

I Roy



**NEW ZEALAND  
ALUMINIUM SMELTERS LIMITED**

***INTERDEPARTMENTAL  
COMMITTEE  
REPORT***

**1993**

REPORT TO THE INTERDEPARTMENTAL COMMITTEE  
ON ENVIRONMENTAL EFFECTS OF THE TIWAI ALUMINIUM SMELTER  
FOR THE YEAR ENDING 31 DECEMBER 1993

MEETING AT TIWAI  
10th JUNE, 1994

aluminum inj =  
computer modelling  
p 4 3B m/c problems in Nov. / what changes with  
p 30. what sheep effects 6ME4+12 instead of scrub  
p 14 1 km had 2 or 3 results  
p 20 computer fig 1 mg / mE immediately  
East How far east.

THE INFORMATION CONTAINED IN THIS REPORT IS CONFIDENTIAL TO  
THE MEMBERS OF THE INTERDEPARTMENTAL COMMITTEE

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## SUMMARY

The overall effect of the smelter on the environment was stable and at similar levels to 1992. The exceptions were decreased vegetation fluoride north of the smelter and increased vegetation fluoride north east of the smelter.

The main stack gaseous fluoride discharge remained within the discharge permit condition of 65 mg/m<sup>3</sup> throughout 1993.

The main stack particulate discharge exceeded the permit conditions at the beginning and the end of 1993. To remedy this the 2B, 3A, and 3B multicyclones were refurbished, as planned, early in the year. The efficiency of the 3B multicyclone reduced in November, while operational problems due to the choking of the baghouse on 2A, 3A and 3B multicyclone occurred on December. Work continued in 1993 to reduce particulate discharge from the main stack.

Improvements proposed to protect the environment were presented in the smelter's application for coastal and discharge permits for discharges to air. These included proposals for dry scrubbing and treatment of spent pot lining material. A prototype dry scrubbing system was installed in 1993. Performance and optimisation trials will continue during 1994.

Problems continue with the north drain fluoride discharge. Work is continuing to develop a solution to reduce the occasional fluoride discharge peak.

The volume of cathode pad leachate discharged to Foveaux Strait decreased during 1993. The number of discharges was 50% lower than in 1992.

Investigation into remediation of ground water contaminated by cathode pad leachate and diesel continued in 1993. Pump and treat trials and laboratory scale bioremediation trials for cathode leachate contamination were undertaken. Sparging and venting trials for remediating the diesel spill were successfully undertaken in late 1993.

At NZAS each Manager is directly accountable for the effect of area operations on the environment. Work continues by each Manager to improve the systems to minimise these effects.



**REPORT TO THE INTERDEPARTMENTAL COMMITTEE ON ENVIRONMENTAL  
EFFECTS OF THE TIWAI ALUMINIUM SMELTER FOR THE YEAR ENDING 31  
DECEMBER, 1993**

**1. INTRODUCTION**

During 1993, NZAS continued with developments aimed at minimising the effects of the smelter's operations on the environment.

Significant developments during 1993 include

- a proposed major upgrade including improved environmental protection equipment,
- development of a full scale prototype dry scrubbing reactor,
- investigation of a process to treat spent pot lining material, and
- application for the renewal of the Discharge to Air Permit.

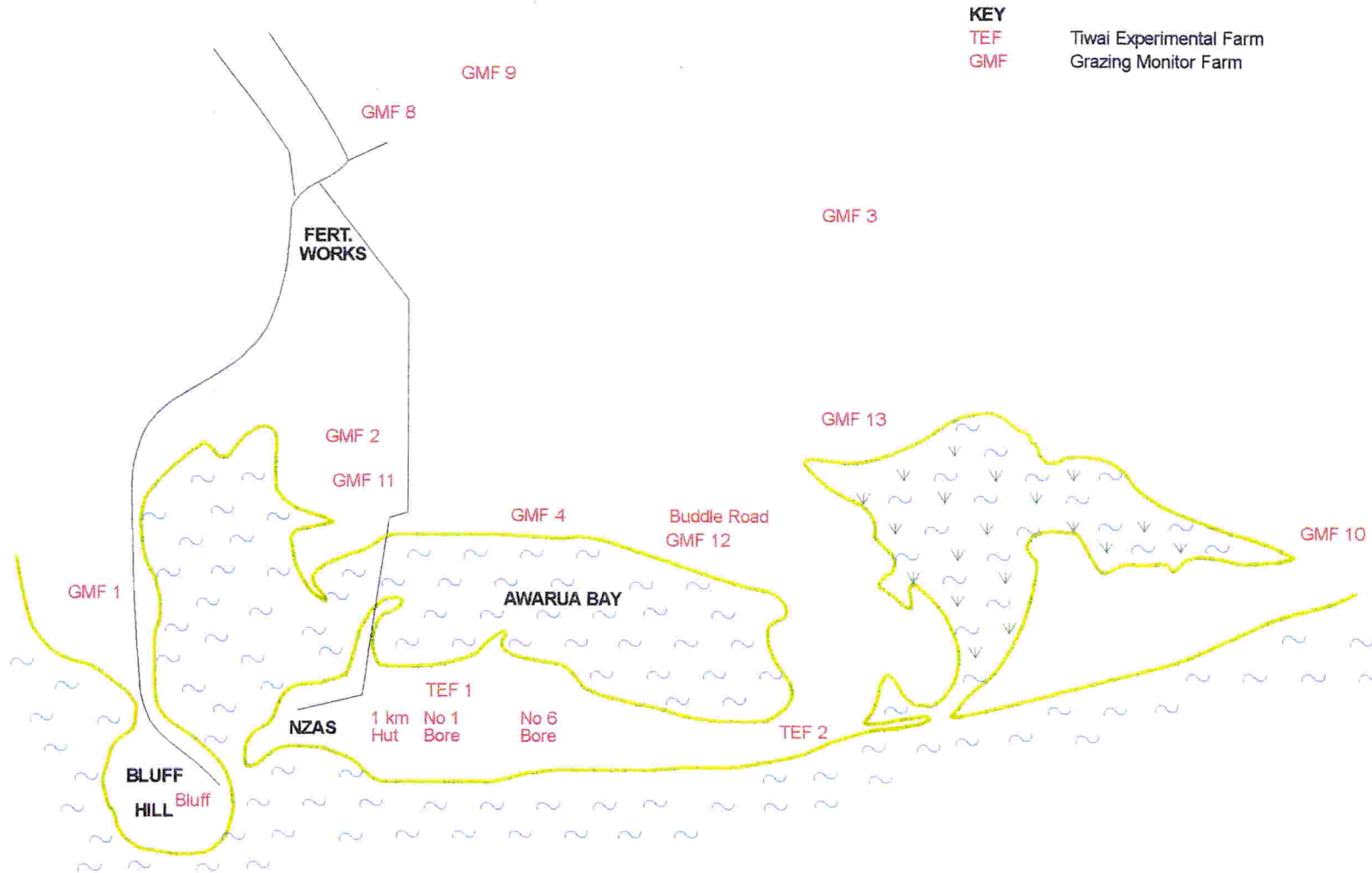
The proposed upgrade includes the installation of dry scrubbing reactors developed at NZAS by the Atmospheric Emissions Control MRU. Trials with a full scale reactor have shown that the new technology has the potential to successfully reduce the smelter's discharge of gaseous fluoride and particulate from the main stack.

A process for treating the spent cell lining material has been successfully developed by Comalco. A treatment plant to handle the existing production of spent cell lining and the stockpile accumulated during the smelter's operation is scheduled to be installed by the end of 1995.

NZAS' application for coastal and discharge permits for discharges to air was granted in April 1994. The permit is for a twelve year period.

The findings of the Environmental Study of the effects of the smelter on the surrounding environment has resulted in changes to the way in which some data is presented and interpreted. These changes have been included in this report.

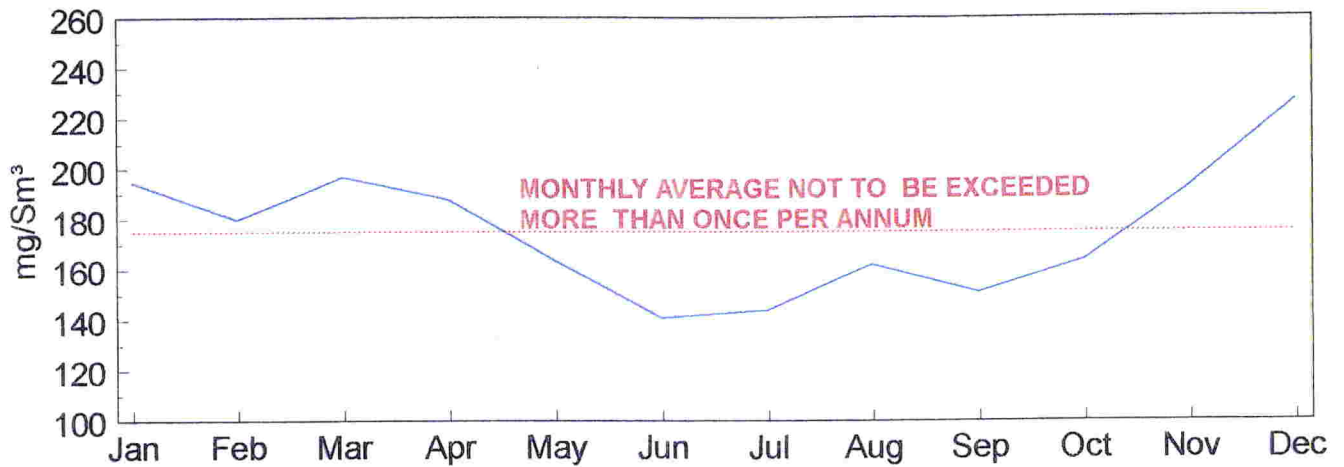
# NZAS MONITORING SITES



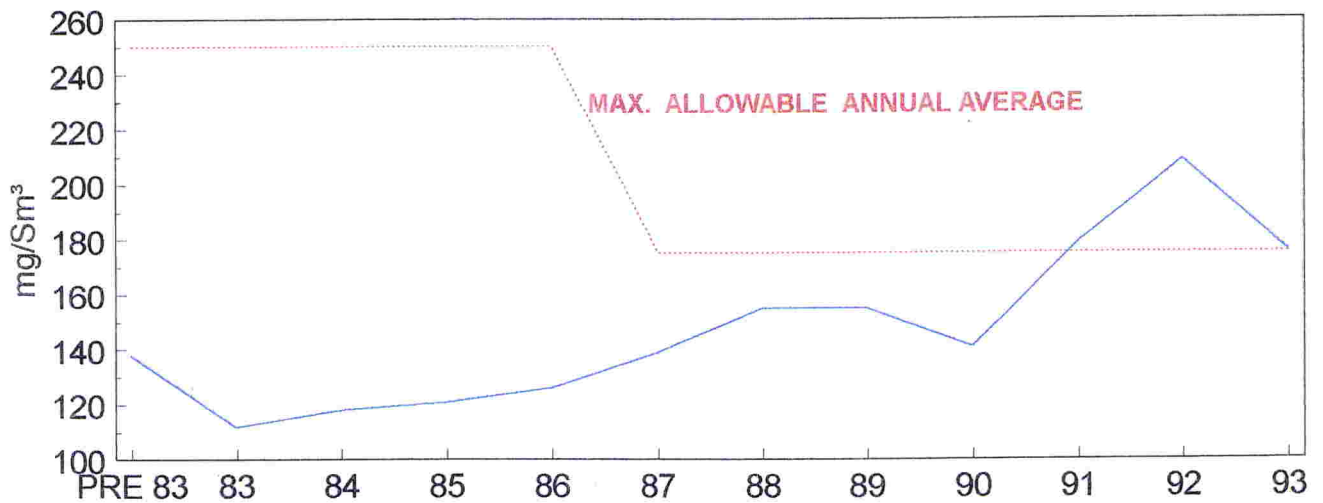
In 1993 discharges to air from the smelter were subject to the Discharge Permit No. HD/19/0006/88. The following sections give details of the discharges and trends observed

**2.1 MAIN STACK DISCHARGES**

**Total Particulate Concentrations  
1993 Monthly Averages**



**Annual Averages**



The refurbishment of the multicyclones on potlines 2B, 3A and 3B was completed in early 1993. Precollectors were installed and commissioned in the latter part of 1993. These improvements were required as the permit condition for the monthly average total particulate concentration for the main stack was exceeded five times in 1993.

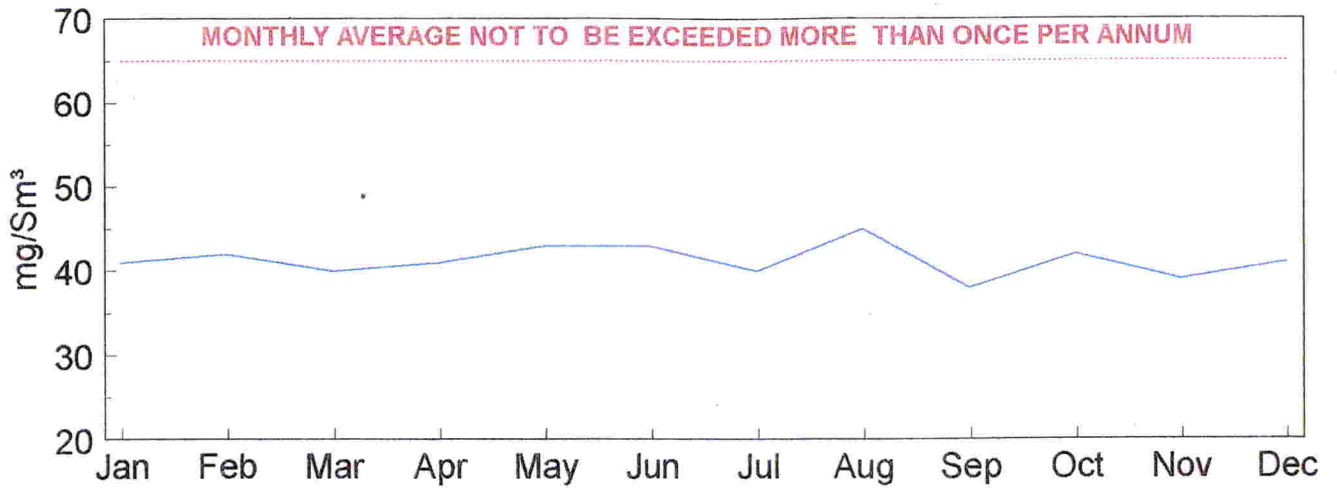
The violation in November was due to a reduced performance of the 3B multicyclone. The multicyclone had been refurbished in early 1993 and the reduction in performance was unexpected. The violation in December was due to the failure of the baghouse system which had become choked. This affected the secondary air system reducing the performance of the multicyclones. To ensure there is no repeat of this incident the hopper emptying procedure has been improved. High level indicators with communication to a control station which is manned 24 hours a day were also installed. All bags in the baghouse have been replaced and the performance has stabilised.

The 1993 annual average total particulate concentration was 176 mg/Sm³. This exceeds the maximum permitted annual average concentration of 175 mg/Sm³.

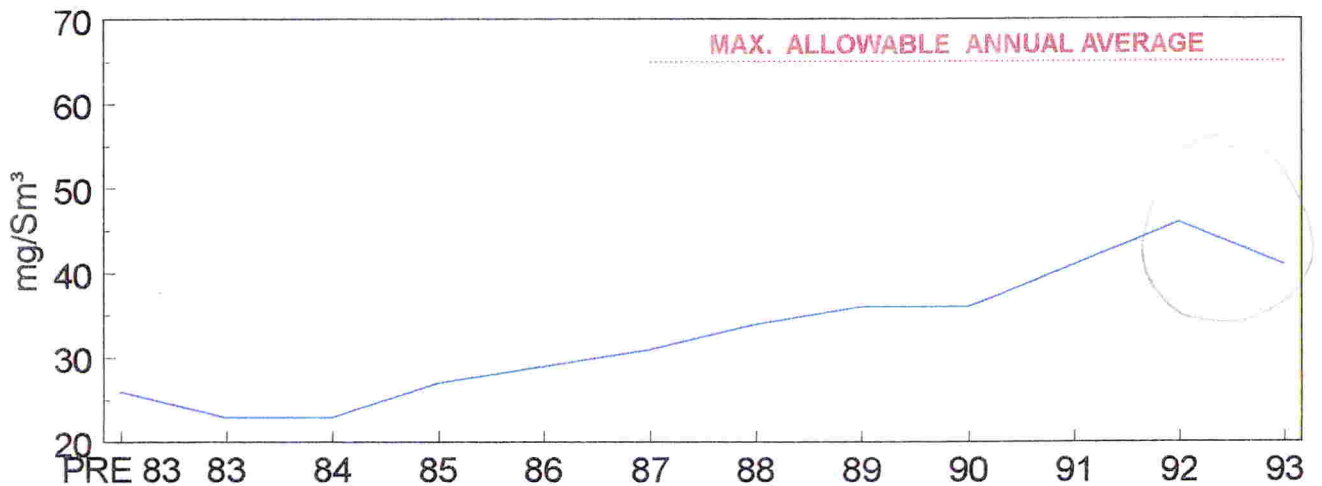
*what caused this?*

*22/11/93  
20/12/93  
21/12/93  
22/12/93  
23/12/93  
24/12/93  
25/12/93  
26/12/93  
27/12/93  
28/12/93  
29/12/93  
30/12/93  
31/12/93*

**2.1.2 Particulate Fluoride Concentration**  
**1993 Monthly Averages**



**Annual Averages**

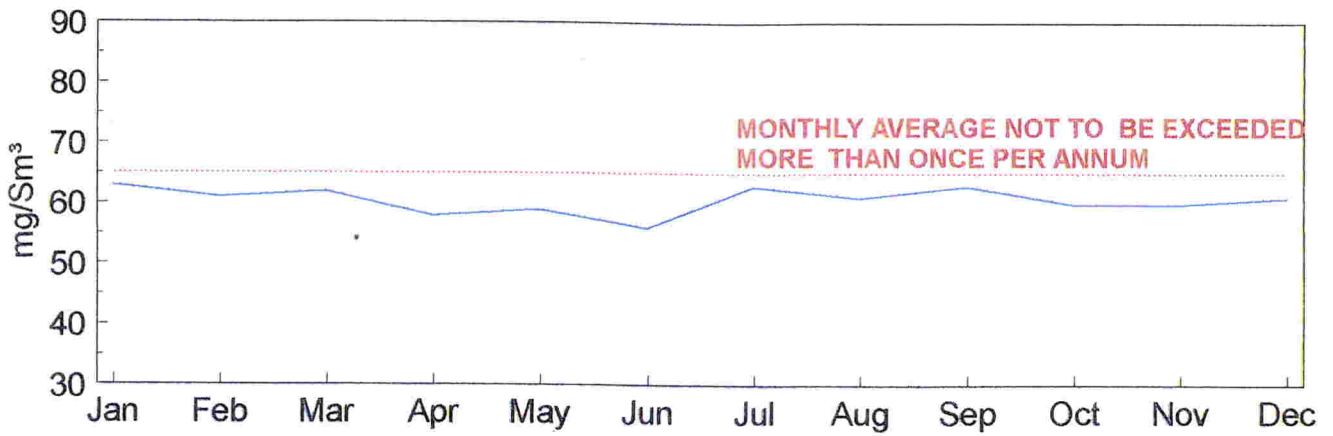


The 1993 annual average particulate fluoride concentration was 41 mg/Sm<sup>3</sup>. This result is lower than the 1992 average and could represent a halt to the upward trend of the previous eight years. The change is likely to be a result of the improved efficiency of the solids collection systems.

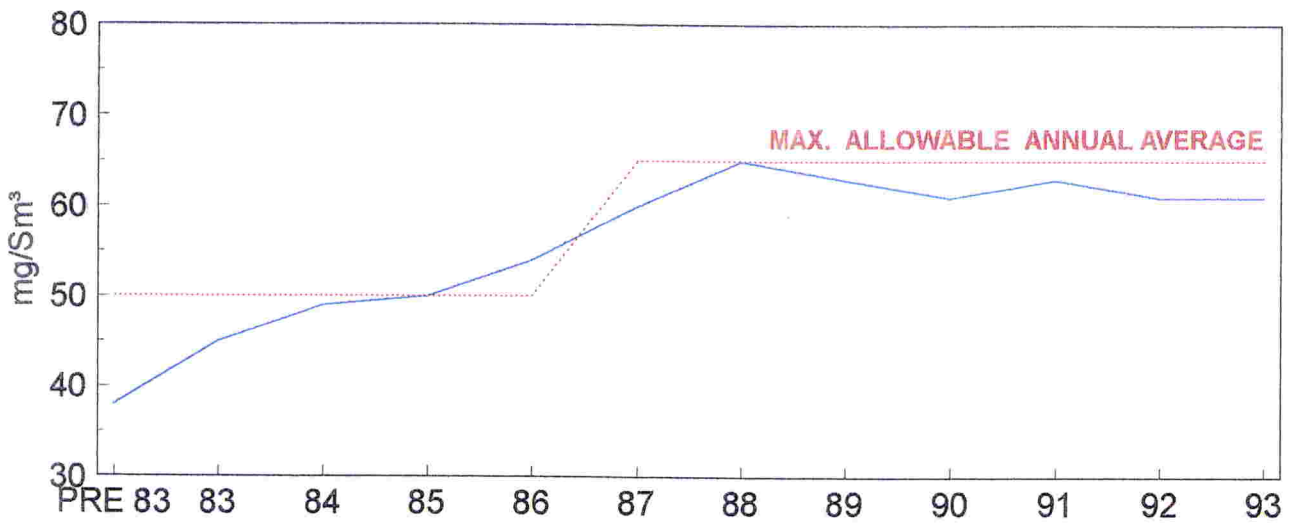
Compliance with both the monthly and annual permit conditions was maintained.

### 2.1.3 Gaseous Fluoride Concentrations

#### 1993 Monthly Averages

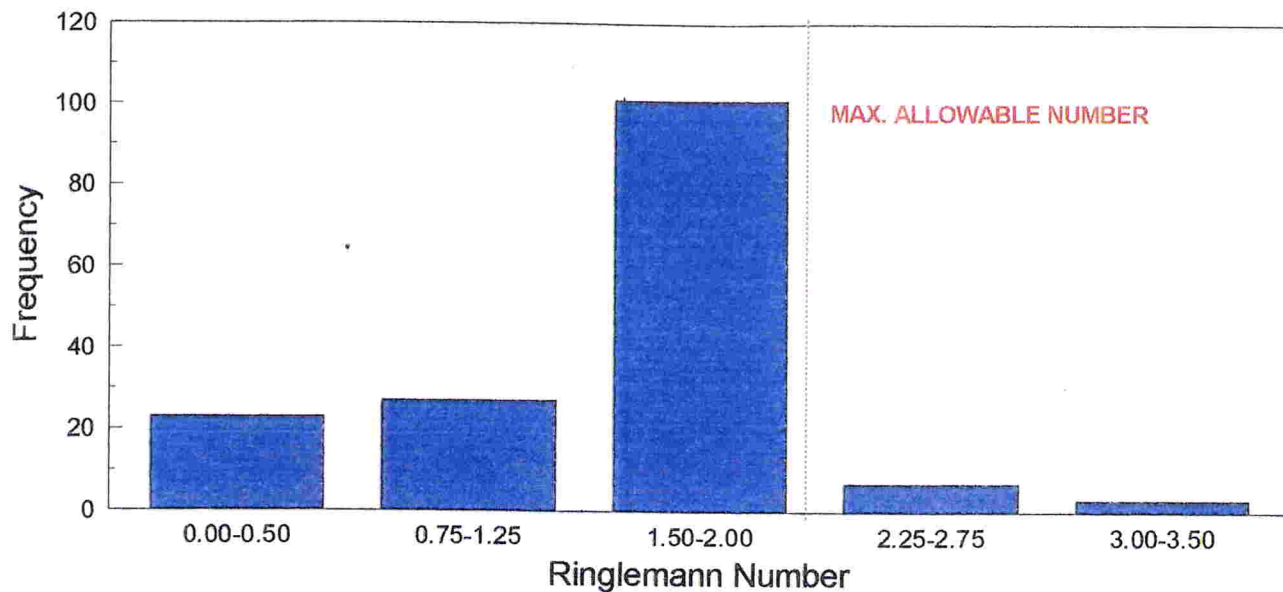


#### Annual Averages



The 1993 annual average gaseous fluoride concentration was 61 mg/Sm<sup>3</sup>, reflecting the improved control of discharges with the alumina injection control system. Compliance with both the monthly and annual permit conditions was maintained.

## 2.1.4 Ringlemann Smoke Density Number Ringlemann Number Distribution



As with previous years, the median stack Ringlemann Smoke Density number was 1.75. There were ten occasions when the consent condition maximum of 2.0 was exceeded. These exceptions do not represent license violations as the discharge consent conditions allow a Ringlemann Smoke Density number of up to 3.5 for 15 minutes each day during fire changes.

8 times?

## 2.1.5 Sulphur Dioxide Concentration

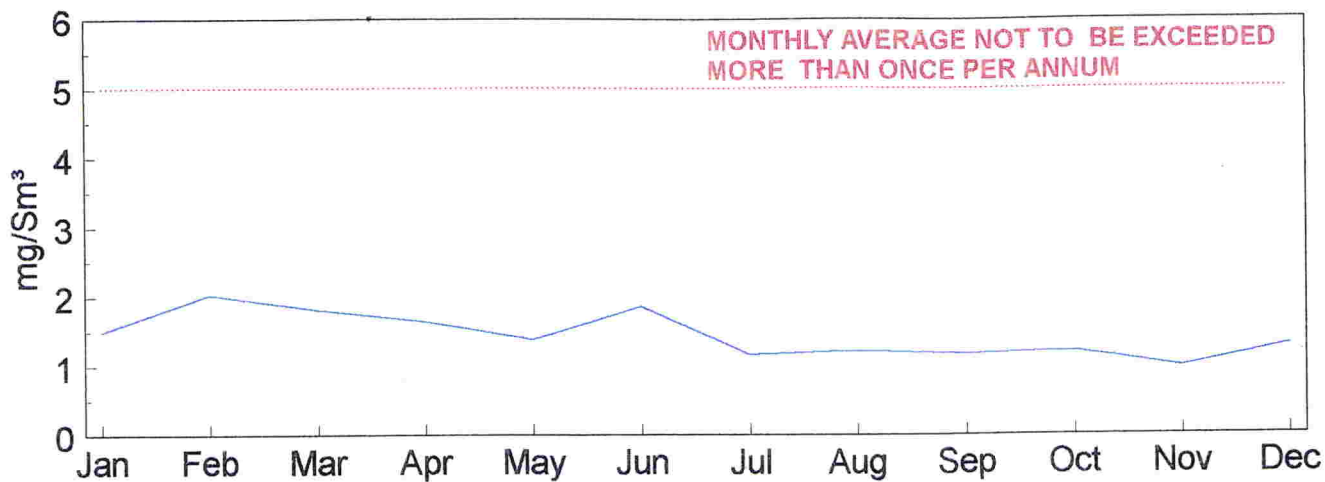
The 1993 average main stack sulphur dioxide concentration was 179 mg/Sm<sup>3</sup>. This result is within range. *normal range.*

## 2.1.6 Dry Scrubbing

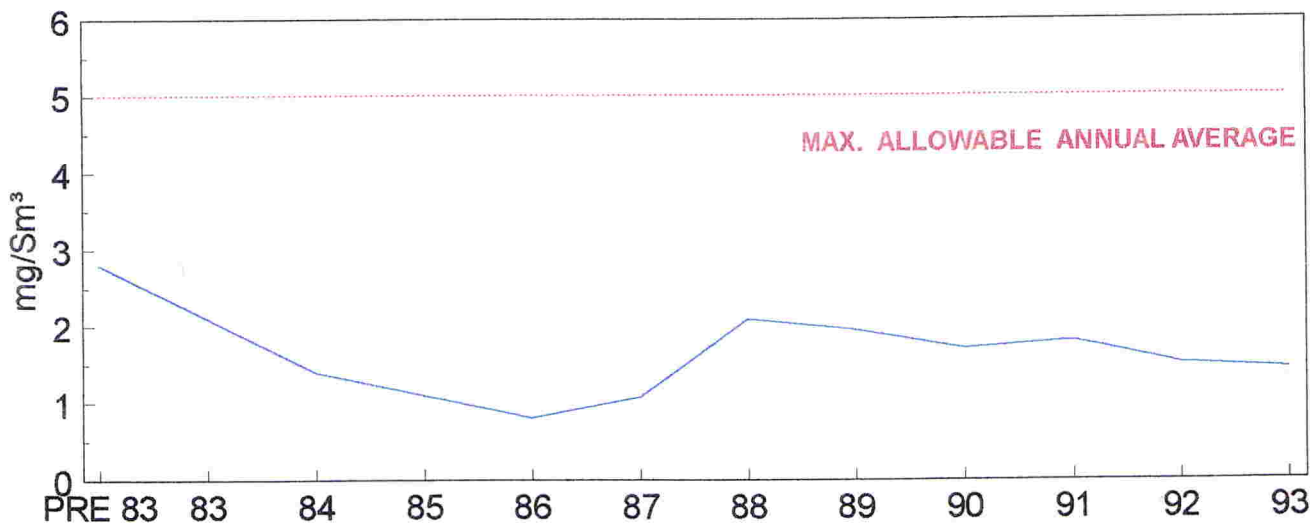
Installation of the Comalco prototype dry scrubbing system started in October 1993 and was commissioned in mid February, 1994. Test work will continue until mid 1994 to verify the performance of the system.



