

**TBME as a Groundwater
Contaminant**
Nature, Behaviour and
Recommendations for Monitoring

G Hyett
NRA Anglian Region, Central Area
Draft Final Report OI/562/2/A

NRA Anglian 124



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Statement of Use:

This research was commissioned to establish the behaviour of TBME in groundwater, especially the distances over which it may travel and the rate at which it degrades. The results and recommendations will be used by pollution prevention officers to comment on planning applications and prosecutions.

Research Contractor:

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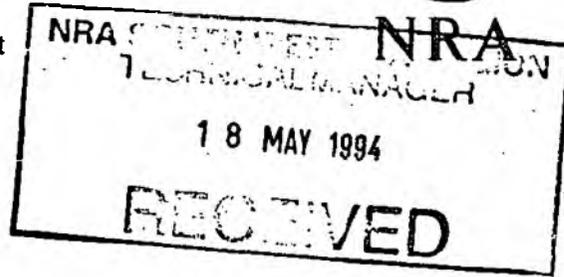
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MEMORANDUM



To: See Distribution
From: Geoff Brighty, Regional R&D Scientist
Our ref: 830/56/20
Your ref:
Date: 16 May 1994



ANGLIAN REGIONAL OPERATIONAL INVESTIGATION 562:

TMBE AS A GROUNDWATER CONTAMINANT: NATURE, BEHAVIOUR AND RECOMMENDATIONS FOR MONITORING

I enclose a Draft Final report for this project which is an Operational Investigation: Reported Nationally. The report has been written by Dr Glynn Hyett, Groundwater Protection Officer at Anglian's Central Area Office, Brampton. It is based on Central Area investigations of a particular groundwater pollution incident, a MSc Thesis from University College, London on that site and further reviews of the literature undertaken by Dr Hyett.

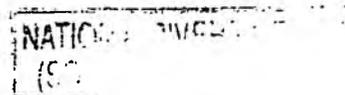
It has been the intention that a short summary document should be produced from the project to inform the wider Authority about this contaminant, which is increasing in use, and its behaviour. It has brought together the various strands investigated and presents recommendations for monitoring and future research.

The project has now reached the Draft Final Report review stage. It has been sent to all Regions to receive feedback on this UK-wide contaminant. The quality review criteria are on the enclosed PM3 form.

Please can you return your comments by the 3 June 1994. If comments are not received, it will be assumed that you are generally happy with the report.

I hope you find the report of interest.

DR G C BRIGHTY
Regional R&D Scientist



18 MAY 1994

MGB

cc G Hyett
P Waldron

Distribution

Ian Davey	Thames Region
Bob Harris	Severn-Trent Region
Peter Chave	Head Office
David Tester	Anglian Region

Regional Water Quality Managers (8) to nominate Pollution Prevention Officer/Groundwater Protection Officer to review on behalf of practitioners

QUALITY REVIEW INVITATION

PM3/cp

Project Reference: Anglian OI 562
 Function: Water Quality
 Region/H.O. Dept Anglian

Prepared by: G Brighty
 Date: 16 May 1994

Project Title

TBME in Groundwaters

Stage (if applicable)

Draft Final Reporting

You are invited to attend a Quality Review of the following Product(s):

Product Code(s)

OI/562/2/A

Product Name(s)

Draft Final Report: TBME as a Groundwater
 Contaminant: Nature, Behaviour and
 Recommendations for Monitoring

Venue (if postal enter, "POSTAL")	POSTAL	Date Time Duration	To be returned by 3 / 6 / 1994
Chairman	David Tester (TAPS Centre)	Project Manager	Paul Waldron
Reviewers	Ian Davey (Thames Region) Bob Harris (Severn-Trent Region, National Groundwater Centre) Peter Chave (Head Office) David Tester (Anglian Region, TAPS Centre) Regional Water Quality Managers to nominate Groundwater Protection Officer/Pollution Prevention Officer to review on behalf of practitioners		

Product Description(s) attached:

Draft Final report from the OI project 562: TBME in groundwaters.

Product(s) attached (where applicable)

TBME as a Groundwater Contaminant: Nature, Behaviour and Recommendations for Monitoring

Please consider the report with reference to these review criteria:

- 1) Will the report, in this format and context, help officers develop a strategy for fuel spill investigations ?
- 2) Is there enough depth given on the behaviour of TBME ? Would more real data be useful ?
- 3) Is there a need to cover analytical procedures ?
- 4) Do the conclusions contradict evidence for other Regions ? Is there / do you have additional evidence on TBME usage and pollution events ?
- 5) Should more incidents be collected nationally ? Will these actually be of any use ?
 Do any Groundwater Monitoring Networks cover TBME ?

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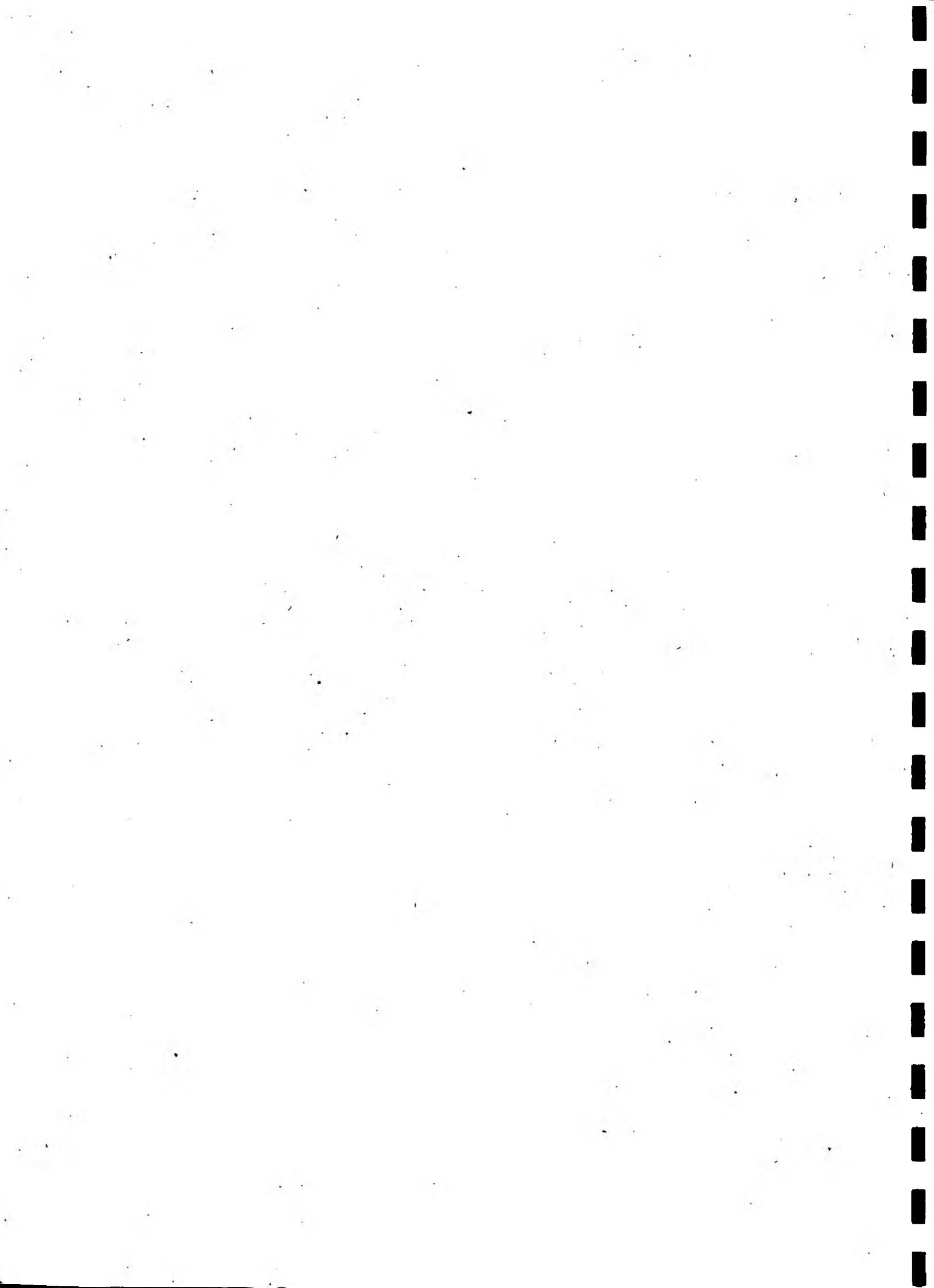
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TBME AS A GROUNDWATER CONTAMINANT
NATURE, BEHAVIOUR AND RECOMMENDATIONS FOR MONITORING

1. OBJECTIVES OF THE RESEARCH

1.1 Brief Background

The project was conceived following the contamination of two major Public Water Supply boreholes in Central Area of Anglian Region. It was apparent that little was known of the fate and behaviour of the compound, and few analytical facilities were available. The two incidents yielded some useful data, eg that TBME can be tasted at very low levels (c 5mg/l). Analytical facilities have since improved with the increasing occurrence of TBME in the UK. Some evidence pointed to a high solubility of TBME, and a possible co-solubility effect with other fuel components, leading to increased solubility and rates of migration for other fuel components. A project was considered necessary to establish clearly how best to deal with future fuel spillage incidents where TBME was present.

1.2 Objectives

- a) To evaluate the usage of TBME in the UK.
- b) To undertake a brief literature review of the chemistry of TBME.
- c) To establish the behaviour and persistence of TBME in groundwater, its fate and its interaction with other fuel contaminants.
- d) Recommend any special monitoring techniques that may be required to assess the extent of a spillage.
- e) Recommend any special remedial actions required after a leak has been identified.

The evaluation of criteria for any change in underground hydrocarbon storage for products containing TBME is considered to be beyond the scope of this note.

1.3 Methodology

A research contractor at UCL was employed to undertake a literature review of TBME. Concurrently NRA Anglian Region undertook a further field study of one TBME spillage in the Great Ouse Chalk Aquifer, with the contractor aiding in collecting samples and reviewing the results. The field study is not reported in detail here.

2. TBME USAGE IN UK FUELS

2.1 Background

TBME is a fuel additive, added as an oxygenate. Oxygenates improve the degree of combustion, and reduce the amount of unburnt fuel pollutants such as oxides of nitrogen, and carbon monoxide. Oxygenates have a substantial molecular content and are added to increase the octane rating and improve fuel quality. Oxygenates are relatively highly polar, and have a higher water solubility compared to most other hydrocarbons.

Whilst first used in the 1920s, it was the 1970s, with the fuel crises and increasing environmental legislation, that led refiners to widen the search for antiknock/octane enhancing alternatives. This limited search was greatly extended during the 1980s, and a wide variety of oxygenate alternatives were examined (Lang et al 1981) as atmospheric emission standards and catalytic converters were introduced.

TBME is now the most widely accepted oxygenate in the US, where other fuel alternatives (eg ethanol, methanol) have not gained a significant market share. TBME is the only ether blended in the US (Unzelmen 1991) and is used extensively worldwide. However, to date it has not been as widely used in leaded or unleaded UK fuels as in many American states.

Contrary to much opinion TBME was not used as a direct replacement to lead in UK fuels, and is used in all grades of petrol.

2.2 Legislative Requirements

2.2.1 Atmospheric Emissions

Two EEC directives (78/665 and 83/351) have been adopted, outlining target emissions for carbon monoxide, nitrous oxides and hydrocarbons. The impact of smog, ozone and acidifiers in the environment is well documented.

The use of leaded fuel is now banned in West Germany and Luxembourg, and it is anticipated that tax incentives will continue to produce a fall in market share of leaded fuels.

2.2.2 Fuel Lists

A further Directive (85/536/EEC) sets allowable limits for the use of monoalcohols and ethers as oxygenate blending agents.

Table 1 shows two lists. List A limits are mandatory, whilst individual states may allow a higher limit up to the levels in List B.

TABLE 1 EEC OXYGENATE LIMITS

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

The UK currently conforms to list A

- 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, eg Tertiary amyl methyl ether, ethyl tertiary butyl ether.
- 5) Oxygen weight, not exceeding the individual limits fixed for each of the above components.

2.3 TBME as an Additive

2.3.1 TBME is less corrosive than methanol, ethanol and TBA. Methanol and ethanol are both water tolerant (preferentially fix in the water phase) and require additional additives. This effect is less apparent with all ethers. TBME does not have a significantly different performance in terms of;

- a) antiknock,
- b) drivability,
- c) fuel economy,
- d) inlet system cleanliness.

when compared to the other additives

The problems of using ethers in older vehicles will decline as the road fleets are continually replaced.

TBME does not significantly increase fuel volatility, at concentrations up to 20%. However other oxygenates like methanol bring about dramatic increases in fuel volatility.

2.3.2 Anticipated Future Usage of TBME Future

TBME is likely to remain significant as an additive as:

- 1) TBME is compatible with other hydrocarbons and requires no cosolvents to improve water tolerance in the presence of other fuel components.
- 2) TBME has a lower blended vapour pressure when compared with methanol, and will probably be more compatible with any forthcoming legislation on fuel volatility, especially in the summer months.
- 3) No engine modifications are required with TBME as compared with higher content methanol blends.
- 4) TBME can be handled and stored like most other fuel components and does not require any special adaptations to a dryer distribution network.
- 5) TBME is far less corrosive than methanol.

2.4 Current use of TBME

2.4.1 Production

TBME can be produced by a number of processes, and rates of production show it to be the fastest growing petrochemical in the world (anticipated at 200,00 barrels per day in US by 1995 (Unzelman 1991)) and actually two billion litres in 1992 (Emsley, 1994).

2.4.2 Uses of TBME

TBME has three main commercial uses:

- a) Fuel additive.
- b) Dissolution of gallstones in humans.
- c) As a carrier fluid in liquid chromatography.

2.4.3 TBME in fuels

Discovering the content of TBME in fuel has proved somewhat problematic. It is thought to vary widely, depending on the refining process and blending properties of individual fuels. In the US and Canada fuels may contain, and often do, up to the 15% limit by volume. The US Government's 1990 Clean Air Act Amendment requires oxygenates to be used to improve combustion. Each winter thirty-nine American cities convert to petrol containing 15% TBME (Emsley, 1994).

The UK limit is 10%, but generally enquires have shown it to be blended to about 1%, where used.

Correspondence with the UK Petroleum Industry Association has discovered that in 1993, and only in 1993,

- 1) TBME was not a component of all UK petrol.
- 2) TBME appears to have been used in about 40% of UK petrol.
- 3) TBME was used in all grades or types of petrol, ~~ie~~ not just unleaded fuels.

- 4) The concentration varied from 0.1% wt to a. 5% wt. However, higher concentrations may have been used on occasions.
- 5) For petrol with TBME added the average concentration was just over 1% wt.
- 6) The concentration of TBME varies for a variety of reasons, within and between different fuels, due to variation in unit availability/reduction and feedstock.

Shell UK Ltd have indicated that they never use TBME, whereas Total Oil Ltd, have confirmed that they have blended up to the 10% maximum.

The above correspondence is reproduced in Appendix 1.

It is possible, that UK fuels will follow the US trend, and therefore that TBME content will increase. However, currently unleaded fuels do NOT all contain TBME, and its relatively high cost may mean that levels will remain as at present for some time to come.

2.5 Summary

2.5.1 TBME is increasingly seen as a useful additive. It has excellent properties as an automotive fuel additive. Generally UK usage is in 40% of fuels, at about 1% by weight.

