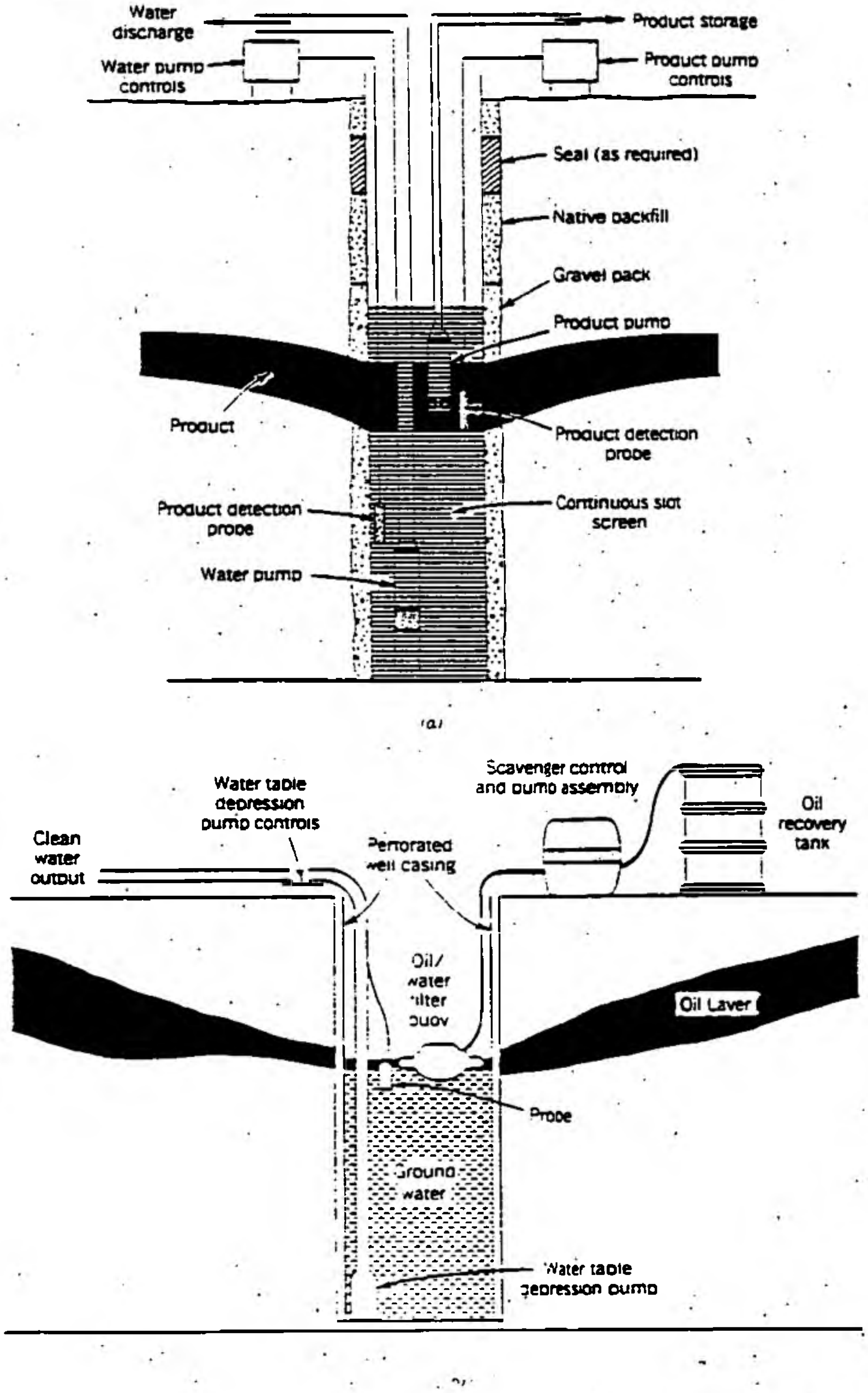


Figure 4.7.4.1.B

The depression pumps at the Beck Row Site were estimated to be pumping at a rate of about 75 to 125 m^3/d. The remediation wells were drilled to 7.5m only in an effort to avoid the basal high transmissivity fracture. The drawdown at the remediation wells has been calculated for a variety of transmissivities.

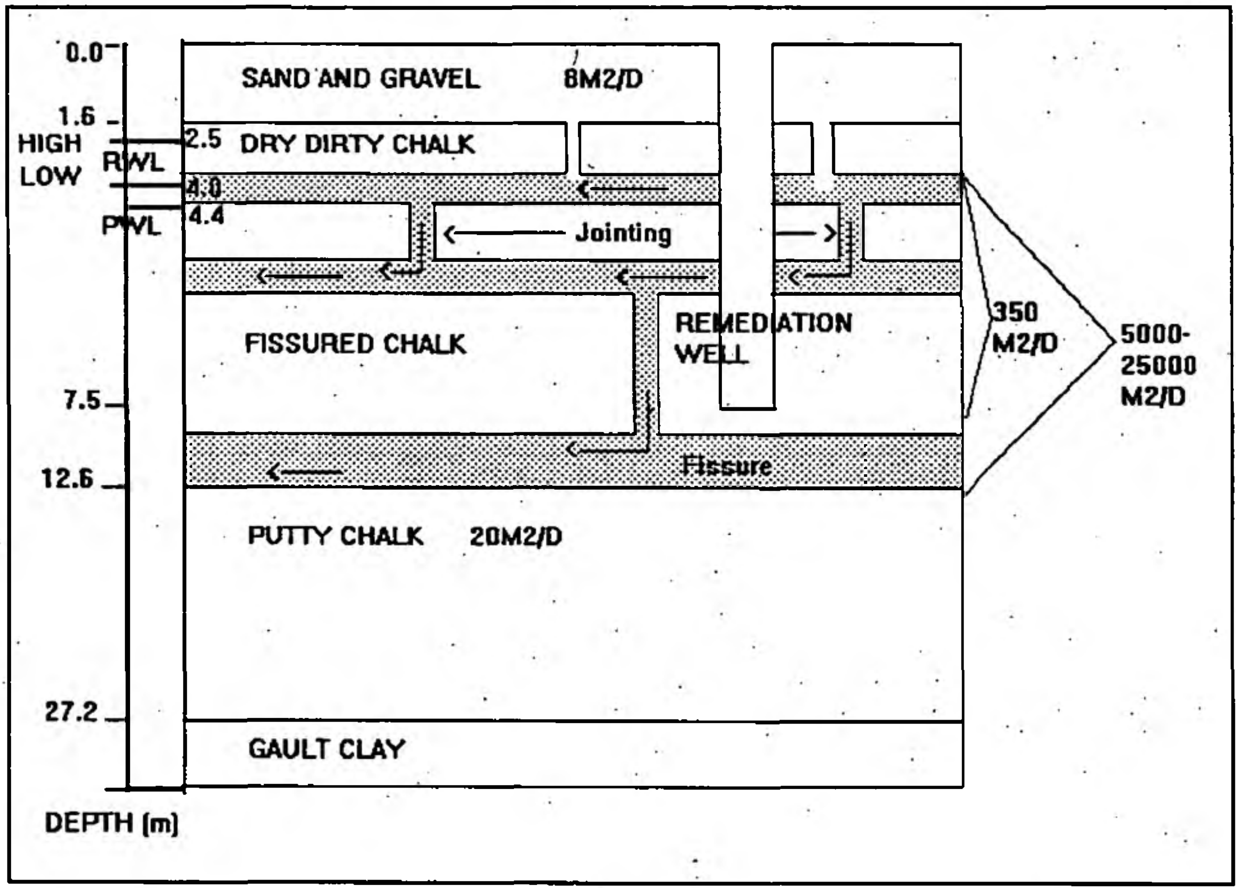


Figure 4.7.4.1.B: Remediation Wells at Beck Row

Table 4.7.4.1 Drawdown at Remediation Wells

Pumping Rate Averaged at 100 m^3/d

Transmissivity (m^2/d)	**Drawdown (m)**
350	0.350
5000	0.024
25000	0.005

No free product phase was recovered at the Beck Row Site

4.7.4.2 Recovery of Aqueous Phase Contaminants

The water recovered from the remediation well depression pumps was passed through an air sparging system prior to discharge to the sewage treatment works. The blended water was sampled at the intake and outlet of the sparging tower. This analysis was used in the mass balance of contaminants at the site.

4.7.5 Mass Balance on Contaminants

Estimates of the amount of free product remaining in the aquifer have been calculated as volume free product layer minus amount removed by remediation wells and amount abstracted at the public supply borehole. These are rough estimates but are valuable indicators of free product remaining in the aquifer and the need for further site remediation.

Estimates of the amount of contaminant released have been made from the contour map of the floating fuel laver as observed in figure Free Product, April 1991, Appendix A.

Table 4.7.5.A Volume Free Floating Fuel Layer

Fuel layer thickness:	.02m
Fuel layer area:	625m
Volume Fuel:	12.5 m^3 (12,500l)

Amount MTBE removed in aqueous phase from the depression pumps at the remediation boreholes.

Table 4.7.5.B Volume Fuel Removed by Remediation Depression Pumps

Average Abstraction Rate:	500 m^3/d	(Dames and Moore)
Time of Abstraction in Days:	600	(1.7 Years)
Volume Abstracted:	300,000 m3/d	
Average MTBE levels:	70 ug/l	(At Tower Inlet, PSA)
Weight MTBE	21 kg	
Volume MTBE (0.704 g/cc)	.0298 m^3 (29.8l)	
Volume Fuel (1% MTBE)	2981 l	

Amount MTBE removed in aqueous phase from the abstraction borehole.

Table 4.7.5.C Volume Fuel Removed by Abstraction Pumping

Time (days)	Abs. Rate (m^3/d)	Volume Water (m^3)	Avg MTBE (ug/l)	Weight MTBE (kg)
90	9,500	855,000	10	8.55
540	4,000	2,160,000	4	8.64
630	4,000	2,520,000	1	2.52
			Total	19.62

Weight MTBE:	19.62 kg
Volume MTBE (0.704 g/cc)	.02787 m^3
	27.9 l
Volume Fuel (1% MTBE)	2791 l

Table 4.7.5.D Mass Balance

	Volume	Percent
Total Fuel Spilled	12,500 l	100
Volume Fuel Removed by Remediation Pumping	2,981 l	24
Volume Fuel Removed by Abstraction Pumping	2,791 l	22
Fuel Remaining in Aquifer	6,728 l	54

4.7.6 Evaluation of Remediation Methods

The pump and treat system failed to recover any of the free product layer that had been detected. The failure of the recovery system is due to one or more reasons:

i) Failure of system to develop significant cone of depression.
ii) Free product layer dissolved in aqueous phase.
iii) Free product migrated away from remediation wells.
iv) Remaining free product "held" or "bound".

The depression pumps did recover almost 25% of the calculated total contamination in the form of an aqueous phase solution. A graph of rainfall verses contaminant levels at Beck Row shows a sharp drop in the MTBE levels after the start of remediation pumping.

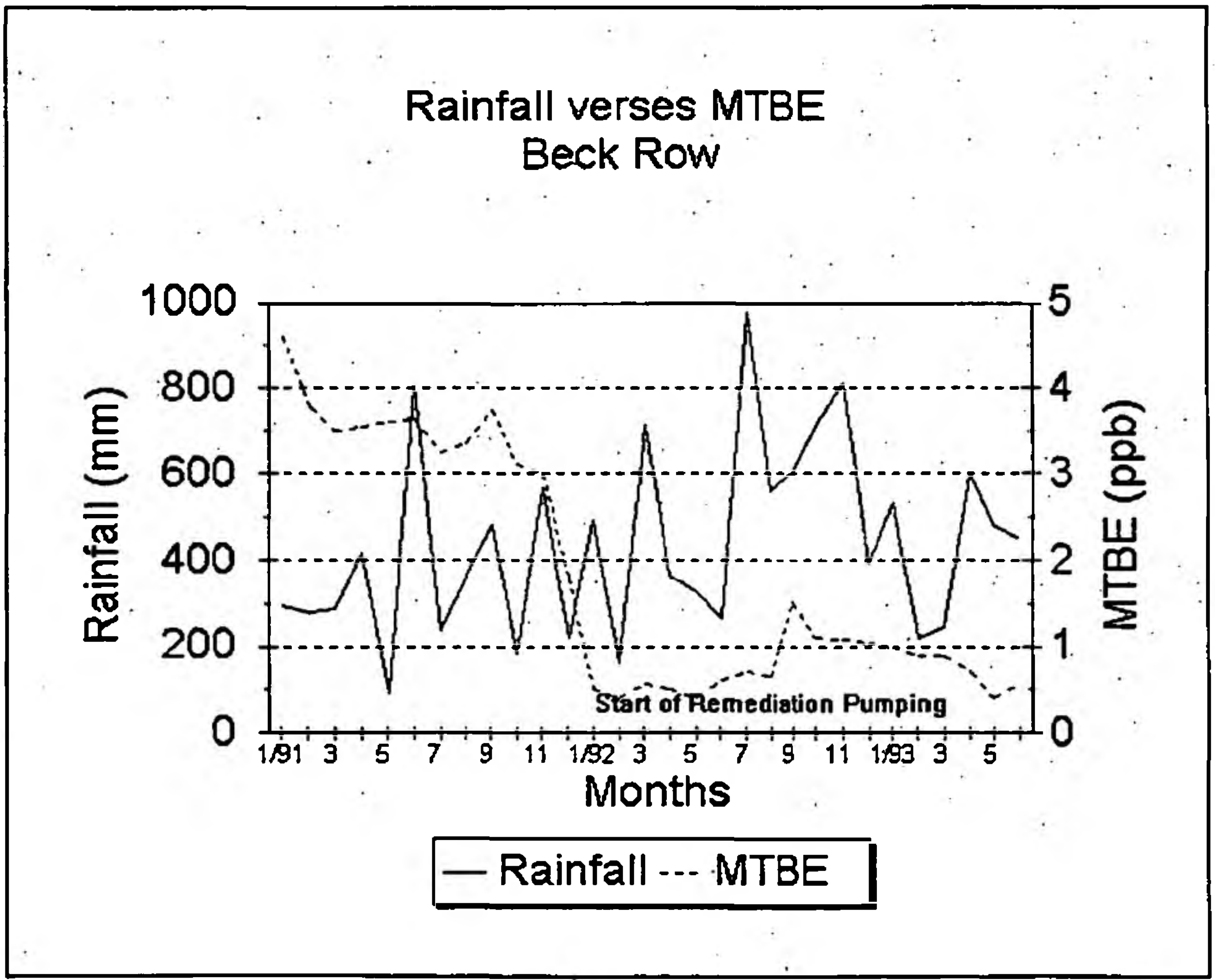


Figure 4.7.6 Rainfall verses MTBE at Beck Row

4.7.7 Location of Remaining Contaminants at Beck Row

The 54% of the contaminants estimated to be remaining in the aquifer and overburden at the Beck Row have been sub-divided into "held" and "bound" phases.

4.7.7.1 Contaminants "Held" at the Beck Row Site

Contaminants described as "held", are those trapped in the aquifer and overburden material by capillary pressure or physical boundaries. The "held" phase at the Beck Row Site are mainly thought to be i) held in intergranular porosity in the drift sands and clays, ii) sitting on impermeable lenses on the upper chalk, and iii) trapped in dead end fractures in the chalk aquifer.

Figure Post Mortem Held Fuel, Appendix A, is the interpreted location of the "held" fuel phase still thought to exist at the Beck Row Site. The location of these contaminants has been estimated from contours on the contaminant plume in combination with the figure Free Product, June 1991, Appendix A.

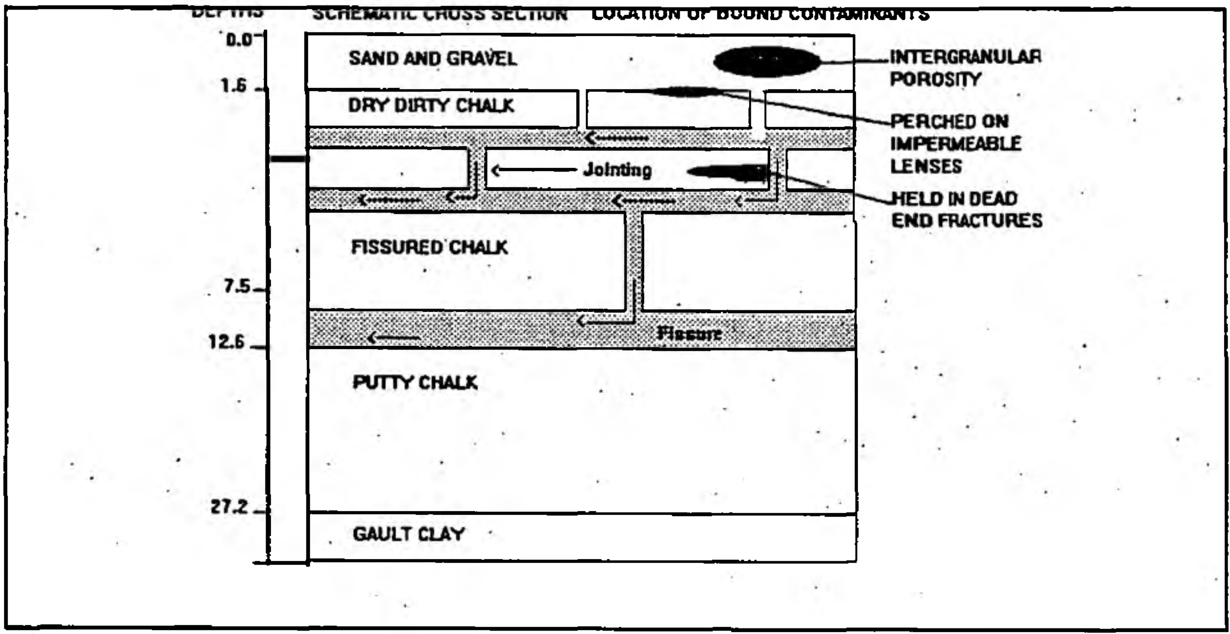


Figure 4.7.7.1 Contaminants "Held" at Beck Row Site

4.7.7.2 Contaminants "Bound" at the Beck Row Site

Unknown quantities of contaminants will be "bound" in the overburden and aquifer. These processes include contaminants sorbed onto organic carbon and mineral surfaces, and contaminants diffused into the matrix of the chalk. No information is known on the sorption or diffusion of MTBE.

4.7.8 Remobilization of "Held" and "Bound" Contaminants

The contaminants "held" an "bound" in the aquifer will be mobilized by the raising and lowering of the water table in the unconfined chalk aquifer and by infiltration. Direct recharge from infiltration will be limited at this site due to the extensive paving. The rainfall is taken as a direct reflection of water levels in the unconfined aquifer. Plots of rainfall verses contaminant levels at Beck Row seem to show a direct relationship ,after the start of remediation pumping, indicating a remobilization of the contaminants.