**2.2.1 Total Particulate Concentrations  
1993 Monthly Averages**

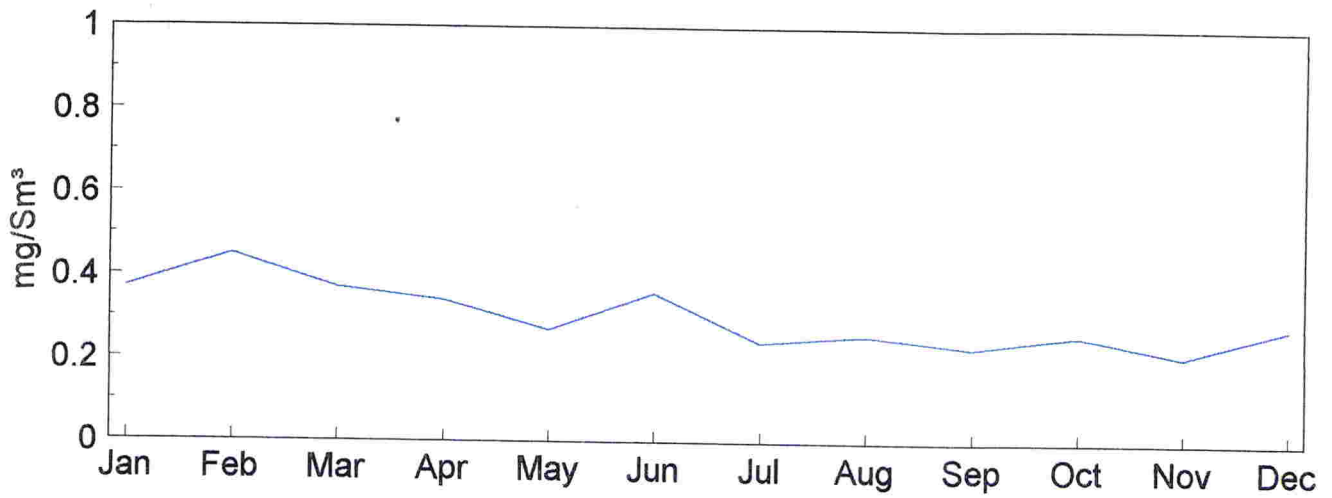


**Annual Averages**

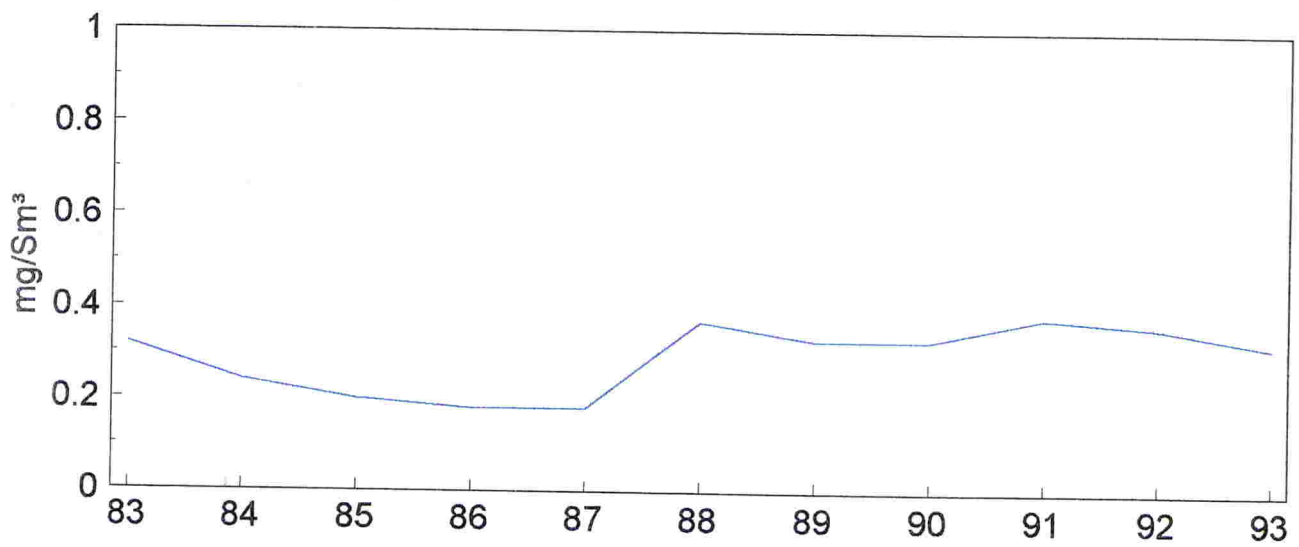


*total particulate* ✓  
The 1993 annual average roof louvre particulate fluoride concentration was 1.43 mg/Sm<sup>3</sup>. Compliance with both the monthly and annual permit conditions was maintained.

## 2.2.2 Particulate Fluoride Concentrations 1993 Monthly Averages



## Annual Averages

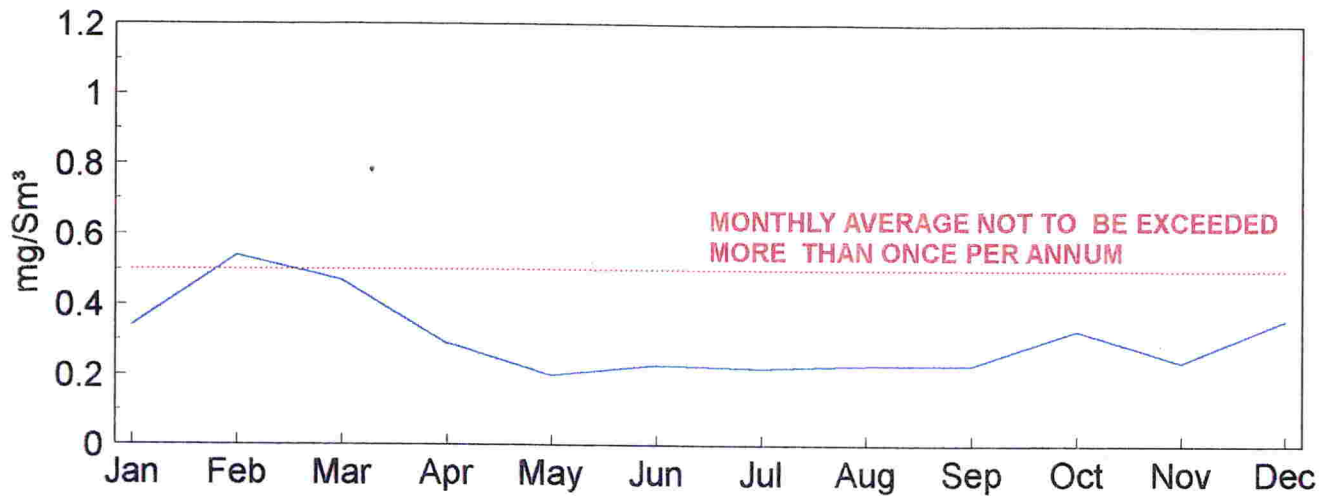


The 1993 annual average roof louvre particulate fluoride concentration was 0.32 mg/Sm<sup>3</sup>. This result is similar to the previous five years.

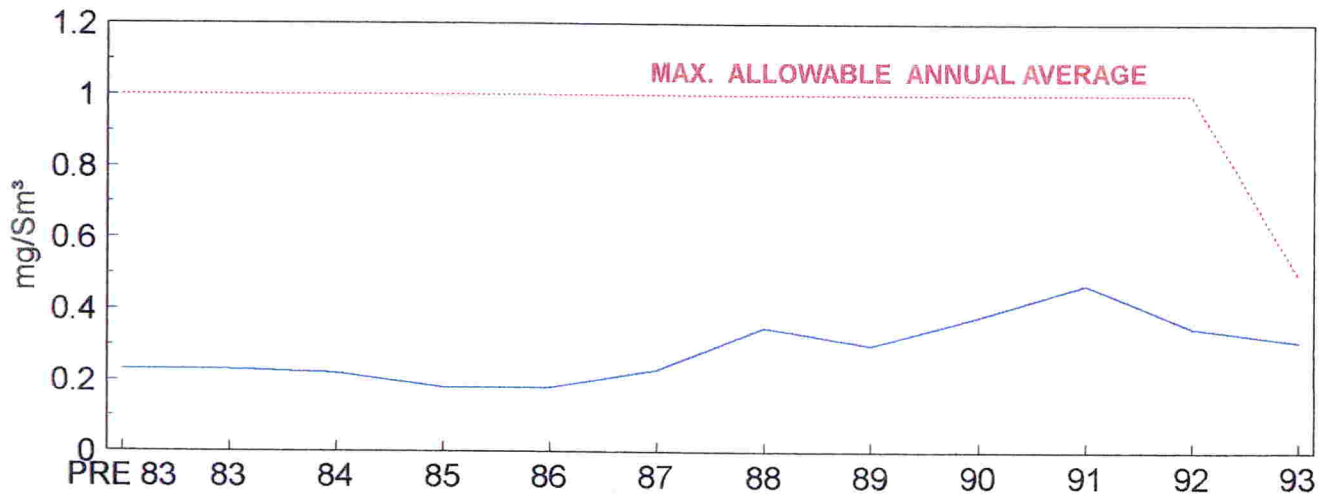


## 2.2.3 Gaseous Fluoride Concentrations

### 1993 Monthly Averages



### Annual Averages



The 1993 annual average roof louvre gaseous fluoride concentration was 0.31 mg/Sm<sup>3</sup>. Compliance with both the monthly and annual permit conditions was maintained.

The elevated gaseous fluoride concentrations recorded in the first quarter of the year were most likely due to process variations caused by the restart of Potline 2 late in 1992.

Don't miss pots in experiments made  
+ where are they located.

### 2.2.4 Sulphur Dioxide Concentration

The 1993 average Potroom roof louvre sulphur dioxide concentration was 0.85 mg/Sm<sup>3</sup>.  
This result is within range *normal*

### 2.3 BAGHOUSE DISCHARGES

The regular visual inspection of baghouse discharges continued. These inspections support the on-going operational surveillance of this equipment that ensure the required standards are maintained.

### 2.4 CARBON MRU

The conditioning tower of the electrostatic precipitator, which removes particulate from the emissions from Carbon Baking Furnace 3 was blown over in high winds on the 30 November, 1993. Operation of the electrostatic precipitator continued with the conditioning tower isolated while a new tower was constructed. The new tower was commissioned on the 11 April, 1994 and is operating satisfactorily.

### 3 DISPERSION AND EFFECTS OF DISCHARGES TO AIR

#### 3.1 METEOROLOGICAL CONDITIONS

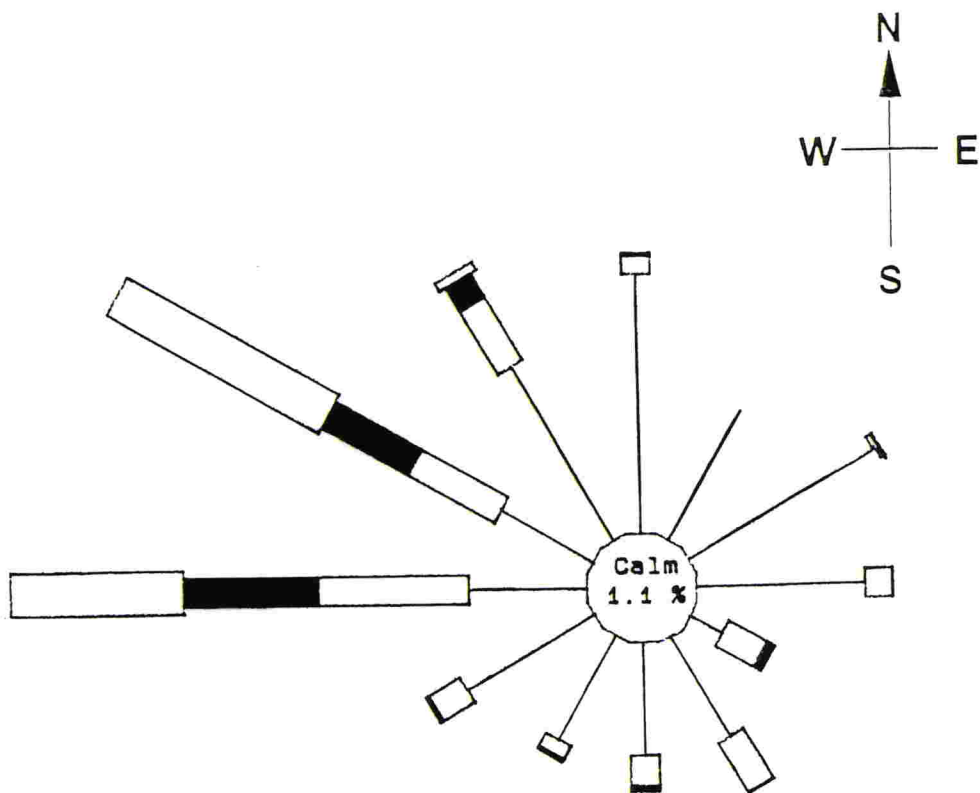
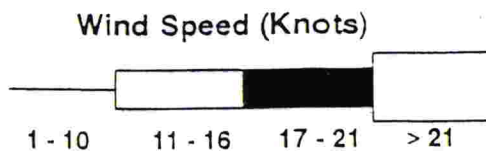
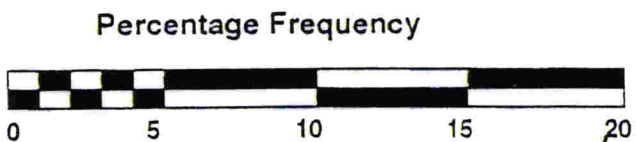
The mean wind frequency diagram shown on the following page shows that the 1993 wind pattern was dominated by westerly and north westerly winds. Compared with 1992 there was an increase in winds from the north and a reduction in winds from the east, south and west.

The following table shows the predominant winds for each month during 1993.

<b>Month</b>	<b>Predominant Wind Direction</b>
January	North west and strong west
February	South, west and north west
March	West and north west
April	Light west and north
May	Strong north west and west
June	Strong north west and west
July	Light north and northeast
August,	North west and west
September	North west and west
October	North west and west
November	North west, west, south east and east
December	South, west and light south east

**TIWAI POINT**  
**MEAN WIND FREQUENCY (%) OF SURFACE WIND DIRECTIONS**  
**FOR THE YEAR 1993**

Scale:



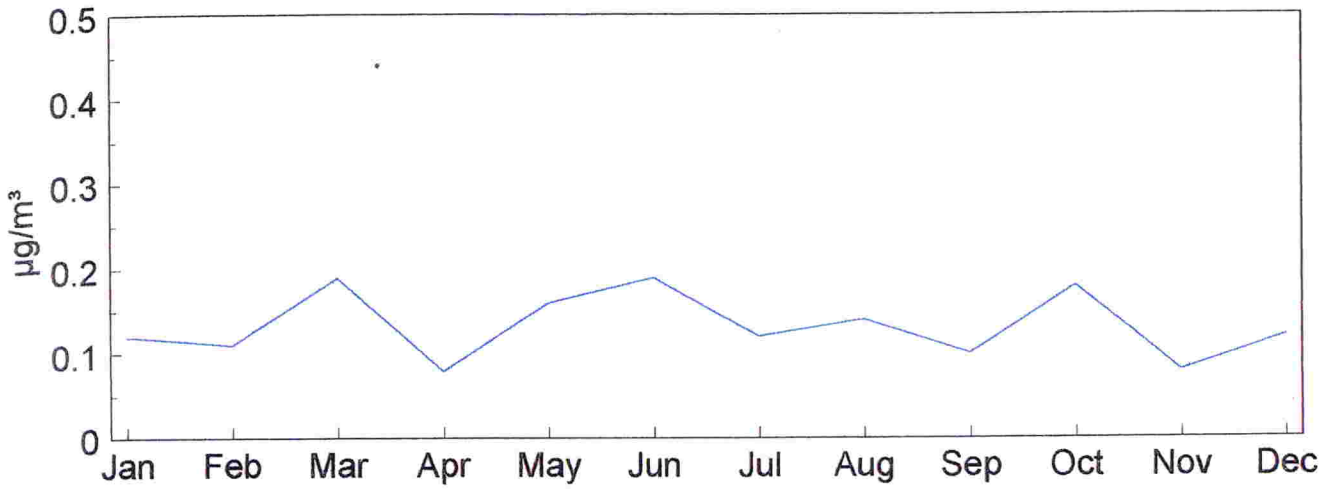
**% Time at**

Calm	1.1
1-10 Knots	57.1
11-16 Knots	18.2
17-21 Knots	9.3
>21 Knots	13.9

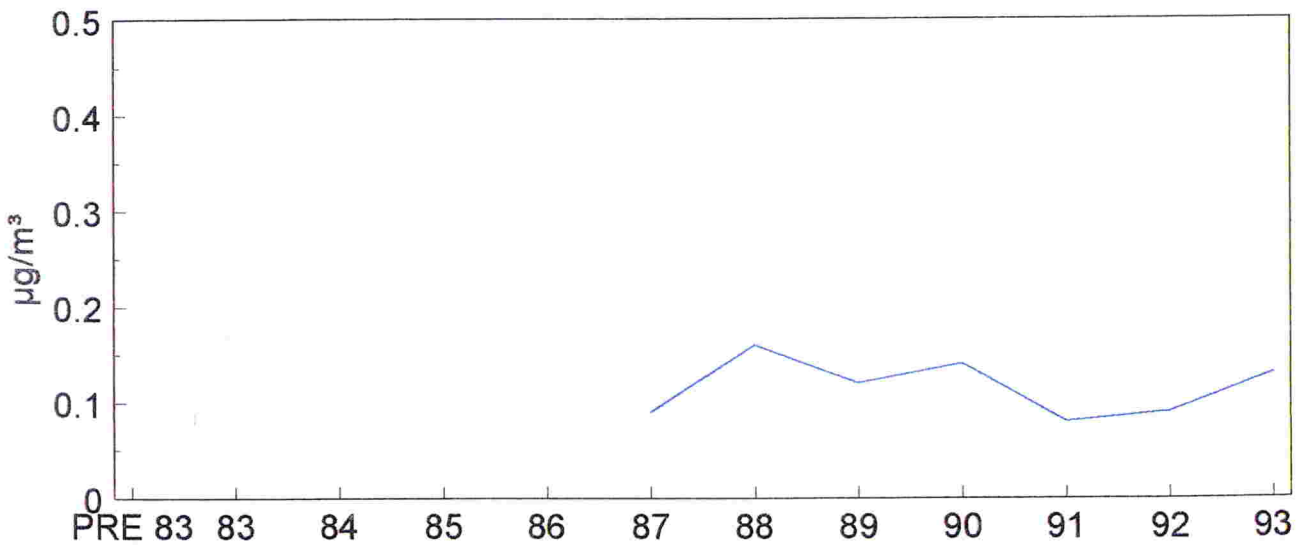
**3.2 AMBIENT AIR GASEOUS FLUORIDE**

**3.2.1 1 km Hut**

**1993 Monthly Averages**



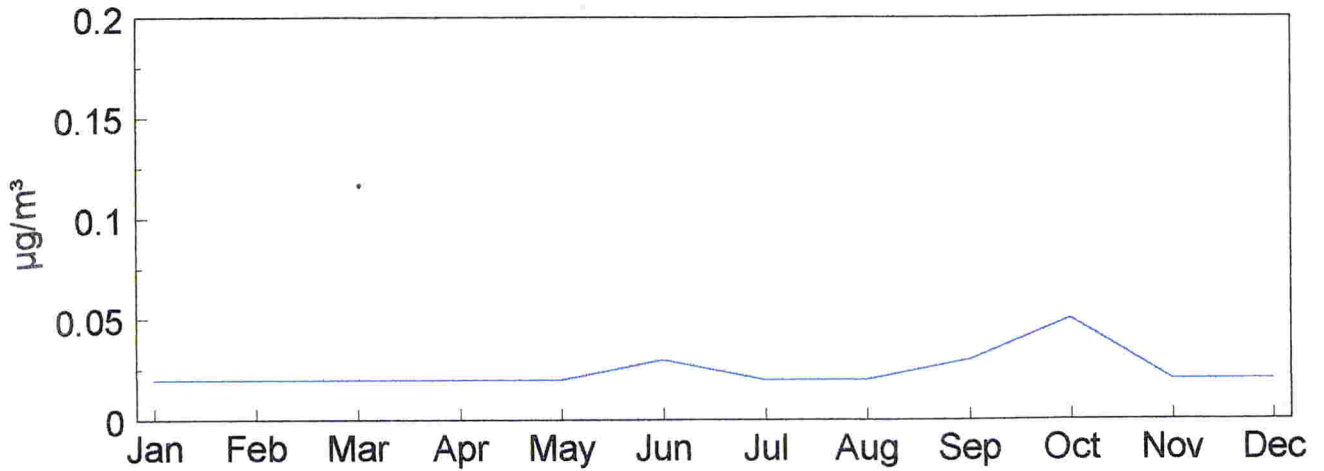
**Annual Averages**



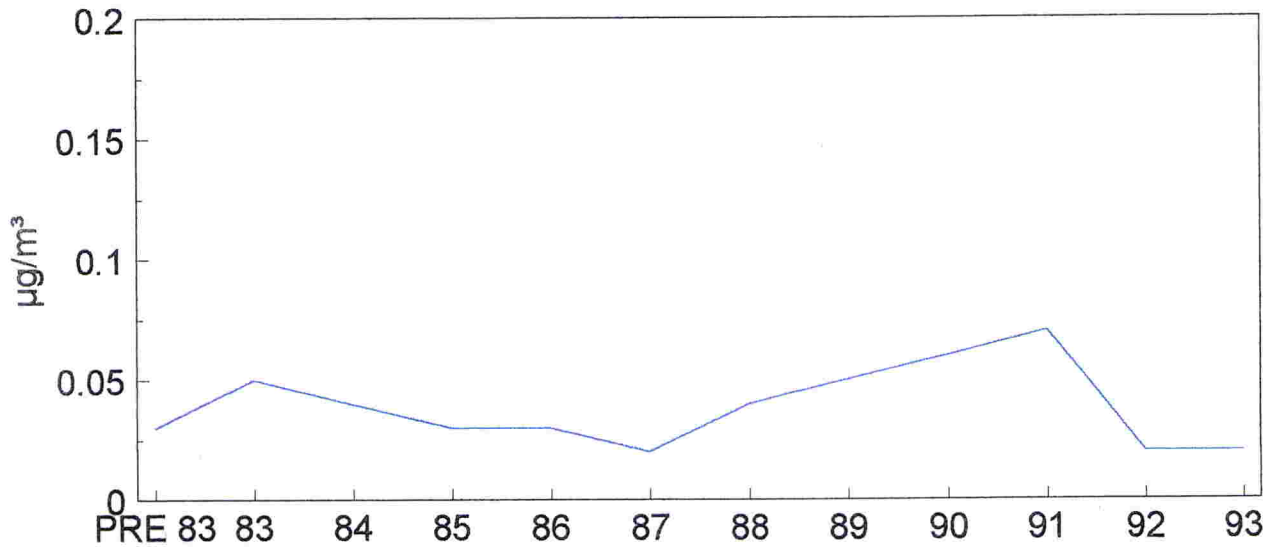
The 1993 average gaseous fluoride concentration of the ambient air at the 1 km hut was 0.13 μg/m³. The highest seven day concentration was 0.44 μg/m³ measured in October. This is within the normal range of results for this site.

*Any 24 hour results ?*

1993 Monthly Averages



Annual Averages

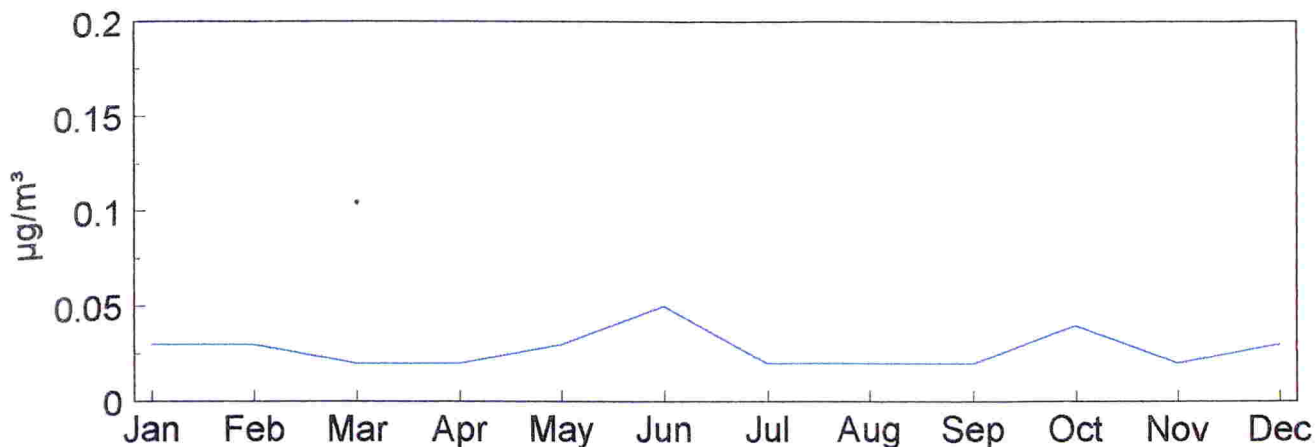


The 1993 average gaseous fluoride concentration of the ambient air at the No. 1 Bore was 0.02 µg/m³. This is the same result as in 1992 and indicates the reversal of the upward trend in this parameter as suggested by the results from 1987 to 1991. The highest seven day concentration at the No. 1 Bore site was 0.11 µg/m³ measured in October.