3. PROPERTIES OF TBME

3.1 Nomenclature and Structure

Tertiary butyl methyl ether is also widely known as methyl tertiary butyl ether, and less common as 2-Methoxy - 2 - methylpropane. It is most commonly described as:

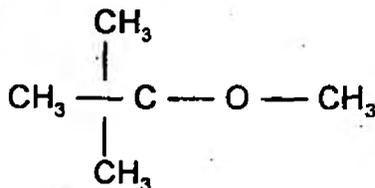


Table 2 presents a summary of its Physical Properties

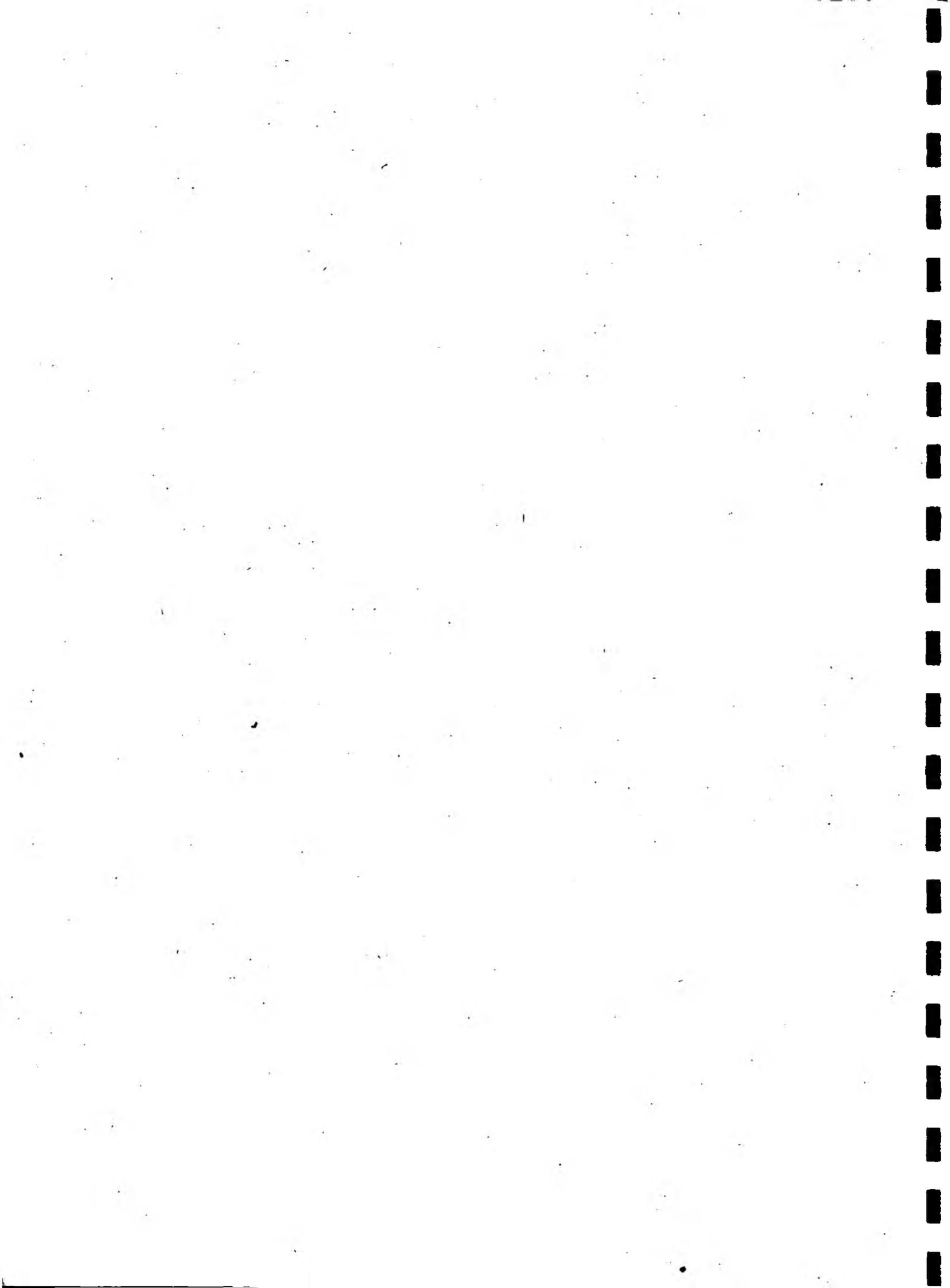


TABLE 2 - SUMMARY OF PHYSICAL PROPERTIES

Physical State	Liquid	(The Merck Index 1989)
Colour	Colourless	(The Merck Index 1989)
Odour Threshold	680µg/l	(Angle C R, 1991)
Taste Threshold	5µg/l, possibly 2-3µg/l	
Water Solubility	48 g/100g 20C	(The Merck Index, 1989)
Cosolubility Effect	Non consolubility effect	(Stephenson RM, 1992)
Density	0.7404 g/ml @ 20C	(The Merck Index, 1989)
Vapour Pressure	32.66 kpa @ 25C	(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	-110C	(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 @ 22C	(Cline et al 1991)
Drinking Water Standards		
EEC, WHO, EPA	None	
Recommendations	200 ppb 50 ppb 5 ppb	(Hartly et al 1992) (Garrett et al 1986) (Anglian Water)

Biodegradation	
Aerobic	Weight of evidence points to Non-biodegradable
Anaerobic	Non-biodegradable
Atmospheric	
Half Life	4 days under summer conditions
Reactivity (OH)	$2.8 \cdot 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{second}^{-1}$

3.2 Chemistry of TBME

3.2.1 Solubility

TBME is relatively water soluble compared to other fuel components. TBME is not relatively strongly dipolar in nature compared to methanol for example. However, it is far more soluble than the monoaromatic constituents of fuel, although no published value for a dipolar measurement for TBME has been discovered. Table 3 below lists the solubility of various fuel components.

TABLE 3 FUEL COMPONENT SOLUBILITIES IN WATER

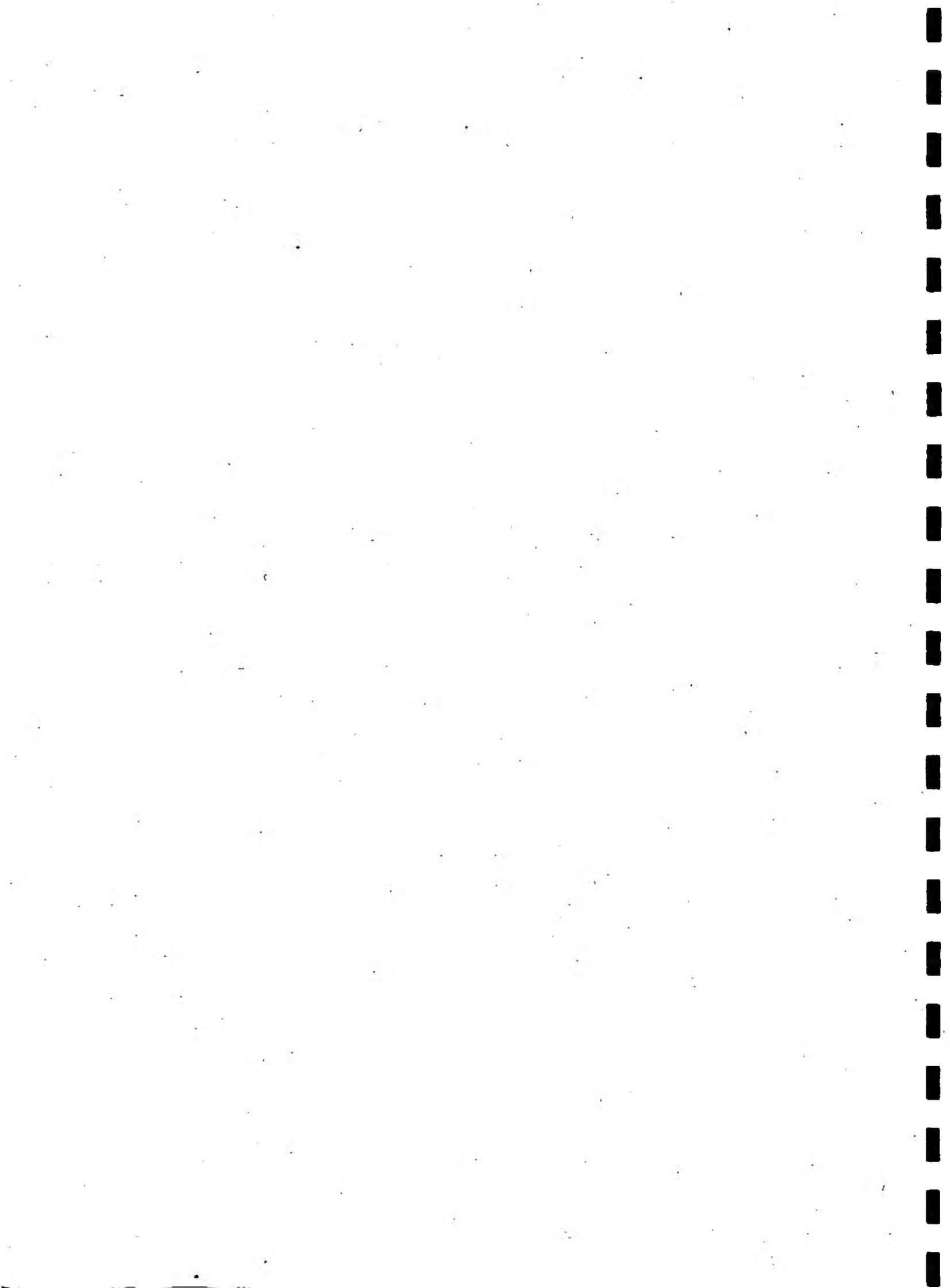
	MG/L	%	RELATIVE TO BENZENE
Methanol	Miscible in all proportions		
TBME	48,000	4.8	27
Benzene	1,780	0.18	1
Toluene	515	0.05	0.3
m-Xylene	170	0.02	0.1

(API, 1985 Table 2.1)

However, the above figures are based on STP, and aquifer conditions will of course vary, together with the actual mix of contaminants. Examination of Figure 1 shows that TBME solubility increases with decreasing temperature (Stephenson 1992). Under typical aquifer conditions it is likely that solubility will increase relative to published STP values.

3.2.2 Cosolubility

Garrett et al (1986) postulated that due to the high binary solubility of TBME with water that its presence may change the solubility of other fuel components. Typically, many spillages are quantified in terms of BTEX concentrations (Benzene, Toluene, Ethylbenzene and Xylenes) whilst fuels are complex mixtures of other several hundred components. The reality is therefore likely to be very complex. API Document 4531 on the Chemical Fate and Impact of Oxygenates in Groundwater: Solubility of BTEX from Gasoline - Oxygenates Compound (1991) contains the most data on the cosolubility effect.



In all, three separate experiments showed either NO EFFECT or actually decreased the solubility of the components of gasoline (API 4531 1991, Groves 1998, Cline et al 1991).

3.2.3 Volatilisation

Henry's Gas Constant for TBME is shown in Table 2. Whilst transferring such a value to natural system is difficult it is probable that TBME is LESS VOLATILE than the aromatic and alcohol portions of most fuels. Table 4 shows the Half-Life of TBME in Aqueous system.

TABLE 4 HALF LIFE IN AQUEOUS SYSTEMS (MINUTES)

TBME	5402 ²
Benzene	37.3 ¹
Toluene	30.6 ¹

1 API, 1985

2 Canadian 1986

TBME in the atmospheric environment will react slowly, with an estimated atmospheric ½-life of about 4 days.

3.2.4 Partitioning

TBME preferentially concentrates in the fuel phase component compared with the aqueous phase. Laboratory studies have indicated the fuel-water partition co-efficient to be temperature dependent, with TBME preferentially partitioning into the fuel phase as temperature decreases. This data also agrees with binary water-TBME solubility relationships with temperature.

At typical aquifer temperatures around 80% of the TBME may remain in the fuel phase.

3.3 Biodegradation

TBME, in common with other ethers, is reported as difficult to degrade. It appears to be non-biodegradable, with only one reference indicating otherwise. These results show TBME to be far MORE PERSISTENT than the typical aromatic and alcohol constituents of fuels.

3.3.1 Aerobic Conditions

Jensen et al (1990) used four material types with varying concentration of TBME in water, in equilibrium with a model gasoline. No biodegradation was observed over 40 and 60 days.

There was some evidence of bacterial inhibition at high concentrations, also reported in other studies (Bolt et al 1992).

3.3.2 Anaerobic Conditions

Suflita et al (1993) tested TBME and other oxygenates in sediment and groundwater from an anoxic aquifer contaminated with domestic landfill leachate. No degradation was observed after 182 days, supporting the above experiments in aerobic conditions.

3.4 Health Standards and Treatment

3.4.1 Maximum Admissible Concentrations

No official drinking water standards specific to TBME were found in British, EC or USA legislation. However the following limits were recommended:

TBME ($\mu\text{g/l}$)	Authority
200	Hardly et al 1990, Tulsa University Medical Centre
50	Garratt et al 1986, State Toxicologist for Maine, USA
5	Anglian Water Services Limited

The Groundwater Directive specifies a maximum admissible concentration of $10\mu\text{g/l}$ for dissolved and emulsified hydrocarbons; mineral oils. The Drinking Water Inspectorate consider that UK advice was that a maximum of $10\mu\text{g/litre}$ for one month would not be expected to be detrimental to Health, but they stressed this was not a standard. The correspondence is reproduced in Appendix 1.

3.4.2 Toxicity

3.4.2 Toxicity

TBME is not particularly toxic, and selected data is shown in Table 5 below (Duff et al 1992). A comprehensive Toxicity Profile is reproduced as Appendix 2, with the kind permission of the British Industrial Biological Research Association.

TABLE 5 SELECTED TOXICITY DATA FOR TBME

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 (Duffy et al 1992)	Response	Not a Skin Sensitizer

The initial effect of acute exposure to TBME is anaesthetic, with some respiratory irritation (at 26 to 33 parts per thousand). TBME whilst readily absorbed by inhalation, oral and dermal routes is rapidly metabolised and excreted in urine as Tertiary Butyl Alcohol or eliminated in exhaled air.

However TBME has been banned in Alaska. Car owners reported headache, nausea and respiratory problems after refuelling in cold temperatures (Crow, 1993). However, other sources suggest it is the smell that leads to the complaints (Emsley 1994).

3.4.3. Treatment Options

TBME is relatively volatile. Treatment by Granular Activated Carbon is thought relatively inefficient compared to average BTEX adsorption rates; 0.004 grams TBME/1.0 gram GAC compared to 0.3 grams BTEX/1.0 gram GAC (API document 4497, 1991).

It has been found that aeration is efficient. Two groundwater sources in Anglian Region, Central Area are currently using aeration towers to remove TBME.

4. TBME AS A GROUNDWATER CONTAMINANT

4.1 Introduction

This section presents a brief review of published and unpublished data on the behaviour of TBME in actual fuel spillages.

4.2 Published Field Data

4.2.1 Introduction

There appears to have been very few well documented incidents. It is apparent that differences in reporting make direct comparisons between the few reported incidents problematic. Indeed, given the known variation in the blending of fuels within the UK, including the TBME content, significant variations in field concentrations and fuel component relationships must be expected.