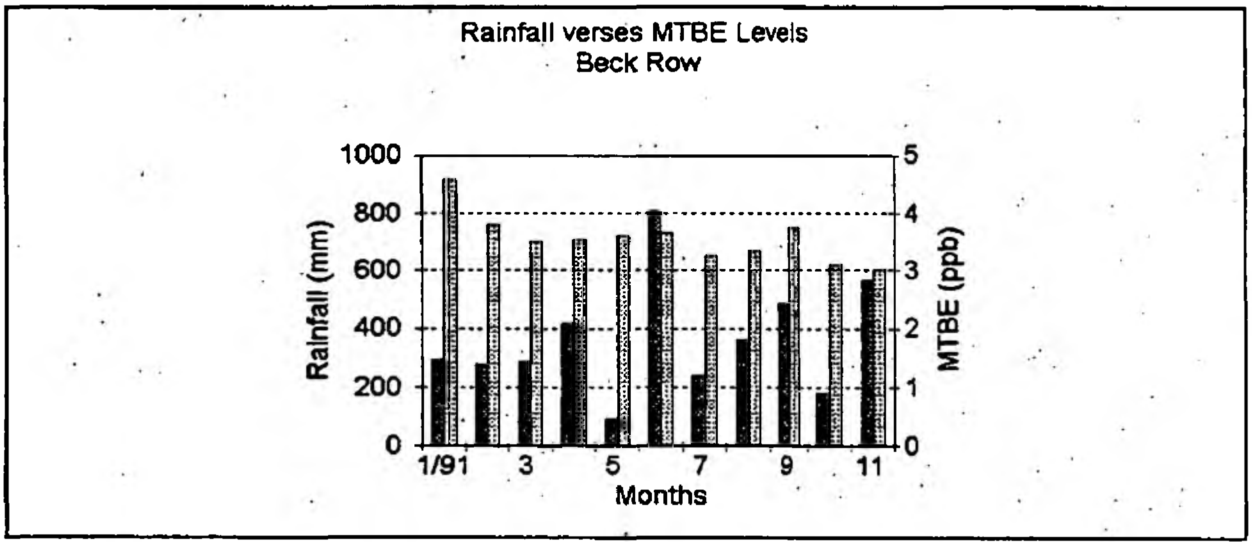


Figure 4.7.8.A Rainfall verses MTBE prior to Remediation Pumping

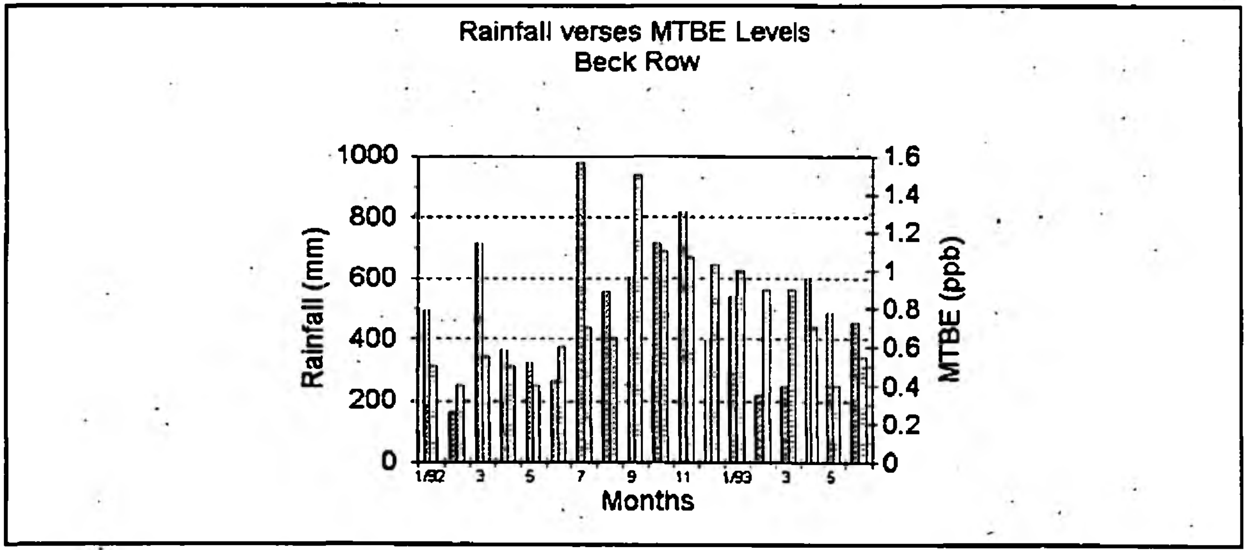


Figure 4.7.8.B Rainfall verses MTBE at Beck Row after start of Remediation Pumping

4.7.9 Endpoint of Pump and Treat Remediation at Beck Row

The Pump and Treat method has been evaluated to determine the effectiveness of the technique and the endpoint (or lowest value) which may be expected for the contaminants. Pump and Treat techniques have been observed to approach a fixed concentration with time, more or less exponentially. The fixed concentration or "asymptote" is approached, but is not theoretically attainable as pumping time is extended (API 4543 1992). Linear regression techniques have been applied to the Beck Row Site using the API Computer Program REGRESS (API 4543 1992) and sample computer runs have been included in Appendix B. Remediation Borehole (RB) 104 was chosen for its proximity to the predicted fuel phase.

Table 4.7.9 Asymptote or Endpoint of Selected Contaminants at Remediation Borehole 104

Contaminant	Asymptote (ug/l)	Time to Asymptote (Days)
MTBE	104	630
Benzene	92	650
Toluene	93	450
Ethylbenzene	63	<320
Xylene	323	<360

The BTEX components are observed to reach a well defined asymptote value (ie: straight line). The MTBE REGRESS analysis shows a tendency to a continuing decline of concentration with time indicating that a true asymptote, or endpoint, has not been established. This is an indicator that the Pump and Treat methods are continuing to be effective in the remediation of the MTBE component.

RB 101 shows current contaminant values typical of that found in RB 104 prior to remediation pumping. RB 101 is in the predicted area of the remaining fuel phase and should show a similar response to RB 104 under remediation pumping. It is recommended that remediation pumping be undertaken at RB 101. There is no need for a two phase recovery system, as the floating free product phase is not evident, and that the equipment should take the form of a scavenger pump only.

Pumping and regular monitoring should continue for MTBE at RB 103, RB 104, RB 106, and RB 203 for both monitoring and research values.

4.8 Remediation of Contaminated Water at Beck Row

Anglian Water has installed, and upgraded, air sparging facilities at the Beck Row Site as well as activated carbon filtering. The air sparging system is estimated to be the most cost effective of the two techniques. The activated carbon will saturate relatively quickly, when compared to the BTEX components, and require frequent changing. The current systems of treatment at Beck Row should be sufficient to handle the current and future anticipated levels of MTBE from the 1988 contaminant release.

Bibliography

Angle, C.D. MD. 1991, "Letters to the Editor", JAMA, Dec. 4, 1991, Vol. 266, No. 21, pp 2986.

API Document 4415 August 1985, "Literature Survey: Unassisted Natural Mechanisms to Reduce Concentrations of Soluble Gas Components", Health and Environmental Sciences, American Petroleum Institute, 1220L Street, Northwest Washington, D.C., 2005.

API Document 4497 May 1991, "Cost-Effective, Alternative Technologies for Reducing the Concentrations of Methyl Tertiary Butyl Ether and Methanol in Groundwater", Health and Environmental Sciences, American Petroleum Institute, 1220L Street, Northwest Washington, D.C., 2005.

API Document 4525 November 1990, "A Compilation of Field-Collected Cost and Treatment Effectiveness for the Removal of Dissolved Gasoline Components from Groundwater", Health and Environmental Sciences, American Petroleum Institute, 1220L Street, Northwest Washington, D.C., 2005.

API Document 4531 November 1991, "Chemical Fate and Impact of Oxygenates in Groundwater: Solubility of BTEX from Gasoline-Oxygenate Mixtures", Health and Environmental Sciences, American Petroleum Institute, 1220L Street, Northwest Washington, D.C., 2005.

API Document 4543 April 1992, "User's Manual for REGRESS: Statistical Evaluation of Asymptotic Limits of Groundwater Remediation", Health and Environmental Sciences, American Petroleum Institute, 1220L Street, Northwest Washington, D.C., 2005.

Barker, J.F., Hubbard, C.E., and Lemon, L.A. Oct-Nov 1990, "Proceedings of the NWWA/API Conference of Petroleum Hydrocarbons and Organic Chemicals in Groundwater", Dublin, Ohio, pp 113-127.

Bott, D.J., Dawson, W.M., Piel, W.J., and Karas, L.J. 1992, "MTBE Environmental Fate", Arco Chemical Company, for Life Cycle Analysis and Eco-Assessment in the Oil Industry, The Institute of Petroleum, London, Nov 26, 1992.

Brown, W.H. 1972, "Introduction to Organic and Biochemistry", Willard Grant Press, Inc., 53 State Street, Boston, Mass. 02109.

Canadian Water Quality Guidelines for Methyl tertiary-Butyl-Ether, December 1991, DRAFT COPY, IWD Scientific Series Report, Environmental Quality Guidelines, Water Quality Branch, Inland Water Directorate, Environment Canada, Ottawa, Ontario.

Cline, P.V., Delfino, J.J., and Rao, P.S.C. 1991, "Partitioning of Aromatic Constituents into Water from Gasoline and Other Complex Solvent Mixtures", Environmental Science and Technology, Vol. 25, No. 5, 1991, pp 914-920.

Crow, P. 1993, "MTBE question in Alaska", Oil and Gas Journal, Mar. 15, 1993, pp 36.

Dames and Moore, "Reports 1 to 5 on the Beck Row MTBE Unleaded Fuel Contamination Incidence", Prepared for PSA, RAF Mildenhall, Mildenhall.

Domenico, P.A. and Schwartz, F.W. 1990, "Physical and Chemical Hydrogeology", John Wiley and Sons, Inc.

Downing, R.A. and Headworth, H.G. 1990, "Hydrogeology of the Chalk in the UK: the evolution of our understanding", in Chalk, Proceedings of the International Chalk Symposium held at Brighton Polytechnic on 4-7 September 1989, Thomas Telford Ltd, Thomas Telford House, 1 Heron Quay, London, E14 9XF. pp 555-571.

Duff, J.S., Del Pup, J.A., and Kniess, J.J. 1992, "Toxicological Evaluation of Methyl Tertiary Butyl Ether (MTBE): Testing Performed under the TSCA Consent Agreement", Journal of Soil Contamination, Vol. 1, No. 1, 1992, pp 29-37.

EEC Enviromental Directives

78/665	Atmospheric Emissions
83/851	Atmospheric Emissions
85/536	Oxygenates as Fuel Additives

European emission, fuel quality regs tighten, Technology, Dec 18, 1989, Oil and Gas Journal, pp 41-47

Fetter 1993, "Contaminant Hydrogeology",Macmillan Publishing Company, 866 Third Avenue, New York, New York, 10022.

Funisaki, N., Hada, S., and Neya, S. 1985, "Partition Coefficients of Aliphatic Ethers-Molecular Surface Area Approach", The Journal of Physical Chemistry, Vol. 89, No. 14, 1985, pp 3046-3049.

Garrett, P., Moreau, M., and Lowry, J.D. 1986, "Proceedings of the NWWA/API Conference of Petroleum Hydrocarbons and Organic Chemicals in Groundwater", Dublin, Ohio, pp 227-238.

Groves, F.R. Jr., 1988, "Effect of Cosolvents on the Solubility of Hydrocarbons in Water", Environmental Science and Technology, Vol. 22, No. 3, 1988, pp 282-286.

Hartley, W.R., and Englande, A.J.Jr. 1992, "Health Assessment of the Migration of Unleaded Gasoline - A Model For Petroleum Products", Water Science Technology, Vol. 25, No.3, 1992, pp 65-72.

Ilett, K.F., Laurence, B.H., and Hackett, L.P. 1990, "Alimentary Tracts and Pancreas", Journal of Gastroenterology and Hepatology, Vol. 5, 1990, pp 499-502.

Jenson, H.M. and Arvin, E. 1990, "Solubility and Degradability of the Gasoline Additive MTBE, methyl-tert.-butyl-ether, and Gasoline Compounds in Water", Contaminated Soils' 90, pp 445-448.

Kerr, J.M. 1990, "Investigation and remediation of VOCs in soil and groundwater", Environmental Science and Technology, Vol. 24, No. 2, 1990, pp 172-173.
Laing, G.J. and Palmer, F.H. 1987, "The use of oxygenates in motor gasolines", BP Research Centre, Chersley Road, Sunbury-on-Thames, Middlesex, TW1671N.

Mackay, D.M. and Cherry, J.A. 1989, "Groundwater contamination: Pump-and-treat remediation", Environmental Science and Technology, Vol. 23, No. 6, 1989, pp 630-636.

Merck Index 1989, "The Merck Index", 11th Edition, pp 5908-5909.

MTBE File, Institute of Petroleum, 61 New Cavendish Street, London, W1M 8 AR.

NRA 1979 - 1993, "NRA File on Beck Row Mildenhall", Brampton Office, Huntingdon.

OGJ Special 1990, "Tough air-quality goals spur quest for transportation fuel changes", OGJ Special, June 18, 1990, Oil and Gas Journal, pp 33-50.

Otto, K.W. 1993, "MTBE will be a boon to U.S. gas processors", Oil and Gas Journal, Jan. 11, 1993, pp 37-39.

Owen 1990, "Automotive Fuels Handbook", Published for the Society of the Chemical Industry by John Wiley and Sons.

Petrochemical Report 1993, "Methanol, MTBE Suppliers will likely keep up with rising demand", OGJ Special, Oil and Gas Journal, Mar. 29, 1993, pp 48-52.

Schmelling, S.G., Keeley, J.W., and Enfield, C.G. 1992, "Critical Evaluation of Treatment Technologies with Particular Reference to Pump and Treat Systems", Contaminated Land Treatment Technologies", Editor Rees, J.F., Elsevier Applied Science, pp 47-57.

Stephenson, R.M. 1992, "Mutual Solubilities: Water-Ketones, Water-Ethers, and Water-Gasoline, Alcohols", Journal of Chemical Engineering Data, Vol. 37, No. 1, 1992, pp 80-95.

Suflita, M.J. and Mormile, M.R. 1993, "Anaerobic Biodegredation of Known and Potential Gasoline Oxygenates in the Terrestrial Subsurface", Environmental Science and Technology, Vol. 27, No. 5, 1993. pp 976-978.

Unzelman, G.H. 1991, "U.S. Clean Air Act expands role for oxygenates", Technology, Apr 15, 1991, Oil and Gas Journal, pp 44-48.

Veith, G.D., Call, D.J., and Brooke, L.T. 1983, "Structure-Toxicity Relationships for the Fathead Minnow, *Pimephales promelas*: Narcotic Industrial Chemicals", Canadian Journal of Fish and Aquatic Science, Vol 40, 1993, pp 743-748.

Wu, H.S., Pividal, K.A., and Sandler, S.I. 1991, "Vapour-Liquid Equilibria of Hydrocarbons and Fuel Oxygenates", Journal of Chemical Engineering Data, Vol. 36, No. 4, 1991, pp 418-421.

Personal Communication

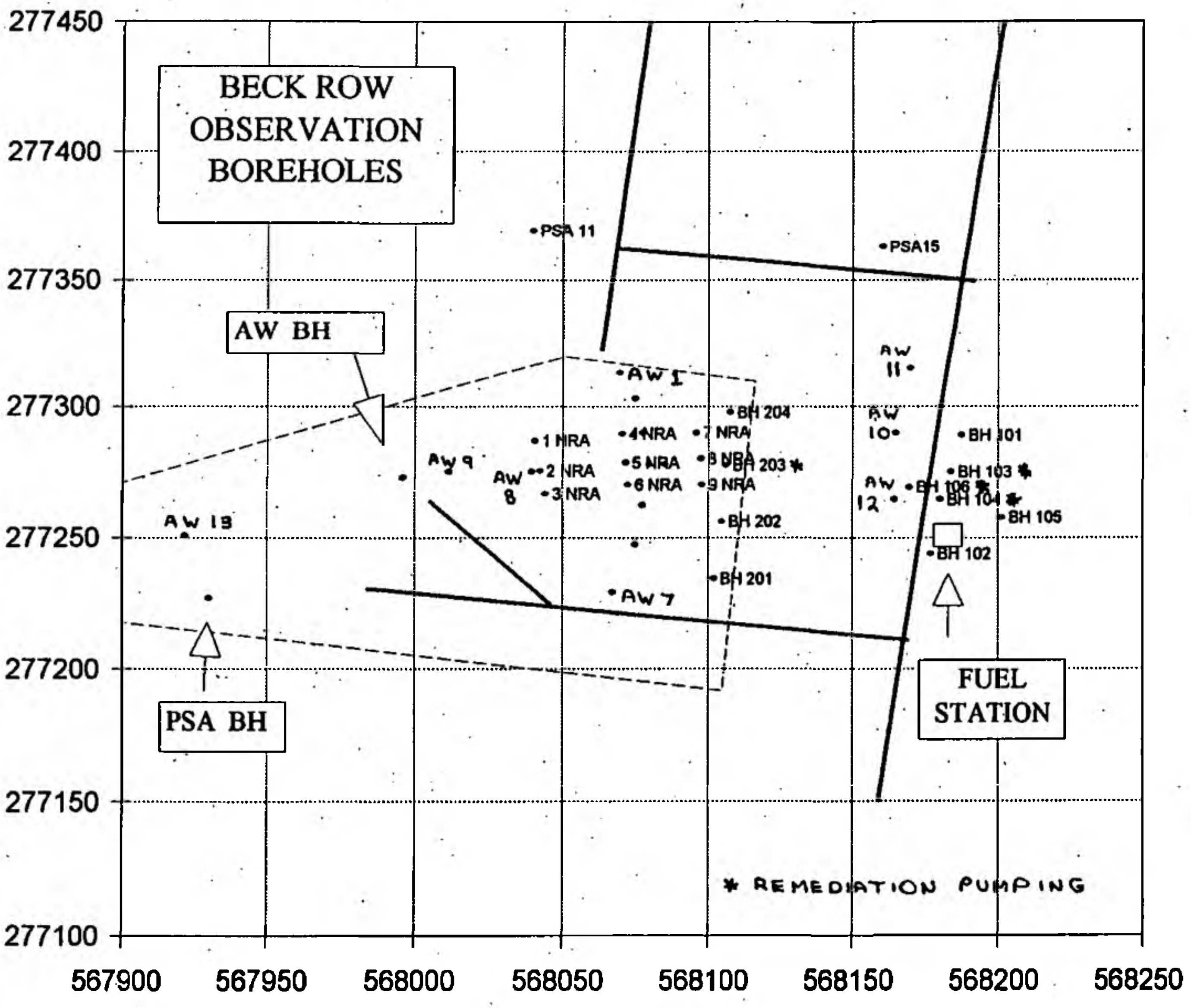
Feltham, J., Department of Industry and Trade - Oil and Gas Division, Rm 4.2, M11, 1 Palace Street, London, SW1E 5HE.

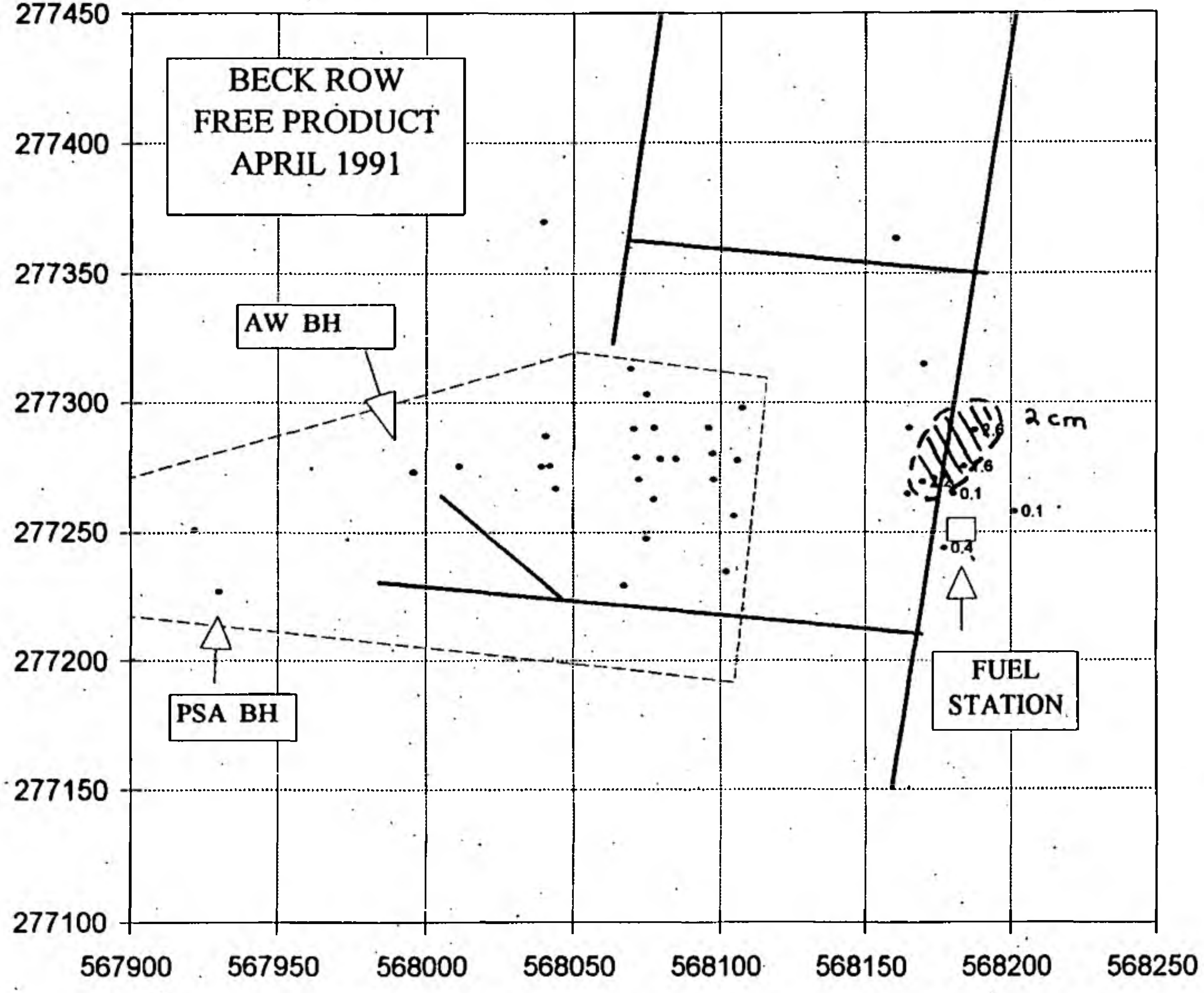
Monger, P., Petrol Retailers Association, 201 Great Portland Street, London, W1N 6AB.