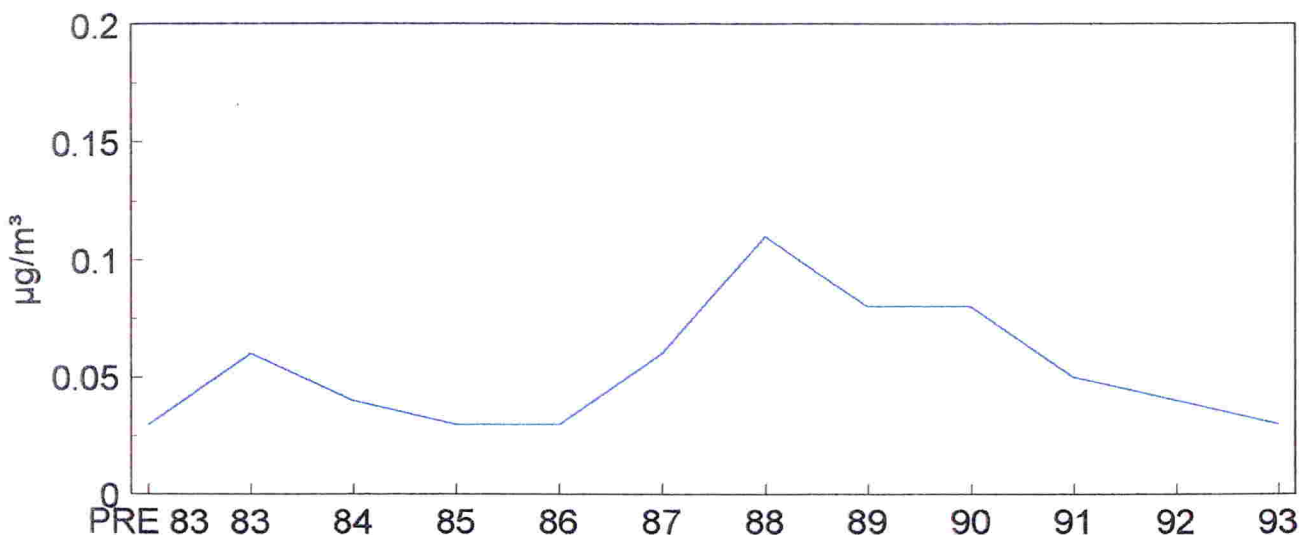
*avg 2x the records*



1993 Monthly Averages



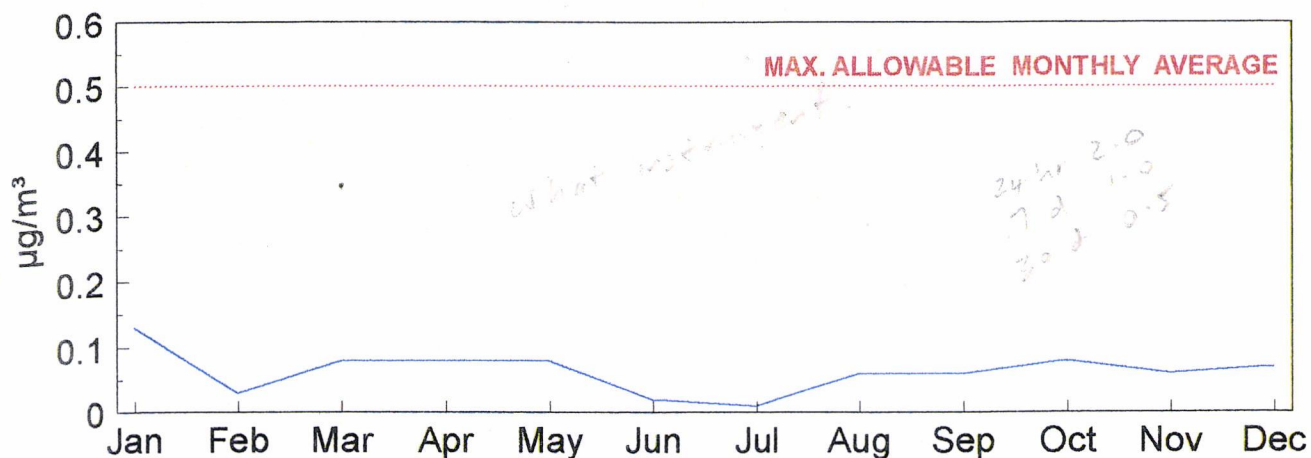
Annual Averages



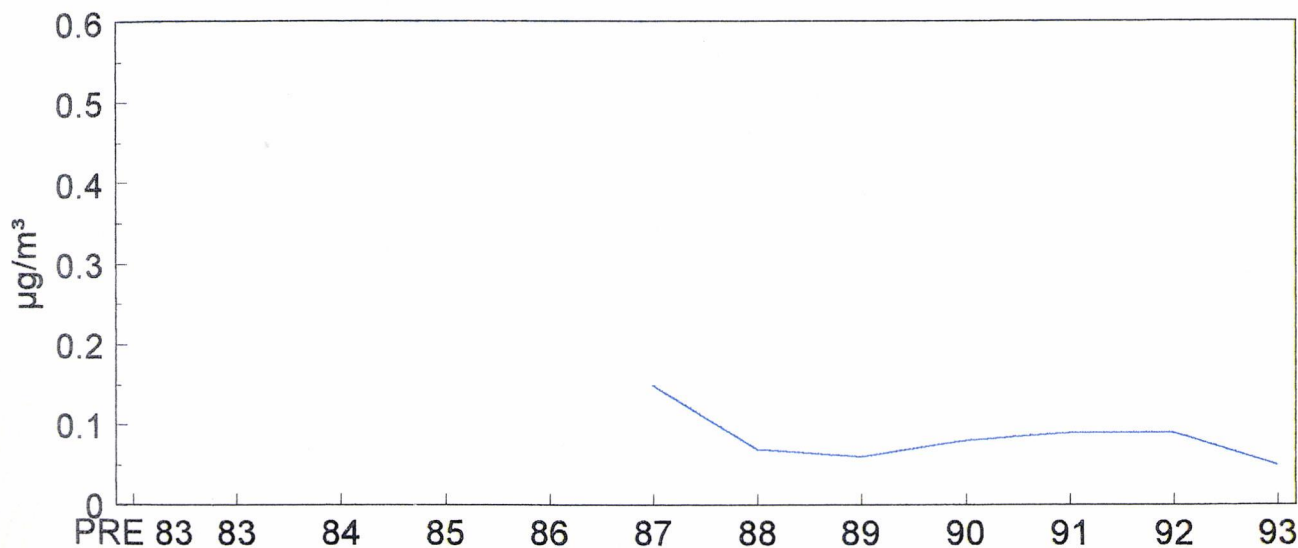
The 1993 average gaseous fluoride concentration of the ambient air at the No. 6 Bore was 0.03 µg/m³. This result continues the downward trend that became evident in 1989. The concentration of gaseous fluoride in this location is influenced by the main stack discharges. Improvements in the alumina injection system have reduced the fluctuations in the concentration of gaseous fluoride emitted from the stack. The progressive elimination of the high summer concentrations of gaseous fluoride have resulted in the downward trend in the annual ambient air gaseous fluoride concentrations. The effect of this reduced variation can best be illustrated by comparing the average results for the first quarter and the winter months of 1989, just after the injection system was installed, with the same months in 1993. The highest seven day concentration measured at No. 6 Bore was 0.16 µg/m³ measured in February.

Year	Period	Main Stack Gaseous F mg/m³	No.6 Bore Gaseous F µg/m³	Annual Average for No. 6 Bore µg/m³
1989	Jan, Feb, Mar	68	0.120	0.08
	Jun, Jul, Aug	60	0.037	
1993	Jan, Feb, Mar	62	0.027	0.03
	Jun, Jul, Aug	60	0.030	

1993 Monthly Averages



Annual Averages



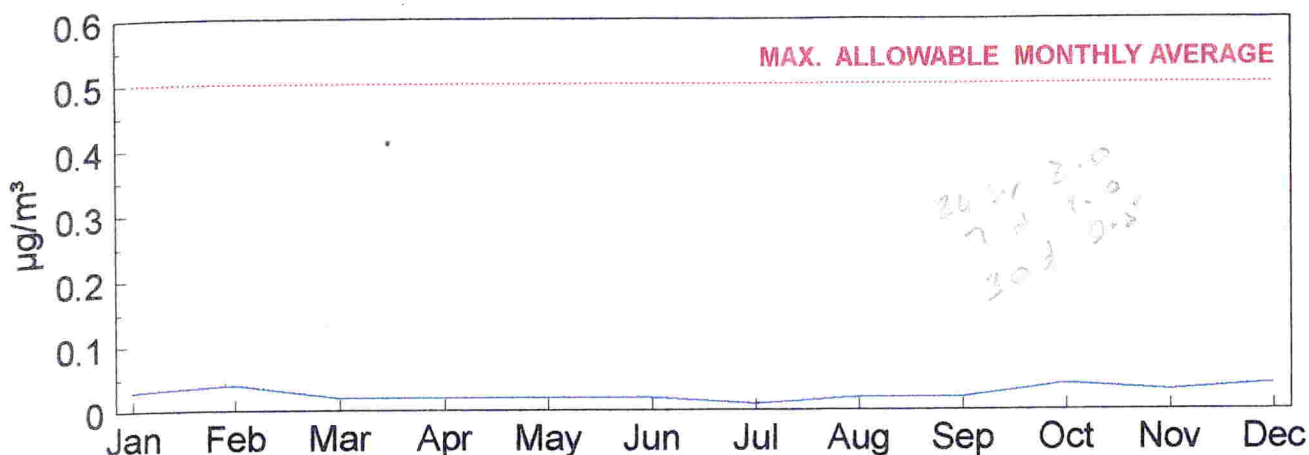
The 1993 average gaseous fluoride concentration of the ambient air at the Buddle Road <sup>site</sup> was 0.05 µg/m³. This is a lower concentration than the 1992 result which was 0.09 µg/m³ but it is within the expected range for this site.

The seven day average gaseous fluoride limit of 1 µg/m³ was not exceeded. The highest seven day concentration at Buddle Road was 0.23 µg/m³ measured in January.

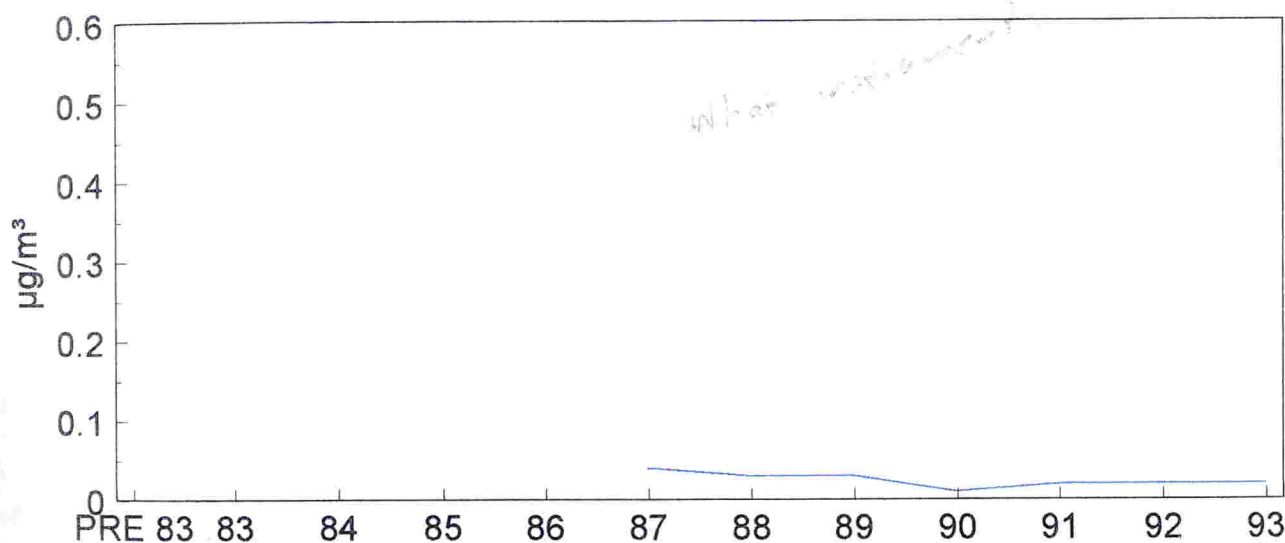


**3.2.5 Bluff**

**1993 Monthly Averages**



**Annual Averages**



The 1993 average gaseous fluoride concentration of the ambient air at Bluff was 0.02 µg/m³.

The seven day average gaseous fluoride limit of 1 µg/m³ was not exceeded. The highest seven day concentration at Bluff was 0.10 µg/m³ measured in February.

*7 d limit is 1.0*

**3.2.6 ATMOSPHERIC DEPOSITION**

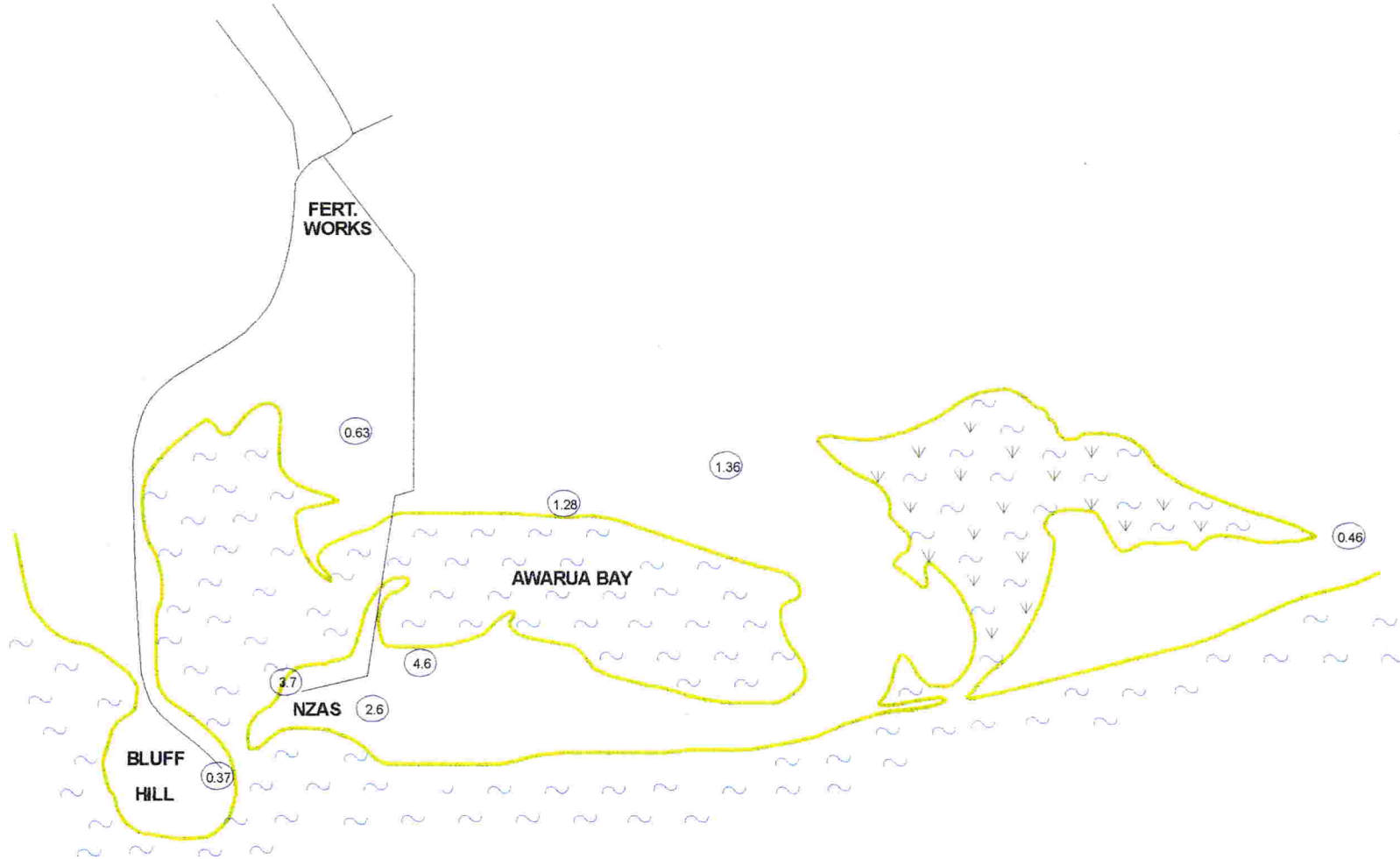
Fluoride deposition in the area surrounding the smelter is shown on the map on page 19. The deposition measured at Bluff has decreased from 0.7 mg/m²/day to 0.36 mg/m²/day. The deposition at the two sites on the north east side of Awarua Bay have increased from about 0.9 mg/m²/day to about 1.4 mg/m²/day.

*can also be seawater effects, street intensity of wind, road dust, fertiliser*

**ATMOSPHERIC DEPOSITION - DEPOSIT GAUGE FLUORIDE CONCENTRATIONS**

**1993 AVERAGE CONCENTRATIONS**

KEY 9 mg/m<sup>2</sup>/day fluoride



### 3.2.6 BLP MODEL PREDICTIONS

Dames and Moore were contracted by the smelter to model the dispersion of the smelter's discharges to air. The Buoyant Line and Point Source (BLP) model was chosen to predict the dispersion of gaseous fluoride discharges. This work was presented in the smelter's application for an air discharge permit in September, 1993. The predicted gaseous fluoride concentrations were compared with the results from the five ambient air monitoring sites near the smelter over a two year period. The comparison showed instances of both over and under estimation by the model. The greater tendency was for over estimation.

The work of Dames and Moore has shown that the BLP model can be used to assess the distribution of gaseous fluoride discharges from the smelter. As such the model is an additional tool for assessing the smelter's environmental effects.

The BLP model predicted mean ambient air gaseous fluoride concentrations caused by the discharge from the smelter during 1993 are shown on the map on page 21.

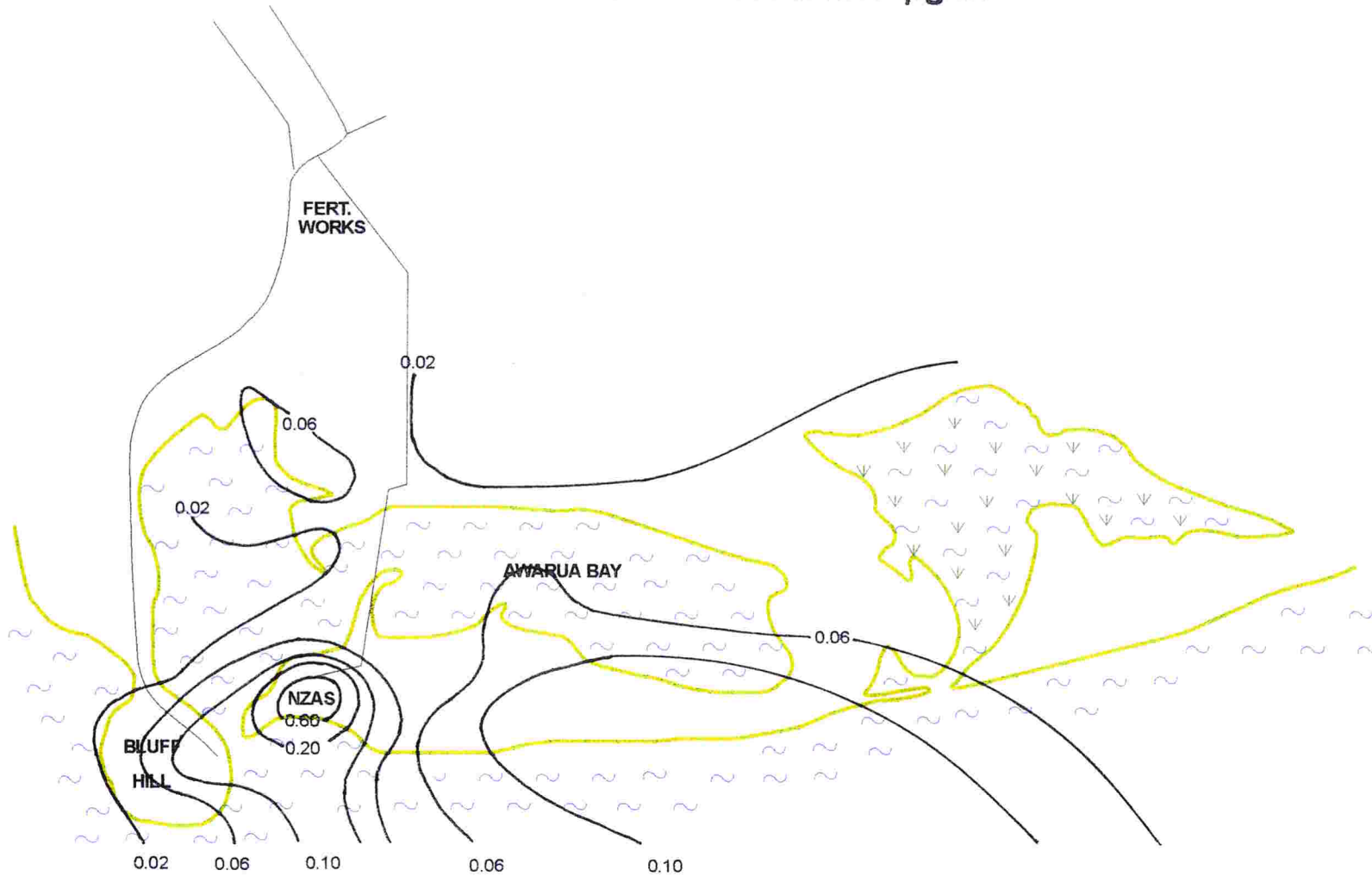
The model predicts mean ambient air gaseous fluoride concentrations of  $1 \mu\text{g}/\text{m}^3$  immediately east of the smelter,  $0.15 \mu\text{g}/\text{m}^3$  on Bluff Hill, and  $0.15 \mu\text{g}/\text{m}^3$  at the east end of Tiwai Peninsula for 1993.

Comparison of the 1993 predicted concentrations with the results of the smelter's ambient air monitoring confirms the model's tendency to over predict. The mean ambient air gaseous fluoride concentration measured at Bluff township was  $0.02 \mu\text{g}/\text{m}^3$  compared with the predicted concentration of  $0.06 \mu\text{g}/\text{m}^3$ . The mean ambient air gaseous fluoride concentration measured at No. 6 Bore was  $0.03 \mu\text{g}/\text{m}^3$  compared with the predicted concentration of  $0.15 \mu\text{g}/\text{m}^3$ . The Buddle Road, 1km Hut, and No. 1 Bore site ambient air monitoring results were all similar to the model's predicted fluoride concentrations. Work to refine the model will be undertaken.

The BLP model was also used to predict short term gaseous concentrations. The model predicts that during 1993 the 24 hour maximum ambient air gaseous fluoride concentration at the Bluff Hill summit would have exceeded the discharge permit condition of  $2 \mu\text{g}/\text{m}^3$  on four days. In their evidence in support of the smelter's application for the air discharge permit, Dames and Moore stated that the BLP model was likely to over estimate the concentration of gaseous fluoride at higher elevations on Bluff Hill. Work on refining the model to improve the predictions on top of Bluff Hill is continuing. The model predicts that the permit condition maximum would not be exceeded at Bluff township.

# BLP MODEL GASEOUS FLUORIDE CONCENTRATION

1993 AVERAGE CONCENTRATION  $\mu\text{g}/\text{m}^3$





### 3.3 UNGRAZED PASTURE

Mean fluoride concentrations of ungrazed pasture are shown on the map on page 23. Comparison with the 1992 mean concentrations show that the overall distribution of fluoride in the pasture is similar to 1993. The fluoride concentrations are lower to the north and west of the smelter in 1993, reflecting the increase in winds from the north west quarter.

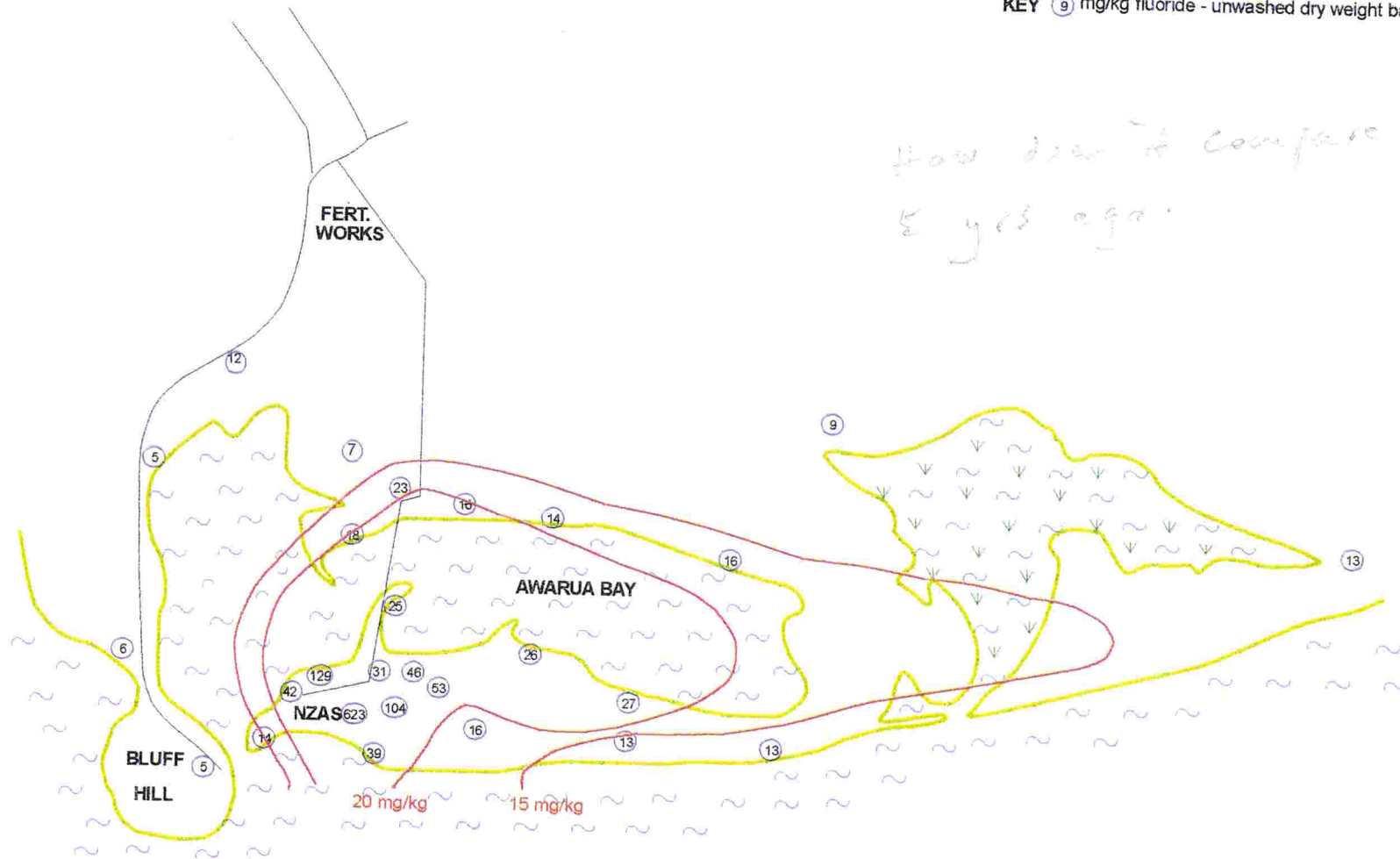
The distance of fluoride concentration isopleths to the north, north east, and east of the smelter are shown in three graphs on page 24. Since 1987 there has been a slow contraction of the 40 mg/kg isopleths from the north. This is consistent with the change in the wind patterns over recent years with the increase in the northerly component. The apparent extension of this isopleth in the north easterly direction is more likely to be natural variation than a real trend. This will need to be reviewed at the end of 1994.