4.2.2 Garret et al 1986

This study quantified the development of a plume in an unconfined sand aquifer. Simplistically three phases of the plume were detected:

- 1) TBME only
- 2) TBME mixed with other fuel components
- 3) Free fuel products

Garret et al suggest TBME travelled the furthest, with the plume encircling the mixed phase in a halo.

4.2.3 Barker et al 1990

The study site was a well documented sand aquifer, with small scale layering and heterogeneities, and with a reported average velocity of 0.09 m/day. Three fuel mixes, gasoline, gasoline and 15% TBME, and an 85% Methanol fuel, were injected side by side via wells. Monitoring results over 480 days from a detailed piezometer network were presented and compared with the movement of a chloride tracer.

The results showed that,

- 1) Methanol and TBME moved at the same rate as the groundwater movement, and BTEX components were relatively retarded.
- 2) TBME appeared recalcitrant. Methanol was virtually completely removed at 476 days, with significant degradation of BTEX. The BTEX/Methanol mix showed some inhibition of BTEX degradation, postulated to be due to toxic inhibition and/or oxygen removed by preferential methanol biodegradation.
- 3) That the presence of oxygenates did not cause any enhanced BTEX mobility.
- 4) The TBME recalcitrance was supported by laboratory microcosm studies.

4.2.4 Summary

The published data indicates that TBME is:

- 1) Relatively mobile compared to other fuel components.
- 2) Relatively persistent compared to other fuel components.

4.3 Unpublished Data

4.3.1 Introduction

This section presents a brief summary of an ongoing monitoring programme in Anglian Region. In spring 1990 a major public water supply borehole in the Chalk Aquifer was found to have been contaminated by TBME. An adjacent fuel station was discovered to be the source. The monitoring programme is still continuing, including the regular review of a dedicated in situ scavenger and containment system installed in October 1991. The source is back on line, with an on site airstripping plant and GAC. This actual incident, and others have been reported elsewhere (Tester and Harker 1981, Burley et al 1991).

4.3.2 Monitoring Programme

Some 30 boreholes have been used to monitor for TBME and other Hydrocarbons. Samples are generally obtained via a portable monitoring pump (Grundfos MP1) and the majority of the analysis was carried out at the NRA Regional Laboratory at Peterborough.

4.3.3 Local Hydrogeology

The source lies in Lower Chalk, is fully penetrating, and overlain by 1 to 1.5 m of a light sandy drift material. Given the very large abstraction rate for a Lower Chalk source the radius of influence is small, with a reported drawdown of about 1 metre at 8,000 cubic metres per day. Transmissivity is very high (c 10,000m³/day), reflecting a highly fractured aquifer and enhanced secondary permeability. Gradients are low, with small head difference across the site of a few centimetres. The principal influence of flow direction is therefore the local borehole abstraction regime. Regionally flows are to the north-west.

4.3.4 Initial Results

The boreholes used in the study are shown in Figure 1. Figure 2 shows the TBME distribution in April 1990 with both the PSA and AWSL boreholes pumping. There is a considerable spreading of the plume, reflecting two sources abstracting. The PSA source was decommissioned in early 1992

In 1992 there is less spread, as only the AWSL borehole was abstracting. Figure 3 to 5 show a narrower plume, and the greater extent of the TBME plume compared to Benzene.

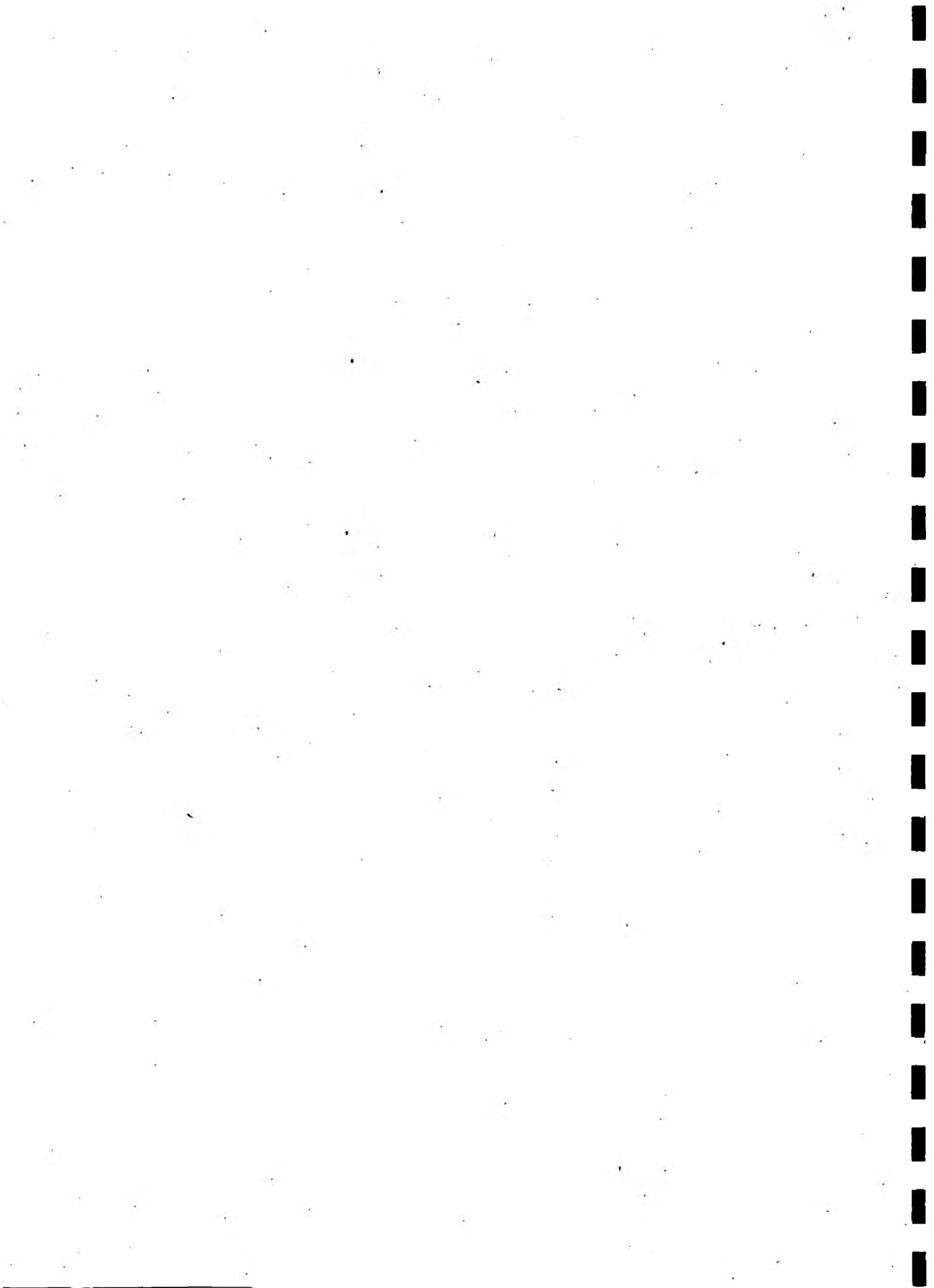
4.3.5 1993 Results

The influence of the now single abstracting source is apparent, with a narrow well defined plume shown in the Figures 6 to 11.

4.3.6 Relative Mobilities

The table below presents data from a transect along boreholes BH101, BH203, BHNRA2, BHNRA5 and AWA9, between the spill and the source shows the relative concentrations of BHNRA5 8.20 LO.1 and TBME, Benzene and Xylene.

DATE: JUNE 1993	BH101	BH203	BH NRA2	BH NRA5	AWA 9
TBME	2,300	6.00	5.10	8.20	1.19
Benzene	390	<0.1	<0.1	<0.1	<0.1
Xylene	6,500	<0.1	<0.1	<0.1	<0.1



DATE: AUGUST 1993	BH101	BH203	BH NRA2	BH NRA5	AWA9
TBME	1,800	1.70	4.90	4.4	1.0
Benzene	2,200	<0.1	<0.1	0.77	<0.1
Xylene	2,000	<0.1	<0.1	0.67	<0.1

The results for the study again indicate that TBME is relatively persistent and mobile.

4.3.7 Other Sites in Anglian Region.

At another major public water supply routine monitoring showed an increase in TBME concentration after the cessation of the drought. It is postulated that this was due to remobilisation by recharge, and rising water levels. It is hoped to continue the existing monitoring programme to evaluate remobilisation effects.

At a further site, an active petrol station, TBME has exhibited a different pattern of behaviour to the other fuel components, though no clear trend is discernable. However, TBME is the only component so far detected in an adjacent surface water body, perhaps indicative of its mobility.

5. CONCLUSIONS

Where TBME is known to have been present in a spillage/leak of a product;

- 1) it may provide 'advance warning' of a fuel plume movement incident due to its mobility, and low odour/taste threshold and,
- 2) as its movement is relatively conservative, and it has a low rate of degradation it may prove helpful in quantifying any fuel loss.

It will be problematic to account for in remediation as;

- 1) it is persistent, even in an aerobic unconfined aquifer, and may preclude any approach of simply monitoring a natural decline in fuel concentrations and,
- 2) it has a low taste threshold, requiring comprehensive treatment in potable supplies.

Several uncertainties still exist, and it is possible that TBME is not widely searched for in UK aquifers.

6. RECOMMENDATION

6.1 Recommendations for Monitoring

- 1) TBME should be looked for in all fuel spills, though its limited occurrence in fuels should be borne in mind.
- 2) As with most fuel spills PVC is not a preferred casing option. Polypropylene should be sufficiently durable. Although stainless steel is the best option to minimise interference it is very expensive.
- 3) TBME's relatively high mobility means that investigation holes may have to cover a wider area than would normally be expected.

6.2 Recommendations for Research

- 1) Further investigations should be made into the occurrence of TBME, and its projected future use. This could be carried out on a National basis in collaboration with an industrial body representing the petroleum producers and refiners.
- 2) Routine groundwater quality monitoring networks should include, even if only a once off, a 'sweep' for TBME in groundwaters. Again, this should be reviewed nationally, or at least regionally. A formal approach should be made to the water companies and other bodies to collect incidents of TBME detections.
- 3) Further investigations should be made into the biodegradability of TBME in the groundwater environment. Often owner/operators suggest to regulators that natural biodegradation may be the best option to remediate a site. This may not be appropriate for TBME.
- 4) Given the mobility of TBME its persistence at the study site suggests it may diffuse into dead acres of strata. In the Chalk, matrix diffusion, and consequent retardation, should be investigated by interstitial porewater analysis. The effect of seasonal water level changes should also be investigated. There may be some merit in undertaking this task at the Central Area, Anglian Region study site.

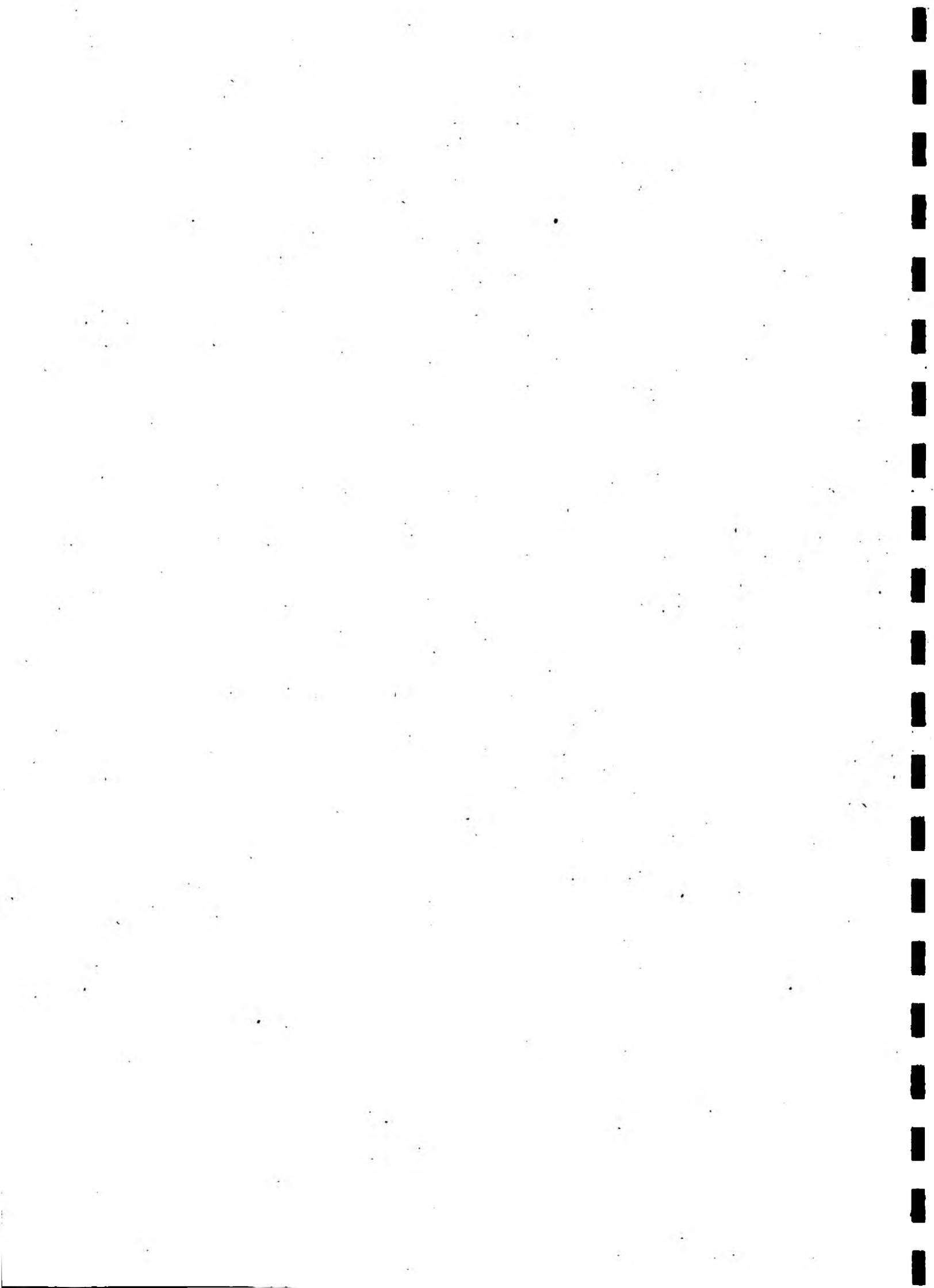
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APPENDIX ONE

Correspondence Relating to TBME Usage

	Company	Date
1.	Total Oil Great Britian Ltd	16th February 1994
2.	United Kingdom Petroleum Industry Association Ltd	22nd February 1994
3.	Drinking Water Inspectorate	24th March 1994



TOTAL



TOTAL OIL GREAT BRITAIN LIMITED

Mr P Waldron
National Rivers Authority
Central Area
Bromholme Lane
Brampton
Huntingdon
Cambs PE18 8NE

16 February, 1994

OUR REF: AD/LW - L18

Dear Mr Waldron

Re: MTBE in UK Gasolines

Thank you for your letter dated 31st January.

I am happy to confirm that we use both MTBE and TAME in all grades of gasoline up to a maximum (combined) of 10% volume.

The actual content varies considerably but the attached sheet gives an indication of levels during 1993.

You should not read too much into the minor variations between seasons and grades, since this can be due to a variety of reasons, including unit availability/production and feedstock availability.

I have also included a toxicity profile for MTBE which you may find useful.