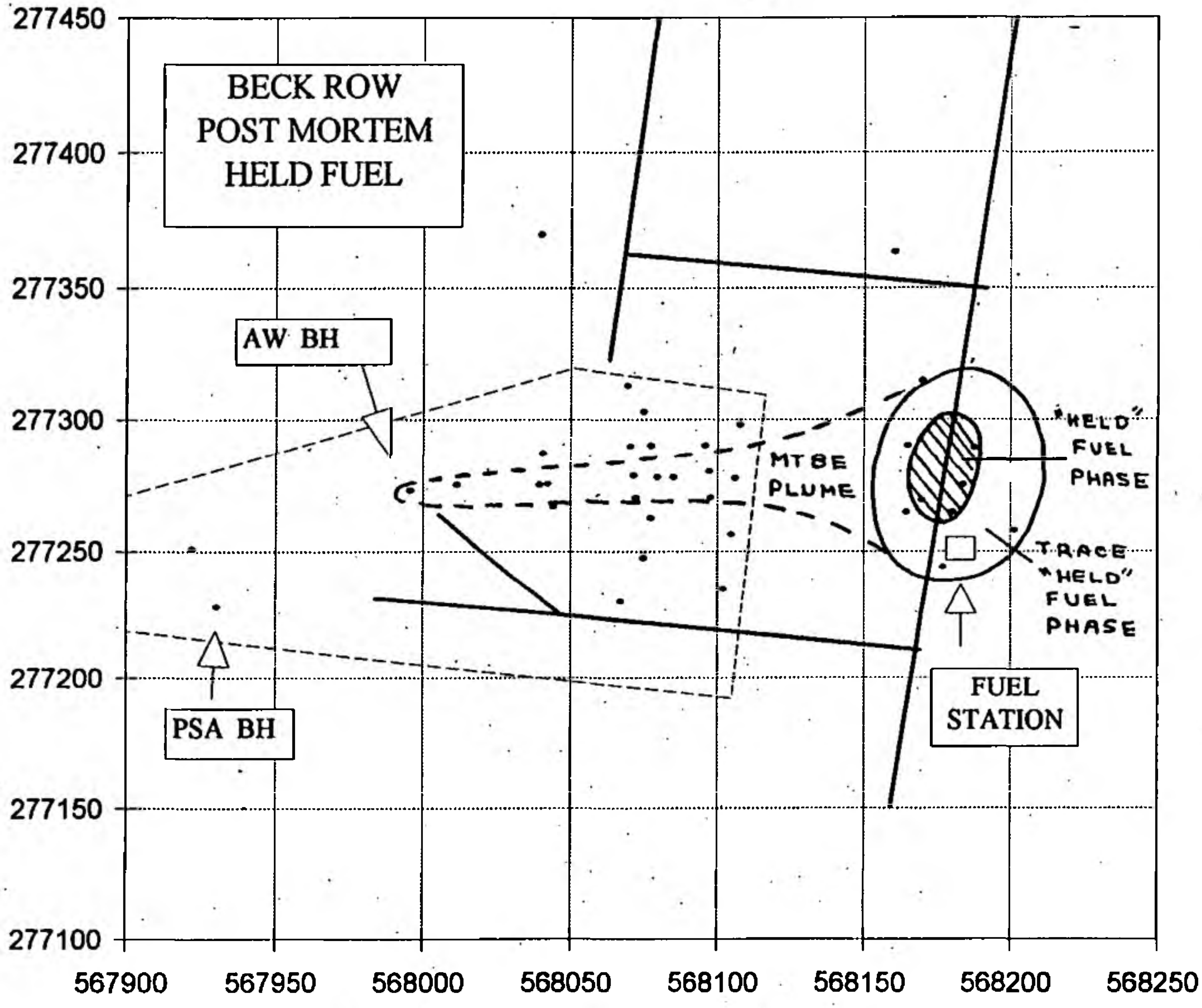
Pedley, J., Supply Fuel Additives, Shell U.K.

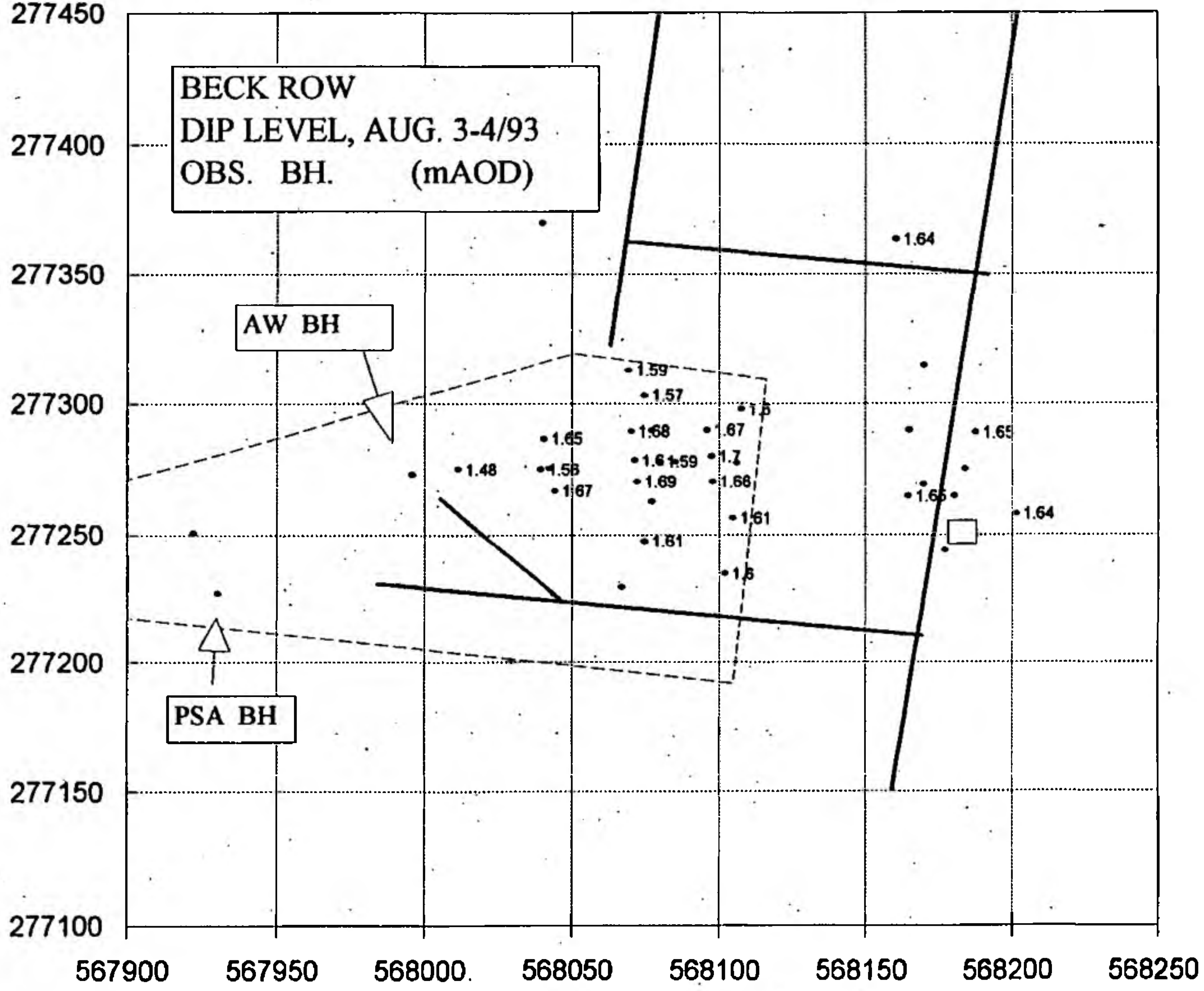
Appendix A

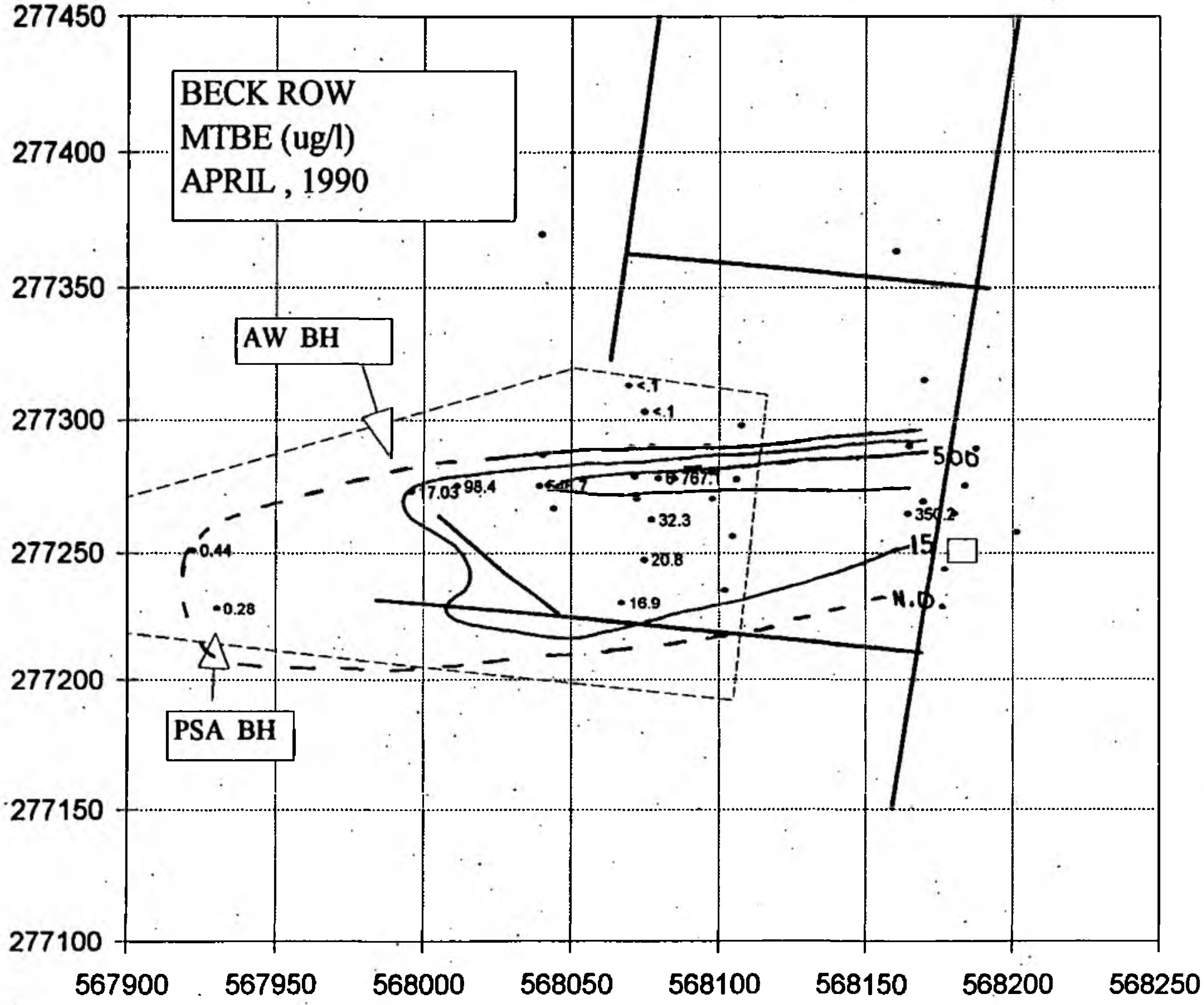
Beck Row Site Map and Contaminant Migration

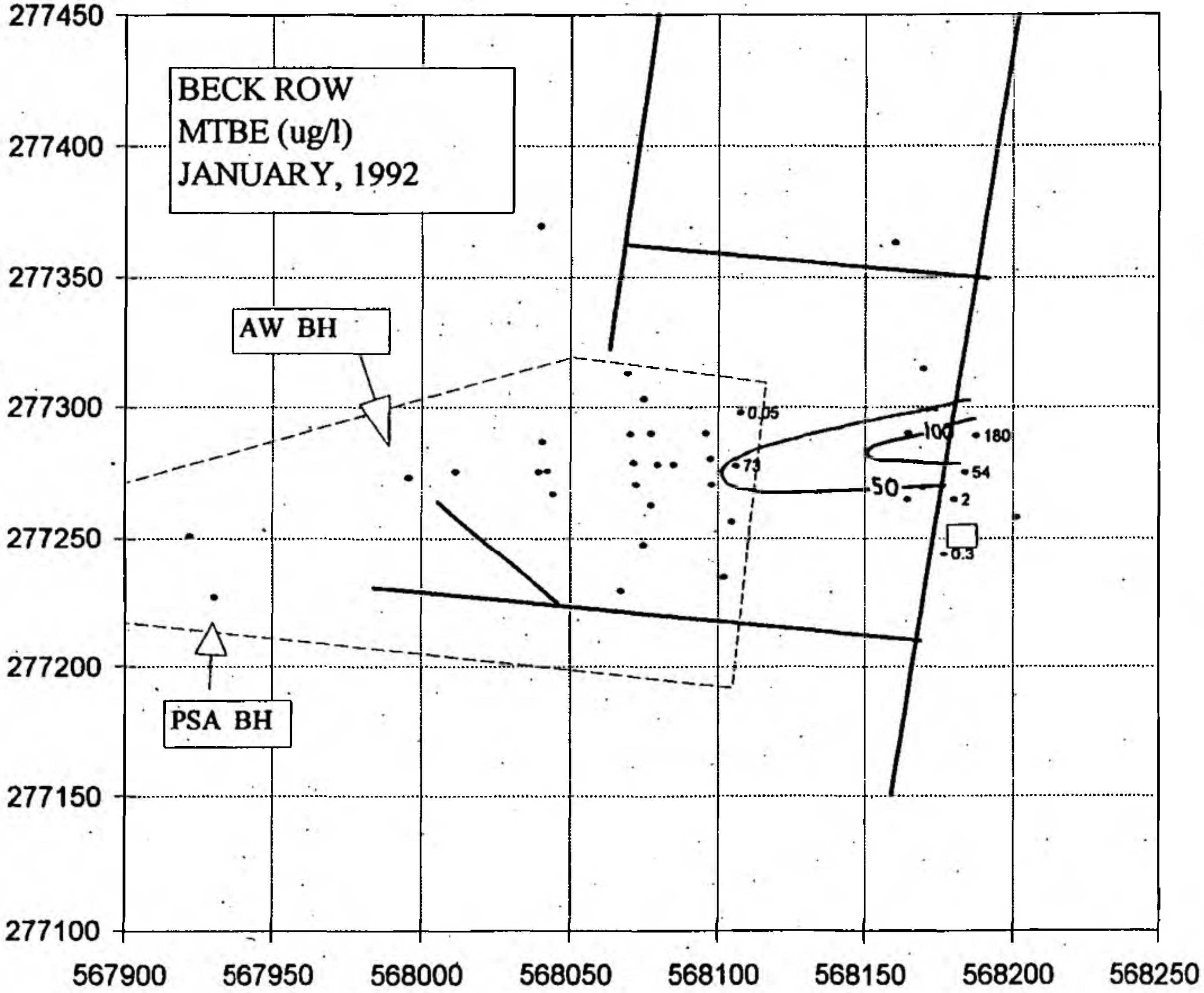

BECK ROW
OBSERVATION
BOREHOLES
AW BH
PSA BH
FUEL
STATION
PSA 11
PSA15
AW 1
AW 11
AW 10
AW 9
AW 8
AW 7
AW 12
AW 13
1 NRA
2 NRA
3 NRA
4 NRA
5 NRA
6 NRA
7 NRA
8 NRA
9 NRA
BH 204
BH 203 *
BH 202
BH 201
BH 101
BH 103 *
BH 106 *
BH 104 *
BH 105
BH 102
* REMEDIATION PUMPING
277450
277400
277350
277300
277250
277200
277150
277100
567900
567950
568000
568050
568100
568150
568200
568250

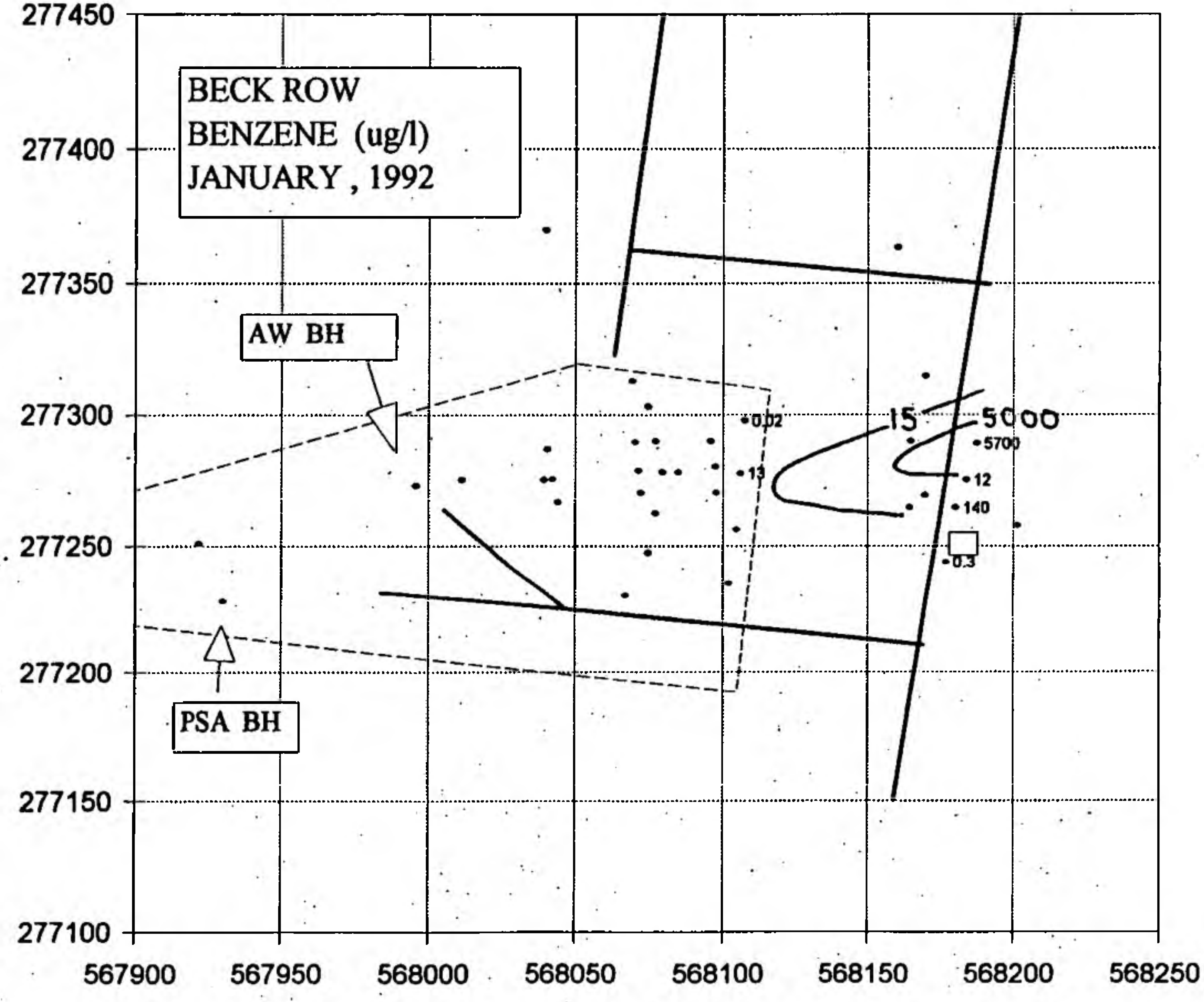

BECK ROW
FREE PRODUCT
APRIL 1991
AW BH
PSA BH
FUEL
STATION
2 cm
2.6
.6
0.1
0.1
0.4
277450
277400
277350
277300
277250
277200
277150
277100
567900
567950
568000
568050
568100
568150
568200
568250