During 1993 the 20 mg/kg isopleth has contracted from the north, north-east, and east. These changes are in agreement with the changes in the wind pattern. No trends are apparent due to the variability of this data.

# UNGRAZED GRASS FLUORIDE CONCENTRATIONS

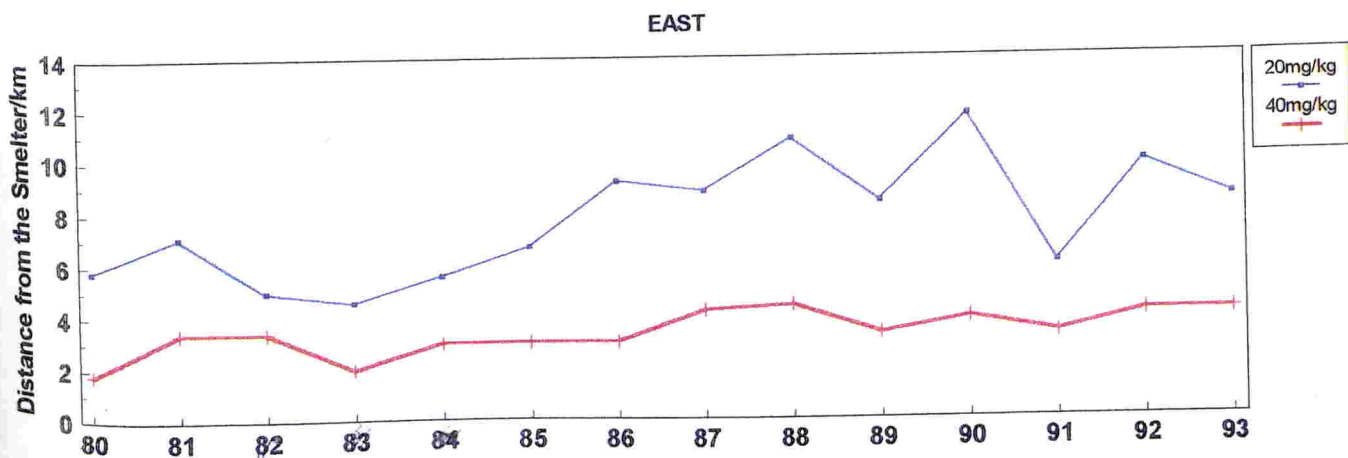
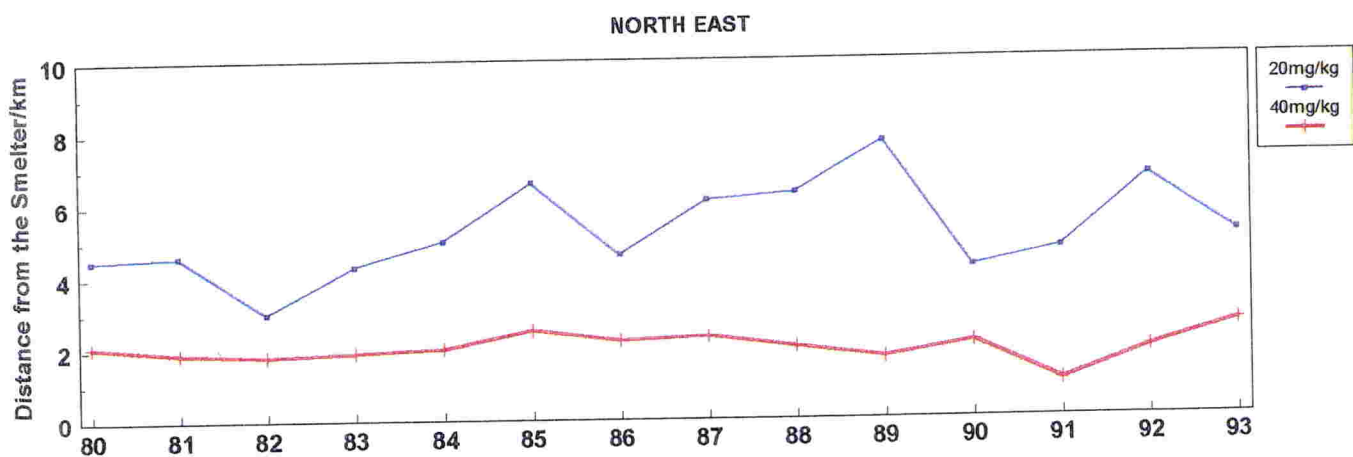
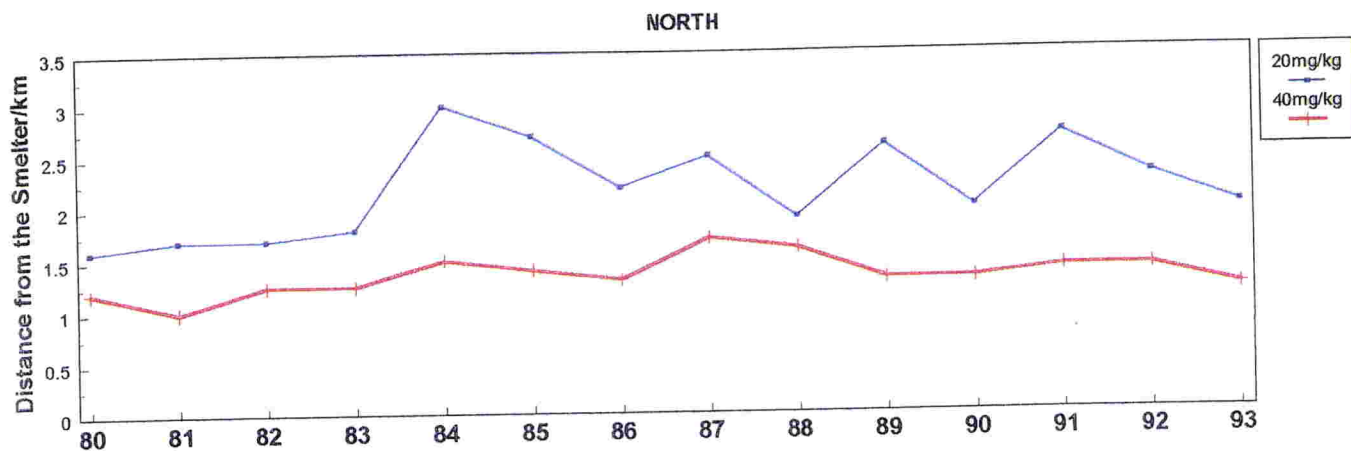
## 1993 AVERAGE CONCENTRATIONS

KEY ⑨ mg/kg fluoride - unwashed dry weight basis



**DISTANCE OF PASTURE FLUORIDE ISOPLETHS FROM NZAS PLANT RELATED TO DIRECTION AND TIME**

*Based on AOAC 26 270.00  
156*

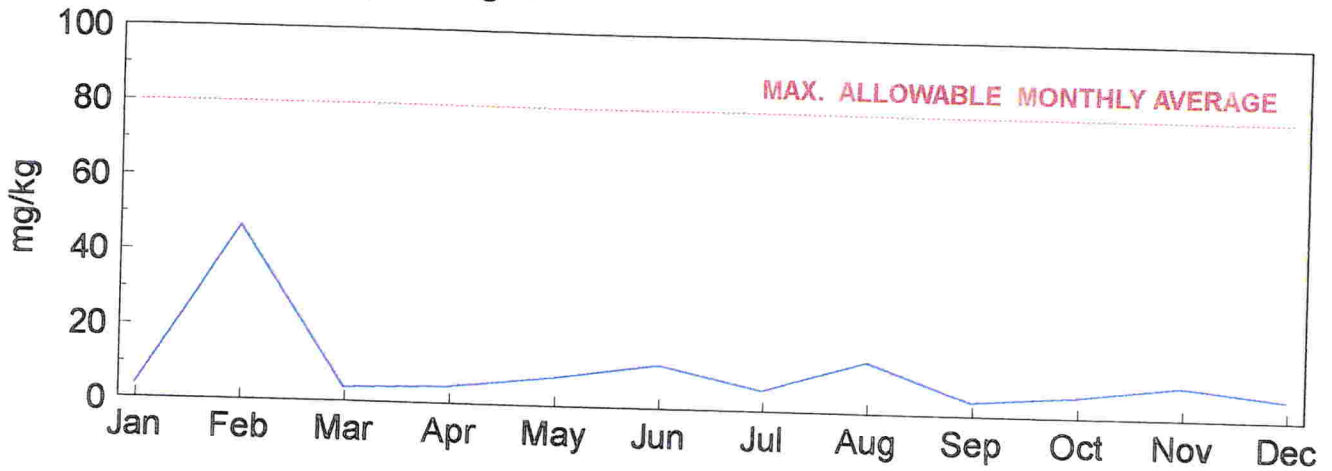


### 3.4 GRAZING MONITOR PROJECT

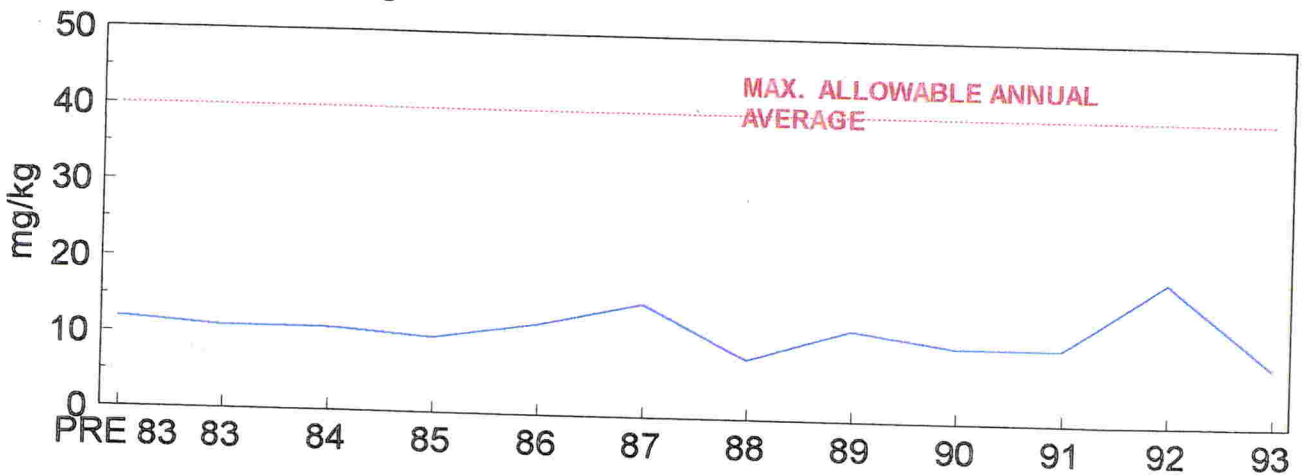
The Grazing Monitoring Project was established in 1969, prior to the smelter's commissioning, to provide a method of assessing the effects on the livestock on productive farms. The project has continued, with minor modifications, as part of the NZAS Environmental Monitoring Program.

#### 3.4.1 Farm No 1

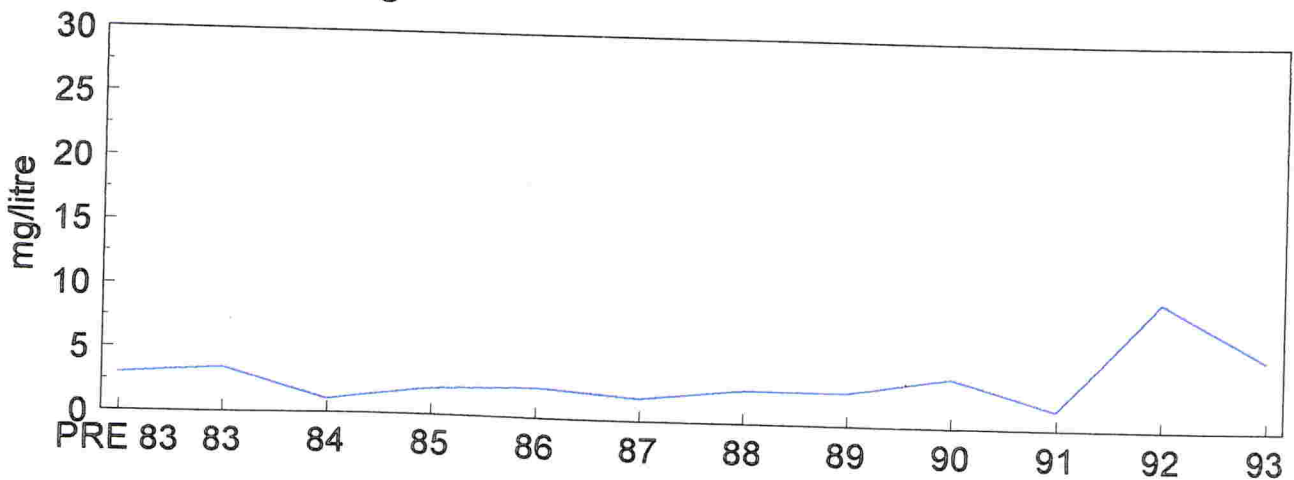
##### **Pasture Fluoride Concentrations 1993 Monthly Averages**



##### **Annual Averages**



##### **Cattle Urinary Fluoride Concentrations Annual Averages**





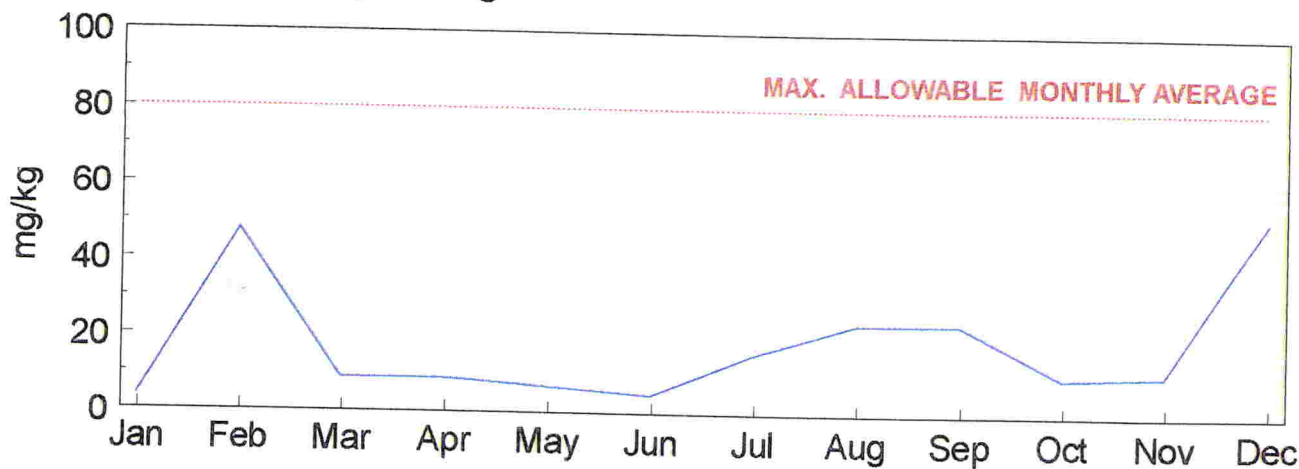
The February pasture fluoride concentration, although elevated, was within the discharge permit condition. The smelter discharges are considered the most likely source of the elevated fluoride concentration in this sample. There was a predominance of winds from the easterly quarter during the week prior to the collection of the sample. All the vegetation samples collected that month from sites to the west of the smelter had similarly elevated fluoride concentrations, further supporting the conclusion that the smelter was the main source of this fluoride.

For all other months of 1993 the fluoride concentration in the pasture samples were at background levels and the annual average fluoride concentration was 8 mg/kg. At no time was the monthly limit of 80 mg/kg, the bimonthly average limit of 60 mg/kg or the annual average limit of 40 mg/kg exceeded.

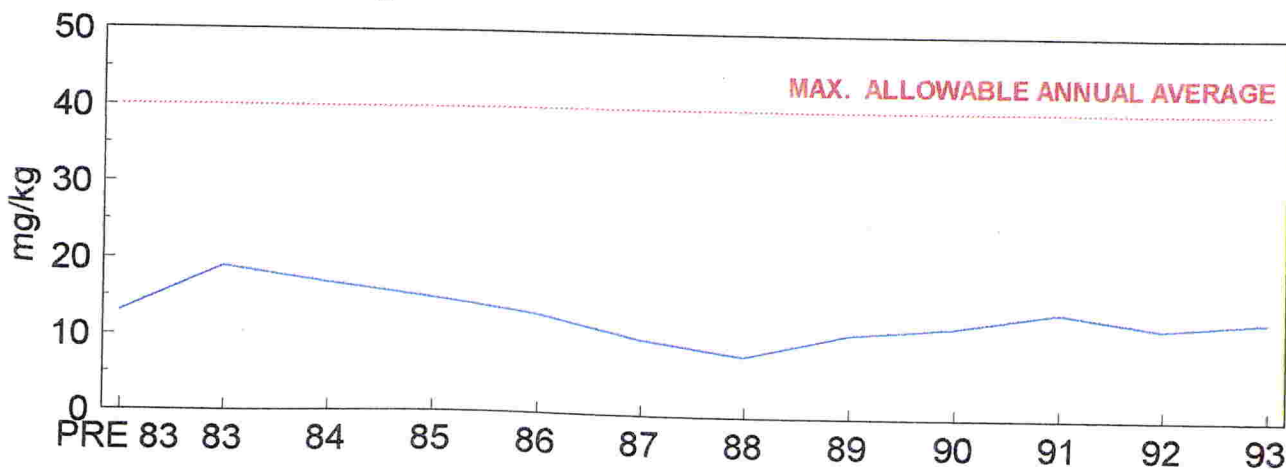
The annual average cattle urinary fluoride concentration was 5.5 mg/litre. This is within the normal range for cattle, (Shupe et al 1964). Chemical analysis of the two bone biopsies showed fluoride concentrations of 995 mg/kg for a two year old and 965 mg/kg for a 6 year old. The results are for fat free bone. In both cases, the fluoride concentration is well below the level that would indicate possible adverse effects. The dental condition of these animals also remains normal with all scores being less than or equal to two on the Suttie scale, showing no adverse effects of fluoride exposure.

### 3.4.2 Farm No 2

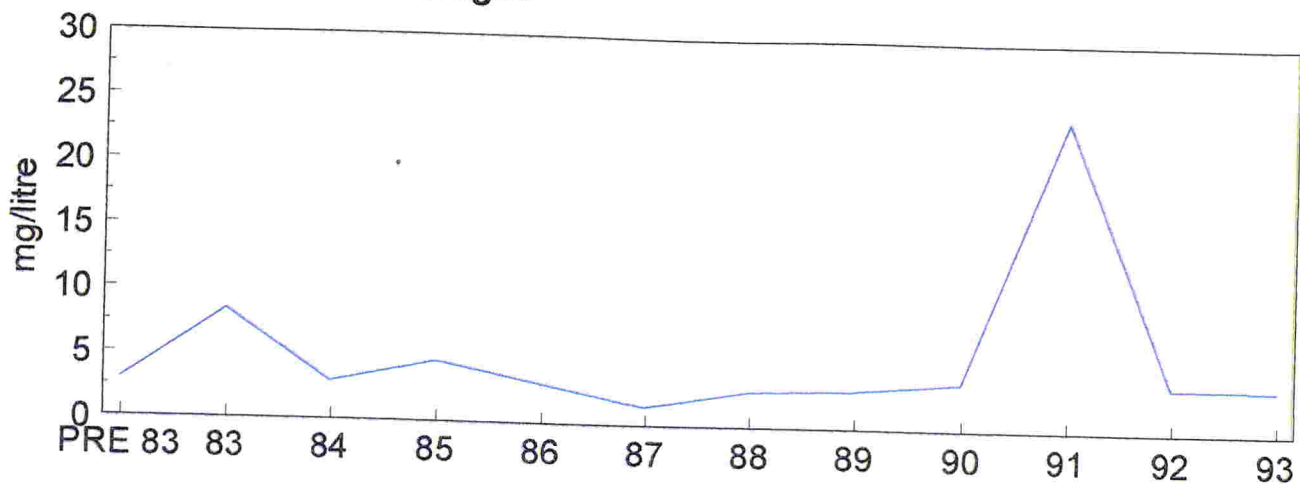
#### Pasture Fluoride Concentrations 1993 Monthly Averages



#### Annual Averages



## Cattle Urinary Fluoride Concentrations 1993 Annual Averages



Farm No. 2 is 6 km north of the smelter. The fluoride concentration in the February pasture sample was effected by the same south-easterly wind pattern as described for Farm No. 1. There was a period of southerlies prior to the collection of the December pasture sample. This would transport the smelter's discharges towards this farm and may explain the elevated December result.

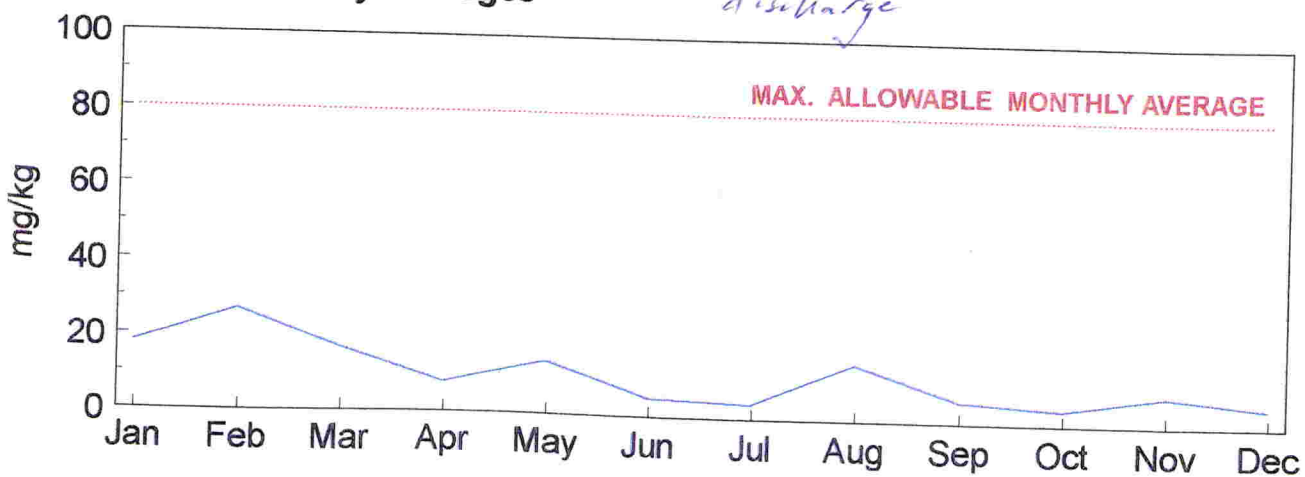
The annual average pasture fluoride concentration was 13 mg/kg. The monthly limit of 80 mg/kg, the bimonthly average limit of 60 mg/kg and the annual average limit of 40 mg/kg were not exceeded during 1993.

The average fluoride concentration in the cattle urine samples collected was 3.5 mg/litre, a similar concentration to previous years.

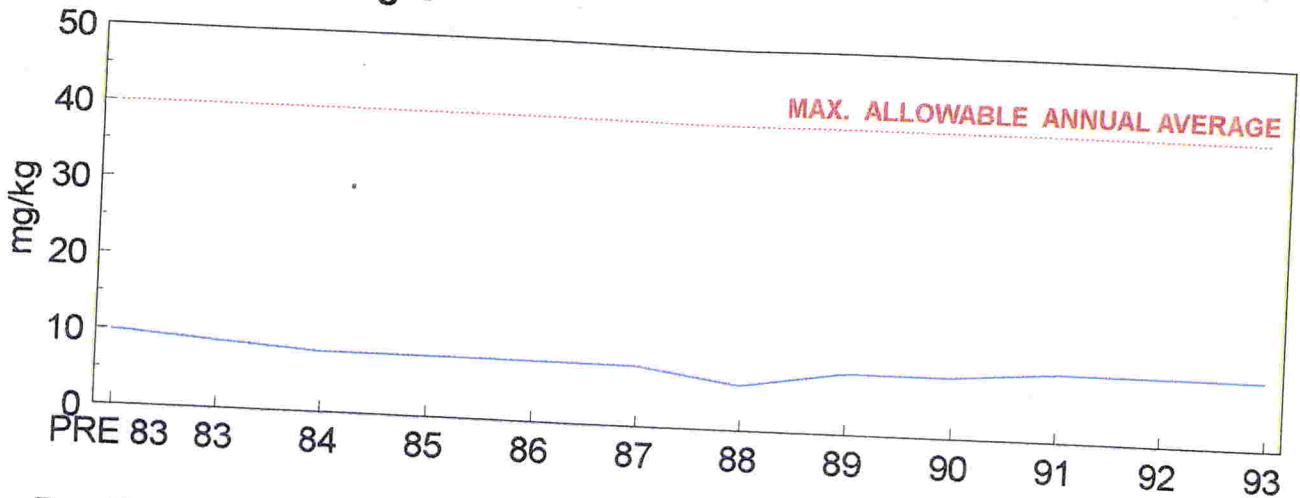
Cattle bone biopsies were conducted. Bone fluoride concentrations were 1485 mg/kg for a four year old, and 1700 mg/kg for two six year olds for fat free bone. The results are higher than previously measured at this farm: 1050 mg/kg for 4 year old in 1991 and 1400 mg/kg for 6 year old in 1988. The results are below the levels where the adverse effects of fluoride exposure would be expected to occur. A dental inspection of six cows using the scoring system of Suttie(1983) resulted in 19 of the 21 teeth scoring two and two teeth scoring three. The predominant tooth scores are indicating no adverse effects from exposure to fluoride.

### 3.4.3 Farm No 3 Pasture Fluoride Concentrations 1993 Monthly Averages

*line on teeth with topdressing  
but scattered with constant  
discharge*



**Pasture Fluoride Concentrations  
Annual Averages**



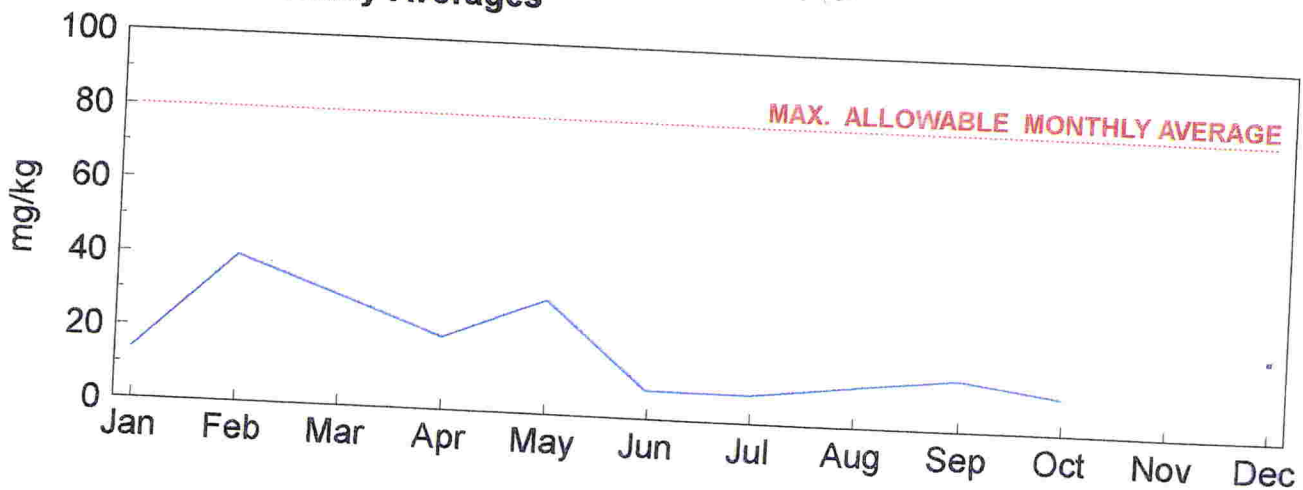
Farm No. 3 is 18 km north east of the smelter. The pasture fluoride concentrations on this farm continue to be low.