Yours sincerely

ARTHUR DEWEY
Product Quality Manager



TOTAL OIL GREAT BRITAIN LIMITED

MTBE/TAME IN UK GASOLINE PRODUCTION 1993

	<u>UNLEADED PREMIUM</u>			<u>LEADED PREMIUM</u>			<u>UNLEADED SUPER</u>		
	<u>SUM</u>	<u>INT</u>	<u>WINT</u>	<u>SUM</u>	<u>INT</u>	<u>WINT</u>	<u>SUM</u>	<u>INT</u>	<u>WINT</u>
MTBE (%VOL) MIN	0.1	0.1	<0.1	0.4	0.3	0.1	0.8	2.9	0.5
MTBE (%VOL) MAX	8.2	8.6	9.4	8.2	8.1	7.7	8.4	8.1	7.6
MTBE (%VOL) AVG	3.457	4.002	2.182	3.476	3.796	2.766	5.471	5.255	4.552
TAME (%VOL) MIN	<0.1	<0.1	<0.1	0.1	0.1	<0.1	<0.1	0.1	0.1
TAME (%VOL) MAX	2.3	2.3	1.3	2.6	2.9	1.9	1.4	1.5	1.1
TAME (%VOL) AVG	0.552	0.985	0.475	0.992	1.494	0.855	0.512	0.823	0.556



Malcolm Watson
Senior Technical Officer

United Kingdom
Petroleum Industry Association Limited

9 Kingsway
London WC2B 6XH
Telephone: (071) 240 0289
Fax: (071) 379 3102

Your ref GAH/HH/581/10/19

Paul Waldron
Water Quality Manager
NRA Anglian Region
Central Area
Bromholme Lane
Brampton
Huntingdon
Cambs PE18 8NE

22 February 1994

Dear Mr Waldron,

MTBE IN GASOLINE

I apologise for the delay in repending to your letter of the 19th January 1994 on the MTBE (or TBME) content of UK gasolines but I have had to obtain the information required from my associations members.

The use of MTBE in a company's gasoline depends on a number of factors particularly its refinery configuration/operation and the availability/price of MTBE (or other oxygenates). The usage will therefore vary with time and between companies. The data quoted below is therefore only typical of 1993 and it could be misleading to extrapolate it to other years. Typically for 1993:-

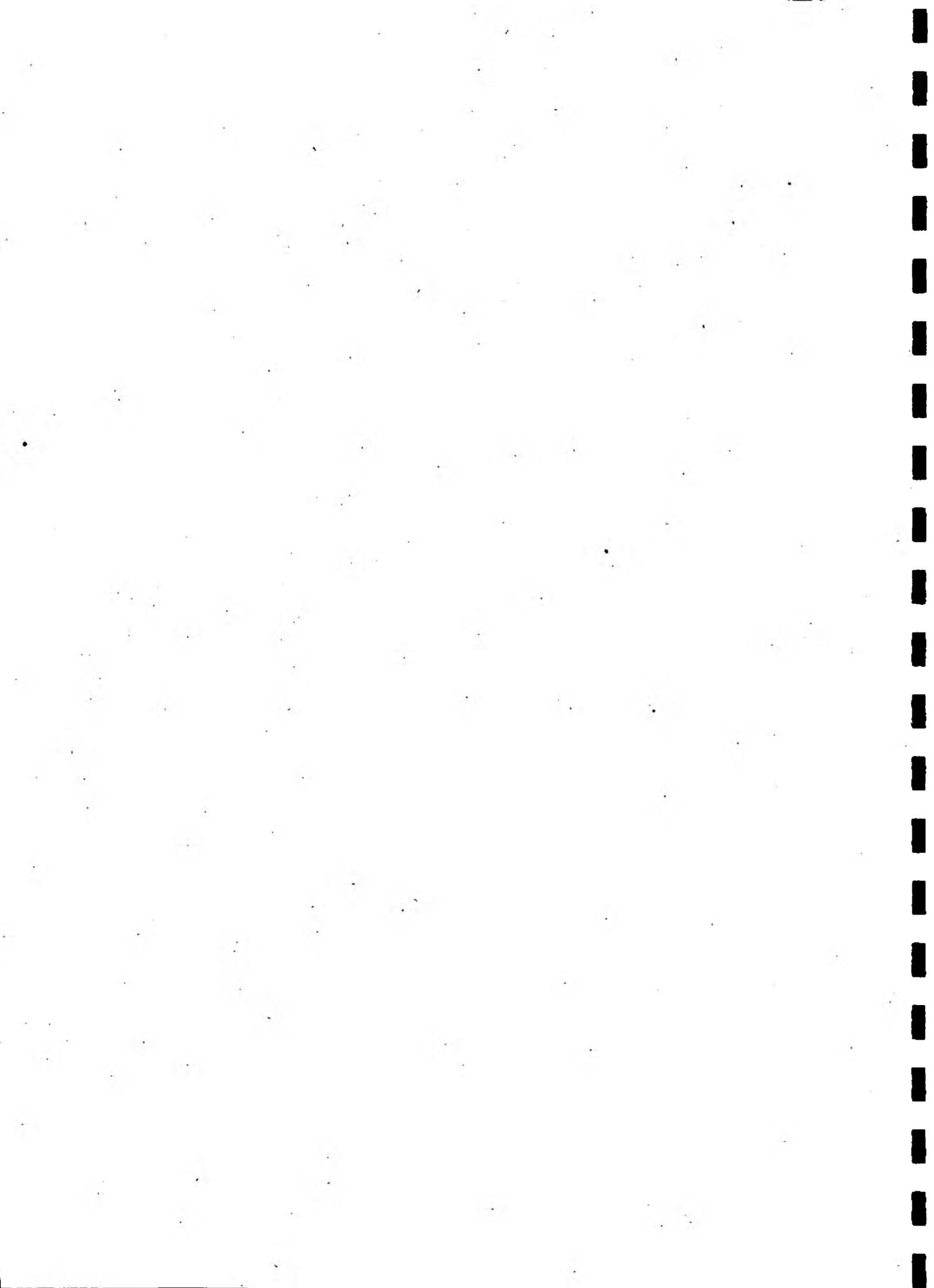
- o MTBE was not a component in all UK petrol
- o MTBE appears to have been used in about 40% of UK petrol
- o MTBE was used in all grades of petrol (leaded and unleaded)
- o The concentration of MTBE varied from 0.1 %wt to about 5 %wt. However higher concentrations may have been used on occasions.
- o For petrol with MTBE added, the average concentration of MTBE was just over 1 %wt

In providing guidance to your officers it is essential to stress the levels of MTBE used can vary from day to day even with petrol from the same refinery. This is an inevitable consequence refinery operations combined with the way petrol is blended from a number of process streams.

If you require any further information please contact me.

Yours sincerely

Malcolm Watson





DRINKING WATER INSPECTORATE

Room B148B
Romney House
43 Marsham Street
London SW1P 3PY
Direct Line : 071-276 8213
Enquiries : 071-276 8808/8666
Facsimile : 071-276 8405

Mr P Waldron
Anglian Region, National Rivers Authority
Bromholme Lane
Brampton
Huntingdon
Cambs PE18 8NE

24 March 1994

Dear Mr Waldron,

Re: MTBE IN DRINKING WATER

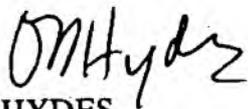
1. In reply to your letter of 16 March 1994 regarding contamination of aquifers with MTBE. An incident occurred at Beck Row, which is next to the Mildenhall airbase, in March 1990 when the aquifer was contaminated by MTBE. The contaminated water from this aquifer entered the public water supply for a period of approximately one month until the GAC had been replaced. There has been a history of contamination of the site by organic solvents and hydrocarbons and Anglian Water Services installed aeration followed by filtration through GAC to treat the water.

2. Investigations at that time found that there was no toxicological information readily available in this country. Data was obtained from the USA on the effects of mice by inhalation. From the data obtained and applying a large safety factor WRC advised Anglian Water Services that up to 100µg/l of MTBE would not pose a risk to health in the water supply in the short term and that the threshold odour concentration is only 10-15 µg/l. In this incident the water entering supply had a slight odour which was detected in the laboratory and the samples contained 8-10 µg/l of MTBE. When investigating this incident the Inspectorate consulted medical advisers at the Department of Health. The advice received was that drinking water containing a maximum of 10 µg/l MTBE for one month would not be expected to be detrimental to health, but the advice did not endorse the WRC view. I stress that this advice only indicates an exposure which is regarded as not detrimental to public health, it is not to be interpreted as a standard for MTBE in drinking water.

3. There was a paper in the American Waterworks Association Journal for May 1984 entitled "Removing Organics from Groundwater through Aeration plus GAC" which discusses ground water pollution by MTBE. I am sure a literature search will provide more information on its toxicology, with the increasing use of MTBE as a petrol additive.

4. I hope that the information will be of some value. I am not aware of any other water companies in England and Wales that have detected MTBE in water supplies.

Yours sincerely

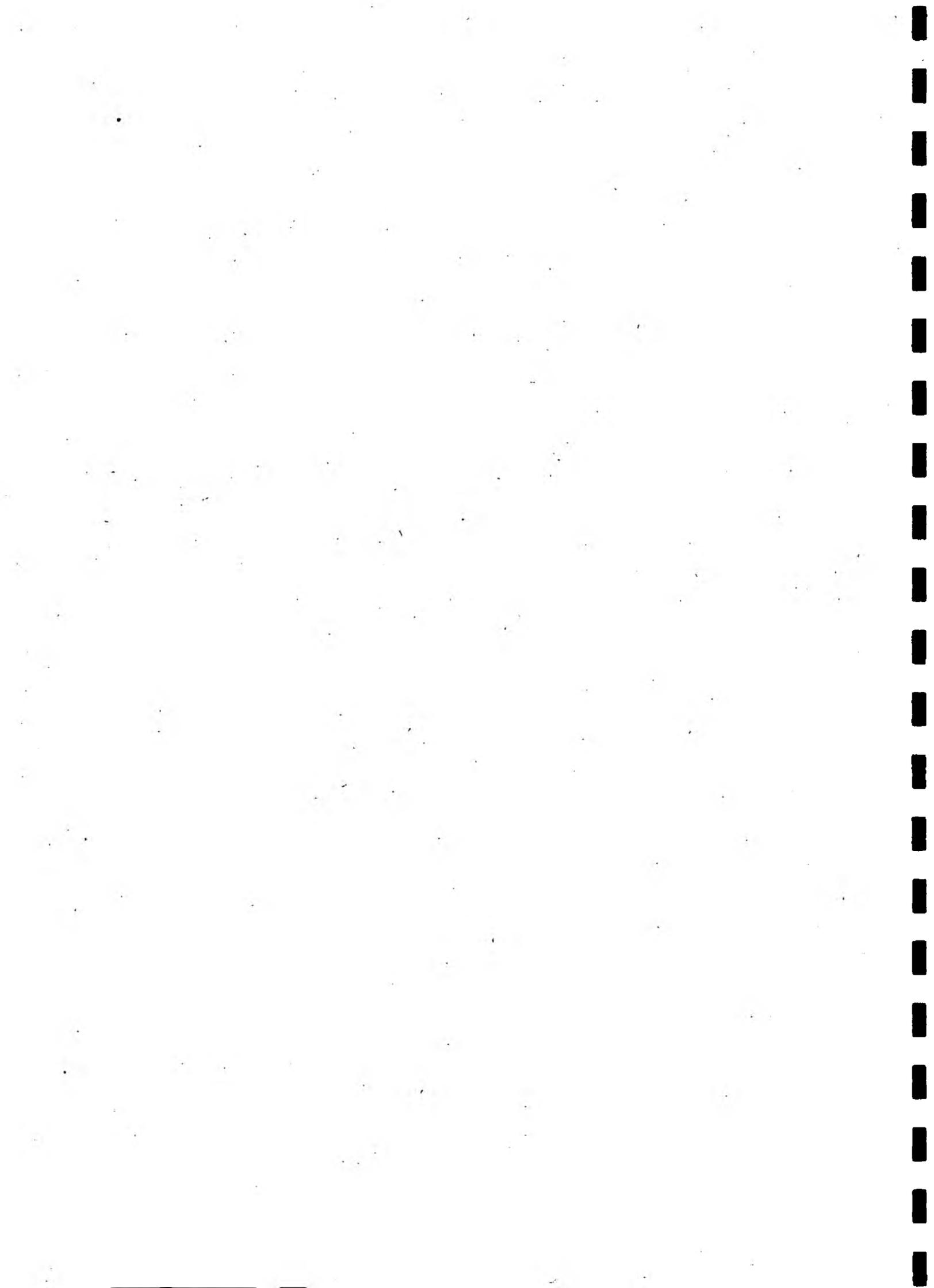


O D HYDES
Deputy Chief Inspector

APPENDIX TWO

TOXICITY PROFILE FOR TBME

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TOXICITY PROFILE



METHYL *tert*-BUTYL ETHER

SUMMARY

Neat methyl *tert*-butyl ether (MTBE) was slightly irritant to the skin and eyes of rabbits. The vapour caused eye irritation in rats and mice, and inflammation of the upper respiratory tract in rats. MTBE was of low acute toxicity to laboratory animals when administered orally, dermally or by inhalation. Single doses given by the oral, inhalation or injection routes have affected the central nervous system and blood circulation in laboratory animals. Repeated exposure of rodents to MTBE vapour resulted in anaesthesia, and effects on various tissues including the liver, kidneys and urinary tract. Inhalation by pregnant mice resulted in foetal toxicity and malformations. Mutagenic activity was reported in mammalian cells in culture, but not in an Ames bacterial test, in yeast, or in the fruit fly. There was no evidence of chromosomal damage in rats treated orally or by inhalation, or in mammalian cells in culture. In humans, the use of MTBE in the treatment of gall stones by direct instillation into the gall bladder has generally produced transient side effects (including nausea, vomiting and sedation).

IDENTIFICATION

STRUCTURAL FORMULA: $\text{CH}_3\text{OC}(\text{CH}_3)_2$

CHEMICAL ABSTRACTS REGISTRY NUMBER: 1634-04-4

RELEVANT PHYSICAL PROPERTIES: Methyl *tert*-butyl ether (MTBE) is a liquid with a boiling point of 55°C. It is soluble in water, ethanol and diethyl ether (EPA, 1986).

LOCAL EFFECTS

SKIN IRRITATION

Non-human. Covered application of neat MTBE to the skin of rabbits for 24 hr produced slight irritation (ARCO Chemical Co., 1980).

EYE IRRITATION

Non-human. The neat liquid caused mild or minimal irritation on instillation of 0.05 or 0.1 ml into the rabbit eye (ARCO Chemical Co., 1980; Snamprogetti, 1980). There were signs of eye irritation in rats and mice exposed to the vapour at concentrations of 7.2-29 g/m³ for 6 hr/day for 13 days or longer (Dodd & Kintigh, 1989), and in rats exposed at 70 g/m³ or more for 4 hr (ARCO Chemical Co., 1980).

OTHER LOCAL EFFECTS

Non-human. Inflammation of the upper respiratory tract membranes developed in rats exposed to vapour concentrations of 3.6 g/m³ or more, 6 hr/day, for 9 days. No such effect was seen in 40 rats exposed at 1.1 g/m³ (Biodynamics Inc., 1984a).

SENSITIZATION AND INTOLERANCE

Non-human. There was no evidence of sensitization in ten guinea-pigs that received repeated intradermal injections of 0.1% MTBE every second day for 3 wk followed by a challenge injection of 0.1% MTBE 2 wk later (ARCO Chemical Co., 1980).