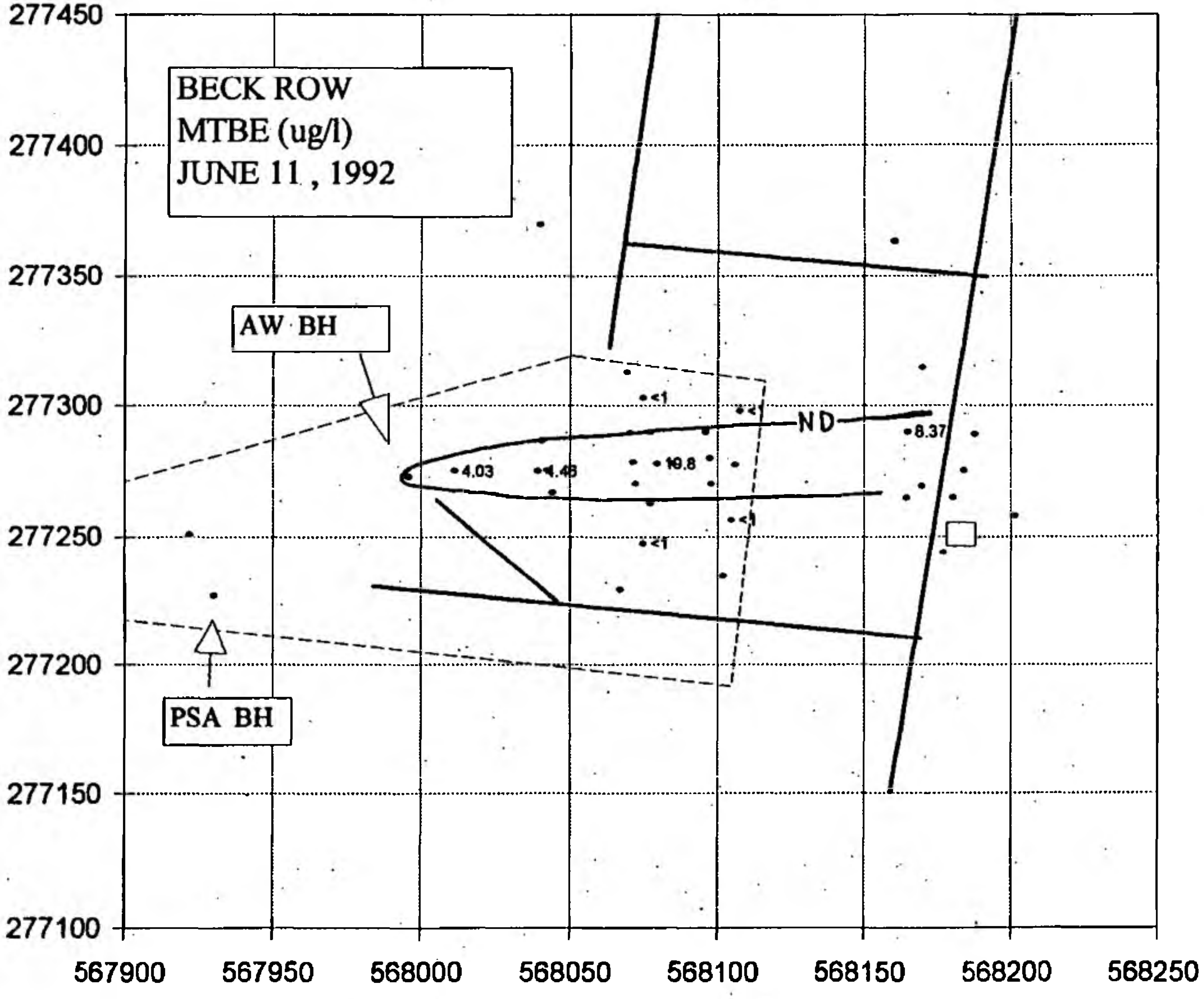

BECK ROW
POST MORTEM
HELD FUEL
AW BH
PSA BH
MTBE
PLUME
"HELD"
FUEL
PHASE
TRACE
"HELD"
FUEL
PHASE
FUEL
STATION
277450
277400
277350
277300
277250
277200
277150
277100
567900
567950
568000
568050
568100
568150
568200
568250

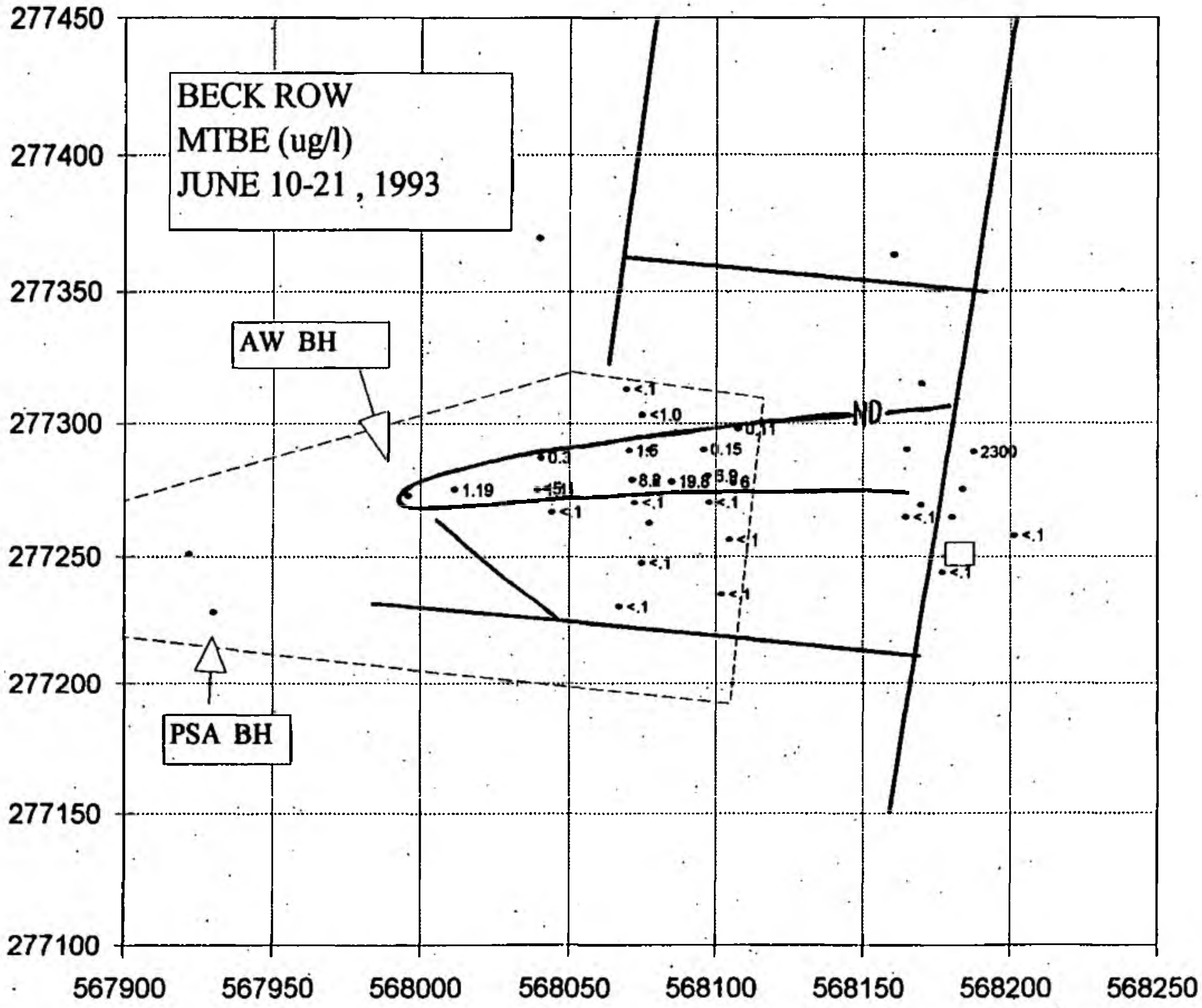

BECK ROW
DIP LEVEL, AUG. 3-4/93
OBS. BH. (mAOD)
AW BH
PSA BH
1.64
1.59
1.57
1.6
1.65
1.68
1.67
1.65
1.48
1.58
1.61
1.59
1.7
1.69
1.66
1.67
1.65
1.64
1.61
1.61
1.6
277450
277400
277350
277300
277250
277200
277150
277100
567900
567950
568000
568050
568100
568150
568200
568250

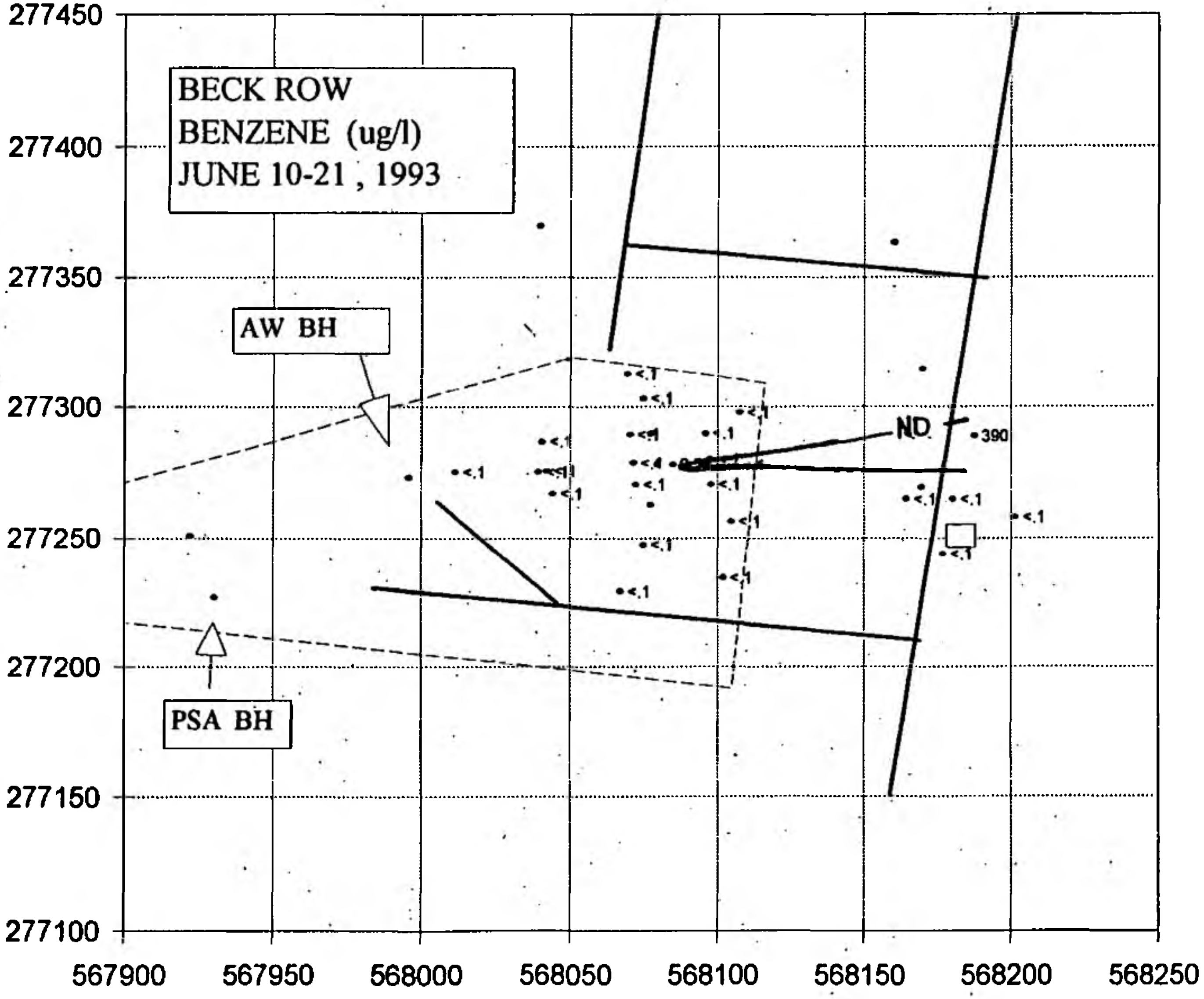

BECK ROW
MTBE (ug/l)
APRIL , 1990
AW BH
PSA BH
<.1
<.1
17.03
98.4
767.
32.3
20.8
16.9
350.2
500
15
N.D.
0.44
0.28
277450
277400
277350
277300
277250
277200
277150
277100
567900
567950
568000
568050
568100
568150
568200
568250

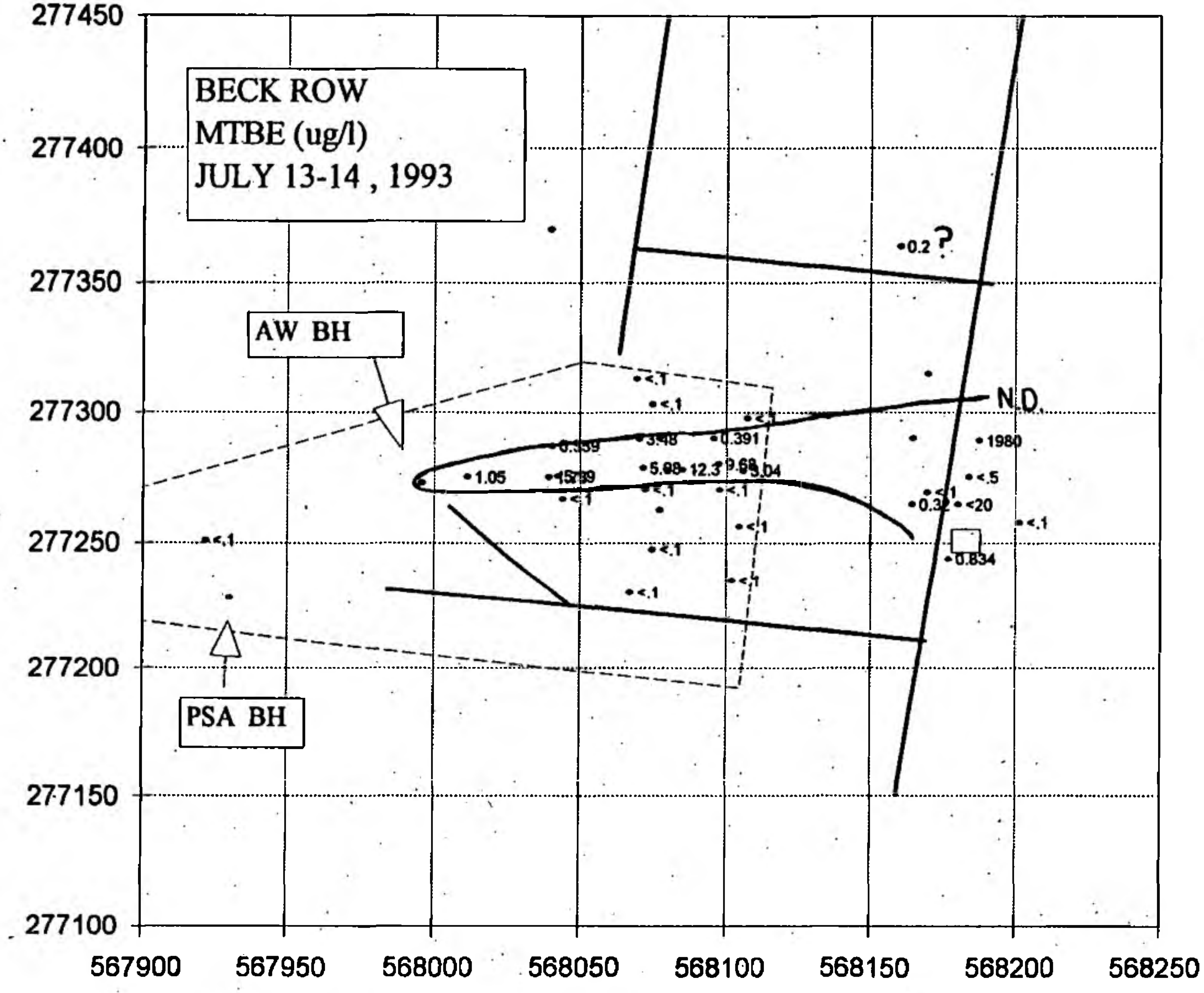

BECK ROW
MTBE (ug/l)
JANUARY, 1992
AW BH
PSA BH
0.05
100
180
73
54
50
2
0.3
277450
277400
277350
277300
277250
277200
277150
277100
567900
567950
568000
568050
568100
568150
568200
568250

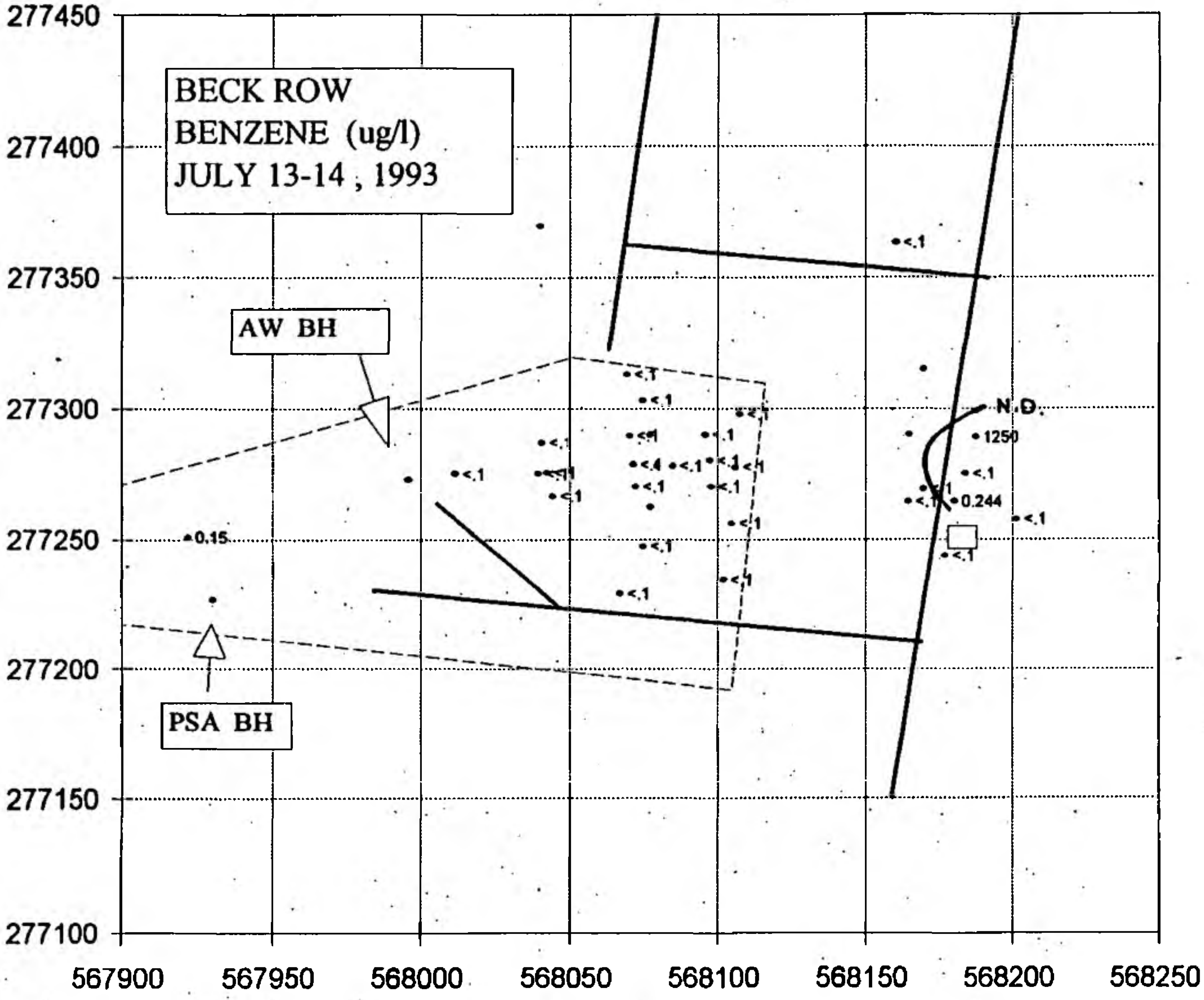

BECK ROW
BENZENE (ug/l)
JANUARY , 1992
AW BH
PSA BH
0.02
13
15
5000
5700
12
140
0.3
277450
277400
277350
277300
277250
277200
277150
277100
567900
567950
568000
568050
568100
568150
568200
568250