The annual average pasture fluoride concentration was 9 mg/kg. The monthly limit of 80 mg/kg, the bimonthly average limit of 60 mg/kg and the annual average limit of 40 mg/kg were not exceeded during 1993.

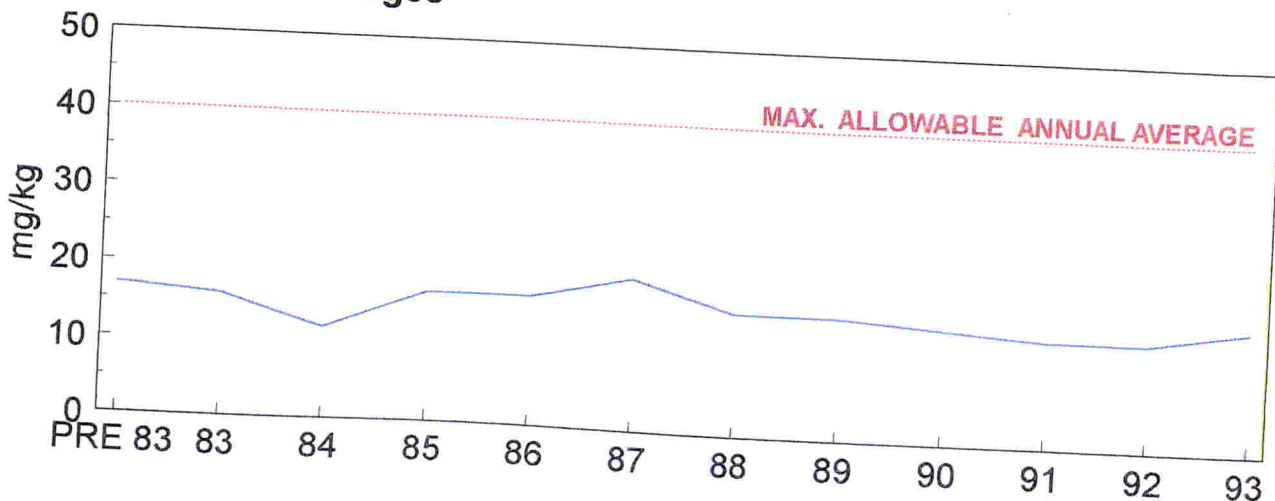
**3.4.4 Farm No 4**

**Pasture Fluoride Concentrations  
1993 Monthly Averages**

*Measurements well below 80 mg/kg*

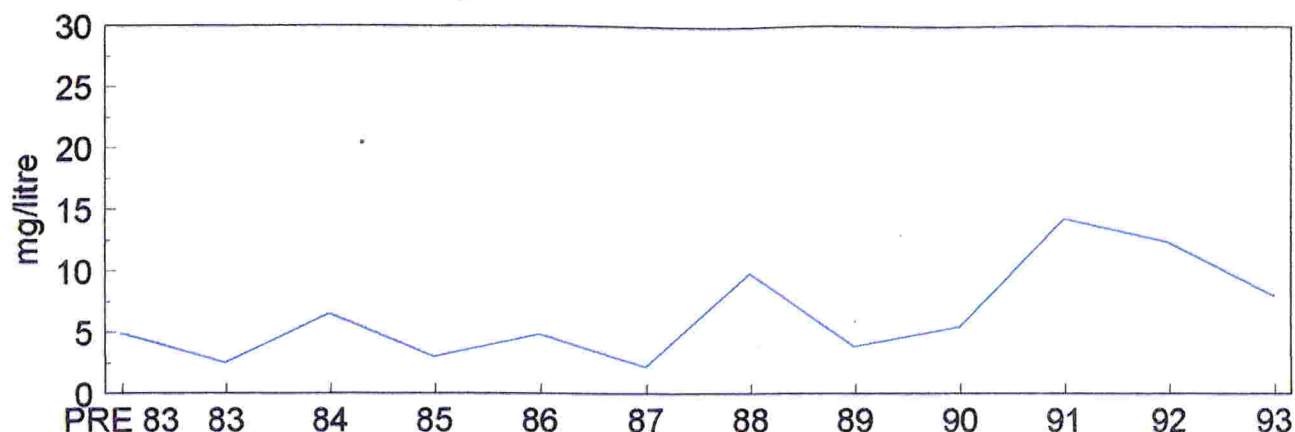


**Annual Averages**





### Cattle Urinary Fluoride Concentrations 1993 Annual Averages

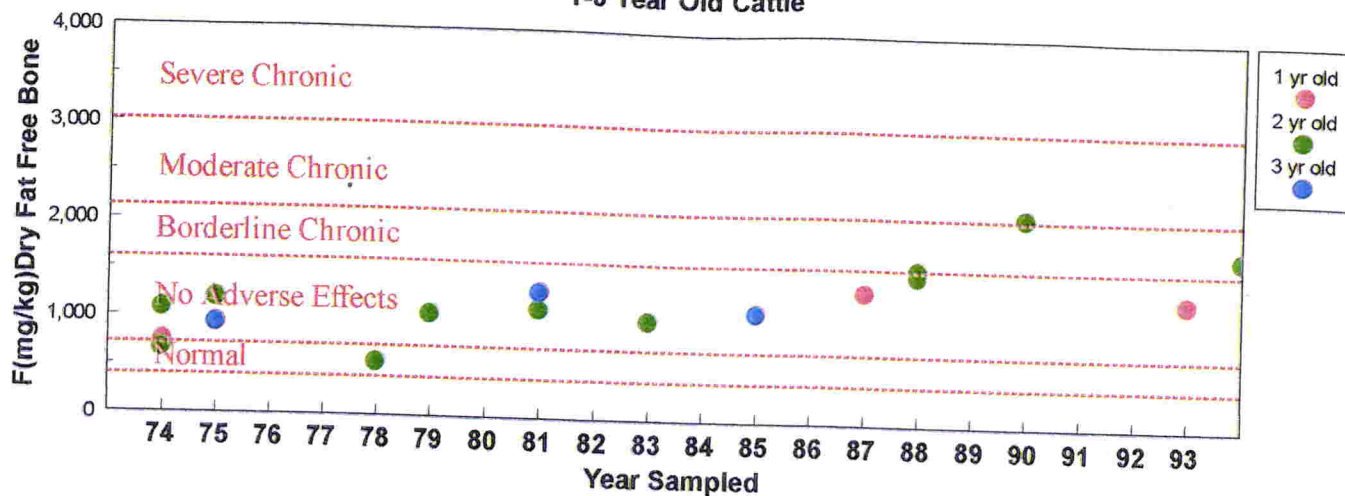


Farm No. 4 is on the northern shore of Awarua Bay, north-east of the smelter. Because of its position this farm is regularly affected by the smelter's discharges. The result of this can be seen in the variation in the fluoride concentrations in the pasture samples through the year.

The farm was topdressed the day before the November sample was collected. The fluoride concentration in the sample was 3100 mg/kg and has not been included in the data analysis.

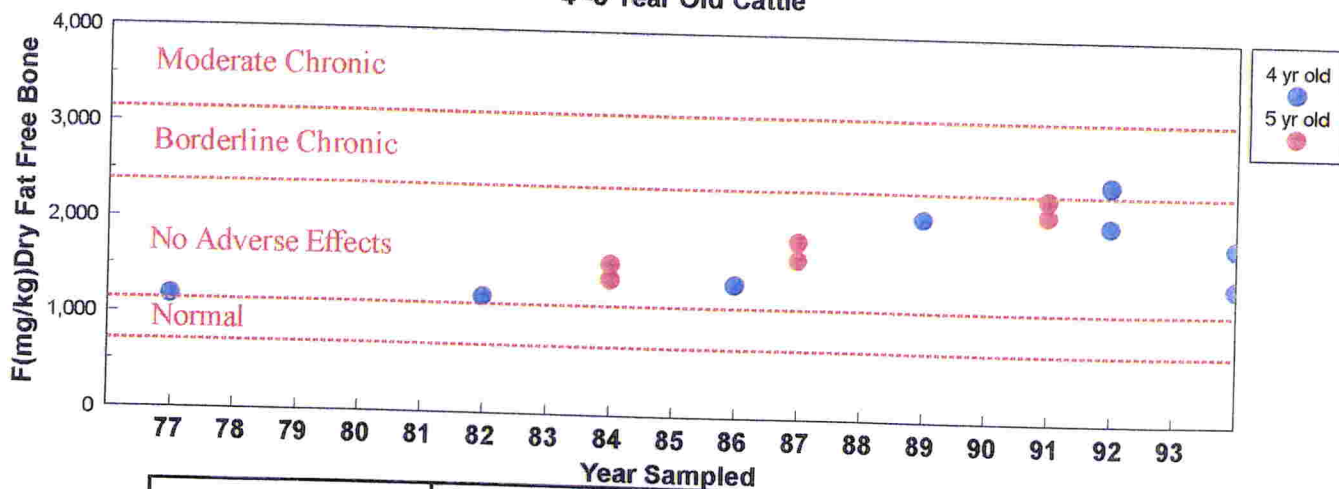
The annual average pasture fluoride concentration was 16 mg/kg. The monthly limit of 80 mg/kg, the bimonthly average limit of 60 mg/kg and the annual average limit of 40 mg/kg were not exceeded during 1993.

The cattle urine sample contained an average fluoride concentration of 8.0 mg/litre. This is within the expected range for this farm. The concentration of fluoride in the bone biopsy taken from a year old cow was 1300 mg/kg fat free bone. This is similar to the 1360 mg/kg for a yearling measured in 1987. These concentrations would suggest the animal was on the borderline of chronic fluorosis. The dental condition of the animals inspected would support this with the most recently erupted teeth scoring two and three on the Suttie scale. The absence of teeth scoring four indicates an improvement compared with teeth erupting in the late 1980's. This is consistent with the improved control of gaseous fluoride emissions from the smelter's main stack.



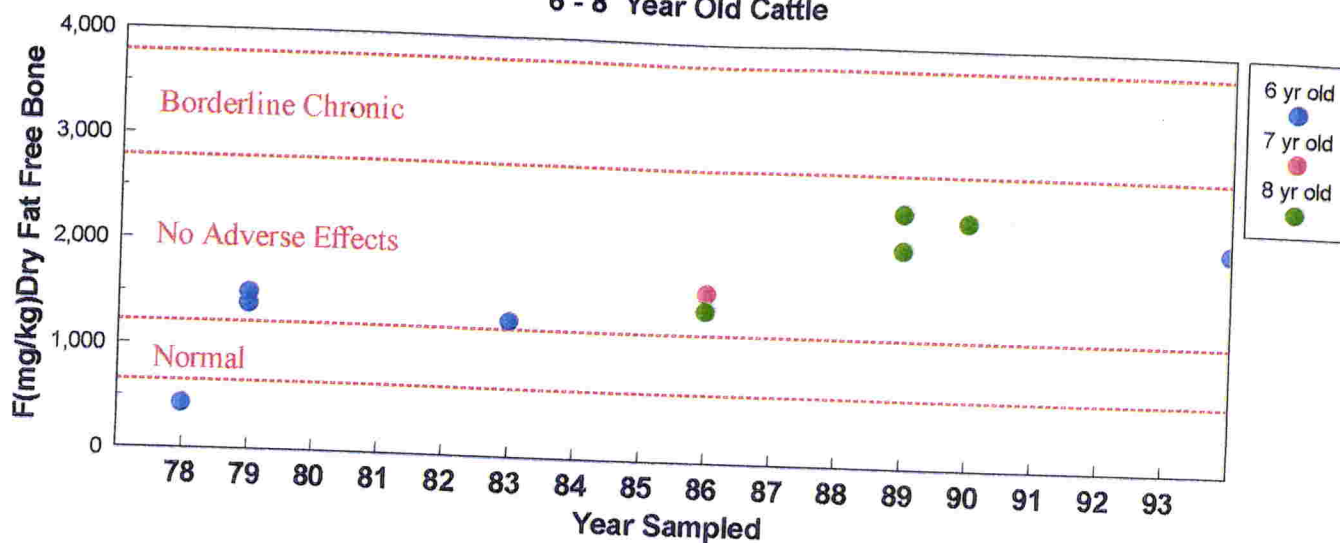
Exposure Levels for a 2 year old	Dry Fat Free Bone F(mg/kg)
Severe Chronic	3027-4206
Moderate Chronic	2130-3027
Borderline Chronic	1605-2130
No Adverse Effects	714-1605
Normal	401-714

GRAZING MONITOR FARM 4  
4-5 Year Old Cattle



Exposure Levels for a 4 year old	Dry Fat Free Bone F(mg/kg)
Severe Chronic	4504-6620
Moderate Chronic	3138-4504
Borderline Chronic	2379-3138
No Adverse Effects	1138-2379
Normal	706-1138

GRAZING MONITOR FARM 4  
6 - 8 Year Old Cattle

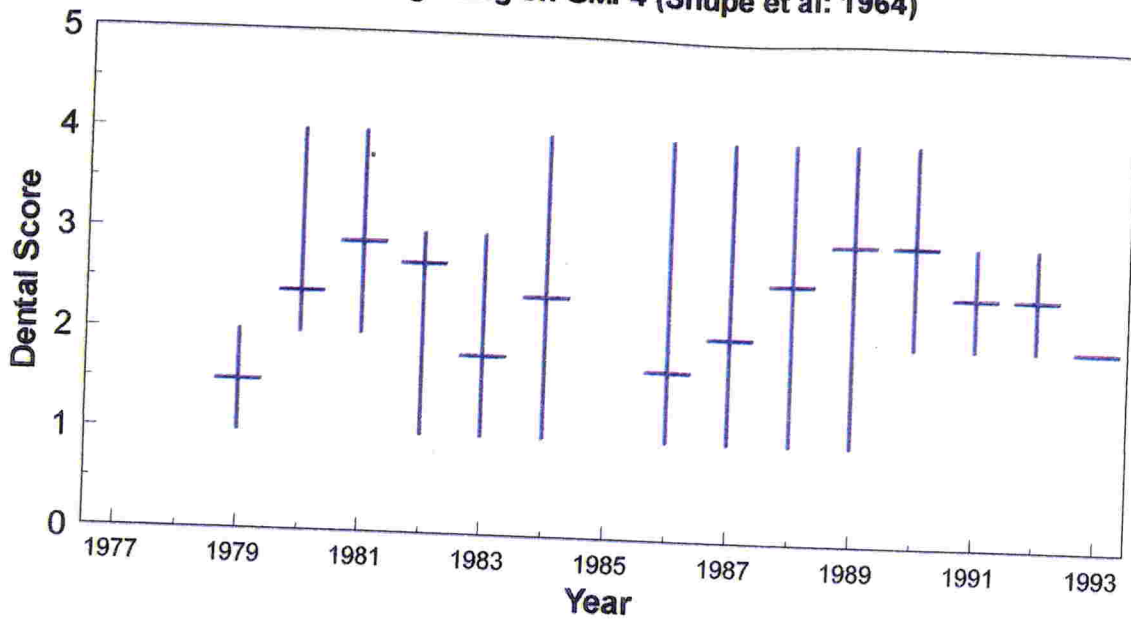


Exposure Levels for a 6 year old	Dry Fat Free Bone F(mg/kg)
Severe Chronic	5622-8676
Moderate Chronic	3788-5622
Borderline Chronic	2794-3788
No Adverse Effects	1221-2794
Normal	653-1221

Changes in the bone fluoride concentrations of cattle grazed on GMF4 are shown in the preceding three graphs. The concentration has increased from about 1500 mg/kg in 1986 to about 2500 mg/kg in 1992 and has not increased since then. The only bone biopsy taken in 1993 was from a yearling heifer which had a fluoride concentration of 1300 mg/kg, similar to a yearling in 1986. The increase in bone fluoride concentrations indicate that the cattle's exposure to fluoride has changed from having no adverse effect to borderline chronic effects. The increasing trend of bone fluoride concentration at GMF 4 appears to have stopped with the concentration stabilised at the 1990 concentration. Bone biopsies collected in early 1994 have been included in these graphs. The 1994 results show that the bone fluoride concentrations are similar to those measured since 1990.

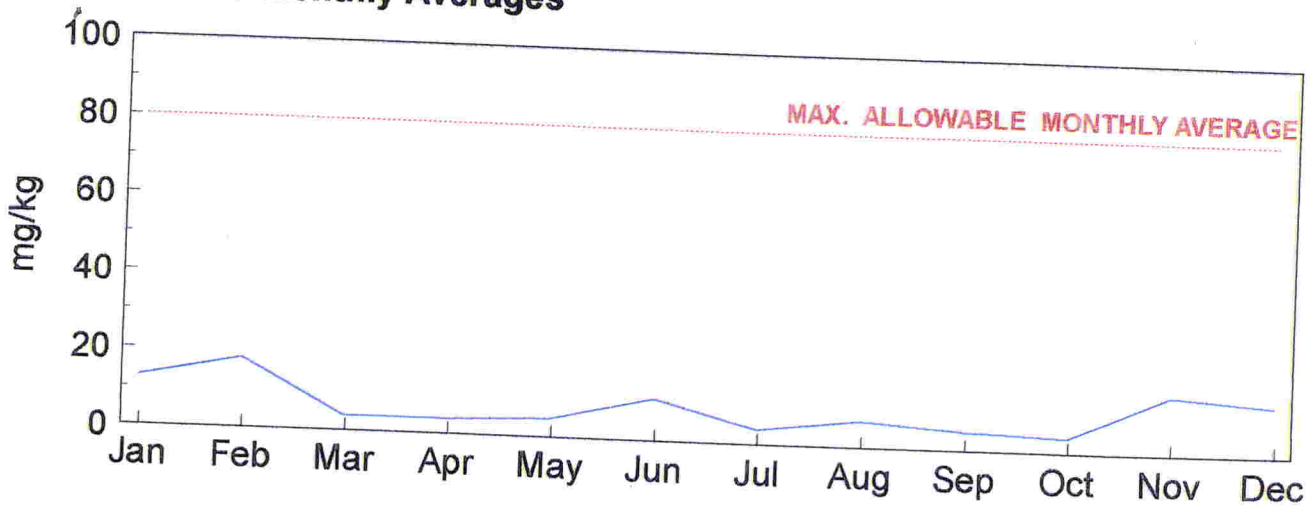
The following graph shows an analysis of the changes in tooth score with time for cattle grazing on GMF4. The time shown in the graph is the time of tooth formation. The score follow the scoring system of Suttie (1983). Since 1985 the average score for teeth formed on GMF4 has risen from 1.7 to about three for teeth formed in 1990.

Dental scores related to year of tooth formation  
in cattle grazing on GMF4 (Shupe et al: 1964)



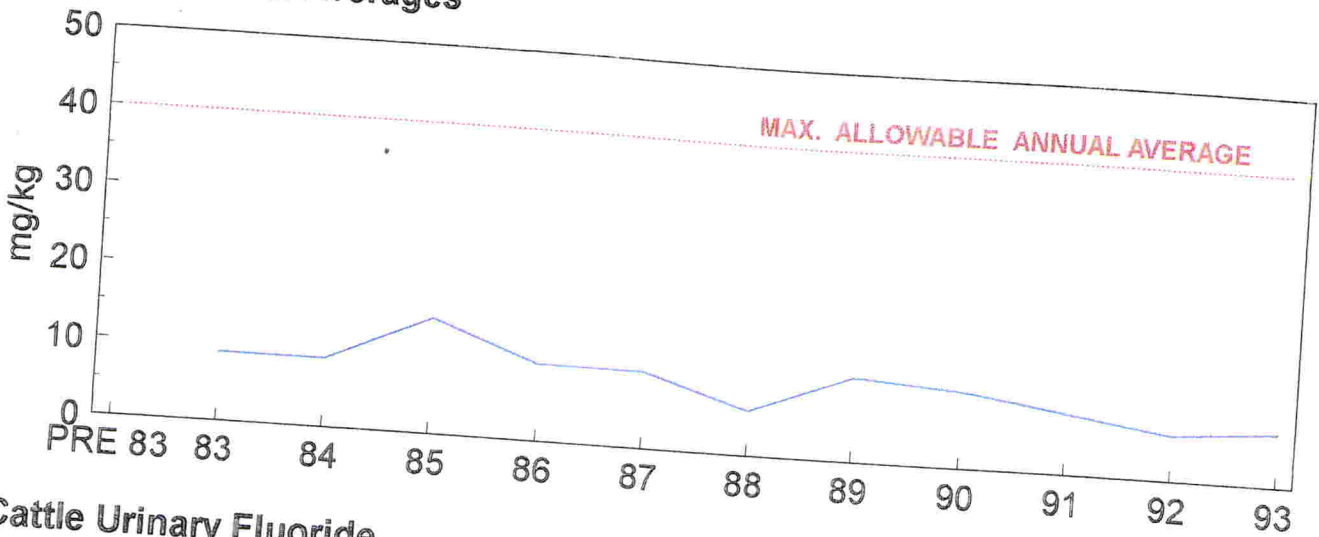
**3.4.6 Farm No 8**

**Pasture Fluoride Concentrations  
1993 Monthly Averages**

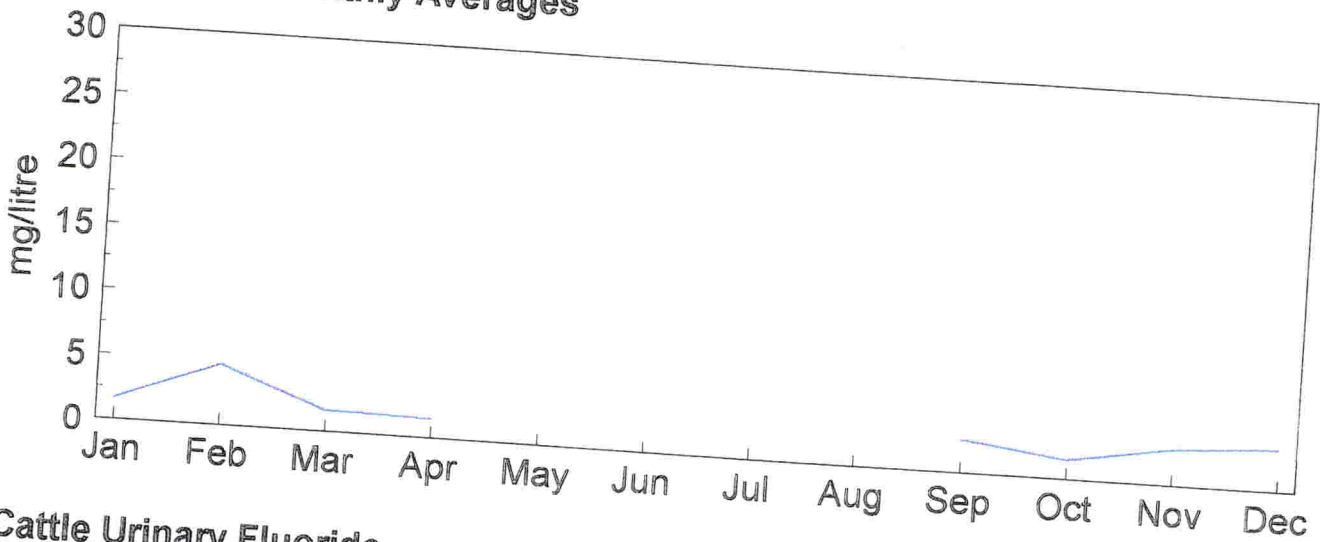




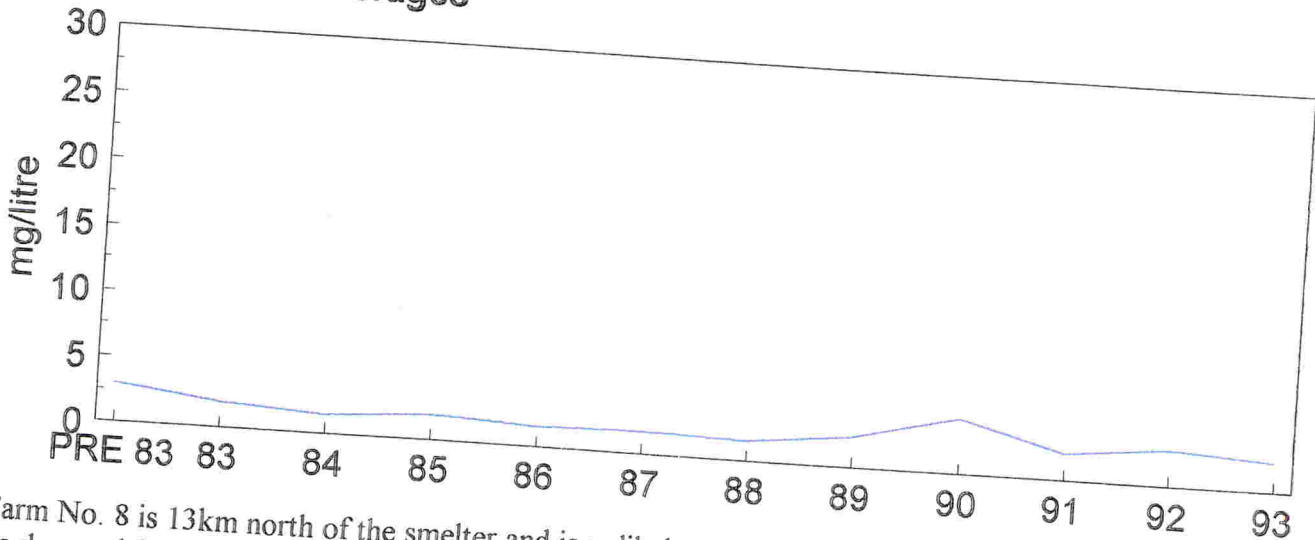
Pasture Fluoride Concentrations  
Annual Averages



Cattle Urinary Fluoride  
1993 Monthly Averages



Cattle Urinary Fluoride  
Annual Averages



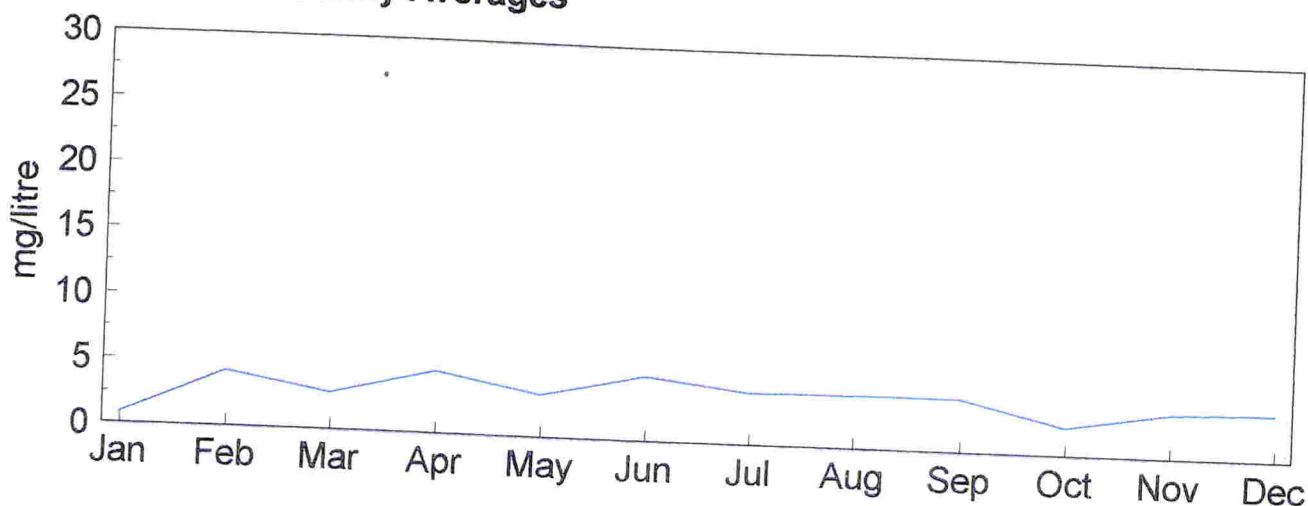
Farm No. 8 is 13km north of the smelter and is unlikely to be affected by the smelter's emissions and will be dropped from the monitoring program from the beginning of 1994. This change is recommended by the IDC and is consistent with the Southland Regional Council's(SRC) proposals for monitoring under the new air discharge permit.