GENERAL SYSTEMIC EFFECTS

SINGLE EXPOSURE

Human. MTBE has been used to dissolve gall stones, by continuous infusion (generally for 5-7 hr) into the gall bladder and aspiration at regular intervals to prevent the liquid from overflowing the gall bladder (Allen *et al.* 1985; Carrick *et al.* 1987; Hellstern *et al.* 1988; Juliani *et al.* 1985; Murray *et al.* 1988; Ponchon *et al.* 1988; Sauerbruch *et al.* 1985; Thistle *et al.* 1989). Side effects of this treatment are normally transient and may include nausea, vomiting and mild sedation, with the odour of MTBE detectable on the patient's breath. A severe complication arose in one patient when aspiration of the liquid was incomplete: the loss (presumably by overflow) of 6 ml [roughly 100 mg/kg bw] caused the patient to become confused whilst another 15 ml loss rendered the patient comatose, with subsequent acute kidney failure, which was thought to be due to MTBE's ability to induce red blood cell damage. The patient recovered after dialysis (Ponchon *et al.* 1988).

Non-human. Oral. LD₅₀ rat: 3.87 g/kg bw (ARCO Chemical Co., 1980).
Symptoms of poisoning in rats included depression of the central nervous system, incoordination, tremors and laboured breathing (ARCO Chemical Co., 1980).

Dermal. LD₅₀ rabbit (24-hr covered contact): >10 g/kg bw
(ARCO Chemical Co., 1980).

Inhalation. 4-hr LC₅₀ rat: 85-120 g/m³ (ARCO Chemical Co., 1980; Sun Petroleum Products Co.)
15-min LC₅₀ mouse: 140 g/m³ (Marsh & Leake, 1950).
10-min LC₅₀ mouse: 650 g/m³ (Snamprogetti, 1980).

Decreased blood pressure and increased heart rate occurred in rabbits and cats exposed to MTBE vapour [details of the exposure conditions were not clearly presented] (Snamprogetti, 1980).

Intraperitoneal. LD₅₀ rat: 1.7 g/kg bw (Snamprogetti, 1980).
In rats, 1-1.5 g/kg bw induced anaesthesia and resulted in the appearance of blood in the urine, suggesting red blood cell damage. No such effects were noted at 0.25-0.5 g/kg bw (Biodynamics Inc., 1980). A slight increase in blood pressure and a reduction in heart rate were seen in rats given 0.5 g/kg bw (Snamprogetti, 1980).

LD₅₀ mouse: 1.4 g/kg bw (Snamprogetti, 1980).

Slight reductions in general activity and co-ordination were reported in mice given 0.1 or 0.4 g/kg bw (Snamprogetti, 1980).

Intravenous. LD₅₀ rat: 0.56 g/kg bw (Snamprogetti, 1980).

Doses of 0.15-0.43 g/kg bw resulted in the appearance of blood in the urine of rats (Biodynamics Inc., 1980). Rats, rabbits and cats given 0.01-0.1 g/kg bw showed an immediate drop in blood pressure, a reduction and subsequent increase in heart rate, and an increase in respiratory rate (Snamprogetti, 1980).

Subcutaneous. LD₅₀ rat: 6.7 g/kg bw (Snamprogetti, 1980).

LD₅₀ mouse: 3.6 g/kg bw (Snamprogetti, 1980).

REPEATED EXPOSURE

Non-human. Inhalation. Rats. In the studies described in the following paragraph, exposure was for 6 hr/day, 5 days/wk.

A transient increase in enzyme activity in the liver and kidneys [not further examined] was seen in males exposed to 0.2 g/m³ or more for 2-15 wk (Savolainen *et al.* 1985). Groups of 20 rats of each sex exposed to vapour concentrations of 0.36 or 1.1 g/m³ for 2 wk showed no clinical effects (Biodynamics Inc., 1984a), although exposure to 0.9 g/m³ or more for 13 wk resulted in anaesthesia (Greenough *et al.* 1980). A concentration of 2.9 g/m³ or higher for 2-13 wk increased liver and kidney weights, decreased lung weight, induced mild effects on blood composition (including increased levels of the red blood cell pigment, haemoglobin), and decreased growth (Biodynamics Inc., 1984a; Dodd & Kintigh, 1989; Greenough *et al.* 1980). Behavioural changes (including reduced activity and muscular incoordination) were seen at 7.2 g/m³ and above for 13 days or more (Biodynamics Inc., 1984a; Dodd & Kintigh, 1989). No tissue abnormalities were apparent in microscopic examinations involving a wide range of organs at concentrations up to 14.4 g/m³ for up to 13 wk in group sizes ranging from 10-25 rats of each sex (Biodynamics Inc., 1984a; Dodd & Kintigh, 1989; Greenough *et al.* 1980). At 14.4 g/m³ or more, adrenal weight was increased and males exposed to 29 g/m³ showed effects on the lymph nodes (cell proliferation), spleen (iron accumulation) and kidneys (hyaline droplets in the tubules) (Dodd & Kintigh, 1989).

In a poorly reported study, there were no overt signs of toxicity in groups of 20-50 rats exposed at 180 or 290 g/m³ for 10 min/day or 290 g/m³ for 5 min/day for 30 or 120 days (Snamprogetti, 1980). No effects were apparently noted in liver function tests, blood and urine analyses or very limited tissue examinations.

Mice. A vapour concentration of 3.7 g/m³ produced no signs of toxicity in 30 female mice exposed for 6 hr/day on days 6-15 of pregnancy (Tyl & Neeper-Bradley, 1989).

Groups of five male and five female mice were exposed to MTBE vapour at concentrations of 7.2, 13.9 or 28.6 g/m³, 6 hr/day, for 13 days. At all exposure levels the animals showed muscular incoordination and decreased activity during exposure, and their liver weight was reduced, although no gross lesions were evident in the major organs (Dodd & Kintigh, 1989).

A brief report of the 'interim' findings [at an unspecified stage] of an 18-month study stated that six out of 50 females and nine out of 50 males exposed at 28.8 g/m³ had died, as well as one of 50 males exposed at 1.4 g/m³. Six of the ten dead males were found to have obstructive uropathy [a disease of the urinary tract] and one of the surviving males in the 28.8 g/m³ group had a distended bladder, indicative of the same condition. There were no indications of urinary tract abnormalities in female mice or in the unexposed controls. The investigators evidently considered that the condition was due to physical matter blocking the urethral canal (known to be narrower in male mice than in females) rather than to an infection, as the tissues of the kidneys and other organs [unspecified] appeared normal on microscopic examination (PTCN, 1990).

In a poorly reported study, there were no overt signs of toxicity in groups of 30 mice exposed at 180 or 290 g/m³ for 10 min/day or 290 g/m³ for 5 min/day for 30 or 120 days (Snamprogetti, 1980). No effects were apparently noted in liver function tests, blood and urine analyses or very limited tissue examinations.

Intraperitoneal. Ten rats that received 0.25 g/kg bw/day for 15 days showed no overt signs of toxicity and the organ weights were unaffected (Snamprogetti, 1980).

REPRODUCTIVE TOXICITY

Non-human. Inhalation. Rats. Reproductive function was apparently unaffected when groups of 15 male rats were exposed to roughly 1.1, 4.4 or 10.5 g MTBE vapour/m³ for 6 hr/day, 5 days/wk, for 12 wk, and mated to females (30/group) exposed to similar concentrations for 3 wk prior to mating and then on days 0-20 of pregnancy (6 hr/day, 7 days/wk) and on days 5-20 of lactation. Each female produced two litters under these conditions. Although pup viability in the second litters was reduced (from a high 99% in controls down to 95.5% at the top two doses), this was not considered by the investigators to be biologically significant. There was no evidence of malformations on gross examination of the offspring, and although some of the offspring from the low- and mid-dose groups showed dilation of the kidney pelvis, the increased incidence was not statistically significant (Biles *et al.* 1987).

There was no evidence of foetotoxicity when groups of 23-25 female rats were exposed at concentrations of about 1, 4 or 12 g/m³ for 6 hr/day on days 6-15 of pregnancy. No malformations were reported on gross examination of the offspring (Conaway *et al.* 1985).

Mice. No overt maternal toxicity was induced when groups of 24-29 female mice were exposed to about 1, 4 or 12 g/m³ for 6 hr/day on days 6-15 of pregnancy. There were some indications of foetotoxicity (early foetal deaths and/or fused sternbrae) at all dose levels although no malformations were reported (Conaway *et al.* 1985).

A vapour concentration of 3.7 g/m³ produced no signs of toxicity in 30 female mice exposed for 6 hr/day on days 6-15 of pregnancy, and examination of the foetuses revealed no abnormalities. A similar exposure regime at higher vapour levels (14.7 and 29.4 g/m³) resulted in clear signs of maternal toxicity (weight loss, muscular incoordination, reduced activity) and evidence of foetotoxicity (reduced foetal body weights, and skeletal variations due to delayed development). Other foetotoxic effects seen only at the highest exposure level (29.4 g/m³) included a reduced number of viable implantations [embryos successfully embedding in the womb] per litter, an increased number of resorptions [early embryo/foetal deaths] and an altered sex ratio (a lower percentage of male foetuses). In addition, an increased incidence of malformations (cleft palate) was seen in the foetuses of the top-dose group (Tyl & Neeper-Bradley, 1989).

CARCINOGENICITY

Non-human. An 18-month inhalation study is currently being conducted in rats and mice, involving the exposure of 50 males and 50 females of each species to vapour concentrations of 1.4, 10.8 and 28.8 g/m³. A brief report of the interim findings provides no data on tumour incidences (PTCN, 1990).

OTHER GENOTOXICITY

Mammals. There was no evidence of chromosomal damage in the bone marrow of rats given a single oral dose (24 rats/group) or five repeated oral doses at 24-hr intervals (8 rats/group) of 0.04, 0.13 or 0.4 g/kg bw (ARCO Chemical Co., 1980). Similarly, groups of ten rats exposed to 2.9, 14.8 or 29 g MTBE vapour/m³, 6 hr/day, for 5 days showed no treatment-related increase in the level of chromosomal damage in the bone marrow cells (Vergnes & Morabit, 1989).

Mammalian cells in culture. There was no convincing evidence of chromosomal damage in mammalian cells in culture, in the presence or absence of an added liver metabolic activation system (ARCO Chemical Co., 1980). In mouse (lymphoma) cells, a dose-related increase in mutagenicity was consistently seen in the presence, but not in the absence, of an added liver metabolic activation system. Replicate tests with a sample of MTBE that was 99.9% pure (as opposed to the 99.1% purity of the initial samples) confirmed this finding (ARCO Chemical Co., 1980).

Microorganisms. MTBE showed no evidence of mutagenic activity in the Ames bacterial test with *Salmonella typhimurium*, or in an assay (for mitotic gene conversion) in the yeast, *Saccharomyces cerevisiae*, either in the presence or absence of a liver metabolic activation system (ARCO Chemical Co., 1980).

Other assays. MTBE was not mutagenic in the fruit fly, *Drosophila melanogaster*, in the sex-linked recessive lethal test (Sernau, 1989).

OTHER TOXICITY CONSIDERATIONS

There was a dose-dependent increase in the concentration of MTBE in the blood, brain and fatty tissue of rats exposed to 0.2-1 g MTBE vapour/m³ for 2 wk or more, and of *tert*-butanol in the blood and brain (Savolainen *et al.* 1985). Following a single intraperitoneal injection of 232 mg MTBE/kg bw in rats, over 90% was exhaled unchanged, with 7.5% exhaled as carbon dioxide and 3.1% excreted in the faeces and urine as formic acid (Biodynamics Inc., 1984b).

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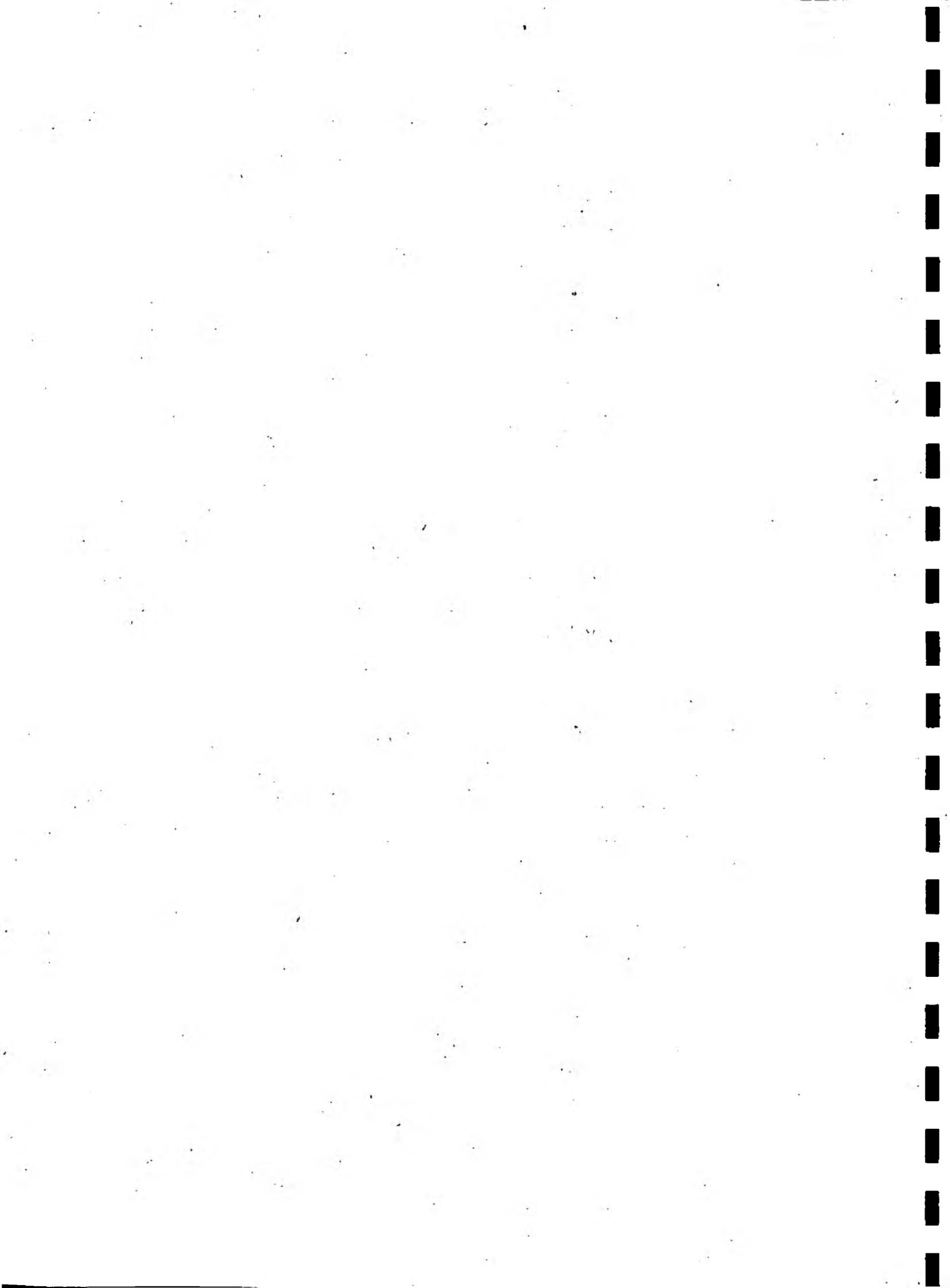
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TR/PA/June 1990(d)/P.337/T.2164(m)/ACN 17163