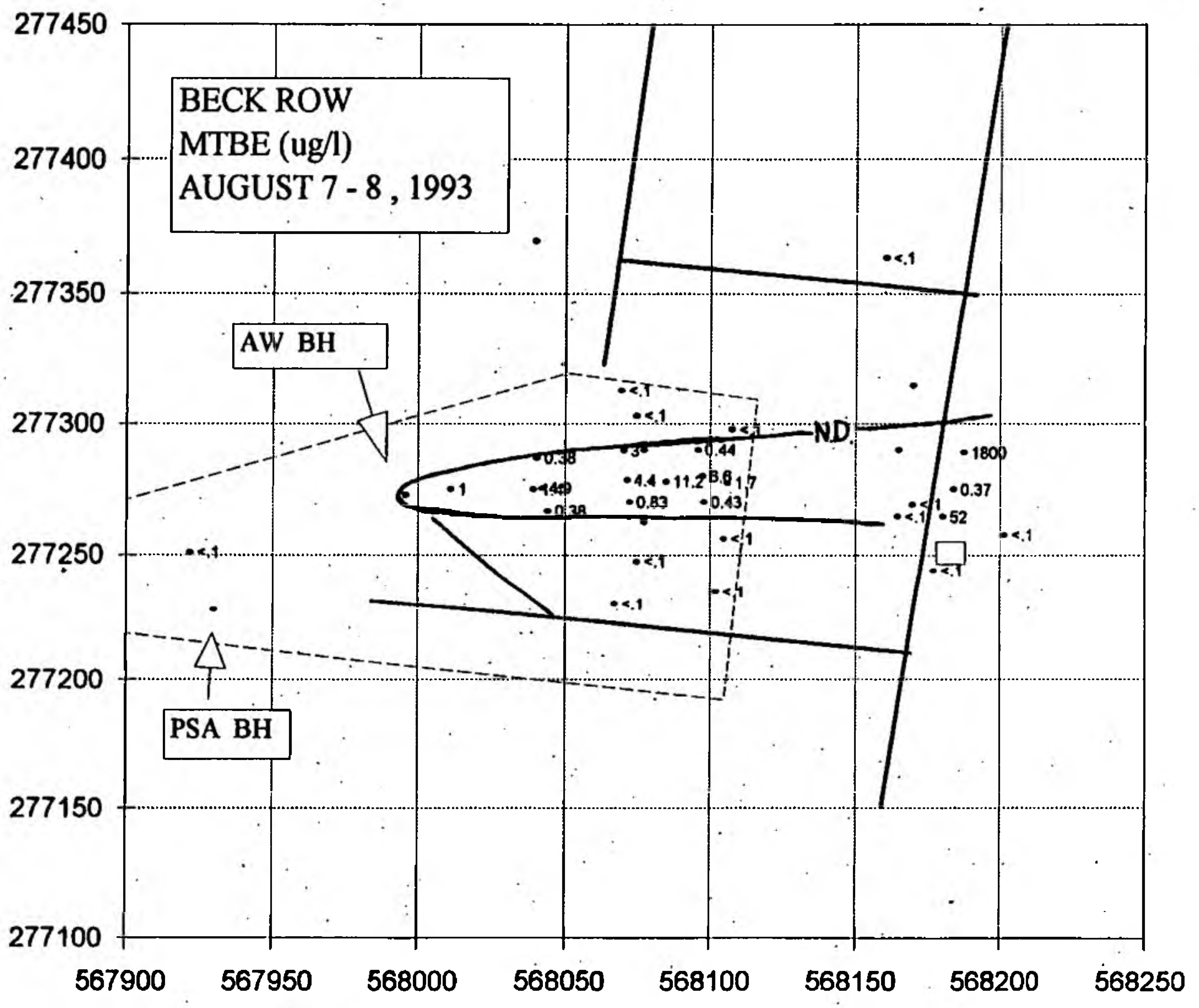

BECK ROW
MTBE (ug/l)
JUNE 11 , 1992
AW BH
PSA BH
ND
<1
<1
<1
<1
4.03
4.46
19.8
8.37
277450
277400
277350
277300
277250
277200
277150
277100
567900
567950
568000
568050
568100
568150
568200
568250

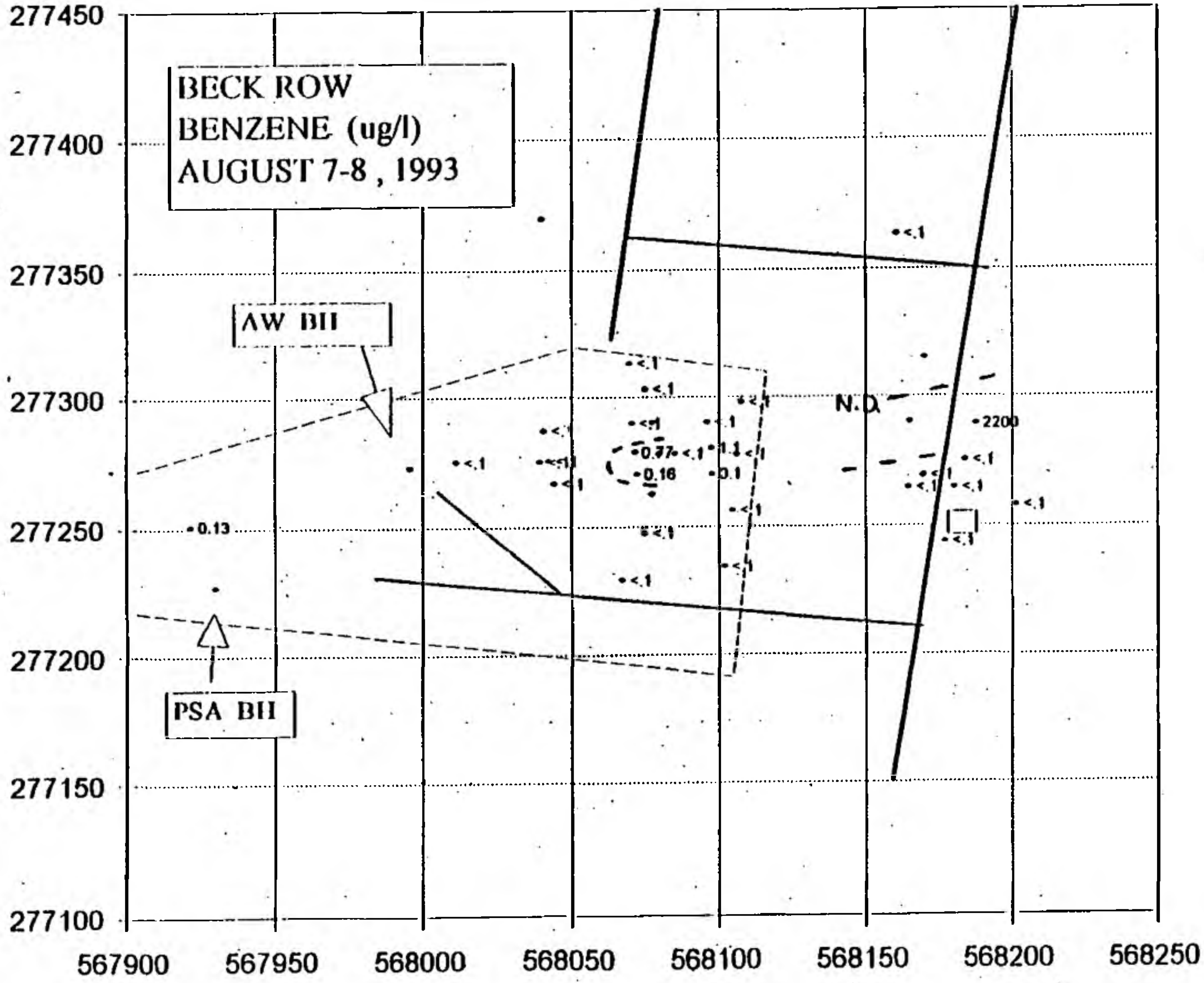

BECK ROW
MTBE (ug/l)
JUNE 10-21 , 1993
AW BH
PSA BH
ND
<.1
<1.0
0.11
0.3
1.6
0.15
2300
1.19
151
8.8
19.8
5.9
6
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
277450
277400
277350
277300
277250
277200
277150
277100
567900
567950
568000
568050
568100
568150
568200
568250


BECK ROW
BENZENE (ug/l)
JUNE 10-21 , 1993
AW BH
PSA BH
ND
390
<.1
<.4
277450
277400
277350
277300
277250
277200
277150
277100
567900
567950
568000
568050
568100
568150
568200
568250


BECK ROW
MTBE (ug/l)
JULY 13-14 , 1993
AW BH
PSA BH
N.D.
?
0.2
<.1
<.1
<.1
0.359
3.48
0.391
1980
1.05
15.39
5.98
12.3
9.68
3.04
<.5
<.1
<.1
<.1
<.1
0.32
<20
<.1
<.1
<.1
0.834
<.1
<.1
<.1
277450
277400
277350
277300
277250
277200
277150
277100
567900
567950
568000
568050
568100
568150
568200
568250


BECK ROW
BENZENE (ug/l)
JULY 13-14 , 1993
AW BH
PSA BH
N.D.
1250
0.244
0.15
<.1
<.1
<.1
<.1
<.1
<.1
<.4
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
277450
277400
277350
277300
277250
277200
277150
277100
567900
567950
568000
568050
568100
568150
568200
568250


BECK ROW
MTBE (ug/l)
AUGUST 7 - 8 , 1993
AW BH
PSA BH
ND
<.1
1800
0.37
52
0.38
3
0.44
4.4
11.2
8.6
1.7
1449
1
0.83
0.43
277450
277400
277350
277300
277250
277200
277150
277100
567900
567950
568000
568050
568100
568150
568200
568250

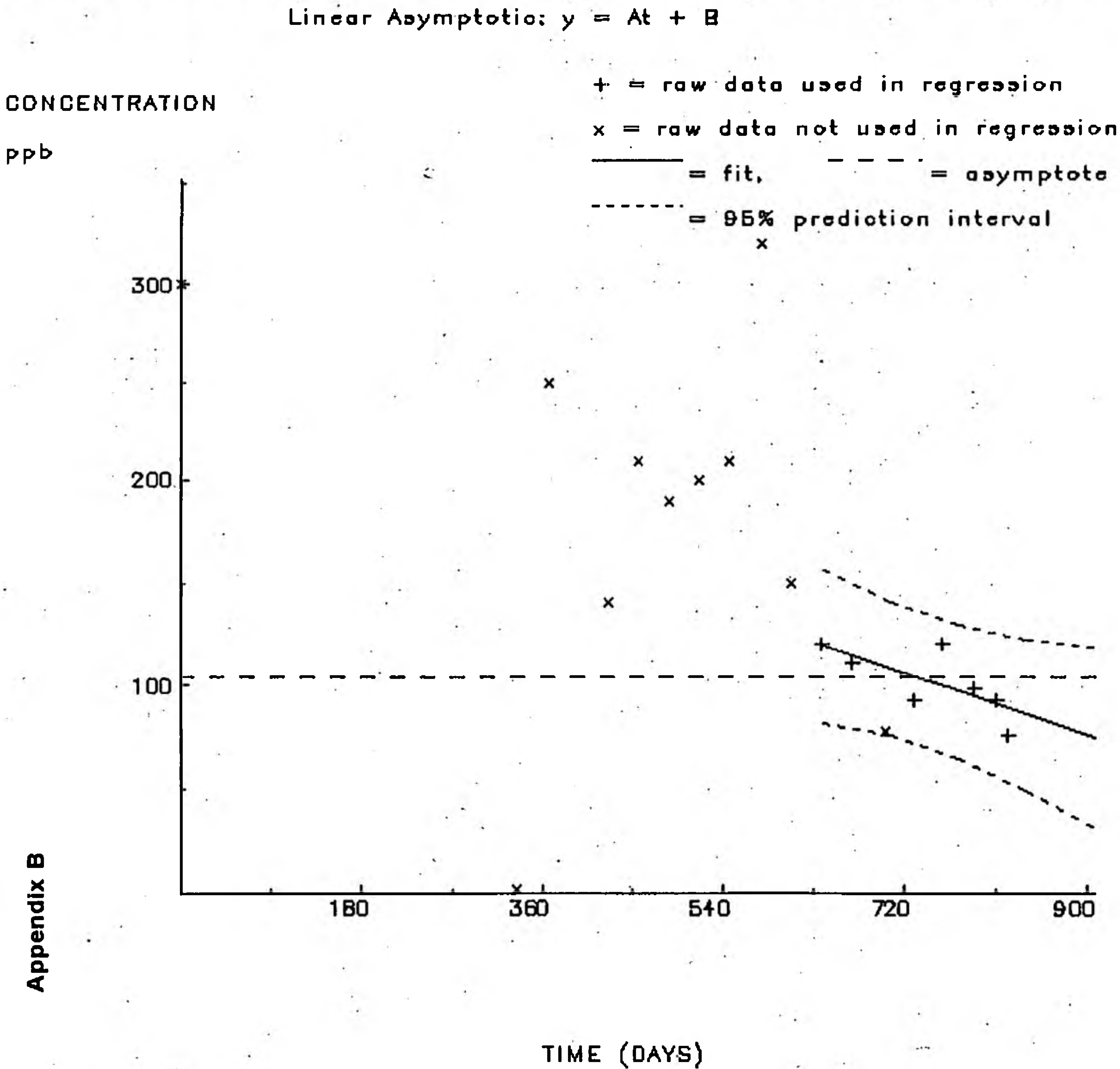

BECK ROW
BENZENE (ug/l)
AUGUST 7-8 , 1993
AW BH
PSA BH
N.D
2200
0.77
0.16
0.1
1.1
0.13
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
<.1
277450
277400
277350
277300
277250
277200
277150
277100
567900
567950
568000
568050
568100
568150
568200
568250

Appendix B

Regression Analysis on Remediation Borehole 104

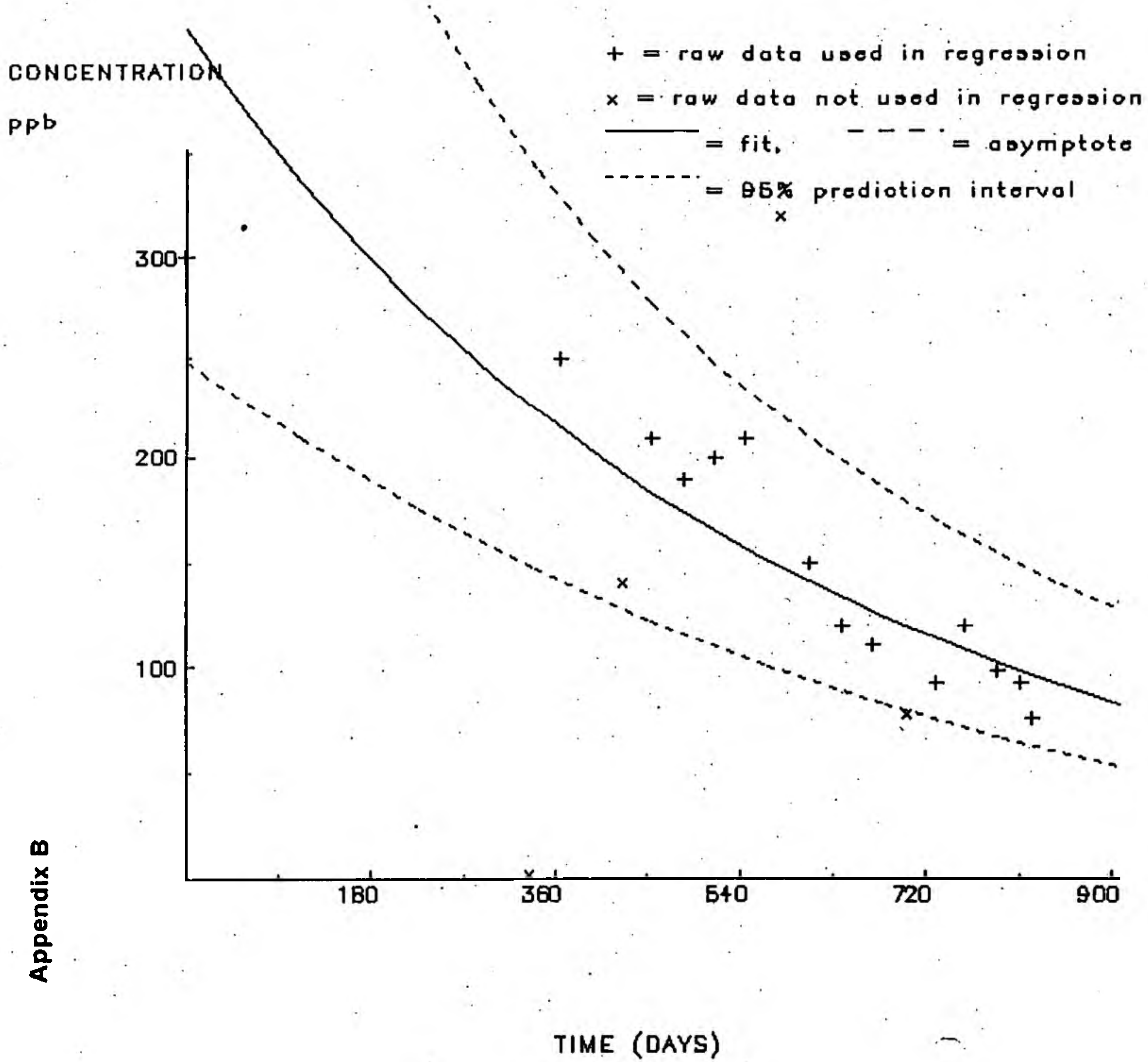
Appendix B

```
DATA MONITORING ANALYSIS REPORT                       07/29/1993, Page 01

  Input data file: C:\REGRESS\BH104M.RAW
     Last revised: 07/24/1993               Fit Performed: 07/29/1993
Total data points: 18                   # Data points used: 7

     Fit equation: 1 - Linear Asymptotic: y = At + B

     Coefficients:  A =    -0.1661,
                    B =   225.1562,
           ASYMPTOTE =    103.71

                                   Sum of (residuals^2): 7.643E+002
Maximum Difference between 95% Confidence Interval and Fit: 19.64
Maximum Difference between 90% Confidence Interval and Fit: 15.39
   Critical Value:  0.3489              Standard Deviation: 16.5572

Data set:  ( Concentration units = ppb )
Point #:  Date:         # Days:  Raw Conc.:   Fit Conc.:      %Error
 1                         334        2.00
 2                         425      140.00
 3                         578      320.00
 11       11/01/1992       639      120.00       118.99         0.8%
 12       12/01/1992       669      110.00       114.01        -3.6%
 6                         700       77.00
 7                           0      300.00
 8                         365      250.00
 9                         455      210.00
 10                        486      190.00
 11                        516      200.00
 12                        547      210.00
 13                        608      150.00
 14       02/01/1993       731       92.00       103.71       -12.7%
 15       03/01/1993       759      120.00        99.05        17.5%
 16       04/02/1993       791       98.00        93.74         4.3%
 17       04/23/1993       812       92.00        90.25         1.9%
 18       05/05/1993       824       76.00        88.25       -16.1%
```


Linear Asymptotic: y = At + B
+ = raw data used in regression
x = raw data not used in regression
= fit,
= asymptote
= 95% prediction interval
CONCENTRATION
ppb
300
200
100
180
360
540
720
900
TIME (DAYS)