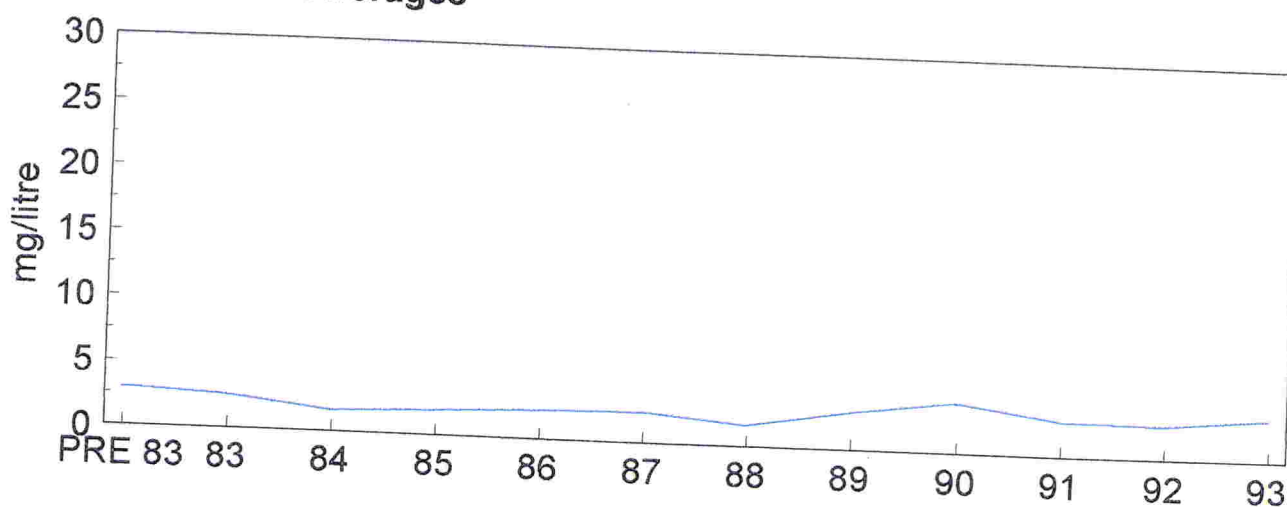
**3.4.7 Farm No 9**

**Cattle Urinary Fluoride**

**1993 Monthly Averages**



**Annual Averages**

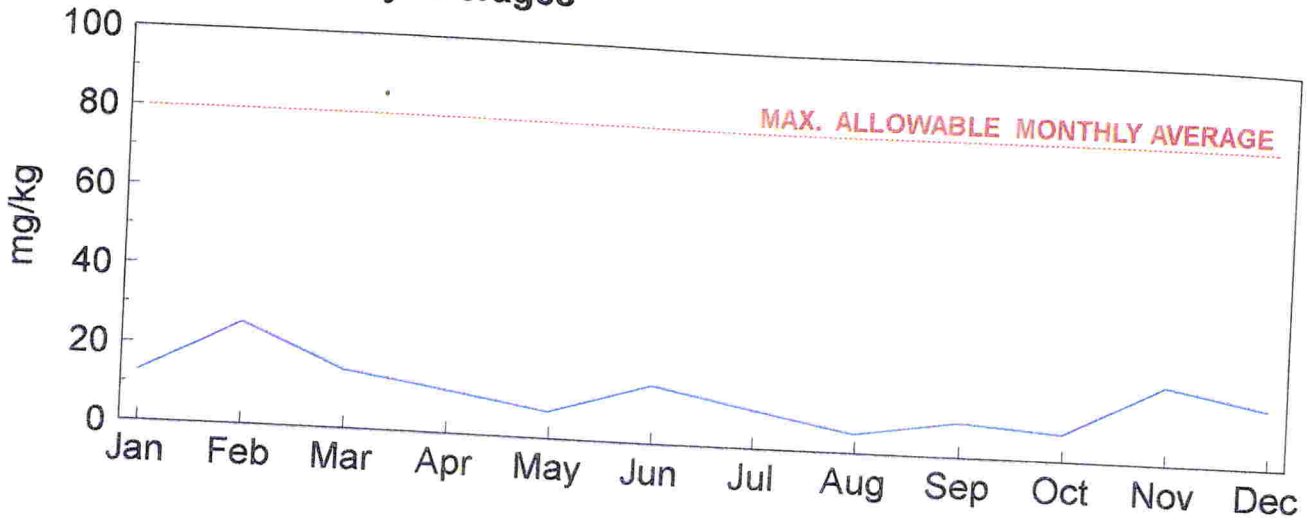


Farm No. 9 is 15.5 km north-west of the smelter and is unlikely to be affected by the smelter's emissions and will be dropped from the monitoring program from the beginning of 1994. This change is recommended by the IDC and is consistent with the SRC's proposals for monitoring under the new air discharge permit.

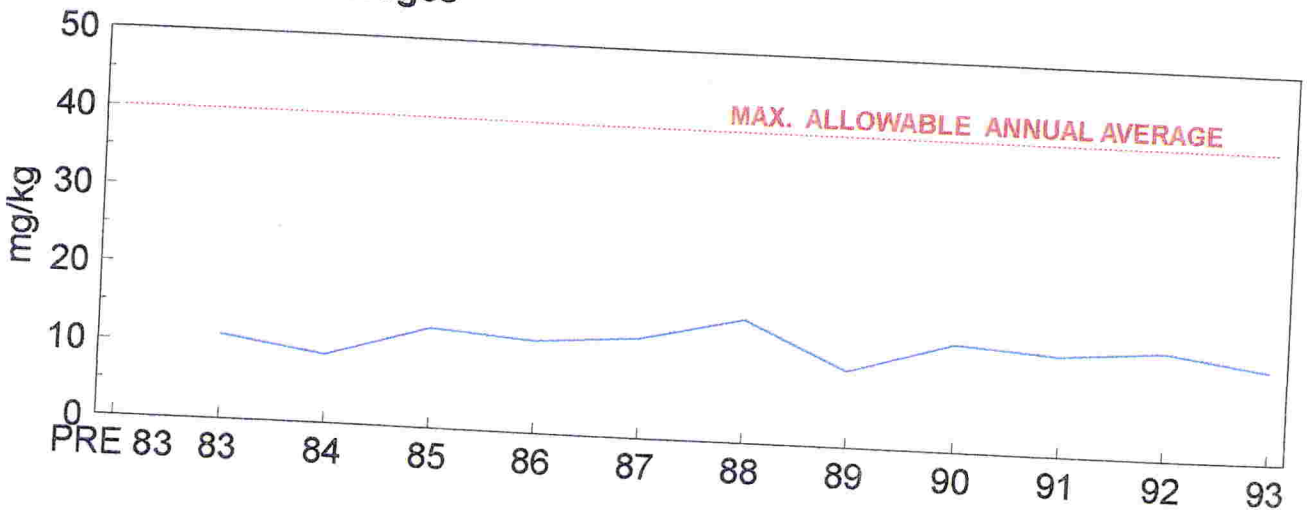
*To be dropped.*

3.4.8 Farm No 10

Pasture Fluoride Concentrations  
1993 Monthly Averages



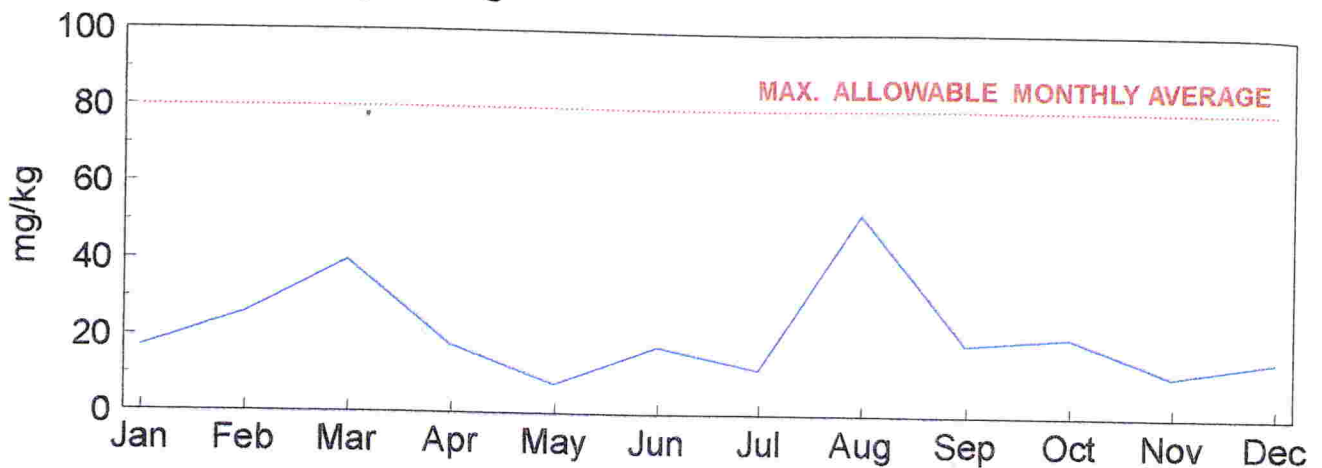
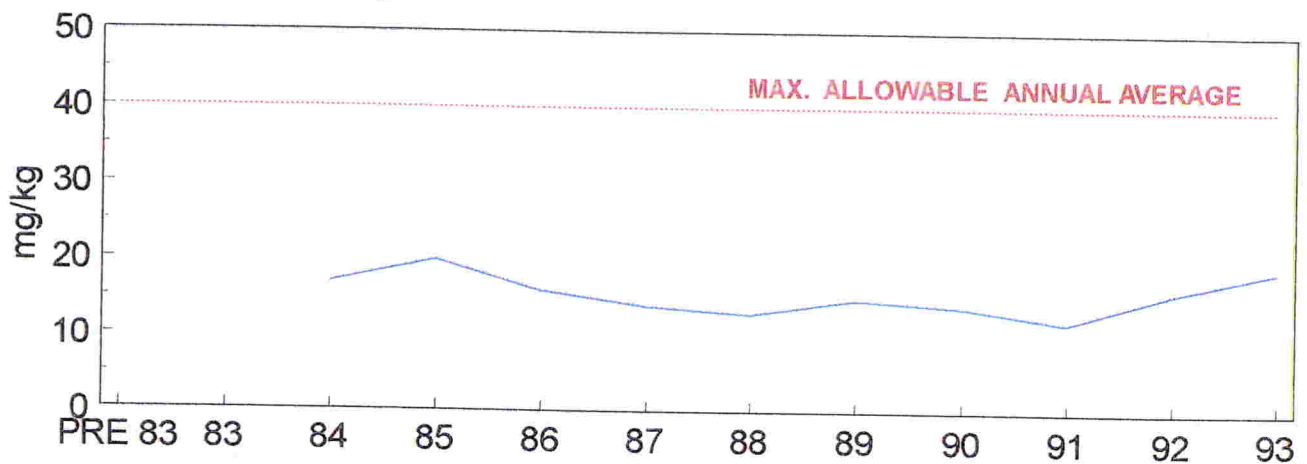
Annual Averages



Farm No. 10 is 25 km east-north-east of the smelter. The 1993 pasture fluoride concentrations were normal.

The annual average pasture fluoride concentration was 12 mg/kg. The monthly limit of 80 mg/kg, the bimonthly average limit of 60 mg/kg and the annual average limit of 40 mg/kg were not exceeded during 1993.

*East of Waituna Lagoon.*

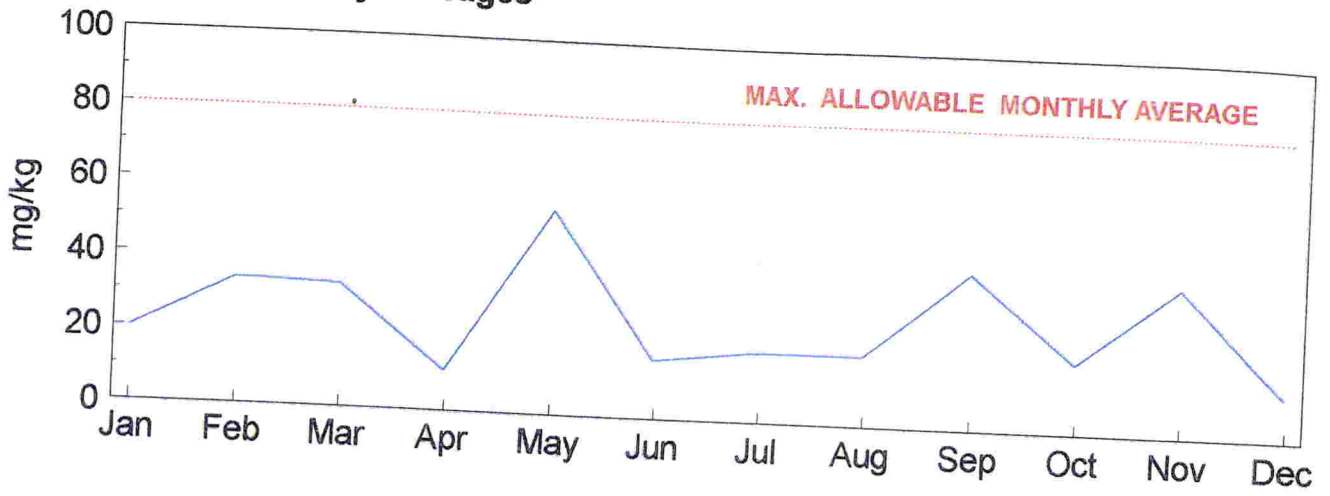
**3.4.9 Farm No 11****Pasture Fluoride Concentrations  
1993 Monthly Averages****Annual Averages**

Farm No. 11 is 5 km north-north-east of the smelter. As with farm No. 4 this farm is periodically affected by the smelter's discharges. Accordingly there is greater variation in the fluoride concentration in the pasture than on more remote farms.

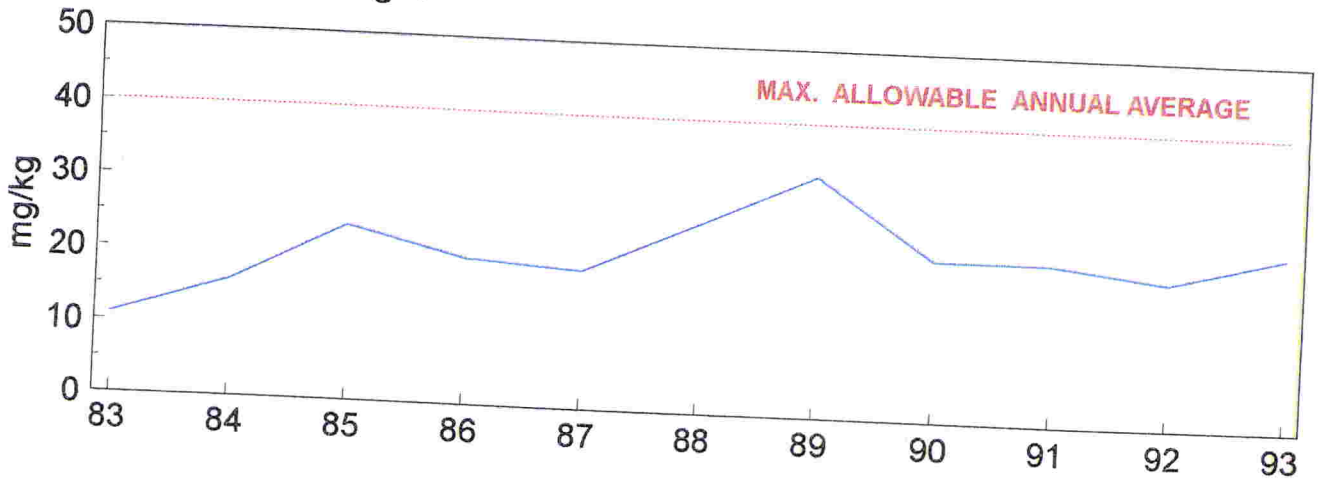
In August there were elevated concentrations of fluoride in the other vegetation samples collected in the vicinity of this farm and at sites further to the north-east. This would suggest the smelter was the main source of this fluoride.

The annual average pasture fluoride concentration was 19 mg/kg. The monthly limit of 80 mg/kg, the bimonthly average limit of 60 mg/kg and the annual average limit of 40 mg/kg were not exceeded during 1993.

Pasture Fluoride Concentrations  
1993 Monthly Averages



Annual Averages



Farm No. 12 is on the northern shore of Awarua Bay, east-north-east of the smelter. Because of its position this farm is regularly affected by smelter discharges. The result of this can be seen in the variation in the fluoride concentrations in the pasture samples through the year. Although significant, the variation in the monitoring results for 1993 is not as great as has been observed in the past. For example in 1991 the fluoride concentration in this farms pasture ranged from less than 10 mg/kg to greater than 75 mg/kg.

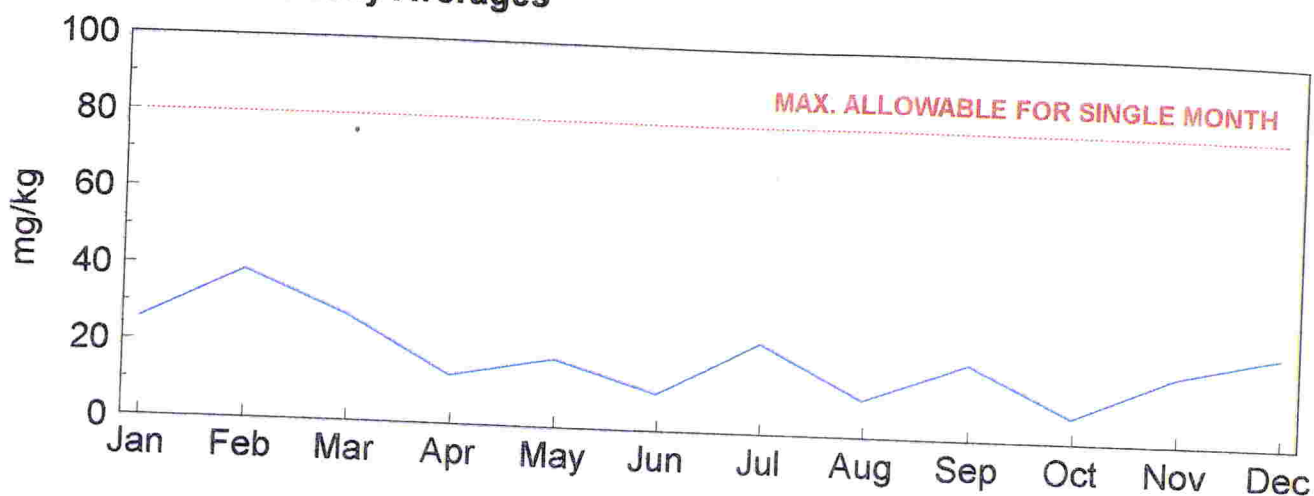
Fertiliser was applied to this farm prior to the May sample collection.

The annual average pasture fluoride concentration was 24 mg/kg. The monthly limit of 80 mg/kg, the bimonthly average limit of 60 mg/kg and the annual average limit of 40 mg/kg were not exceeded during 1993.

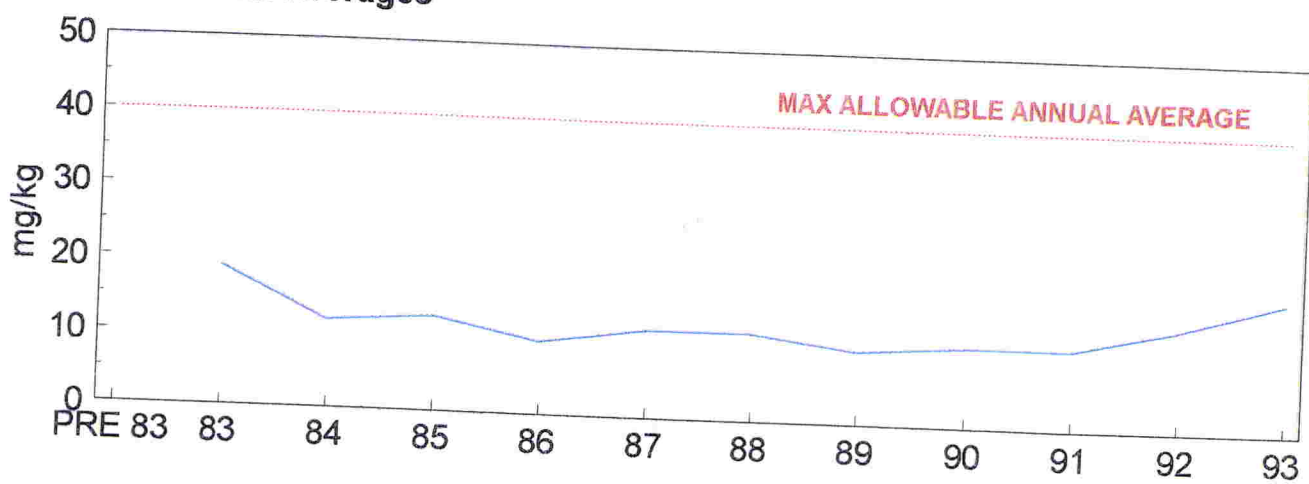


### 3.4.11 Farm No 13

#### Pasture Fluoride Concentrations 1993 Monthly Averages



#### Annual Averages



Farm No. 13 is 15km east-north-east of the smelter. At the recommendation of the IDC this site will be deleted from the monitoring project. It will be replaced by two sites, one slightly closer to the smelter and one further away. This will provide improved monitoring coverage of an area that has been shown to be affected by the smelter's discharges. This is consistent with the SRC's proposals for monitoring under the new air discharge permit.

The annual average pasture fluoride concentration was 18 mg/kg. The monthly limit of 80 mg/kg, the bimonthly average limit of 60 mg/kg and the annual average limit of 40 mg/kg were not exceeded during 1993.

## 3.5 TIWAI EXPERIMENTAL FARMS

### 3.5.1 Introduction

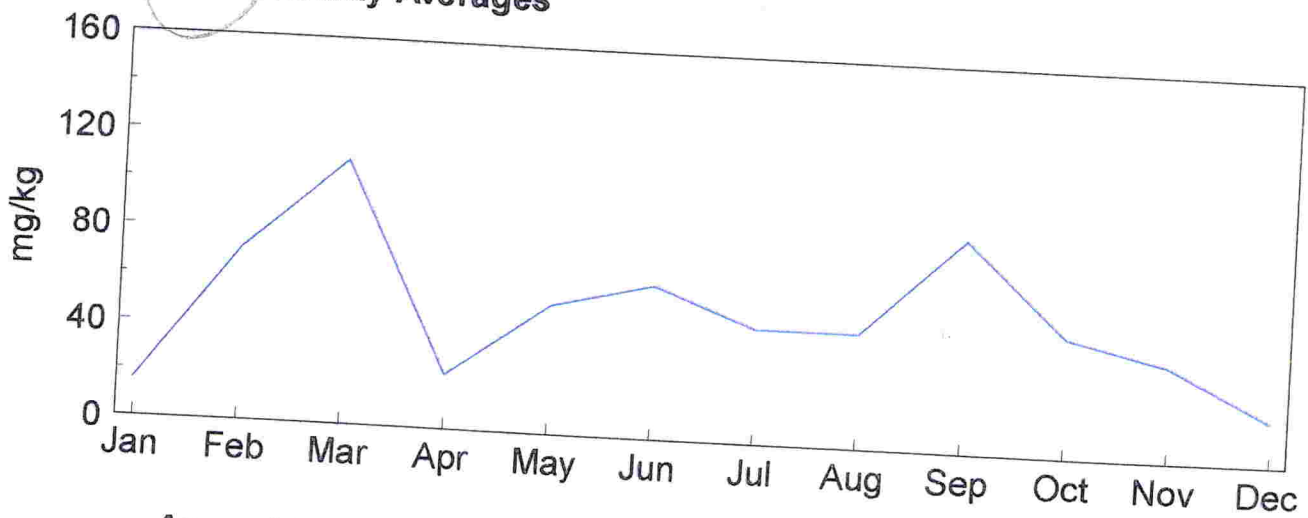
This project was established to support the Grazing Monitor Farms Project. Its aims were to assess the effects of the smelter's discharges into air on sheep and to provide local veterinary officers with experience in diagnosing fluorosis.

The No. 1 Farm is on the Tiwai Peninsula, 3.5 km east of the smelter. It was established in 1971. The No. 2 Farm is at the eastern end of the Tiwai Peninsula, 10 km downwind of the smelter and was established in 1973.