FIGURES

- Figures
1. Borehole Locations
 2. TBME Distribution, April 1990
 3. TBME Distribution, January 1992
 4. Benzene Distribution, January 1992
 5. TBME Distribution, June 1992
 6. TBME Distribution, June 1993
 7. Benzene Distribution, June 1993
 8. TBME Distribution, July 1993
 9. Benzene Distribution, July 1993
 10. TBME Distribution, August 1993
 11. Benzene Distribution, August 1993

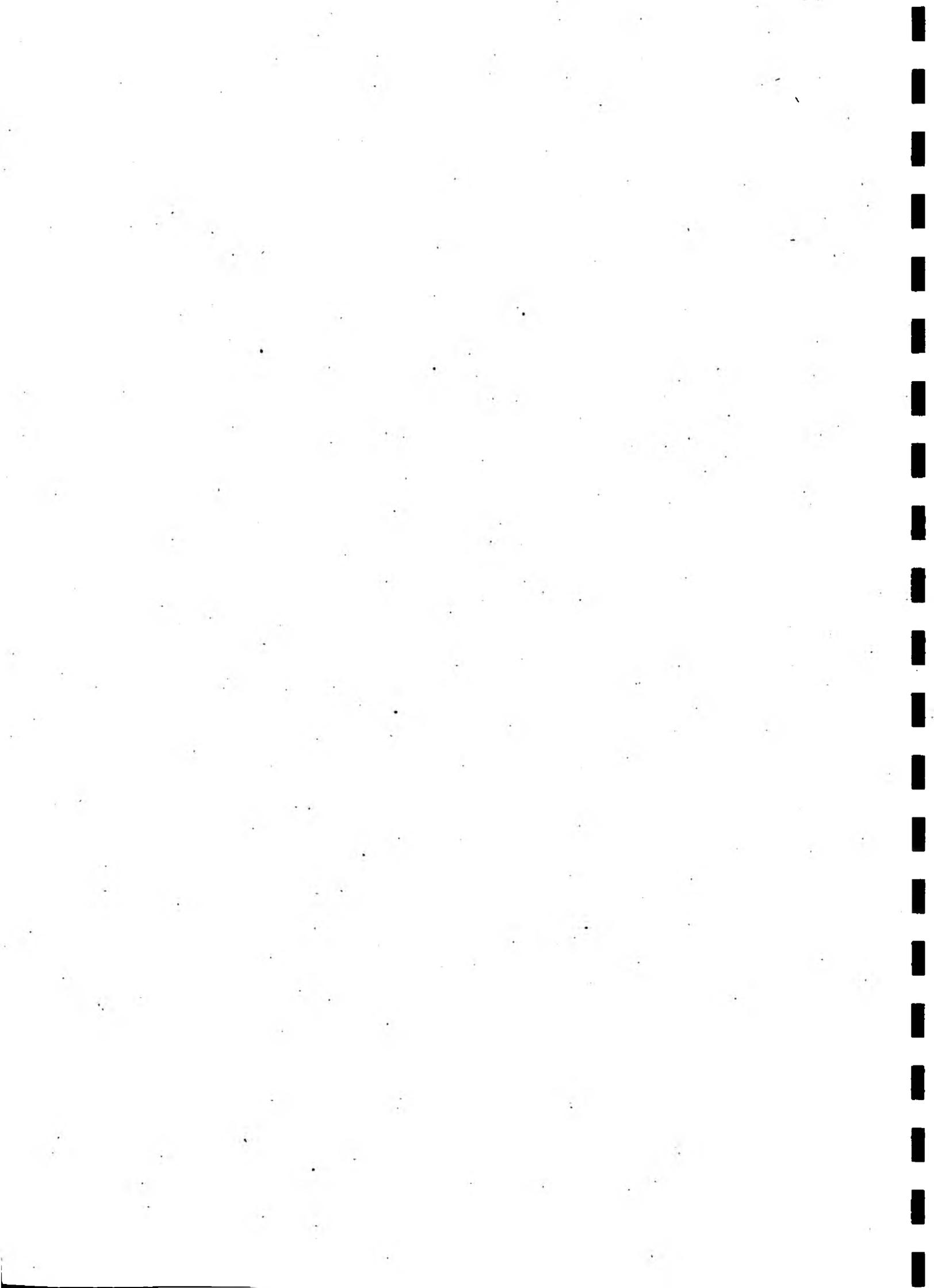


FIGURE 1

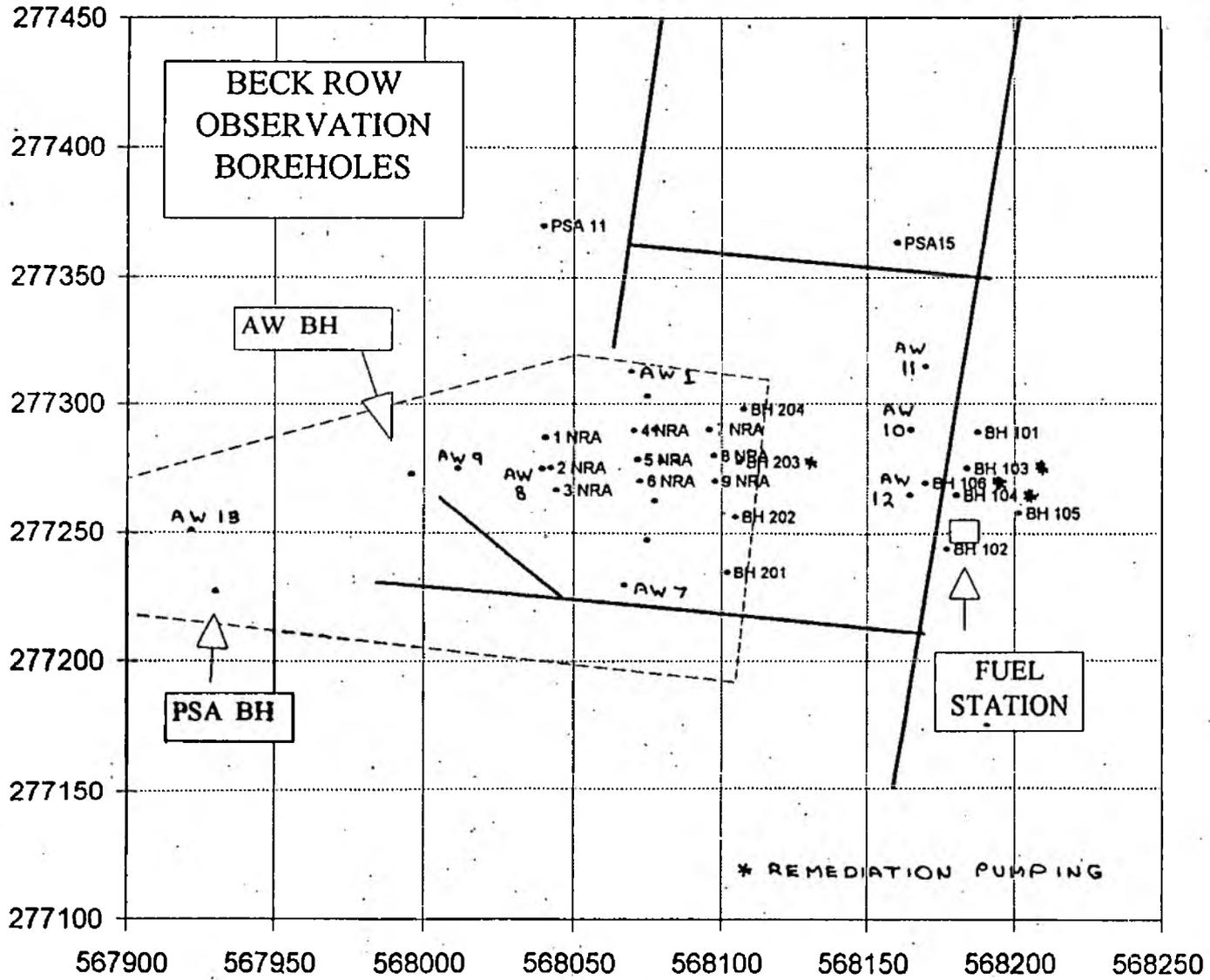


FIGURE 2

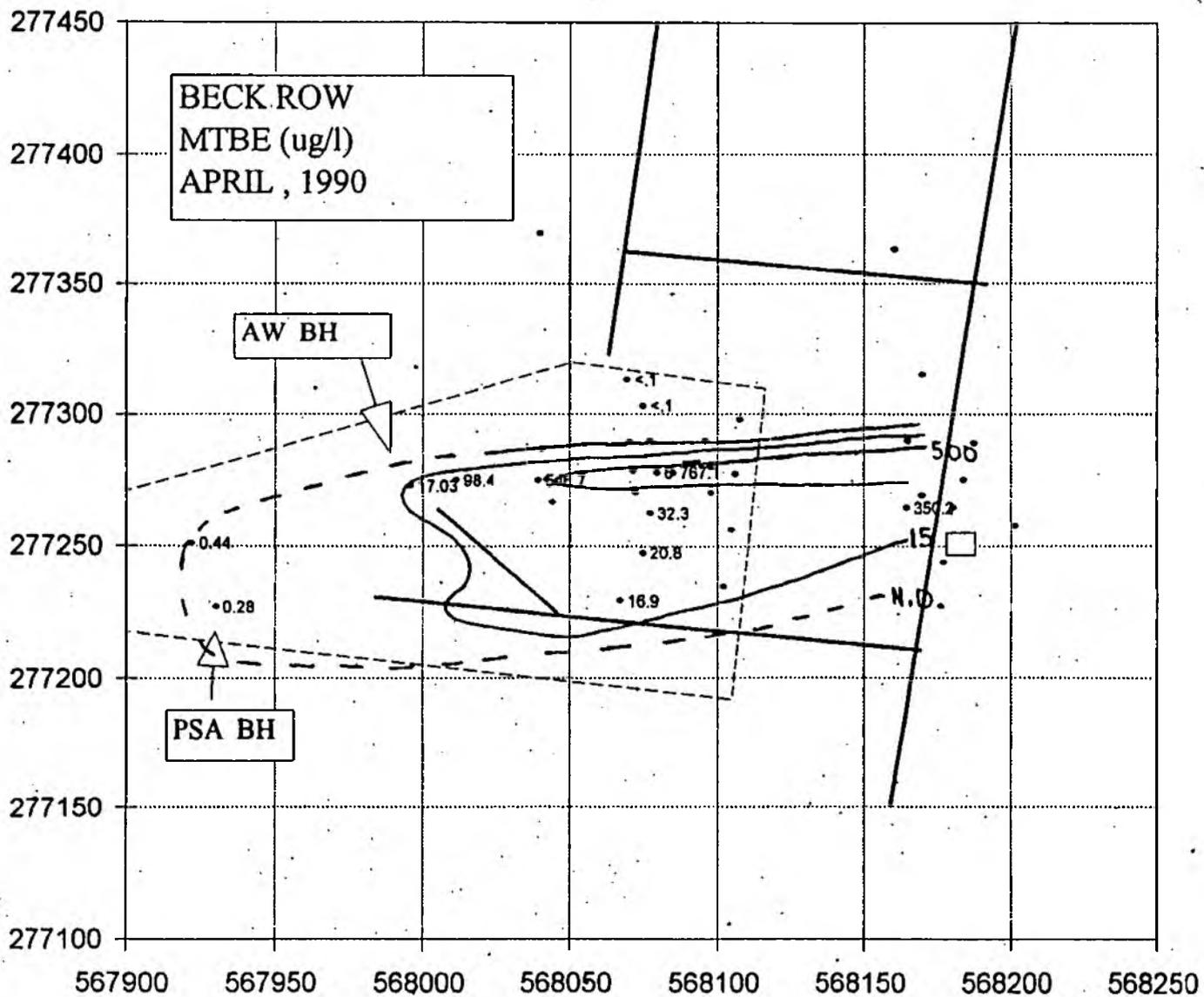
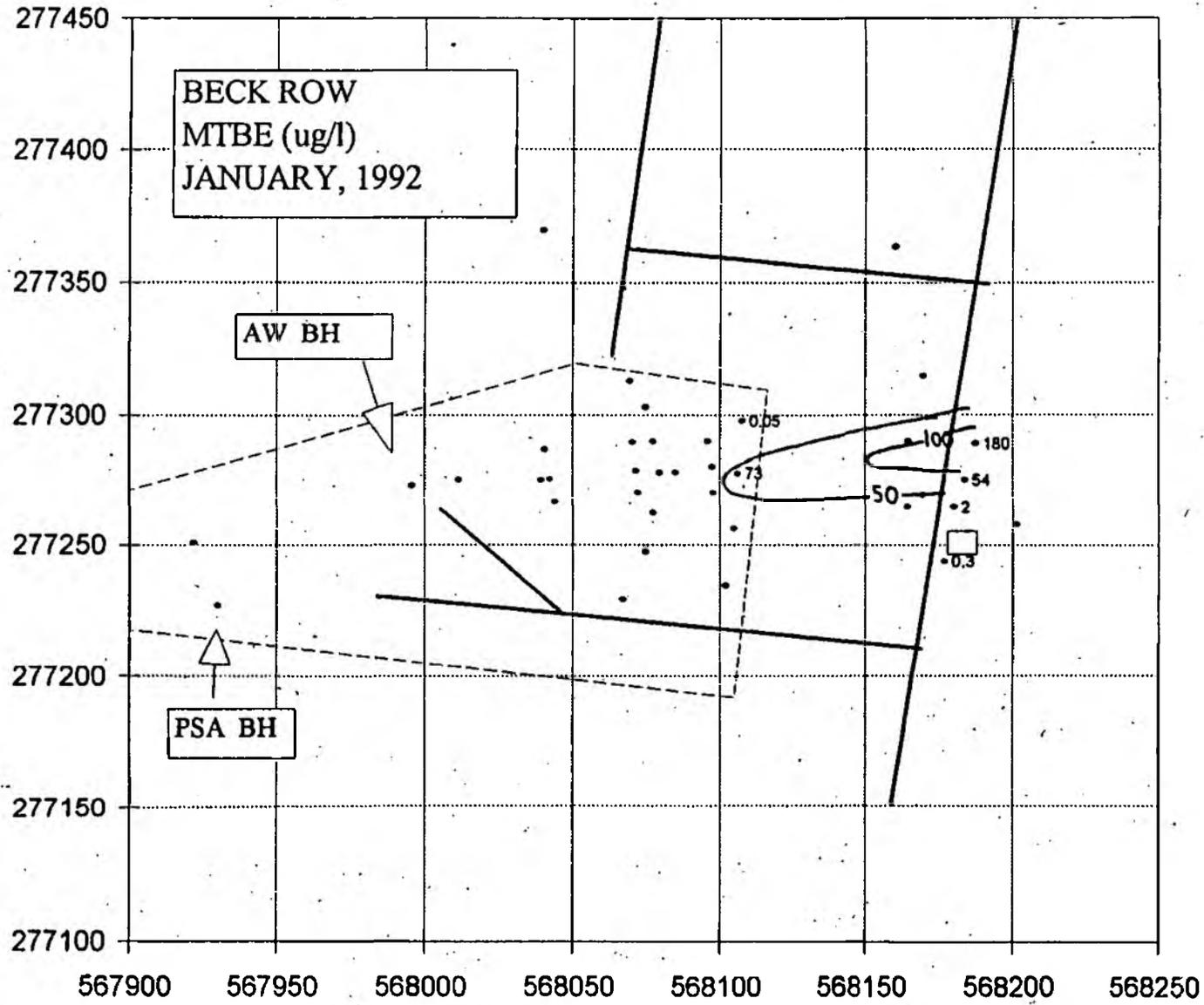