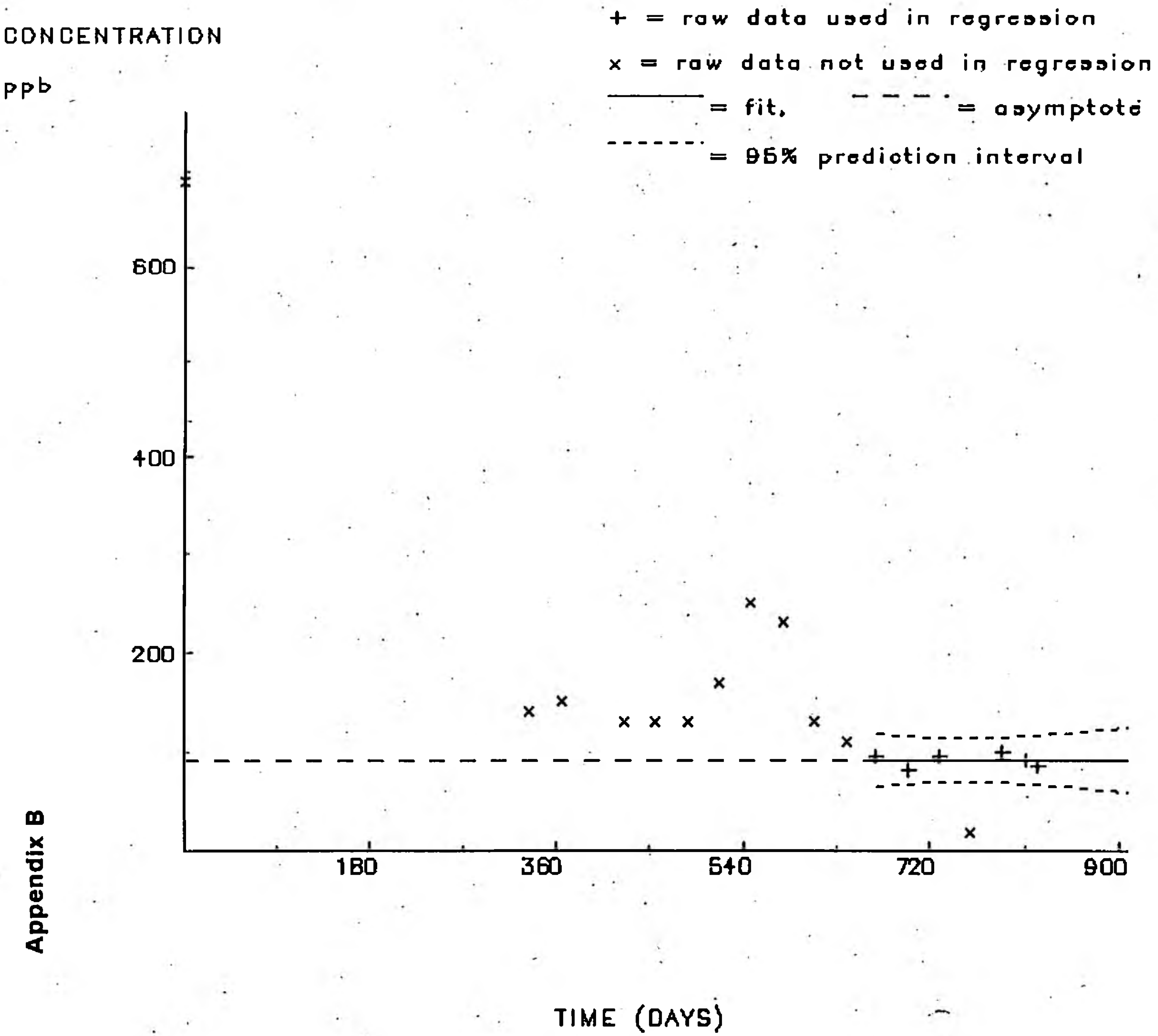
Appendix B

```
DATA MONITORING ANALYSIS REPORT                    07/24/1993, Page 0

  Input data file: C:\REGRESS\BH104M.RAW
     Last revised: 07/24/1993              Fit Performed: 07/24/199
Total data points: 18                    # Data points used: 14

     Fit equation: 3 - Exponential:        y = Ae^(Bt)

     Coefficients:  A =    409.9583,
                    B =     -0.0018,
            ASYMPTOTE =      0.00

            R^2: 1.3941          Sum of (residuals^2): 2.002E+00

Data set:  ( Concentration units = ppb )
Point #:  Date:        # Days:   Raw Conc.:   Fit Conc.:      %Erro
 1        02/01/1991        0       300.00       409.96       -36.7
 2                        334         2.00
 3        02/01/1992      365       250.00       214.89        14.0
 4                        425       140.00
 5        05/01/1992      455       210.00       183.25        12.7
 6        06/01/1992      486       190.00       173.47         8.7
 7        07/01/1992      516       200.00       164.50        17.7
 8        08/01/1992      547       210.00       155.72        25.8
 9                        578       320.00
 10       10/01/1992      608       150.00       139.79         6.8
 11       11/01/1992      639       120.00       132.32       -10.3
 12       12/01/1992      669       110.00       125.48       -14.1
 13                       700        77.00
 14       02/01/1993      731        92.00       112.44       -22.2
 15       03/01/1993      759       120.00       107.01        10.8
 16       04/02/1993      791        98.00       101.12        -3.2
 17       04/23/1993      812        92.00        97.43        -5.9
 18       05/05/1993      824        76.00        95.38       -25.5
```


+ = raw data used in regression
x = raw data not used in regression
= fit,
= asymptote
= 95% prediction interval
CONCENTRATION
ppb
300
200
100
180
360
540
720
900
TIME (DAYS)

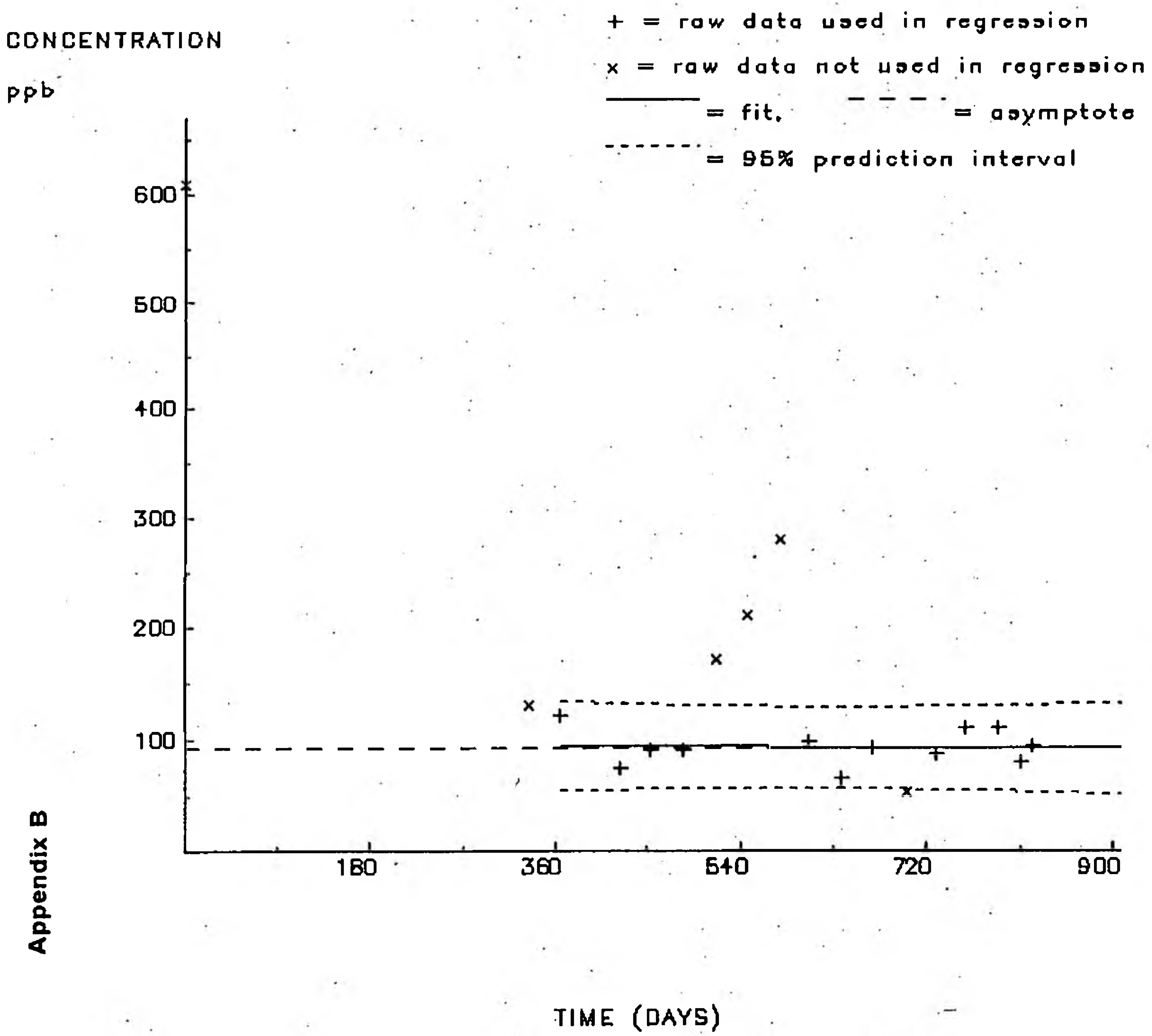
Appendix B

```
DATA MONITORING ANALYSIS REPORT                         07/24/1993, Page 0

  Input data file: C:\REGRESS\BH104B.RAW
     Last revised: 07/24/1993             Fit Performed: 07/24/199
Total data points: 18                   # Data points used: 6

     Fit equation: 1 - Linear Asymptotic: y = At + B

     Coefficients:  A =      0.0019,
                    B =     90.4025,
           ASYMPTOTE =      91.82

                                     Sum of (residuals^2): 2.528E+00
Maximum Difference between 95% Confidence Interval and Fit: 13.24
Maximum Difference between 90% Confidence Interval and Fit: 10.17
   Critical Value:  0.1568                Standard Deviation: 7.111

Data set:  ( Concentration units = ppb )
Point #:  Date:        # Days:   Raw Conc.:   Fit Conc.:      %Erro
 1                       547      250.00
 2                       578      230.00
 12       12/01/1992     669       96.00        91.67           4.5
 13       01/01/1993     700       81.00        91.73         -13.2
 14       02/01/1993     731       96.00        91.79           4.4
 6                       759       20.00
 7                         0      690.00
 8                       334      140.00
 9                       365      150.00
 10                      425      130.00
 11                      455      130.00
 12                      486      130.00
 13                      516      170.00
 14                      608      130.00
 15                      639      110.00
 16       04/02/1993     791      100.00        91.90           8.1
 17       04/23/1993     812       92.00        91.94           0.1
 18       05/05/1993     824       86.00        91.97          -6.9
```


CONCENTRATION
ppb
+ = raw data used in regression
x = raw data not used in regression
= fit,
= asymptote
= 95% prediction interval
600
400
200
180
360
540
720
900
TIME (DAYS)

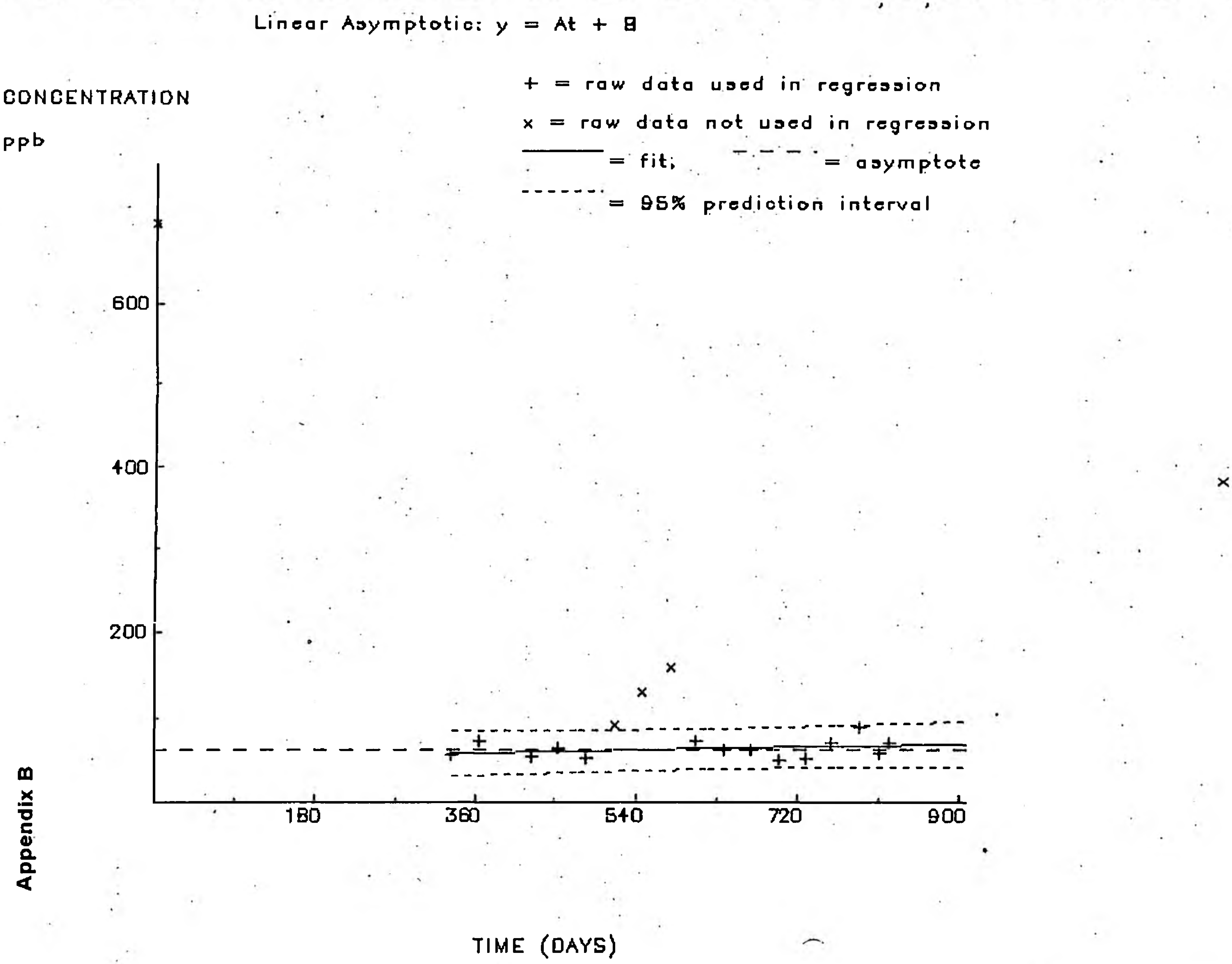
Appendix B

```
DATA MONITORING ANALYSIS REPORT                    07/24/1993, Page 0

  Input data file: C:\REGRESS\BH104T.RAW
     Last revised: 07/24/1993          Fit Performed: 07/24/199
Total data points: 18              # Data points used: 12

     Fit equation: 1 - Linear Asymptotic: y = At + B

     Coefficients:  A =     -0.0041,
                    B =     95.3370,
           ASYMPTOTE =      92.90

                                   Sum of (residuals^2): 2.611E+00
Maximum Difference between 95% Confidence Interval and Fit: 17.76
Maximum Difference between 90% Confidence Interval and Fit: 14.45
   Critical Value:  0.0711              Standard Deviation: 15.42

Data set:  ( Concentration units = ppb )
Point #:  Date:       # Days:   Raw Conc.:   Fit Conc.:     %Erro
 3        02/01/1992    365       120.00        93.84        21.8
 4        04/01/1992    425        75.00        93.59       -24.8
 5        05/01/1992    455        91.00        93.47        -2.7
 6        06/01/1992    486        91.00        93.34        -2.6
 5                      516       170.00
 6                      547       210.00
 7                      578       280.00
 10       10/01/1992    608        97.00        92.84         4.3
 11       11/01/1992    639        66.00        92.71       -40.5
 12       12/01/1992    669        93.00        92.59         0.4
 11                     700        52.00
 12                       0       610.00
 13                     334       130.00
 14       02/01/1993    731        87.00        92.34        -6.1
 15       03/01/1993    759       110.00        92.22        16.2
 16       04/02/1993    791       110.00        92.09        16.3
 17       04/23/1993    812        79.00        92.00       -16.5
 18       05/05/1993    824        94.00        91.96         2.2
```


CONCENTRATION
ppb
+ = raw data used in regression
x = raw data not used in regression
= fit,
= asymptote
= 95% prediction interval
600
500
400
300
200
100
180
360
540
720
900
TIME (DAYS)

Appendix B

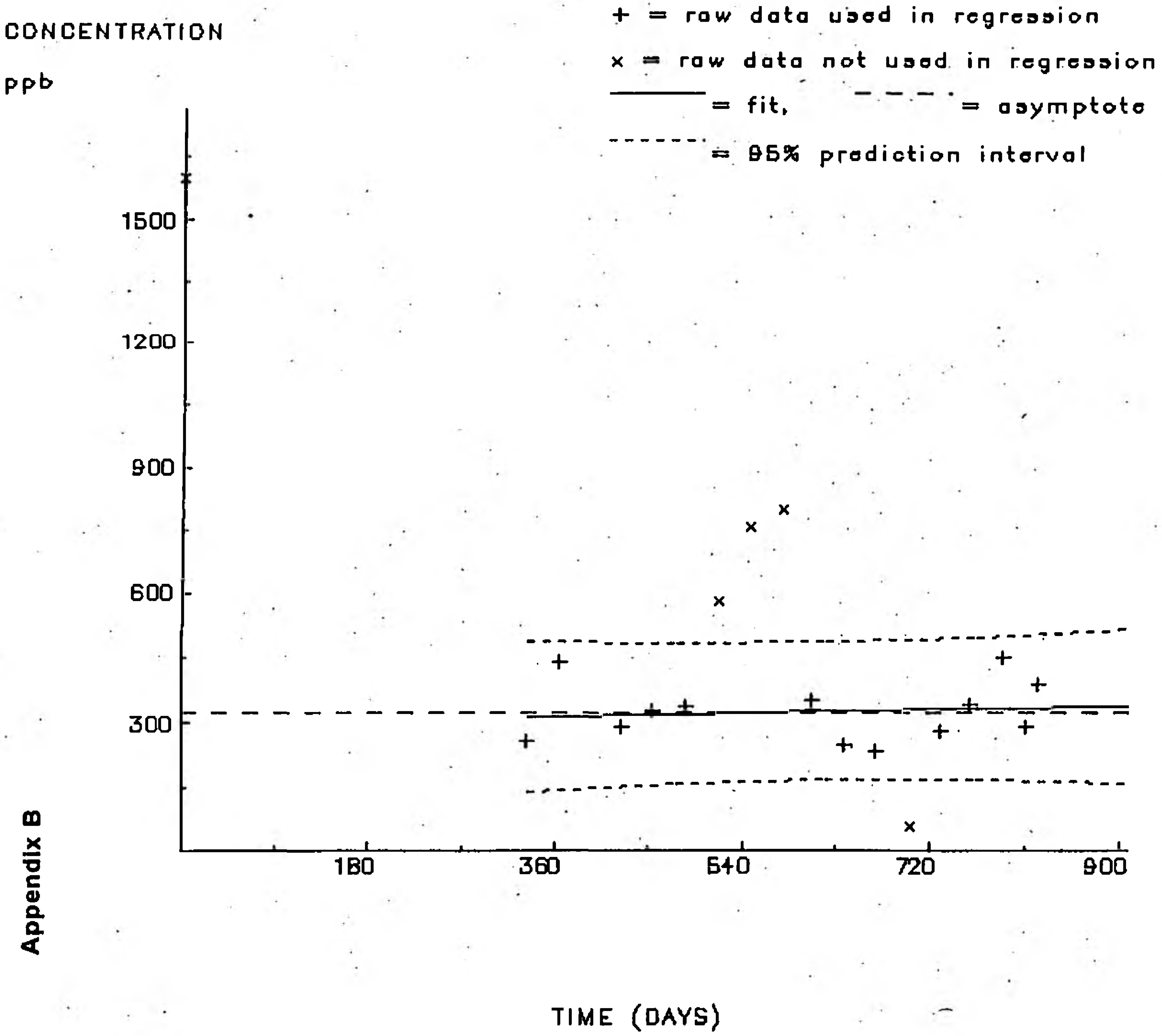
```
DATA MONITORING ANALYSIS REPORT                07/24/1993, Page 0

  Input data file: C:\REGRESS\BH104E.RAW
     Last revised: 07/24/1993            Fit Performed: 07/24/199
Total data points: 18               # Data points used: 14

     Fit equation: 1 - Linear Asymptotic: y = At + B

     Coefficients: A =     0.0160,
                   B =    53.7705,
            ASYMPTOTE =    63.01

                                  Sum of (residuals^2): 1.451E+00
Maximum Difference between 95% Confidence Interval and Fit: 10.92
Maximum Difference between 90% Confidence Interval and Fit: 8.93
   Critical Value:  0.0549                Standard Deviation: 10.92

Data set:  ( Concentration units = ppb )
Point #:  Date:       # Days:   Raw Conc.:    Fit Conc.:     %Erro
 2        01/01/1992     334        57.00        59.10        -3.7
 3        02/01/1992     365        73.00        59.60        18.4
 4        04/01/1992     425        54.00        60.55       -12.1
 5        05/01/1992     455        64.00        61.03         4.6
 6        06/01/1992     486        53.00        61.53       -16.1
 6                       516        91.00
 7                       547       130.00
 8                       578       160.00
 9                         0       700.00
 10       10/01/1992     608        73.00        63.47        13.1
 11       11/01/1992     639        62.00        63.97        -3.2
 12       12/01/1992     669        62.00        64.45        -3.9
 13       01/01/1993     700        51.00        64.94       -27.3
 14       02/01/1993     731        52.00        65.44       -25.8
 15       03/01/1993     759        70.00        65.88         5.9
 16       04/02/1993     791        90.00        66.39        26.2
 17       04/23/1993     812        58.00        66.73       -15.0
 18       05/05/1993     824        71.00        66.92         5.7
```