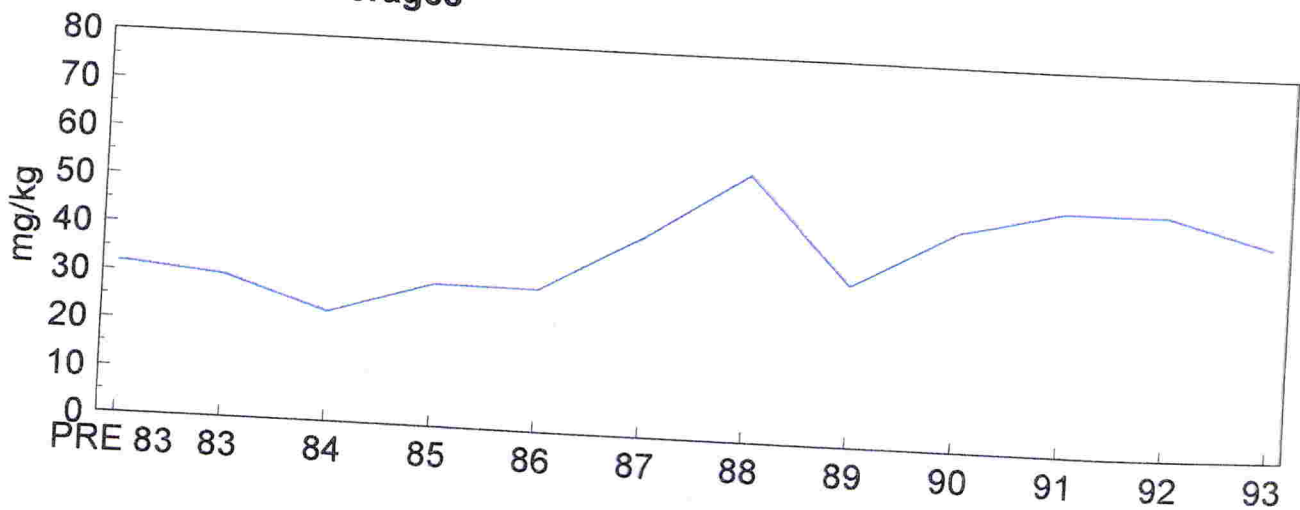
### 3.5.2 Farm No 1

#### Pasture Fluoride Concentrations

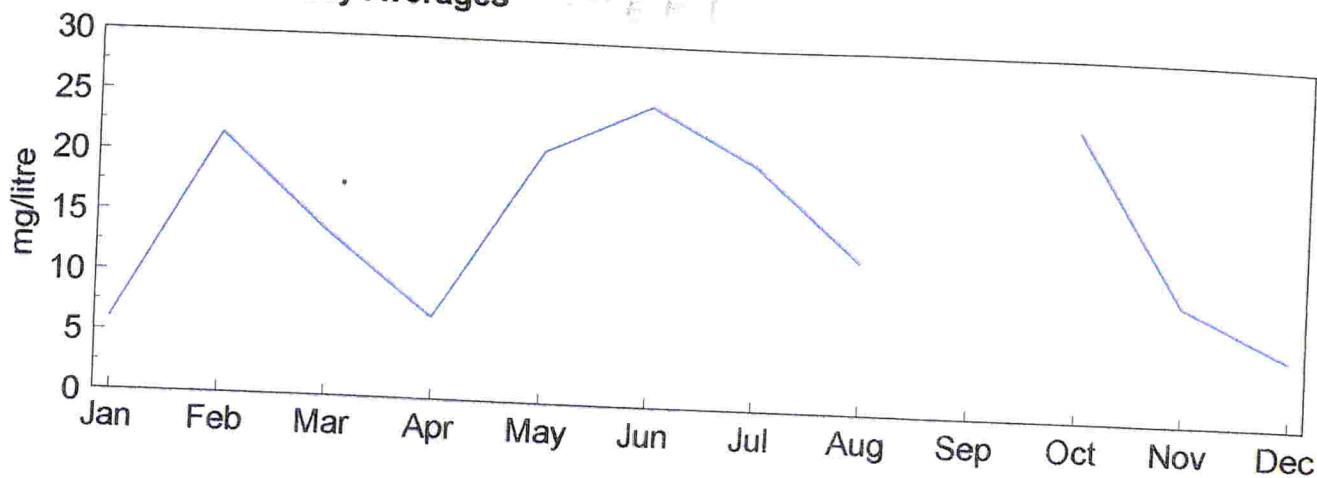
#### 1992 Monthly Averages



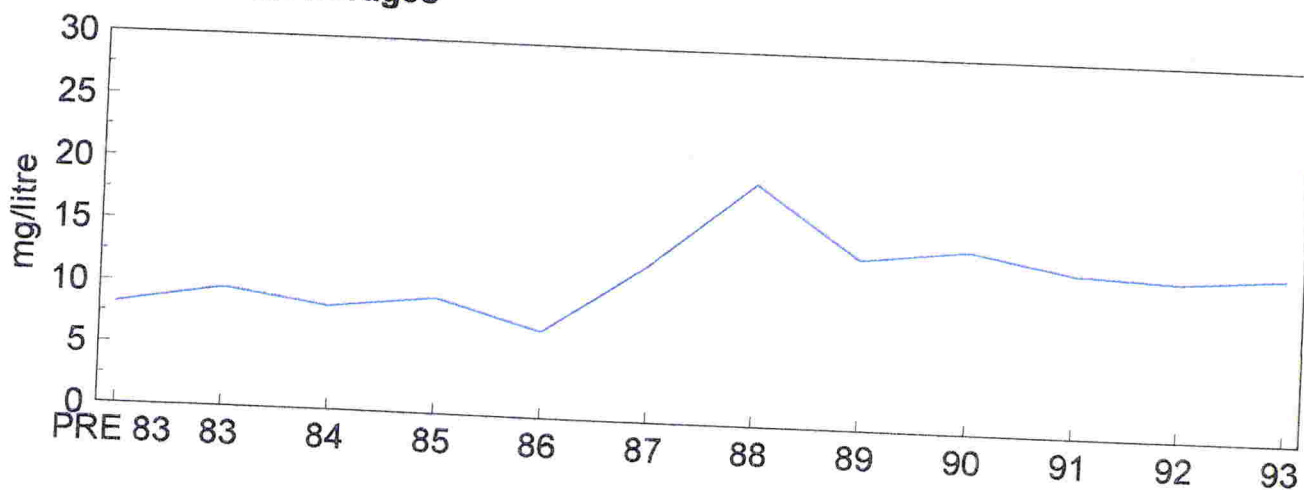
#### Annual Averages



Sheep Urinary Fluoride  
1993 Monthly Averages



Annual Averages



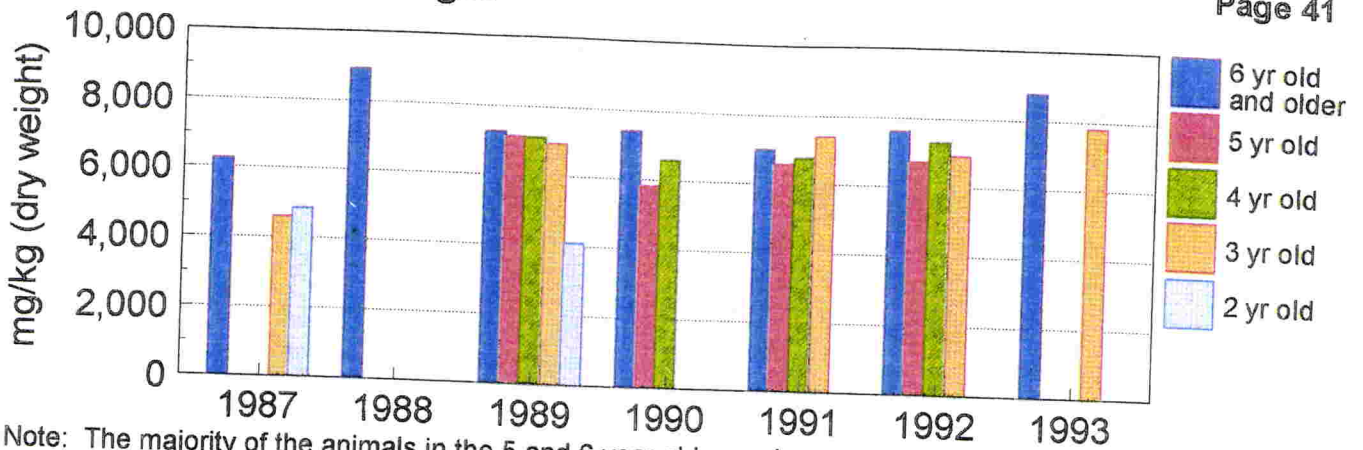
As there is no fertiliser containing fluoride applied to the Tiwai Experimental Farms (TEF), all the variation observed in the fluoride concentrations in both the pasture and the sheep urine is due to smelter discharges. The extent of the variation is similar to previous years with no recent trends evident in the annual averages of either parameter.

No urine sample was collected in September to reduce the disturbance to the flock during lambing.

The annual average pasture fluoride concentration was 45 mg/kg. The annual average urinary fluoride concentration was 13 mg/litre.



## Sheep Jaw Bone Fluoride Concentrations Annual Averages



Note: The majority of the animals in the 5 and 6 year old samples are the culled stock. The samples of the younger animals come from stock deaths during the year. There is often only one animal per age group

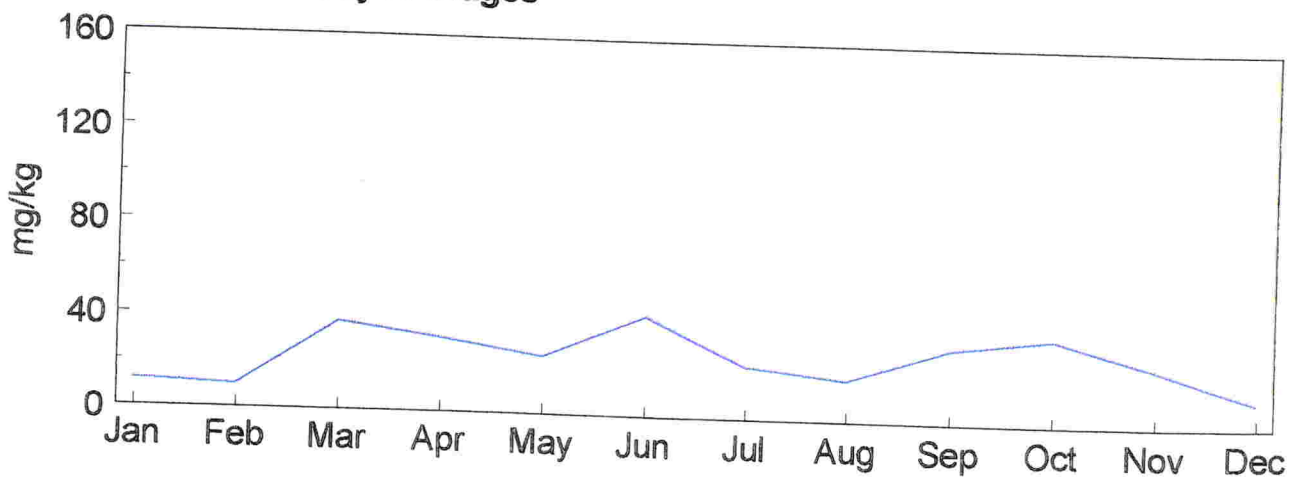
Jaw bone samples were collected and the fluoride concentration in the bone measured. In both age groups represented in the sample the average fluoride concentration was higher than has been observed in recent years. This is attributed to natural variation in a relatively small sample size. Over the years these animals have been growing there has been no upward trends in the pasture fluoride concentrations nor has the concentration of fluoride in their urine showed any upward trend.

The dental condition of the sheep was assessed by the NZAS veterinary consultant. The average and range of tooth condition was similar to previous years. The range of results using the Suttie system was two to four with an average of 2.9.

A management change noted in the 1989 IDC report has resulted in lower exposure to fluoride in the first year for stock raised in the Tiwai Experimental Farm Project. The change was to send weaned lambs to TEF2. Some of these animals return as replacement stock a year later. The lower exposure will depress the bone fluoride concentrations, particularly in young stock and would be expected to produce lower tooth scores in the first pair of permanent teeth. The management of the TEF is being reviewed and a more consistent approach will be recommended.

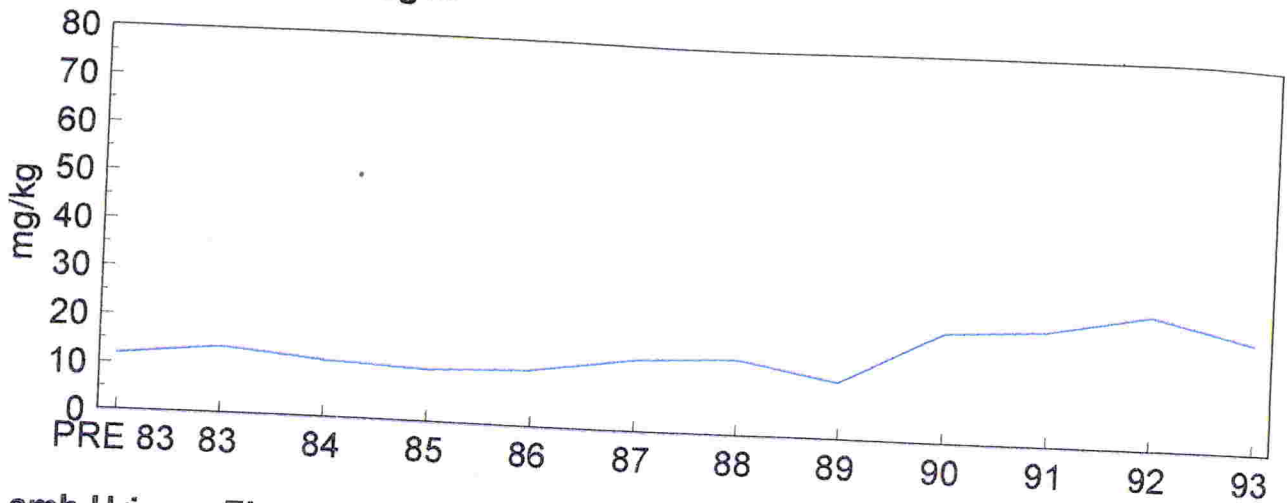
### 3.5.3 Farm No 2

#### Pasture Fluoride Concentrations 1993 Monthly Averages

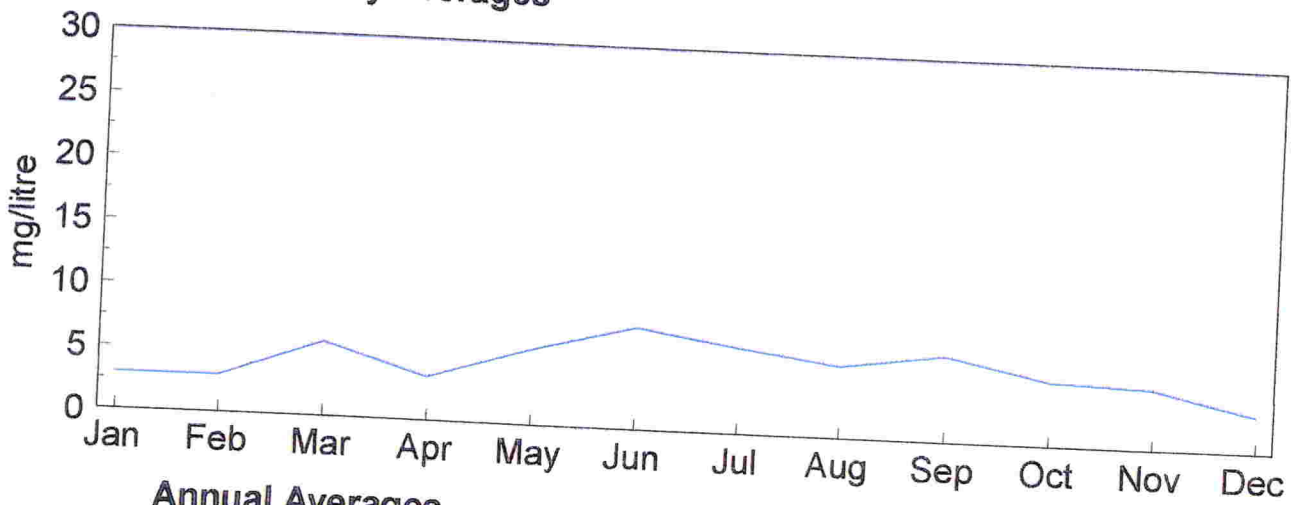


# Pasture Fluoride Concentrations Annual Averages

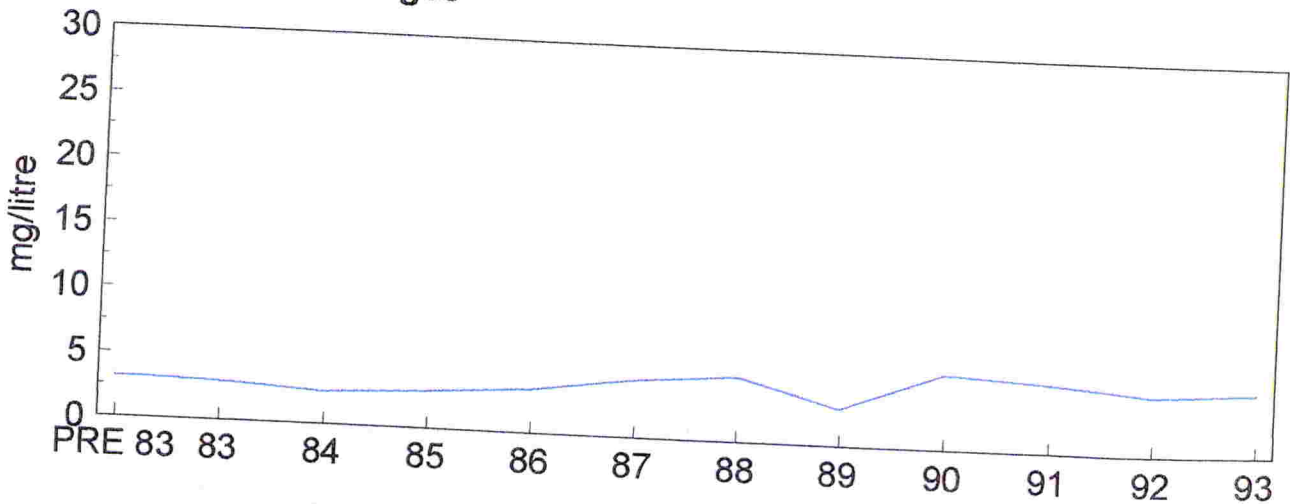
TEF 2



# Lamb Urinary Fluoride 1993 Monthly Averages



# Annual Averages



The 1993 annual average pasture fluoride concentration for TEF No.2 was 23 mg/kg. This is similar to the concentration for the previous three years.

The 1993 annual average lamb urinary fluoride concentration was 4.7 mg/kg which is similar to the previous three years.

### 3.6 Pasture Fluoride Analysis Methods

Investigation into pasture fluoride analysis methods continued during 1993.

The investigation indicates the following

- In 1986 NZAS changed from the Jacobson Heller method to the Association of Official Analytical Chemists (AOAC) method number 26. Statistical analysis of the results of reference materials showed no significant change due to the change in method.
- AOAC method 26 produced significantly lower fluoride results than the AOAC method 26 modified for hot acid extraction. *15-20%*
- AOAC method 26 (modified) produced similar results to the reference method ASTM D3269 for total fluoride in pasture grasses.

Discussion with the Southland Regional Council resolved that measurements of total fluoride were required because most of the fluoride toxicity research on grazing animals was conducted using the ASTM D3269 method. As an interim move NZAS will use the AOAC 26 modified method from January, 1994. Pasture fluoride results will increase by approximately 15 to 20%. NZAS will also investigate the development of more practical methods of measuring total fluoride. The ASTM D3269 method has very significant safety and productivity issues which must be overcome.

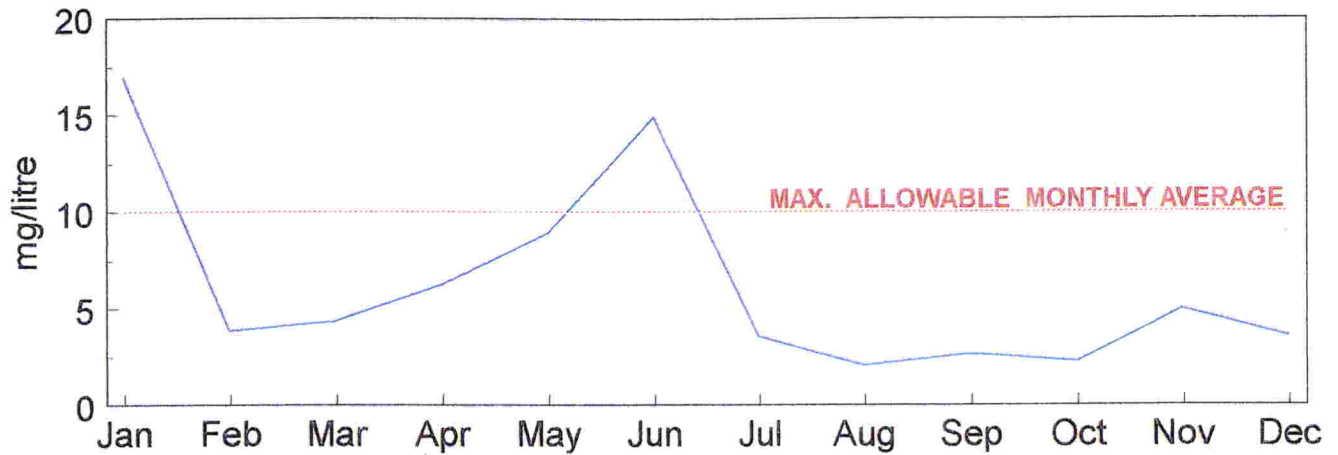
*AOAC 26 modified uses  
heated acid.*



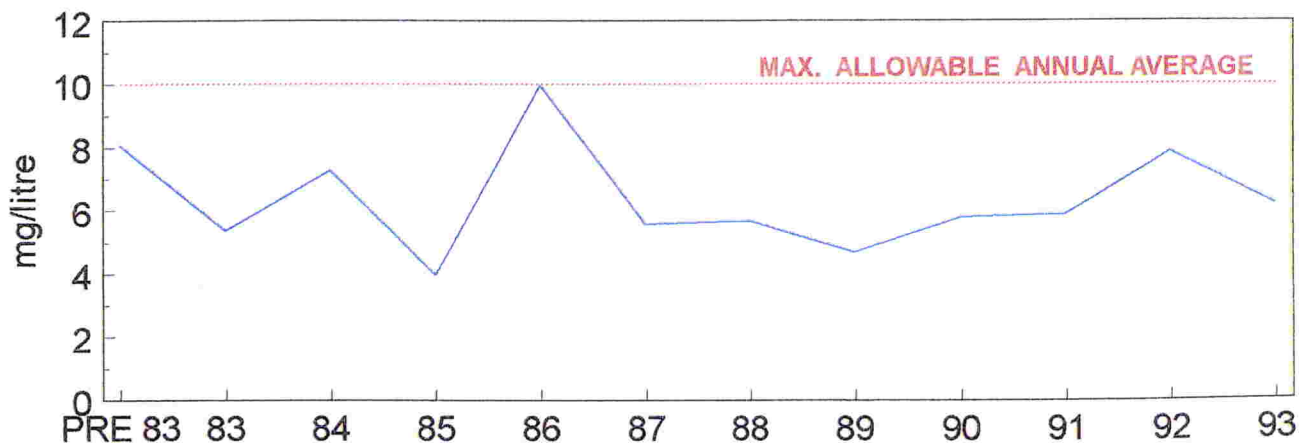
The smelter's liquid discharges are subject to five Coastal permits. The following sections give details of trends for each permit.

4.1 COASTAL PERMIT No 90057 - NORTH DRAIN

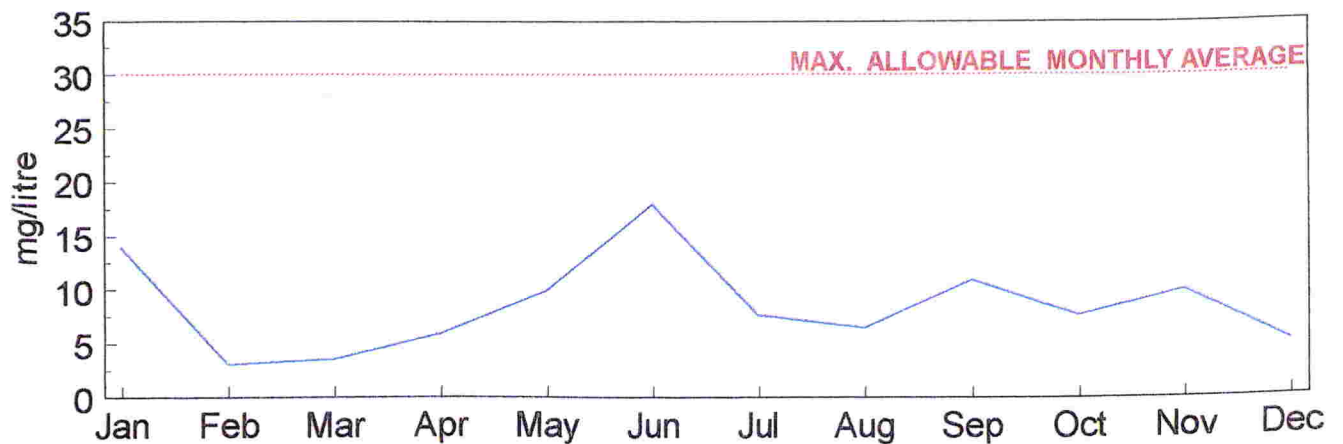
Discharge Fluoride Concentrations  
1993 Monthly Averages



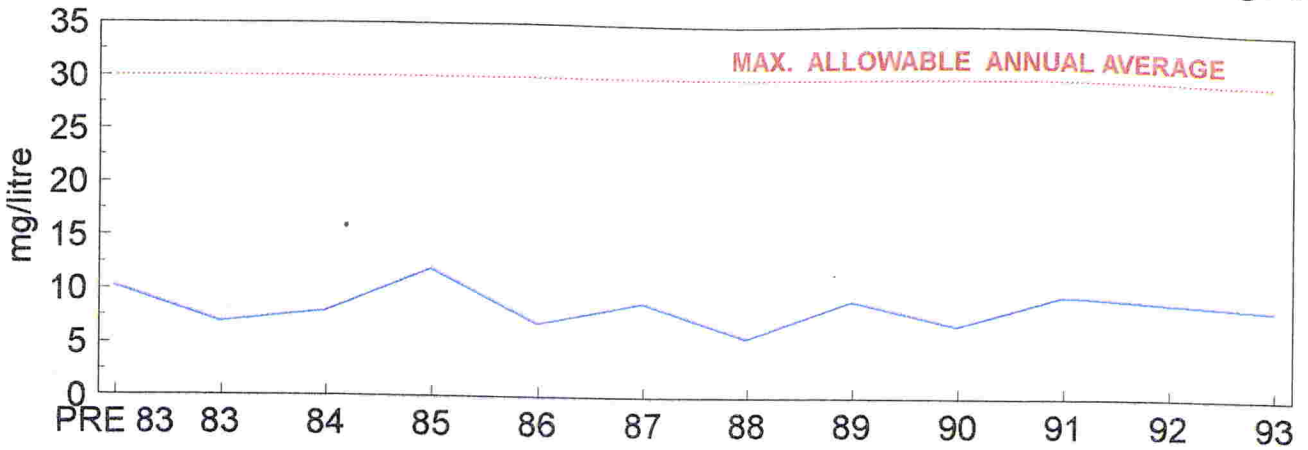
Discharge Fluoride Concentrations  
Annual Averages



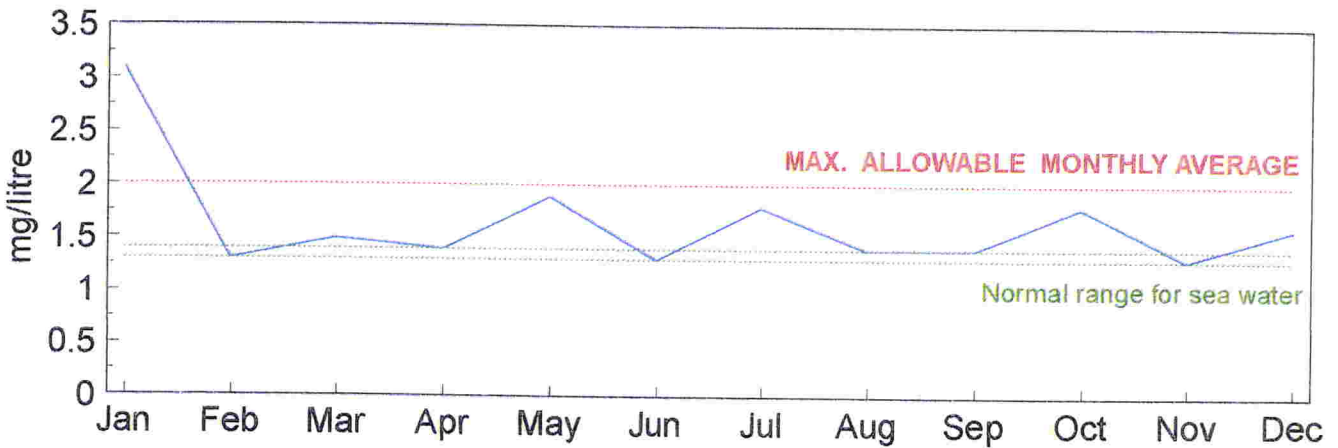
Discharge Suspended Solids Concentrations  
1993 Monthly Averages