FIGURE 3



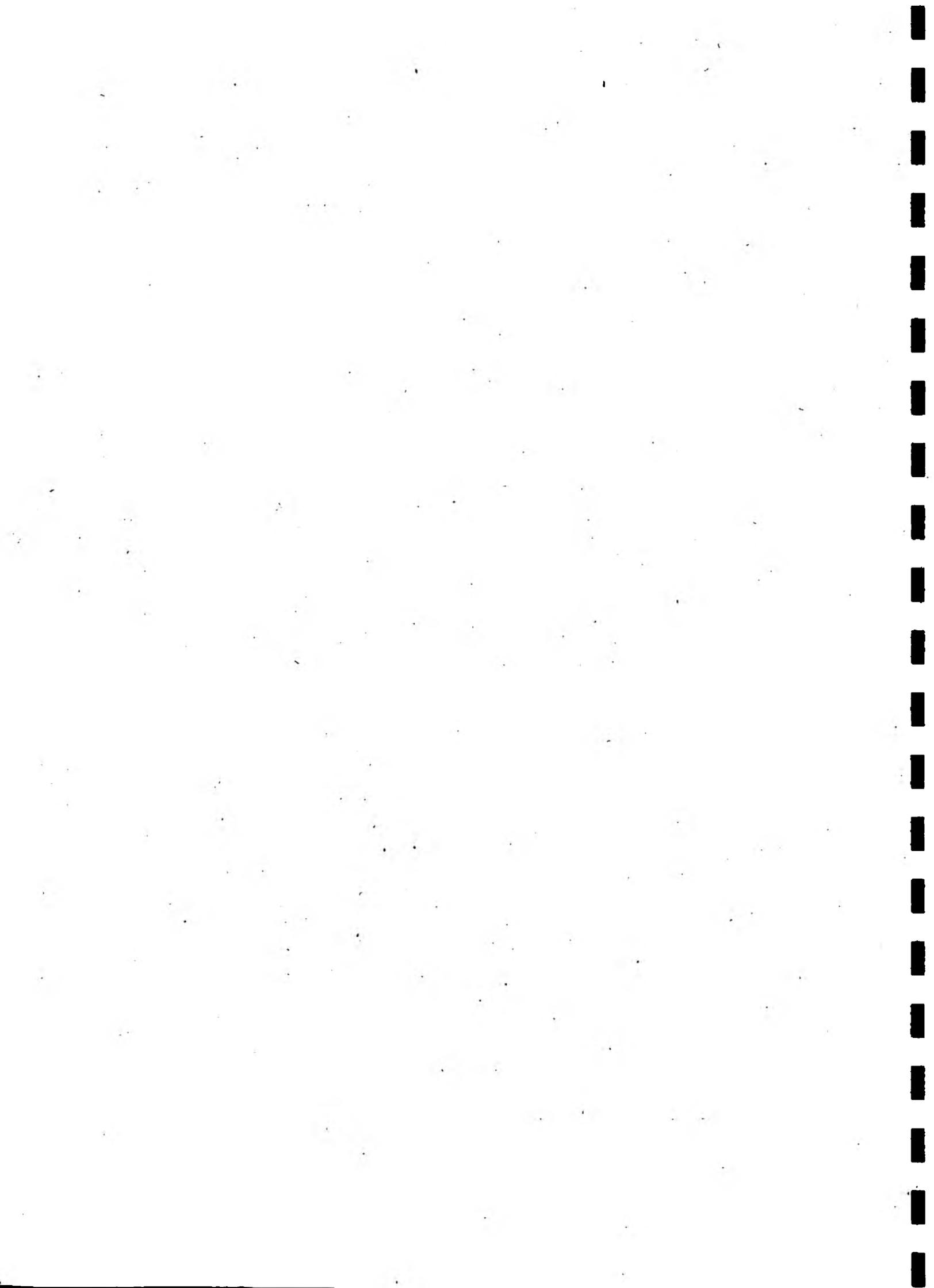


FIGURE 4

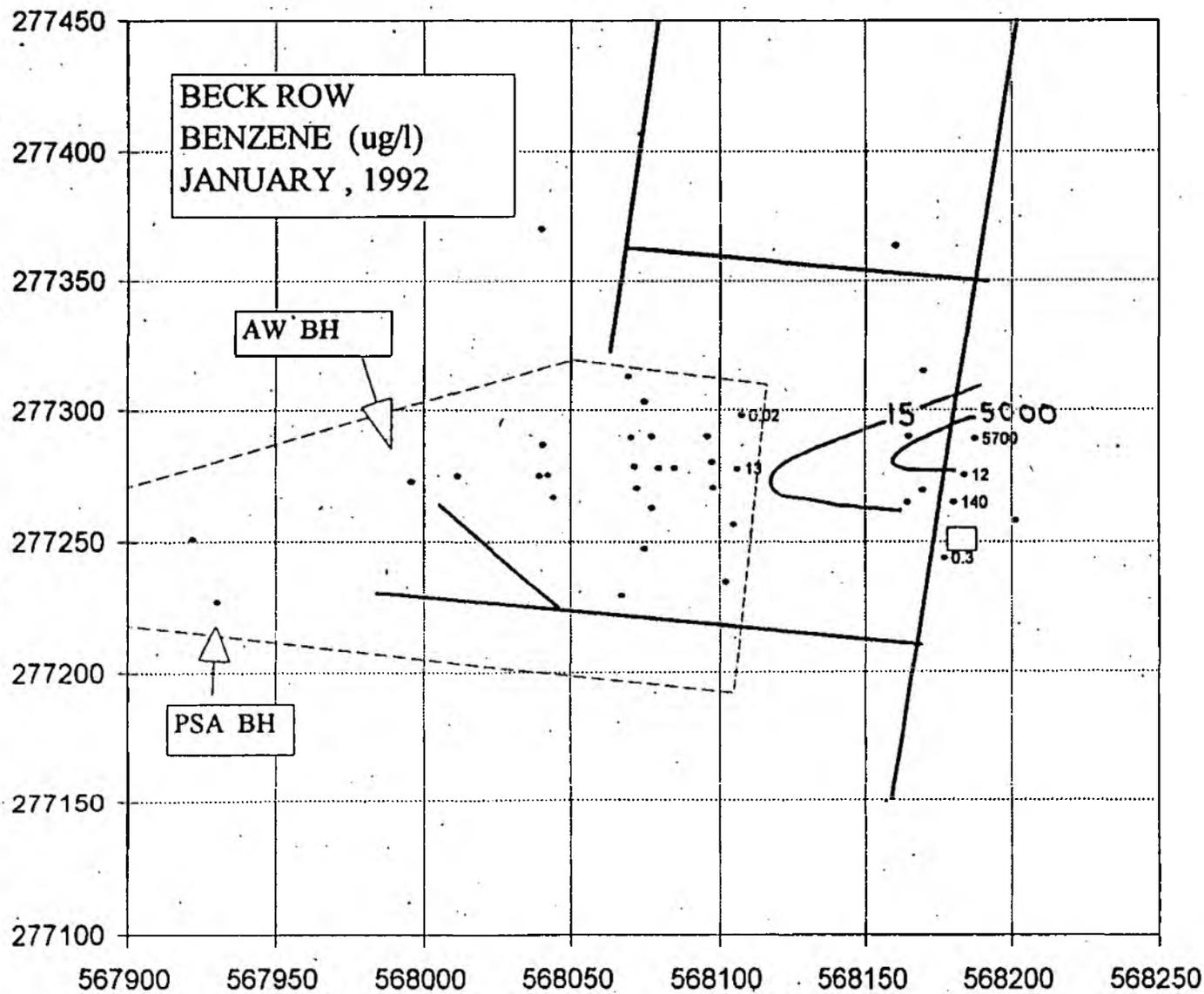


FIGURE 5

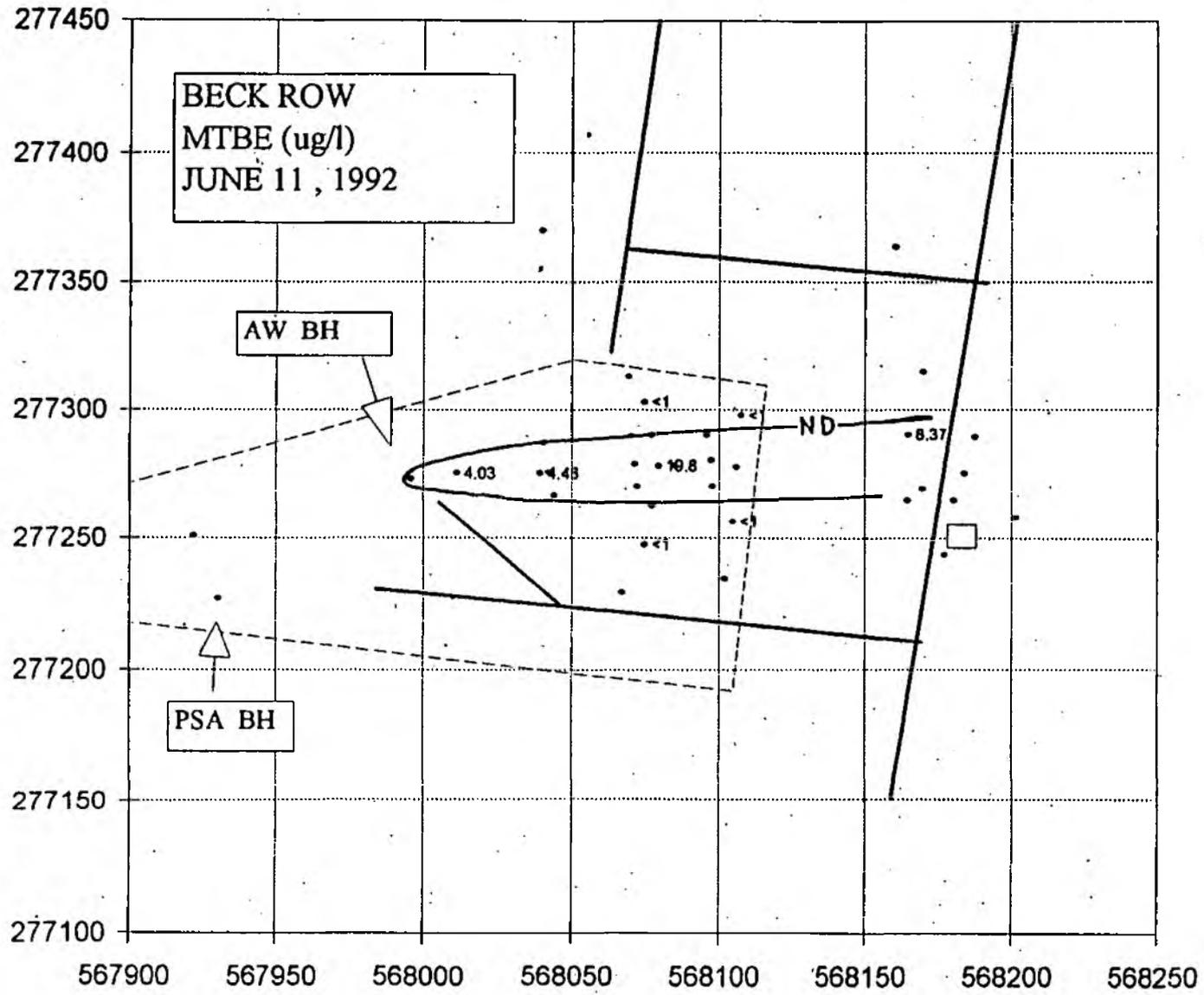
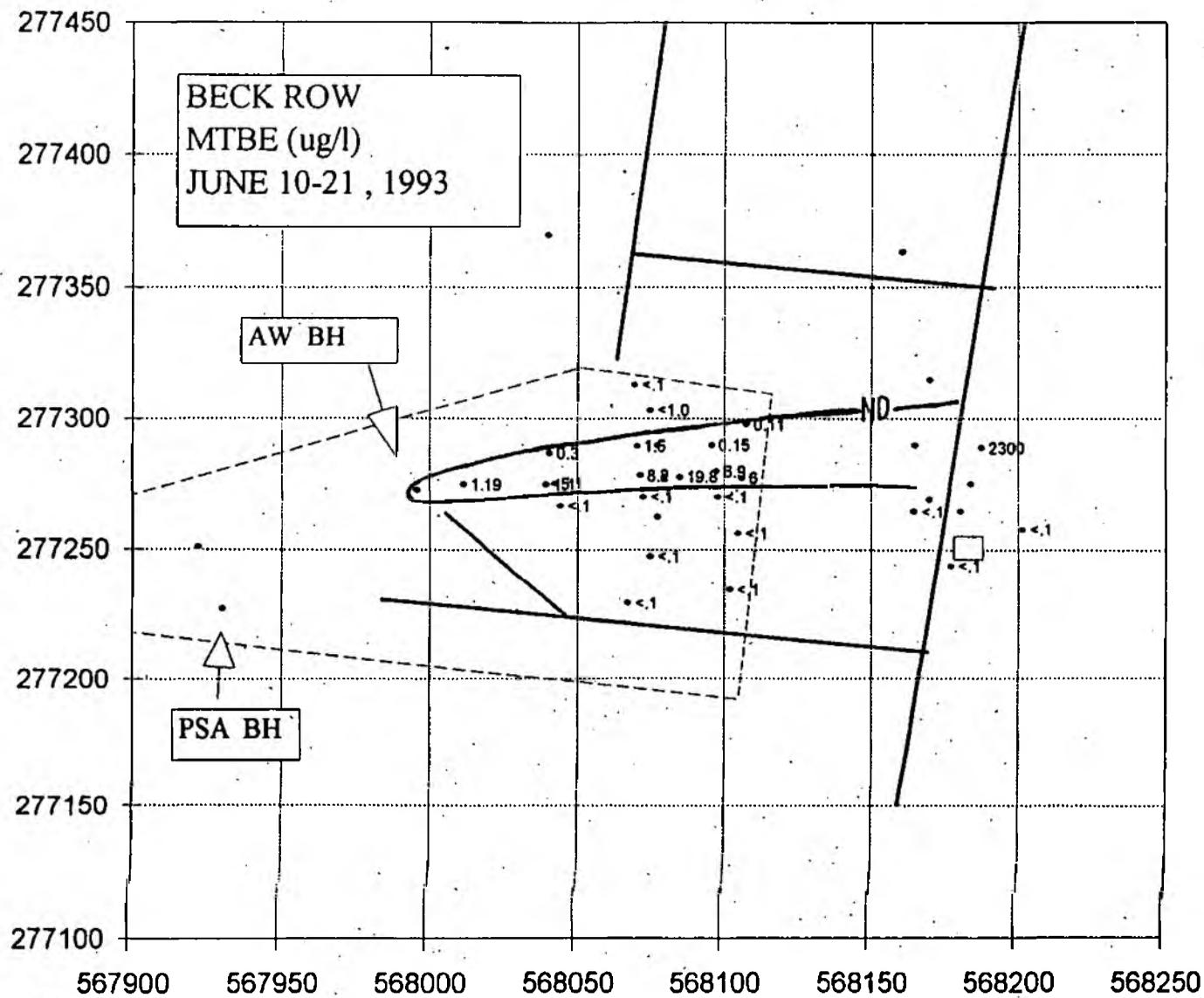
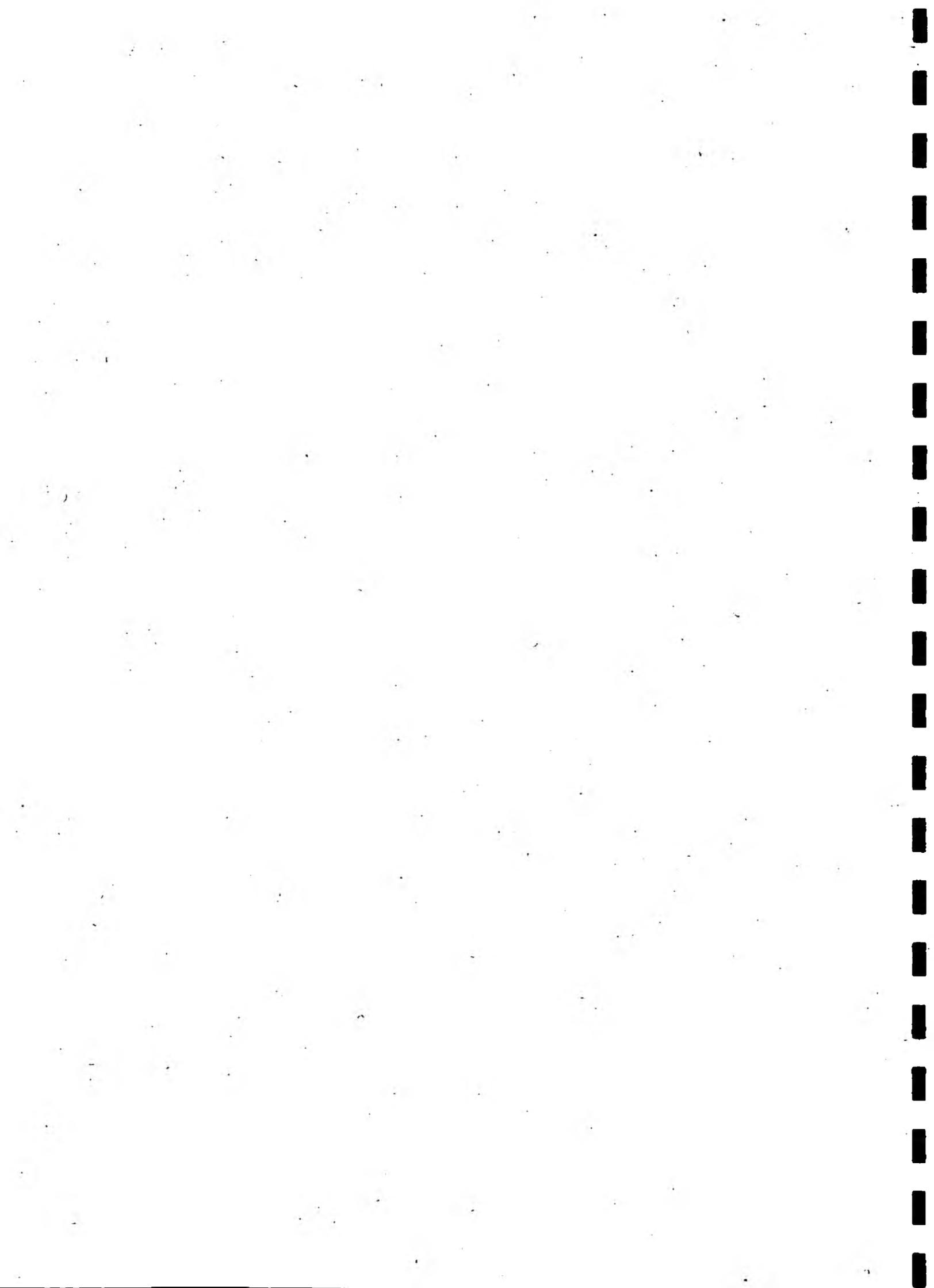