Linear Asymptotic: y = At + B
+ = raw data used in regression
x = raw data not used in regression
= fit;
= asymptote
= 95% prediction interval
CONCENTRATION
ppb
600
400
200
180
360
540
720
900
TIME (DAYS)

Appendix B

Appendix B

```
DATA MONITORING ANALYSIS REPORT                   07/24/1993, Page 0

  Input data file: C:\REGRESS\BH104X.RAW
     Last revised: 07/24/1993            Fit Performed: 07/24/199
Total data points: 18                  # Data points used: 13

     Fit equation: 1 - Linear Asymptotic: y = At + B

     Coefficients:  A =     0.0407,
                    B =   299.3580,
           ASYMPTOTE =    322.92

                                   Sum of (residuals^2): 5.785E+00
Maximum Difference between 95% Confidence Interval and Fit: 71.75
Maximum Difference between 90% Confidence Interval and Fit: 58.55
   Critical Value:  0.3030                  Standard Deviation: 69.81

Data set:  ( Concentration units = ppb )
Point #:  Date:       # Days:   Raw Conc.:    Fit Conc.:       %Erro
 2        01/01/1992     334       254.00        312.95        -23.2
 3        02/01/1992     365       438.00        314.21         28.3
 4        04/01/1992     425       288.00        316.65         -9.9
 5        05/01/1992     455       326.00        317.87          2.5
 6        06/01/1992     486       334.00        319.13          4.5
 6                       516       580.00
 7                       547       760.00
 8                       578       800.00
 10       10/01/1992     608       350.00        324.10          7.4
 11       11/01/1992     639       246.00        325.36        -32.3
 12       12/01/1992     669       230.00        326.58        -42.0
 12                      700        58.00
 13                        0      1600.00
 14       02/01/1993     731       281.00        329.10        -17.1
 15       03/01/1993     759       340.00        330.24          2.9
 16       04/02/1993     791       450.00        331.54         26.3
 17       04/23/1993     812       287.00        332.40        -15.8
 18       05/05/1993     824       389.00        332.88         14.4
```


CONCENTRATION
ppb
+ = raw data used in regression
x = raw data not used in regression
= fit,
= asymptote
= 95% prediction interval
1500
1200
900
600
300
180
360
540
720
900
TIME (DAYS)

Appendix C - Dip Levels

Site Name (-)	Grid Ref (ref)	Eastings (m)	Northings (m)	Datum Elevation AOD (m)	BH Depth (m)	June 10-15/93 Dip Level (m)	AOD (m)
Beck Row	TL6799 7	567996	277273	4.90			
PSA Supply		567930	277227				
PSA 11		568040	277370				
PSA 15		568160	277364	5.63	28.67		
AWA 1		568069	277313	4.99	11.27	3.30	1.69
AWA 2		568075	277303	5.08	4.49	3.39	1.69
AWA 3		568078	277290				
AWA 4		568080	277278	5.31	9.10	3.60	1.71
AWA 4A		568085	277278				
AWA 5		568078	277263				
AWA 6		568075	277247	4.88	7.14	3.18	1.70
AWA 7		568067	277229		7.50		
AWA 8		568040	277275	5.02	5.03	3.33	1.69
AWA 9a		568012	277275	5.36	13.55	3.75	1.61
AWA 10		568165	277290				
AWA 11		568170	277315				
AWA 12		568165	277265	5.81	10.50		
AWA 13		567922	277251		28.18		
BH 101		568188	277289	6.00	7.32	4.20	1.80
BH 102		568177	277244		7.92		
BH 103		568184	277275	5.53			
BH 104		568180	277265	5.58			
BH 105		568202	277258	5.66	7.70	3.91	1.75
BH 106		568170	277269	5.75			
BH 201		568102	277234	5.25	7.39		
BH 202	TL6810 7	568105	277256	5.17	7.53		
BH 203		568106	277278	4.93			
BH 204	TL6811 7	568108	277298	4.95	7.70		
1 NRA	TL6803 7	568041	277287	4.62	7.94	2.84	1.78
2 NRA	TL6804 7	568042	277276		7.93	2.93	
3 NRA	TL6804 7	568044	277267	4.79	7.92	2.99	1.80
4 NRA	TL6807 7	568070	277290	4.80	7.94	2.90	1.90
5 NRA	TL6807 7	568071	277279	4.72	7.94	2.99	1.73
6 NRA	TL6807 7	568072	277270	4.81	7.93	2.99	1.82
7 NRA	TL6810 7	568096	277290	4.87	7.92	3.05	1.82
8 NRA	TL6810 7	568097	277280	4.84	7.93	3.01	1.83
9 NRA	TL6810 7	568098	277270	5.01	7.93	3.22	1.79

Appendix C - Dip Levels

Site Name	July 14 /93		Aug. 3-4 /93	
(-)	Dip Level (m)	AOD (m)	Dip Level (m)	AOD (m)
Beck Row				
PSA Supp				
PSA 11				
PSA 15			3.99	1.64
AWA 1			3.40	1.59
AWA 2			3.51	1.57
AWA 3				
AWA 4			3.72	1.59
AWA 4A				
AWA 5				
AWA 6			3.27	1.61
AWA 7			3.46	
AWA 8			3.46	1.56
AWA 9a			3.88	1.48
AWA 10				
AWA 11				
AWA 12	4.11	1.70	4.16	1.65
AWA 13			3.98	
BH 101	4.30	1.70	4.35	1.65
BH 102	3.81		3.86	
BH 103				
BH 104				
BH 105	3.93	1.73	4.02	1.64
BH 106				
BH 201			3.65	1.60
BH 202			3.56	1.61
BH 203				
BH 204			3.35	1.60
1 NRA			2.97	1.65
2 NRA			3.07	
3 NRA			3.12	1.67
4 NRA			3.12	1.68
5 NRA			3.12	1.60
6 NRA			3.12	1.69
7 NRA			3.20	1.67
8 NRA			3.14	1.70
9 NRA			3.35	1.66

Appendix C - Chemical Data

Site Name (-)	PSA Dip Free Prod. April 1991 (cm)	NRA 1 MTBE Date	Pumped ug/l	Static Sample Prepump ug/l	Static Sample Postpump ug/l	NRA 2 MTBE Jun 26/90 ug/l
Beck Row		April 4/90	17.03			
PSA BH		April 4/90	0.28	0.21	Treated	
PSA 11		Jan 11/90		0.10		0.15
PSA 15						
AWA 1		April 17/90	<.1		948.20	
AWA 2		April 17/90	<.1			
AWA 3		April 17/90				
AWA 4		April 10/90	6.00			
AWA 4A		April 10/90	767.10			
AWA 5		April 10/90	32.30			
AWA 6		April 10/90	20.80			
AWA 7		April 10/90	16.90			
AWA 8		April 10/90	546.70			
AWA 9a		April 9/90	98.40			
AWA 10						
AWA 11						
AWA 12		April 11/90	350.20		563.50	
AWA 13		April 11/90	0.44			
BH 101	2.6					
BH 102	0.4					
BH 103	1.6					
BH 104	0.1					
BH 105	0.1					
BH 106	2.2					
BH 201						
BH 202						
BH 203						
BH 204						
1 NRA						
2 NRA						
3 NRA						
4 NRA						
5 NRA						
6 NRA						
7 NRA						
8 NRA						
9 NRA						
Catchwater Drain						

Appendix C - Chemical Data

Site Name	MOD1 MTBE Feb 91	Benzene	Toluene	Ethylbenzene	Xylene
(-)	ug/l	ug/l	ug/l	ug/l	ug/l
Beck Row					
PSA BH					
PSA 11					
PSA 15					
AWA 1					
AWA 2					
AWA 3					
AWA 4					
AWA 4A					
AWA 5					
AWA 6					
AWA 7					
AWA 8					
AWA 9a					
AWA 10					
AWA 11					
AWA 12					
AWA 13					
BH 101	1700.00	6400.00	9200.00	1800.00	12000.00
BH 102	0.00	2.00	10.00	6.00	35.00
BH 103	0.00	420.00	600.00	190.00	860.00
BH 104	300.00	690.00	610.00	700.00	1600.00
BH 105					
BH 106					
BH 201					
BH 202					
BH 203					
BH 204					
1 NRA					
2 NRA					
3 NRA					
4 NRA					
5 NRA					
6 NRA					
7 NRA					
8 NRA					
9 NRA					
Catchwater Drain					

Appendix C - Chemical Data

Site Name (-)	PSA1 MTBE Jan 92 ug/l	Benzene ug/l	Toluene ug/l	Ethylbenzene ug/l	Xylene ug/l
Beck Row					
PSA BH					
PSA 11					
PSA 15					
AWA 1					
AWA 2					
AWA 3					
AWA 4					
AWA 4A					
AWA 5					
AWA 6					
AWA 7					
AWA 8					
AWA 9a					
AWA 10					
AWA 11					
AWA 12					
AWA 13					
BH 101	180.00	5700.00	7600.00	140.00	8700.00
BH 102	0.30	0.30	0.80	0.07	2.00
BH 103	54.00	12.00	37.00	6.00	610.00
BH 104	2.00	140.00	130.00	57.00	254.00
BH 105					
BH 106					
BH 201					
BH 202					
BH 203	73.00	13.00	0.20	2.00	2.00
BH 204	0.05	0.02	0.20	0.07	0.20
1 NRA					
2 NRA					
3 NRA					
4 NRA					
5 NRA					
6 NRA					
7 NRA					
8 NRA					
9 NRA					
Catchwater Drain					

Appendix C - Chemical Data

Site Name	PSA2 MTBE Feb 92	Benzene	Toluene	Ethylbenzene	Xylene
(-)	ug/l	ug/l	ug/l	ug/l	ug/l
Beck Row					
PSA BH					
PSA 11					
PSA 15					
AWA 1					
AWA 2					
AWA 3					
AWA 4					
AWA 4A					
AWA 5					
AWA 6					
AWA 7					
AWA 8					
AWA 9a					
AWA 10					
AWA 11					
AWA 12					
AWA 13					
BH 101					
BH 102	0.00	0.00	0.00	0.00	0.00
BH 103	16.00	11.00	28.00	82.00	729.00
BH 104	250.00	150.00	120.00	73.00	438.00
BH 105					
BH 106					
BH 201					
BH 202					
BH 203	32.00	8.00	0.30	0.00	0.00
BH 204	0.00	0.30	0.20	0.03	0.10
1 NRA					
2 NRA					
3 NRA					
4 NRA					
5 NRA					
6 NRA					
7 NRA					
8 NRA					
9 NRA					
Catchwater Drain					

Appendix C - Chemical Data

Site Name (-)	PSA3 MTBE Apr 92 ug/l	Benzene ug/l	Toluene ug/l	Ethylbenzene ug/l	Xylene ug/l
Beck Row					
PSA BH					
PSA 11					
PSA 15					
AWA 1					
AWA 2					
AWA 3					
AWA 4					
AWA 4A					
AWA 5					
AWA 6					
AWA 7					
AWA 8					
AWA 9a					
AWA 10					
AWA 11					
AWA 12					
AWA 13					
BH 101					
BH 102					
BH 103	10.00	4.00	7.00	44.00	334.00
BH 104	140.00	130.00	75.00	54.00	288.00
BH 105					
BH 106					
BH 201					
BH 202					
BH 203	24.00	4.00	0.10	0.00	0.08
BH 204	0.00	0.00	0.10	0.09	0.10
1 NRA					
2 NRA					
3 NRA					
4 NRA					
5 NRA					
6 NRA					
7 NRA					
8 NRA					
9 NRA					
Catchwater Drain					

Appendix C - Chemical Data

Site Name (-)	PSA4 MTBE May 92 ug/l	Benzene ug/l	Toluene ug/l	Ethylbenzene ug/l	Xylene ug/l
Beck Row					
PSA BH					
PSA 11					
PSA 15					
AWA 1					
AWA 2					
AWA 3					
AWA 4					
AWA 4A					
AWA 5					
AWA 6					
AWA 7					
AWA 8					
AWA 9a					
AWA 10					
AWA 11					
AWA 12					
AWA 13					
BH 101					
BH 102	0.00	0.00	0.10	0.00	0.01
BH 103	7.00	2.00	3.00	34.00	199.00
BH 104	210.00	130.00	91.00	64.00	326.00
BH 105					
BH 106					
BH 201					
BH 202					
BH 203	31.00	3.00	0.10	0.05	0.04
BH 204	0.00	0.00	0.10	0.04	0.05
1 NRA					
2 NRA					
3 NRA					
4 NRA					
5 NRA					
6 NRA					
7 NRA					
8 NRA					
9 NRA					
Catchwater Drain					

Appendix C - Chemical Data

Site Name (-)	NRA 3 MTBE June 11/92 ug/l	Benzene ug/l	Toluene ug/l	Ethylbenzene ug/l	Xylene ug/l
Beck Row					
PSA BH					
PSA 11					
PSA 15					
AWA 1					
AWA 2	<1	<.1	<.2	statc	<.3
AWA 3					
AWA 4	19.80	0.55	<.2	static	<.3
AWA 4A					
AWA 5					
AWA 6	<1	<.1	<.2	static	<.3
AWA 7					
AWA 8	4.46	<.1	<.2	static	<.3
AWA 9a	4.03	<.1	<.2	static	<.3
AWA 10	8.37	<.1	<.2	static	<.3
AWA 11					
AWA 12					
AWA 13					
BH 101					
BH 102					
BH 103					
BH 104					
BH 105					
BH 106					
BH 201					
BH 202	<1	<.1	<.2	static	<.3
BH 203					
BH 204	<1	<.1	<.2	static	<.3
1 NRA					
2 NRA					
3 NRA					
4 NRA					
5 NRA					
6 NRA					
7 NRA					
8 NRA					
9 NRA					
Catchwater Drain					

Appendix C - Chemical Data

Site Name (-)	PSA 5 MTBE June/92 ug/l	Benzene ug/l	Toluene ug/l	Ethylbenzene ug/l	Xylene ug/l
Beck Row					
PSA BH					
PSA 11					
PSA 15					
AWA 1					
AWA 2					
AWA 3					
AWA 4					
AWA 4A					
AWA 5					
AWA 6					
AWA 7					
AWA 8					
AWA 9a					
AWA 10					
AWA 11					
AWA 12					
AWA 13					
BH 101					
BH 102	0.00	0.00	0.03	0.00	0.00
BH 103	0.00	2.00	3.00	30.00	175.00
BH 104	190.00	130.00	91.00	53.00	334.00
BH 105					
BH 106					
BH 201					
BH 202					
BH 203	28.00	3.00	0.08	0.00	0.01
BH 204	0.00	0.00	0.00	0.00	0.00
1 NRA					
2 NRA					
3 NRA					
4 NRA					
5 NRA					
6 NRA					
7 NRA					
8 NRA					
9 NRA					
Catchwater Drain					

Appendix C - Chemical Data

Site Name (-)	PSA 6 MTBE July/92 ug/l	Benzene ug/l	Toluene ug/l	Ethylbenzene ug/l	Xylene ug/l
Beck Row					
PSA BH					
PSA 11					
PSA 15					
AWA 1					
AWA 2					
AWA 3					
AWA 4					
AWA 4A					
AWA 5					
AWA 6					
AWA 7					
AWA 8					
AWA 9a					
AWA 10					
AWA 11					
AWA 12					
AWA 13					
BH 101					
BH 102	0.00	0.05	1.00	0.05	0.37
BH 103	0.00	3.00	6.00	26.00	152.00
BH 104	200.00	170.00	170.00	91.00	580.00
BH 105					
BH 106					
BH 201					
BH 202					
BH 203	41.00	5.00	0.60	0.06	0.10
BH 204	0.10	0.00	0.30	0.07	0.10
1 NRA					
2 NRA					
3 NRA					
4 NRA					
5 NRA					
6 NRA					
7 NRA					
8 NRA					
9 NRA					
Catchwater Drain					

Appendix C - Chemical Data

Site Name (-)	PSA 7 MTBE Aug/92 ug/l	Benzene ug/l	Toluene ug/l	Ethylbenzene ug/l	Xylene ug/l
Beck Row					
PSA BH					
PSA 11					
PSA 15					
AWA 1					
AWA 2					
AWA 3					
AWA 4					
AWA 4A					
AWA 5					
AWA 6					
AWA 7					
AWA 8					
AWA 9a					
AWA 10					
AWA 11					
AWA 12					
AWA 13					
BH 101					
BH 102	0.00	0.00	0.06	0.00	0.00
BH 103	0.00	2.00	5.00	14.00	90.00
BH 104	210.00	250.00	210.00	130.00	760.00
BH 105					
BH 106					
BH 201					
BH 202					
BH 203	31.00	5.00	0.20	0.06	0.00
BH 204	0.00	0.00	0.03	0.00	0.01
1 NRA					
2 NRA					
3 NRA					
4 NRA					
5 NRA					
6 NRA					
7 NRA					
8 NRA					
9 NRA					
Catchwater Drain					

Appendix C - Chemical Data

Site Name	PSA 8 MTBE Sept/92	Benzene	Toluene	Ethylbenzene	Xylene
(-)	ug/l	ug/l	ug/l	ug/l	ug/l
Beck Row					
PSA BH					
PSA 11					
PSA 15					
AWA 1					
AWA 2					
AWA 3					
AWA 4					
AWA 4A					
AWA 5					
AWA 6					
AWA 7					
AWA 8					
AWA 9a					
AWA 10					
AWA 11					
AWA 12					
AWA 13					
BH 101					
BH 102	0.00	0.06	0.40	0.70	0.00
BH 103	4.00	5.00	4.00	30.00	84.00
BH 104	320.00	230.00	280.00	160.00	800.00
BH 105					
BH 106					
BH 201					
BH 202					
BH 203	17.00	4.00	3.00	0.30	2.30
BH 204	0.00	0.00	0.04	0.00	0.09
1 NRA					
2 NRA					
3 NRA					
4 NRA					
5 NRA					
6 NRA					
7 NRA					
8 NRA					
9 NRA					
Catchwater Drain					

Appendix C - Chemical Data

Site Name	PSA 9 MTBE Oct/92	Benzene	Toluene	Ethylbenzene	Xylene
(-)	ug/l	ug/l	ug/l	ug/l	ug/l
Beck Row					
PSA BH					
PSA 11					
PSA 15					
AWA 1					
AWA 2					
AWA 3					
AWA 4					
AWA 4A					
AWA 5					
AWA 6					
AWA 7					
AWA 8					
AWA 9a					
AWA 10					
AWA 11					
AWA 12					
AWA 13					
BH 101					
BH 102	0.00	0.03	3.00	0.00	0.20
BH 103	0.00	0.20	1.00	2.00	14.00
BH 104	150.00	130.00	97.00	73.00	350.00
BH 105					
BH 106					
BH 201					
BH 202					
BH 203	28.00	6.00	0.00	0.00	0.30
BH 204	0.00	0.03	0.07	0.00	0.20
1 NRA					
2 NRA					
3 NRA					
4 NRA					
5 NRA					
6 NRA					
7 NRA					
8 NRA					
9 NRA					
Catchwater Drain					

Appendix C - Chemical Data

Site Name (-)	PSA 10 MTBE Nov/92 ug/l	Benzene ug/l	Toluene ug/l	Ethylbenzene ug/l	Xylene ug/l
Beck Row					
PSA BH					
PSA 11					
PSA 15					
AWA 1					
AWA 2					
AWA 3					
AWA 4					
AWA 4A					
AWA 5					
AWA 6					
AWA 7					
AWA 8					
AWA 9a					
AWA 10					
AWA 11					
AWA 12					
AWA 13					
BH 101					
BH 102	0.00	0.00	0.00	0.00	0.00
BH 103	3.00	4.00	1.00	13.00	45.00
BH 104	120.00	110.00	66.00	62.00	246.00
BH 105					
BH 106					
BH 201					
BH 202					
BH 203	18.00	4.00	0.05	0.00	0.01
BH 204	0.00	0.00	0.00	0.00	0.00
1 NRA					
2 NRA					
3 NRA					
4 NRA					
5 NRA					
6 NRA					
7 NRA					
8 NRA					
9 NRA					
Catchwater Drain					

Appendix C - Chemical Data

Site Name	PSA 11 MTBE Dec/92	Benzene	Toluene	Ethylbenzene	Xylene
(-)	ug/l	ug/l	ug/l	ug/l	ug/l
Beck Row					
PSA BH					
PSA 11					
PSA 15					
AWA 1					
AWA 2					
AWA 3					
AWA 4					
AWA 4A					
AWA 5					
AWA 6					
AWA 7					
AWA 8					
AWA 9a					
AWA 10					
AWA 11					
AWA 12					
AWA 13					
BH 101					
BH 102	0.00	0.00	0.00	0.00	0.03
BH 103	4.00	2.00	2.00	3.00	27.00
BH 104	110.00	96.00	93.00	62.00	230.00
BH 105					
BH 106					
BH 201					
BH 202					
BH 203	9.00	1.00	0.04	0.00	0.02
BH 204	0.00	0.02	0.10	0.00	0.03
1 NRA					
2 NRA					
3 NRA					
4 NRA					
5 NRA					
6 NRA					
7 NRA					
8 NRA					
9 NRA					
Catchwater Drain					

Appendix C - Chemical Data

Site Name	PSA 12 MTBE Jan/93	Benzene	Toluene	Ethylbenzene	Xylene
(-)	ug/l	ug/l	ug/l	ug/l	ug/l
Beck Row					
PSA BH					
PSA 11					
PSA 15					
AWA 1					
AWA 2					
AWA 3					
AWA 4					
AWA 4A					
AWA 5					
AWA 6					
AWA 7					
AWA 8					
AWA 9a					
AWA 10					
AWA 11					
AWA 12					
AWA 13					
BH 101					
BH 102	0.00	0.00	0.03	0.00	0.01
BH 103	0.70	0.50	0.60	4.00	9.00
BH 104	77.00	81.00	52.00	51.00	58.00
BH 105					
BH 106					
BH 201					
BH 202					
BH 203	6.00	0.70	0.03	0.00	0.10
BH 204	0.00	0.00	0.03	0.00	0.00
1 NRA					
2 NRA					
3 NRA					
4 NRA					
5 NRA					
6 NRA					
7 NRA					
8 NRA					
9 NRA					
Catchwater Drain					

Appendix C - Chemical Data

Site Name	PSA 13 MTBE Feb/93	Benzene	Toluene	Ethylbenzene	Xylene
(-)	ug/l	ug/l	ug/l	ug/l	ug/l
Beck Row					
PSA BH					
PSA 11					
PSA 15					
AWA 1					
AWA 2					
AWA 3					
AWA 4					
AWA 4A					
AWA 5					
AWA 6					
AWA 7					
AWA 8					
AWA 9a					
AWA 10					
AWA 11					
AWA 12					
AWA 13					
BH 101					
BH 102	0.00	0.04	0.20	0.00	0.11
BH 103	0.30	0.30	0.40	4.00	8.00
BH 104	92.00	96.00	87.00	52.00	281.00
BH 105					
BH 106					
BH 201					
BH 202					
BH 203	4.00	0.60	0.09	0.00	0.00
BH 204	0.00	0.00	0.09	0.00	0.00
1 NRA					
2 NRA					
3 NRA					
4 NRA					
5 NRA					
6 NRA					
7 NRA					
8 NRA					
9 NRA					
Catchwater Drain					

Appendix C - Chemical Data

Site Name (-)	PSA 14 MTBE March 23/93 ug/l	Benzene ug/l	Toluene ug/l	Ethylbenzene ug/l	Xylene ug/l
Beck Row					
PSA BH					
PSA 11					
PSA 15					
AWA 1					
AWA 2					
AWA 3					
AWA 4					
AWA 4A					
AWA 5					
AWA 6					
AWA 7					
AWA 8					
AWA 9a					
AWA 10					
AWA 11					
AWA 12					
AWA 13					
BH 101					
BH 102					
BH 103	0.00	0.22	4.00	0.90	1.00
BH 104	120.00	20.00	110.00	70.00	340.00
BH 105					
BH 106	85.00	91.00	150.00	45.00	194.00
BH 201	0.00	0.06	3.00	0.01	0.25
BH 202	0.00	0.10	2.00	0.06	0.40
BH 203	8.00	0.10	2.00	0.00	0.10
BH 204	0.00	0.06	2.00	0.00	0.10
1 NRA					
2 NRA					
3 NRA					
4 NRA					
5 NRA					
6 NRA					
7 NRA					
8 NRA					
9 NRA					
Catchwater Drain					

Appendix C - Chemical Data

Site Name	PSA 15 MTBE April 2/93	Benzene	Toluene	Ethylbenzene	Xylene
(-)	ug/l	ug/l	ug/l	ug/l	ug/l
Beck Row					
PSA BH					
PSA 11					
PSA 15					
AWA 1					
AWA 2					
AWA 3					
AWA 4					
AWA 4A					
AWA 5					
AWA 6					
AWA 7					
AWA 8					
AWA 9a					
AWA 10					
AWA 11					
AWA 12					
AWA 13					
BH 101					
BH 102					
BH 103	0.00	0.40	1.00	0.60	4.00
BH 104	98.00	100.00	110.00	90.00	450.00
BH 105					
BH 106	0.00	0.10	1.00	0.40	0.50
BH 201	0.00	0.01	3.00	0.00	0.22
BH 202	0.00	0.03	5.00	0.00	0.38
BH 203	4.00	1.00	1.00	0.00	0.05
BH 204	0.00	0.02	1.00	0.00	0.04
1 NRA					
2 NRA					
3 NRA					
4 NRA					
5 NRA					
6 NRA					
7 NRA					
8 NRA					
9 NRA					
Catchwater Drain					

Appendix C - Chemical Data

Site Name (-)	PSA 16 MTBE April 23/93 ug/l	Benzene ug/l	Toluene ug/l	Ethylbenzene ug/l	Xylene ug/l
Beck Row					
PSA BH					
PSA 11					
PSA 15					
AWA 1					
AWA 2					
AWA 3					
AWA 4					
AWA 4A					
AWA 5					
AWA 6					
AWA 7					
AWA 8					
AWA 9a					
AWA 10					
AWA 11					
AWA 12					
AWA 13					
BH 101					
BH 102					
BH 103	0.00	0.10	0.50	0.20	0.90
BH 104	90.00	92.00	79.00	58.00	287.00
BH 105					
BH 106	0.00	0.10	0.50	0.80	1040.00
BH 201	0.00	0.00	0.40	0.00	0.00
BH 202	0.00	0.00	0.30	0.00	0.04
BH 203	8.00	0.03	0.40	0.00	0.02
BH 204	0.00	0.00	0.40	0.00	0.09
1 NRA					
2 NRA					
3 NRA					
4 NRA					
5 NRA					
6 NRA					
7 NRA					
8 NRA					
9 NRA					
Catchwater Drain					

Appendix C - Chemical Data

Site Name	PSA 17 MTBE May 5/93	Benzene	Toluene	Ethylbenzene	Xylene
(-)	ug/l	ug/l	ug/l	ug/l	ug/l
Beck Row					
PSA BH					
PSA 11					
PSA 15					
AWA 1					
AWA 2					
AWA 3					
AWA 4					
AWA 4A					
AWA 5					
AWA 6					
AWA 7					
AWA 8					
AWA 9a					
AWA 10					
AWA 11					
AWA 12					
AWA 13					
BH 101					
BH 102					
BH 103	0.00	2.00	1.00	2.00	4.00
BH 104	76.00	86.00	94.00	71.00	389.00
BH 105					
BH 106	0.00	0.06	0.40	2.00	3.60
BH 201	0.00	0.00	0.20	0.00	0.00
BH 202	0.00	0.00	0.40	0.00	0.10
BH 203	4.00	1.00	0.40	0.00	0.00
BH 204	0.00	0.00	0.20	0.00	0.00
1 NRA					
2 NRA					
3 NRA					
4 NRA					
5 NRA					
6 NRA					
7 NRA					
8 NRA					
9 NRA					
Catchwater Drain					

Appendix C - Chemical Data

Site Name (-)	UCL 1 MTBE JUNE 10 ug/l	Benzene 21, 1993 ug/l	Toluene ug/l	Xylene ug/l	Ethylbenzene ug/l
Beck Row					
PSA BH					
PSA 11					
PSA 15					
AWA 1	<.1	<.1	<.1	<.1	<.1
AWA 2	<1.0	<.1	<.1	<.1	<.1
AWA 3					
AWA 4					
AWA 4A	19.80	0.55	<.2	<.3	
AWA 5					
AWA 6	<.1	<.1	<.1	<.1	<.1
AWA 7	<.1	<.1	<.1	<.1	<.1
AWA 8	1.10	<.1	<.1	<.1	<.1
AWA 9a	1.19	<.1	<.1	<.1	<.1
AWA 10					
AWA 11					
AWA 12	<.1	<.1	<.1	<.1	<.1
AWA 13					
BH 101	2300.00	390.00	<70	6500.00	<70
BH 102	<.1	<.1	<.1	<.1	<.1
BH 103					
BH 104		<.1	<.1	<.1	<.1
BH 105	<.1	<.1	<.1	<.1	<.1
BH 106					
BH 201	<.1	<.1	<.1	<.1	<.1
BH 202	<.1	<.1	<.1	<.1	<.1
BH 203	6.00	<.1	<.1	<.1	<.1
BH 204	0.11	<.1	<.1	<.1	<.1
1 NRA	0.30	<.1	<.1	<.1	<.1
2 NRA	5.10	<.1	<.1	<.1	<.1
3 NRA	<.1	<.1	<.1	<.1	<.1
4 NRA	1.50	<.1	<.1	<.1	<.1
5 NRA	8.20	<.1	<.1	<.1	<.1
6 NRA	<.1	<.1	<.1	<.1	<.1
7 NRA	0.15	<.1	<.1	<.1	<.1
8 NRA	6.90	<.1	<.1	<.1	<.1
9 NRA	<.1	<.1	<.1	<.1	<.1
Catchwater Drain					

Appendix C - Chemical Data

Site Name	UCL3 MTBE	Benzene	Toluene	Xylene	Ethylbenzene
	AUG 7-8	1993			
(-)	ug/l	ug/l	ug/l	ug/l	ug/l
Beck Row					
PSA BH					
PSA 11					
PSA 15	<.1	<.1	<.1	<.1	<.1
AWA 1	<.1	<.1	<.1	<.1	<.1
AWA 2	<.1	<.1	<.1	<.1	<.1
AWA 3					
AWA 4					
AWA 4A	11.20	<.1	<.1	<.1	<.1
AWA 5					
AWA 6	<.1	<.1	<.1	<.1	<.1
AWA 7	<.1	<.1	<.1	<.1	<.1
AWA 8	1.40	<.1	<.1	<.1	<.1
AWA 9a	1.00	<.1	<.1	<.1	<.1
AWA 10					
AWA 11					
AWA 12	<.1	<.1	<.1	<.1	<.1
AWA 13	<.1	0.13	<.1	<.1	<.1
BH 101	1800.00	2200.00	2000.00	6200.00	<70
BH 102	<.1	<.1	<.1	<.1	<.1
BH 103	0.37	<.1	<.1	<.1	<.1
BH 104	52.00	<.1	<.1	<.1	<.1
BH 105	<.1	<.1	<.1	<.1	<.1
BH 106	<.1	<.1	<.1	<.1	<.1
BH 201	<.1	<.1	<.1	<.1	<.1
BH 202	<.1	<.1	<.1	<.1	<.1
BH 203	1.70	<.1	<.1	<.1	<.1
BH 204	<.1	<.1	<.1	<.1	<.1
1 NRA	0.38	<.1	<.1	<.1	<.1
2 NRA	4.90	<.1	<.1	<.1	<.1
3 NRA	0.38	<.1	<.1	<.1	<.1
4 NRA	3.00	<.1	<.1	<.1	<.1
5 NRA	4.40	0.77	0.67	0.91	0.27
6 NRA	0.83	0.16	0.48	0.73	0.27
7 NRA	0.44	<.1	0.79	0.89	0.27
8 NRA	6.60	1.10	0.71	0.97	0.29
9 NRA	0.43	0.10	0.60	0.83	0.25
Catchwater Drain					

Appendix D

Analysis of Fuel Sold in the Mildenhall Area

Location	Date	Type Fuel	%MTBE
1)Motorpoint Garage Beck Row	April 10, 1990	unleaded	0.15
2)Field Road Garage Mildenhall	April 10, 1990	unleaded	0.64
3)BP Garage Mildenhall	April 10, 1990	unleaded	0.49
4)AFEES Station RAF Mildenhall	April 11, 1990	unleaded	0.30
	April 11, 1990	leaded?	0.43
	April 30, 1990	leaded	0.00

Appendix D

Table B-1. Specifications of PS-6 Gasoline (from MacFarland <u>et al.</u>, 1984).

Research octane number	92.0
Motor octane number	84.1
(R + M)/2	88.1
Reid vapor pressure, psia	9.5
Distillation, ASTM D-86	
Initial boiling point, °F	93
5% distilled, °F	105
10% distilled, °F	116
20% distilled, °F	138
30% distilled, °F	164
40% distilled, °F	190
50% distilled, °F	216
60% distilled, °F	238
70% distilled, °F	256
80% distilled, °F	294
90% distilled, °F	340
95% distilled, °F	388
100% distilled, °F	428
Recovery, %	97
10% evaporated, °F	112
50% evaporated, °F	211
90% evaporated, °F	331
API gravity	60.6
Gum, ASTM D-381, g/gal	1
Sulfur, ppm	97
Phosphorus, g/gal	<0.005
Lead, g/gal	<0.05
Stability, hrs	>24

Appendix D

Table B-2. Molecular composition of PS-6 Gasoline. (from Brookman *et al.*, 1985).

COMPOUNDS	VOLUME %	WEIGHT %	MOLAR WEIGHT (g/mole)	WEIGHT % / MOLAR WEIGHT (moles/100g)
n-PARAFFINS				
n-butane		3.83	58	0.0660
n-pentane	10.19	3.11	72	0.0432
n-hexane		1.58	86	0.0184
C3,C7-C10, n-alkanes	1.21	1.21 e	121 a	0.0100
ISO-PARAFFINS				
isobutane	1.14	1.14 e	58	0.0197
isopentane	10.26	8.72	72	0.1211
2-methylpentane		3.93	86	0.0457
3-methylpentane	8.81	2.36	86	0.0274
2,3-dimethylbutane		1.66	86	0.0193
C6-isoalkane	0.18	0.18 e	86	0.0021
2-methylhexane		1.08 e	100	0.0108
3-methylhexane	4.54	1.30	100	0.0130
2,3-dimethylhexane		1.08 e	100	0.0108
2,4-dimethylpentane		1.08 e	100	0.0108
C7-isoalkanes	0.23	0.23	100	0.0023
2,2,4-trimethylpentane		5.22	114	0.0458
2,3,4-trimethylpentane	11.74	2.99	114	0.0262
2,3,3-trimethylpentane		2.85	114	0.0250
2,2,3-trimethylpentane		0.68 e	114	0.0060
C8-isoalkanes	4.98	4.98 e	114	0.0437
2-methyloctane			128	0.0000
3-methyloctane	1.51	1.51 e	128	0.0118
4-methyloctane			128	0.0000
2,2,5-trimethylhexane			128	0.0000
C9-isoalkanes	0.50	0.50 e	128	0.0039
C10 - C13-isoalkanes	2.65	2.65 e	163 a	0.0163

(cont'd)

Table B-2. (cont'd)

COMPOUNDS	VOLUME %	WEIGHT %	MOLAR WEIGHT (g/mole)	WEIGHT % / MOLAR WEIGHT (moles/100g)
CYCLOPARAFFINS				
cyclopentane	0.15	0.15 e	70	0.0021
methylcyclopentane	0.97	0.97 e	84	0.0115
cyclohexane	0.08	0.08 e	84	0.0010
methylcyclohexane				
1,trans,3-dimethylcyclopentane	0.77	0.77 e	98	0.0079
1,cis,3-dimethylcyclopentane				
C7-cycloalkanes	0.32	0.32 e	98	0.0033
C8-cycloalkanes	0.74	0.74 e	112	0.0066
C9-cycloalkanes	1.03	1.03 e	126	0.0082
C10 - C13-cycloalkanes	0.62	0.62 e	161 a	0.0039
MONO-OLEFINS				
propylene	0.03	0.03 e	42	0.0007
trans-butene-2	0.75	0.75 e	56	0.0134
cis-butene-2			56	0.0000
C4-alkenes	0.15	0.15 e	56	0.0027
pentene-1			70	0.0000
trans-pentene-2	1.22	1.22 e	70	0.0174
cis-pentene-2			70	0.0000
C5-alkenes	0.07	0.07 e	70	0.0010
C6-alkenes	0.14	0.14 e	84	0.0017
2-methylpentene-1	1.26	1.26 e	84	0.0150
2-methylpentene-2			84	0.0000
C7 - C12-alkenes	5.34	5.34 e	133 a	0.0402

(cont'd)

Appendix D

Table B-2. (cont'd)

COMPOUNDS	VOLUME %	WEIGHT %	MOLAR WEIGHT (g/mole)	WEIGHT % / MOLAR WEIGHT (moles/100g)
AROMATICS				
benzene	1.69	1.94	78	0.0249
toluene	3.99	4.73	92	0.0514
ethylbenzene	1.69 e	2.00	106	0.0189
o-xylene	1.91 e	2.27	106	0.0214
m-xylene	4.78 e	5.66	106	0.0534
p-xylene	1.45 e	1.72	106	0.0162
1-methyl-3-ethylbenzene	5.33	1.54	120	0.0128
1-methyl-4-ethylbenzene		1.56	120	0.0130
1,2,4-trimethylbenzene		3.26	120	0.0272
C9-alkylbenzenes	2.40	2.51 e	120	0.0209
C10-alkylbenzenes	2.11	2.21 e	134	0.0165
C11-alkylbenzenes	0.52	0.57 e	148	0.0039
C12-alkylbenzenes	0.21	0.21 e	162	0.0013
C9 - C13-indans/tetralins	1.54	1.59 e	147 a	0.0108
C10 - C12-naphthalenes	0.74	0.74 e	144 a	0.0051
TOTAL	99.94	100.02		1.0334

MOLAR WEIGHT OF PS-6 GASOLINE = 96.77 g

NOTES:

e - weight % estimated as equivalent to volume %
a - assumed average group molecular weight

Appendix D

Table B-3. Molar fraction to volume fraction ratios for BTEX in PS-6 gasoline.

Compound	Molar Fraction	Volume Fraction	Molar Fraction/ Volume Fraction
benzene	0.024	0.0169	1.42
toluene	0.050	0.0399	1.25
ethylbenzene	0.018	0.0169	1.08
o-xylene	0.021	0.0191	1.09
m-xylene	0.052	0.0478	1.08
p-xylene	0.016	0.0145	1.08

Table B-4. Experimentally determined volume fractions and calculated molar fractions for BTEX in PS-6 gasoline.

Compound	Volume Fraction yg	Molar Fraction xg
benzene	0.02082	0.02965
toluene	0.03519	0.04388
ethylbenzene	0.01570	0.01696
o-xylene	0.02088	0.02266
m-xylene	0.04072	0.04402
p-xylene	0.01809	0.01959
TOTAL	0.15140	0.17676