FIGURE 6





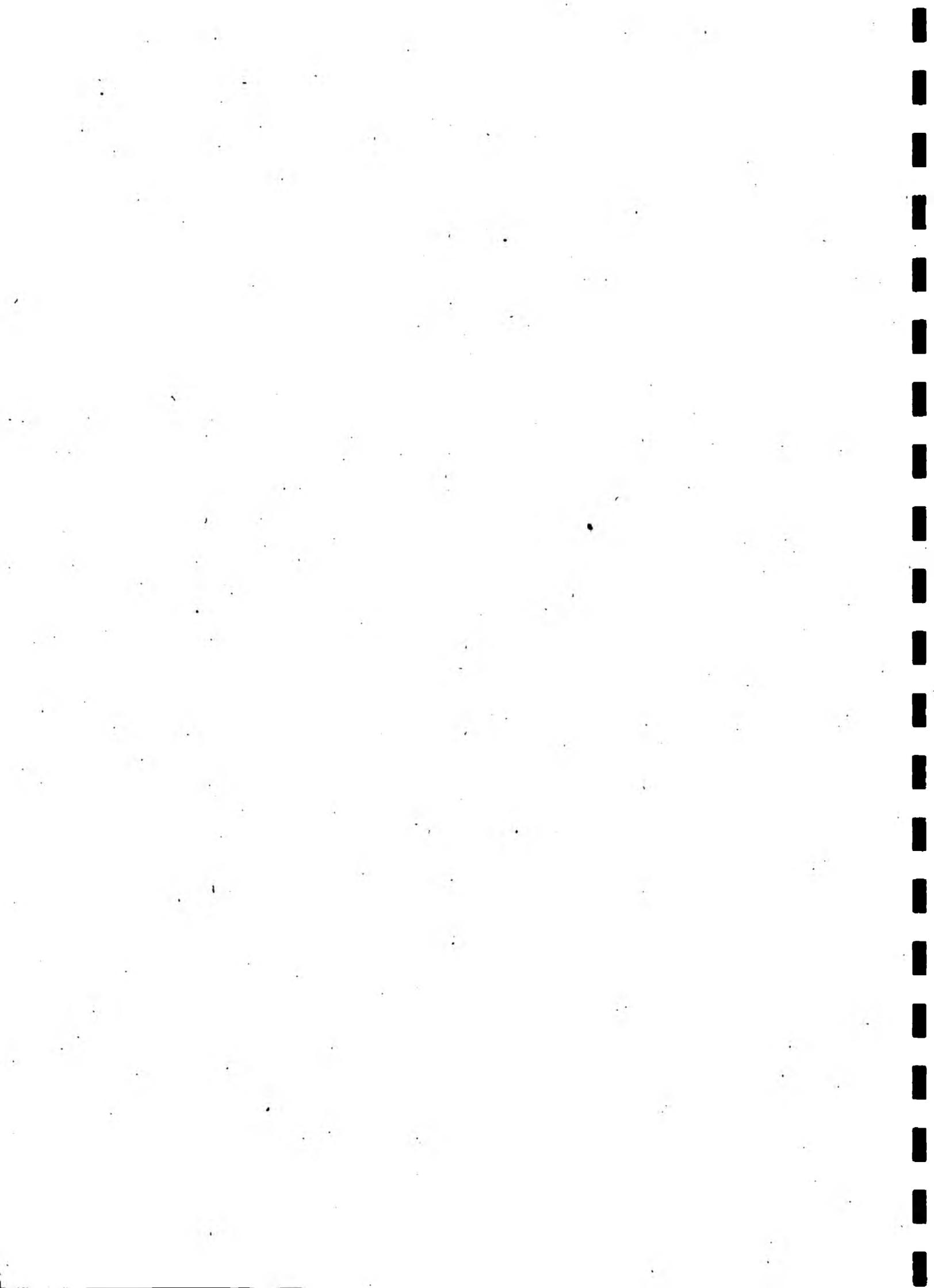


FIGURE 8

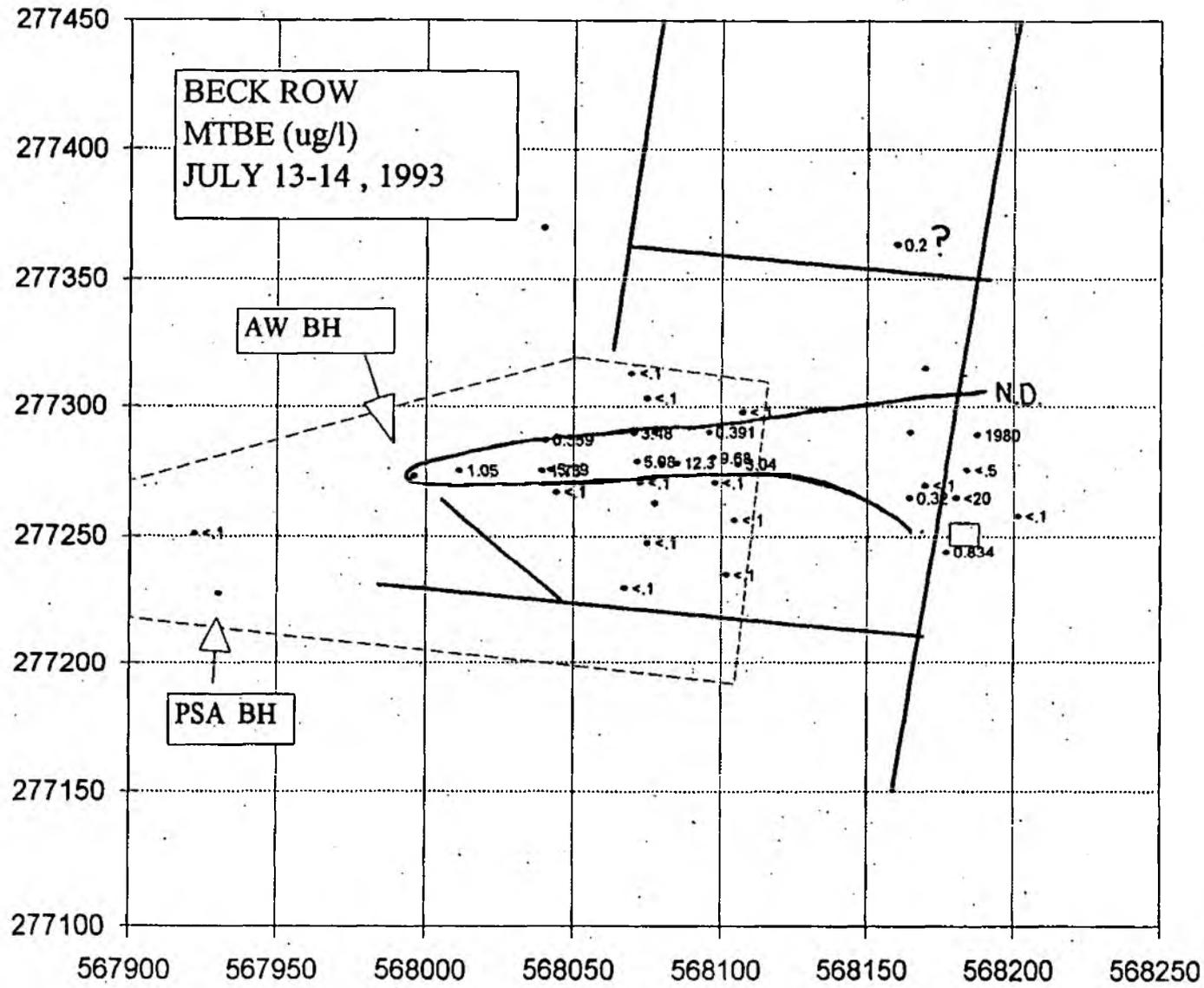


FIGURE 10

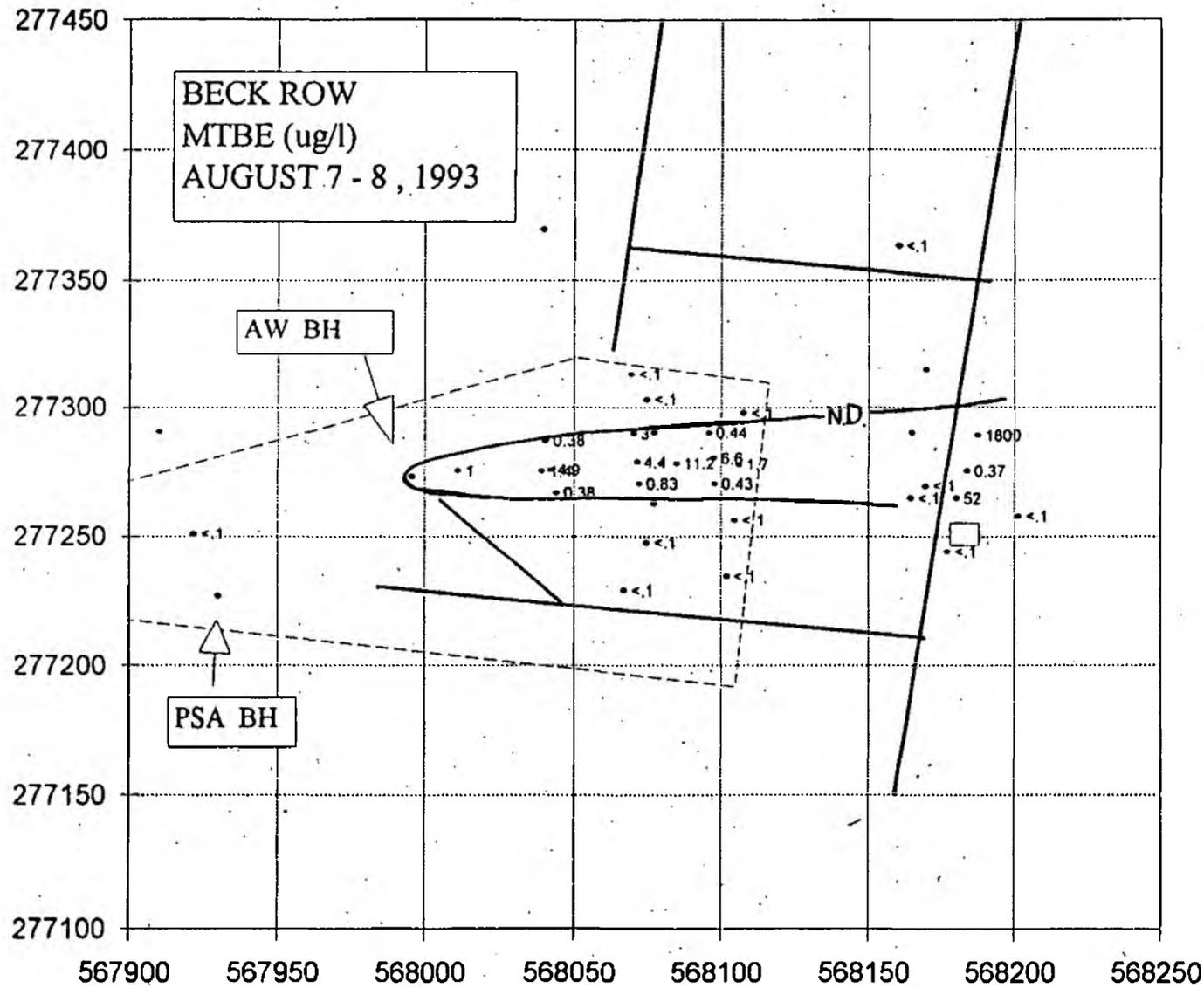


FIGURE 11