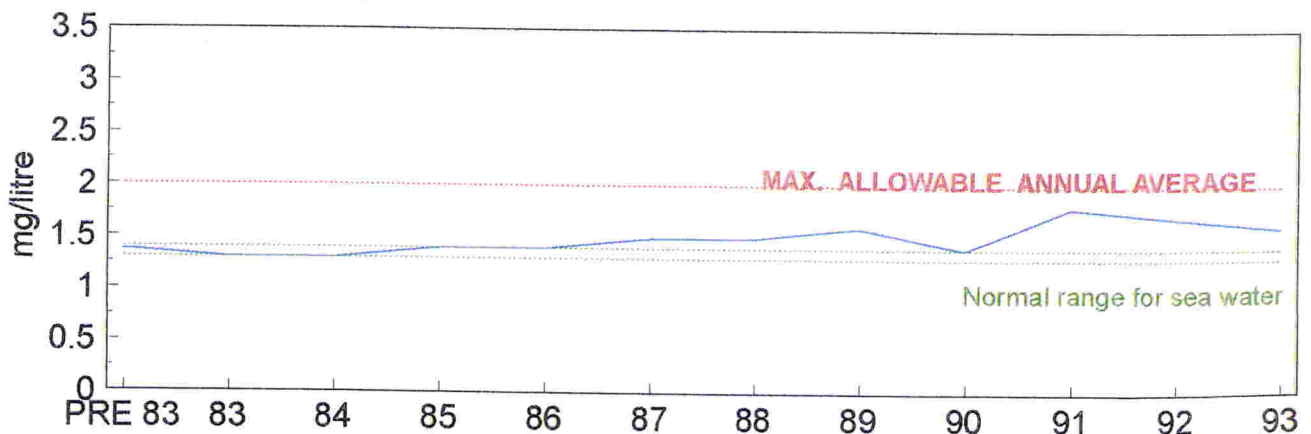
**Discharge Suspended Solids Concentrations  
Annual Averages**



**Receiving Water Fluoride Concentrations  
1993 Monthly Averages**



**Annual Averages**

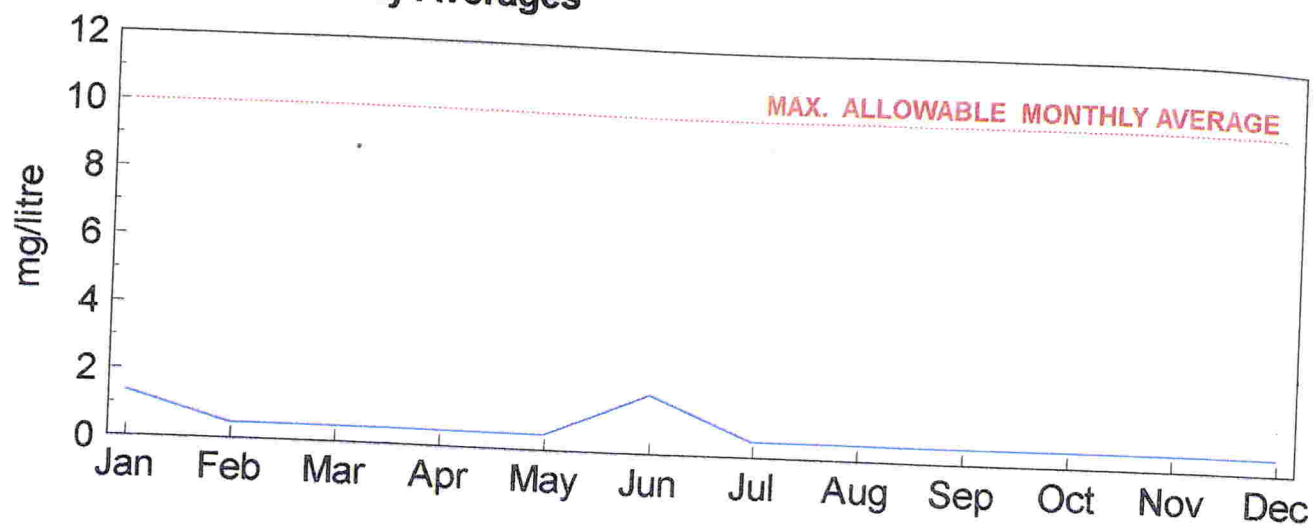


The discharge fluoride concentration permit condition for the North drain was exceeded in January and June during 1993. The receiving water fluoride concentration permit condition was also exceeded in January. The factors contributing to these incidents have been discussed in previous reports. Continuous flow data coupled with meteorological data have been collected throughout 1993 from all three site drains. This information, along with routine monitoring data and data collected from other investigations has now been forwarded to a consultant. Once NZAS is satisfied the consultant has recommended effective, long term solutions to this problem, a decision to proceed with the implementation of these solutions will be taken.

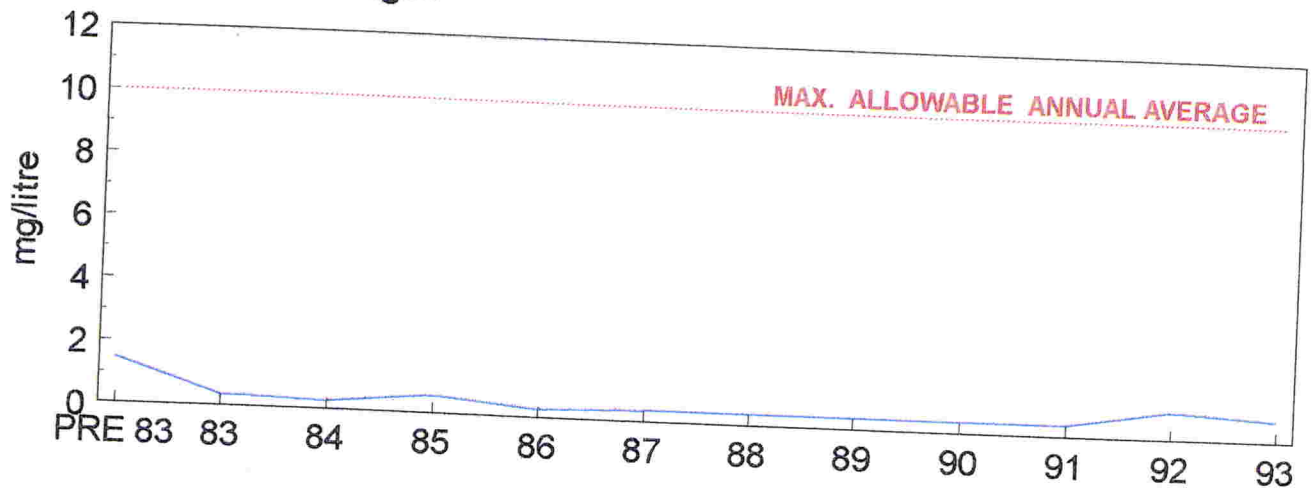
**4.2 COASTAL PERMIT No 90058 - WEST DRAIN**

**Discharge Fluoride Concentrations**

**1993 Monthly Averages**

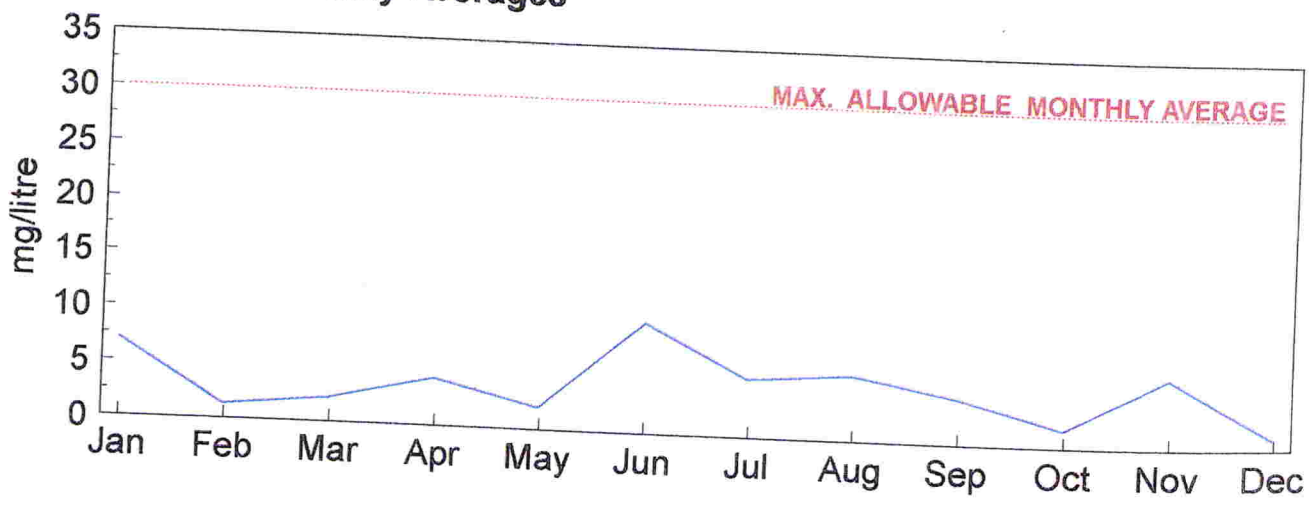


**Annual Averages**



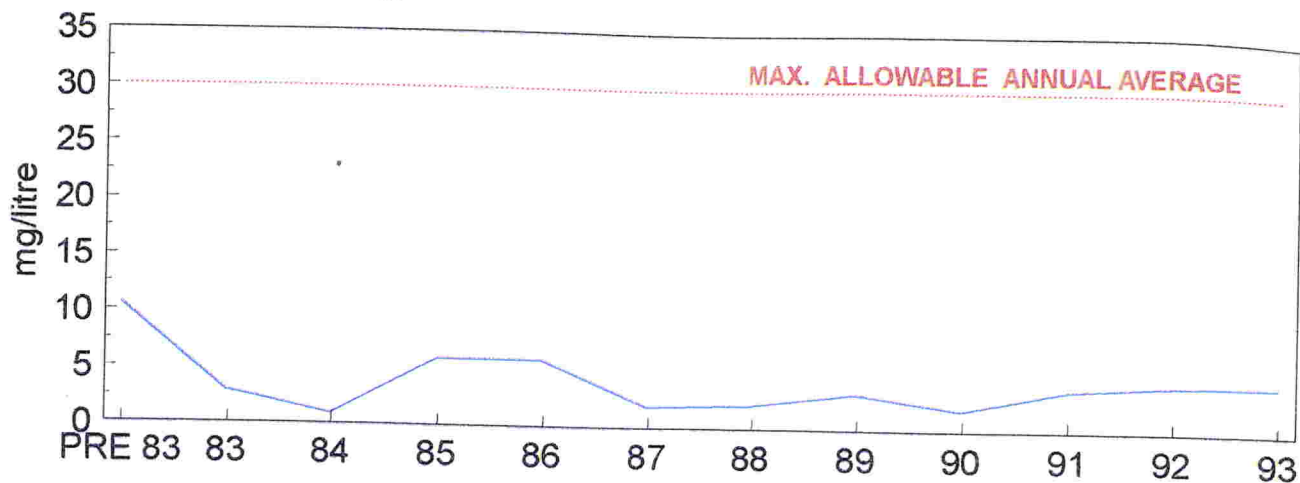
**Discharge Suspended Solids Concentrations**

**1993 Monthly Averages**

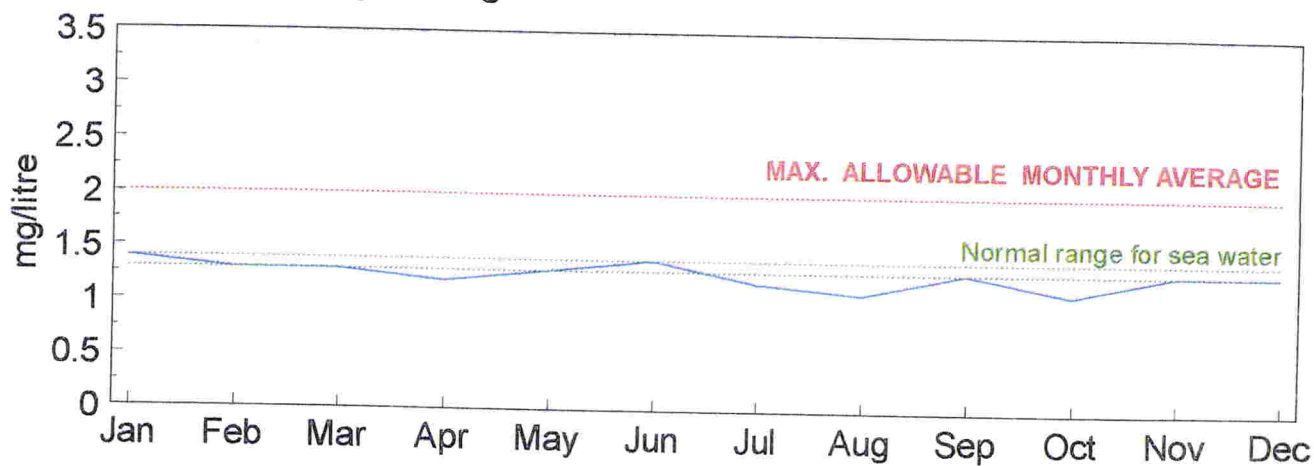




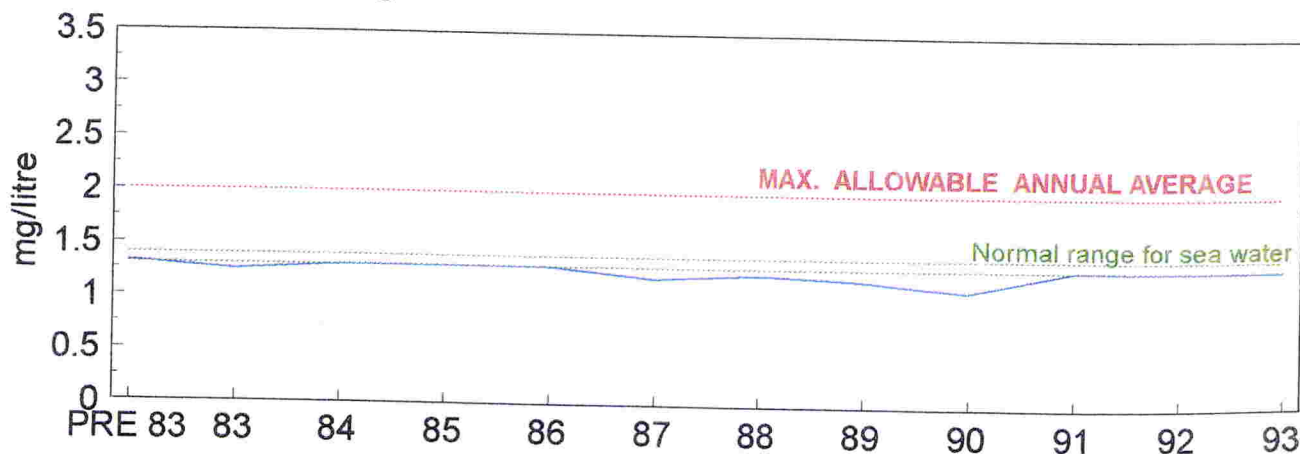
### Discharge Suspended Solids Concentrations Annual Averages



### Receiving Water Fluoride Concentrations 1993 Monthly Averages

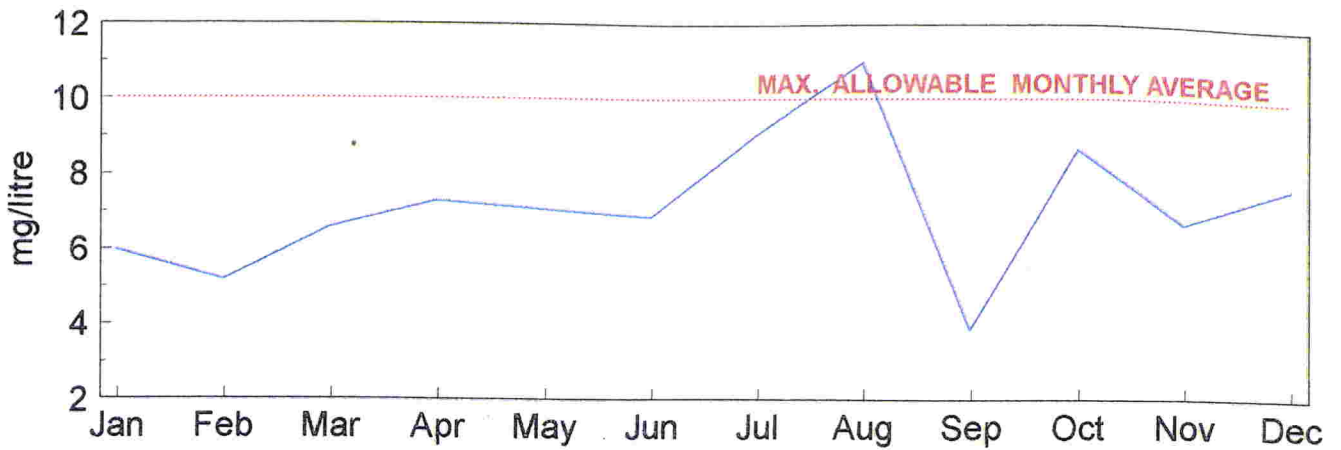


### Receiving Water Fluoride Concentrations Annual Averages

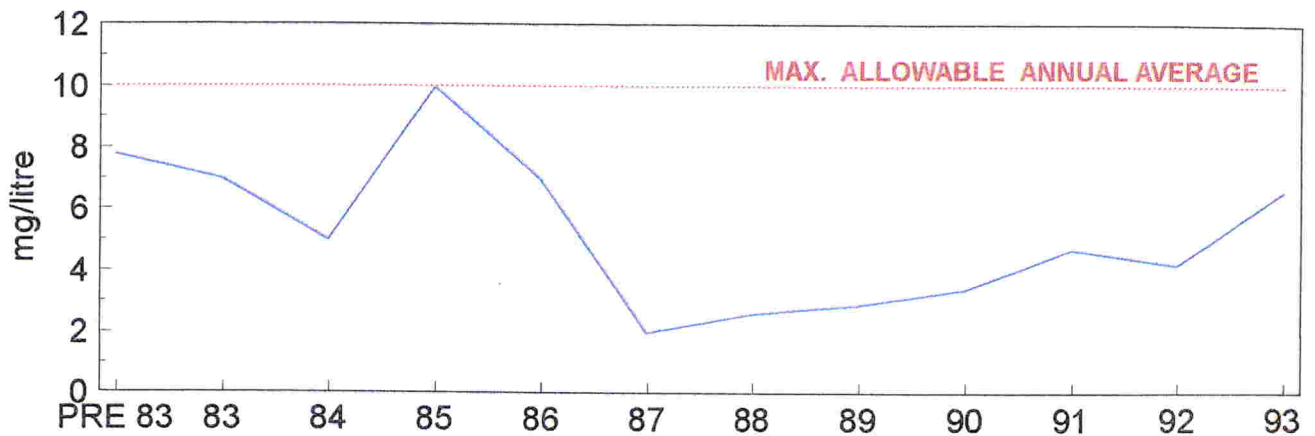


All the measured parameters in the West drain's discharges and receiving water are stable and within the permit conditions.

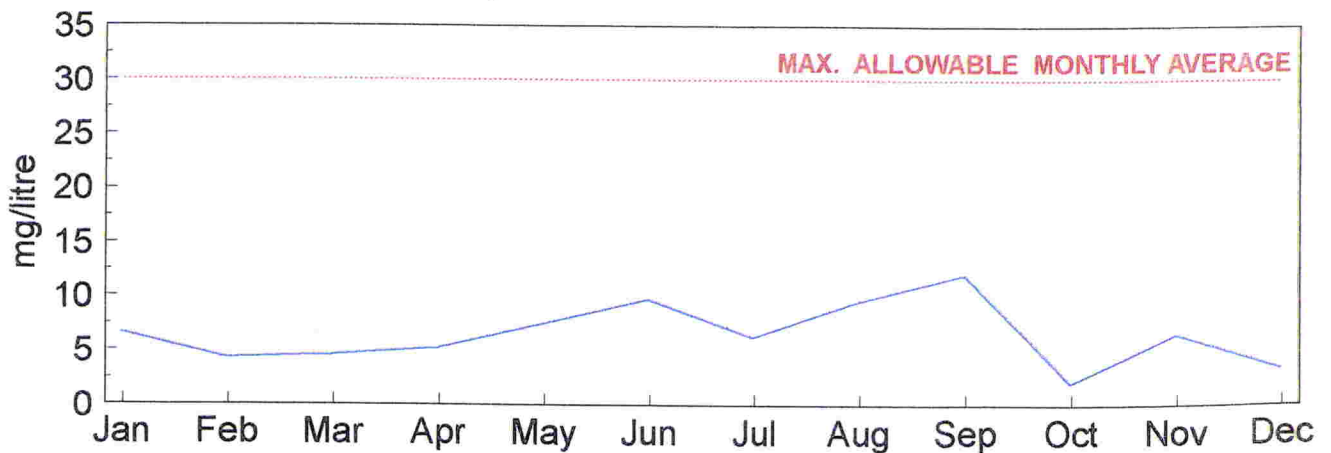
**Discharge Fluoride Concentrations  
1993 Monthly Averages**



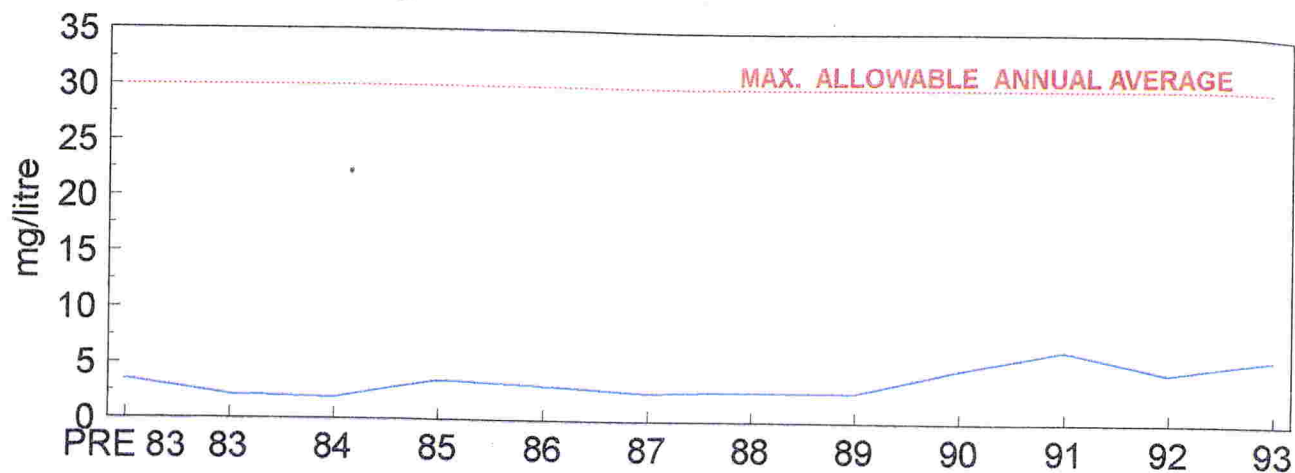
**Annual Averages**



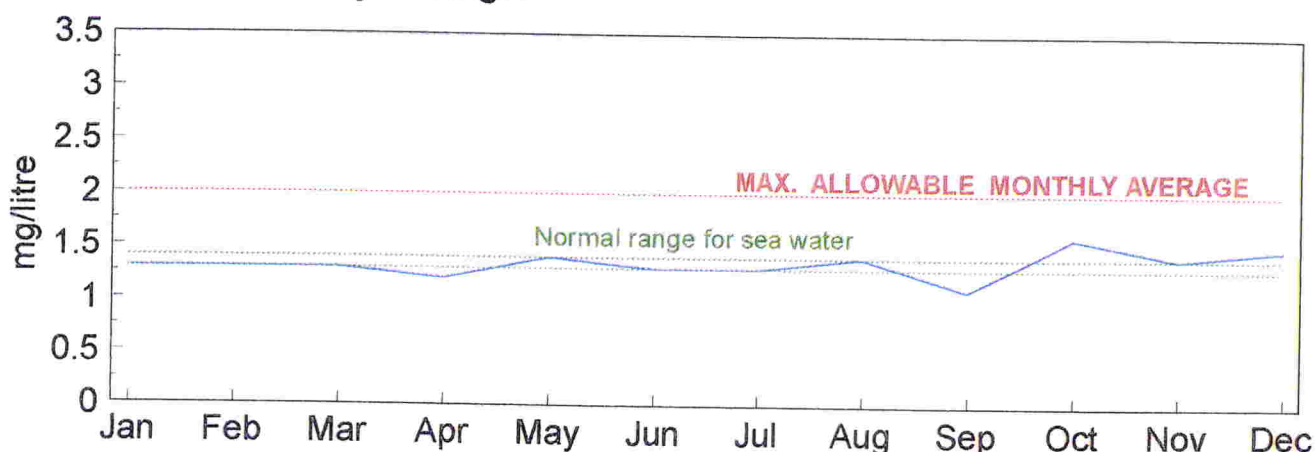
**Discharge Suspended Solids Concentrations  
1993 Monthly Averages**



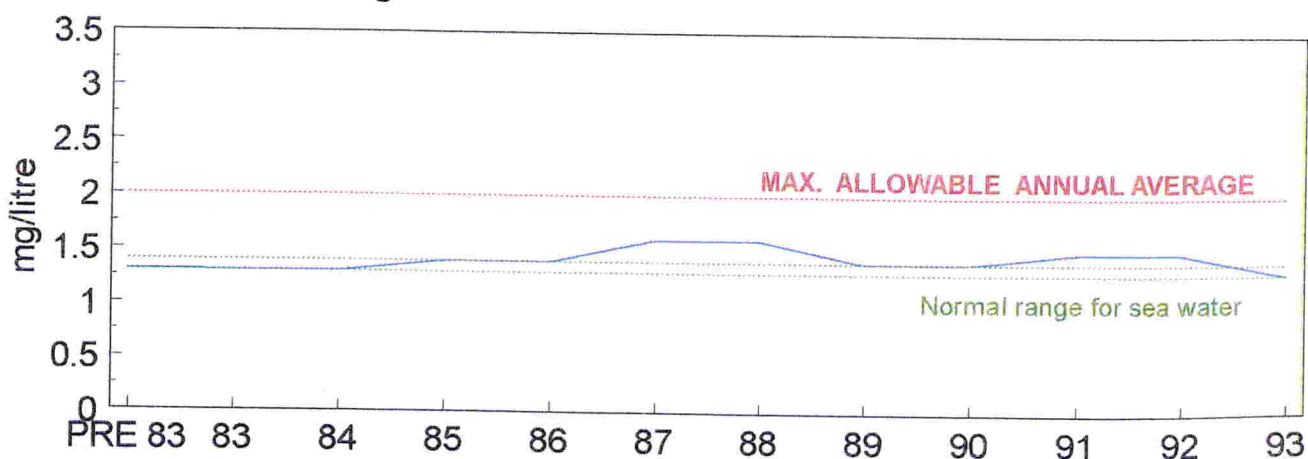
### Discharge Suspended Solids Concentrations Annual Averages



### Receiving Water Fluoride Concentrations 1993 Monthly Averages



### Annual Averages



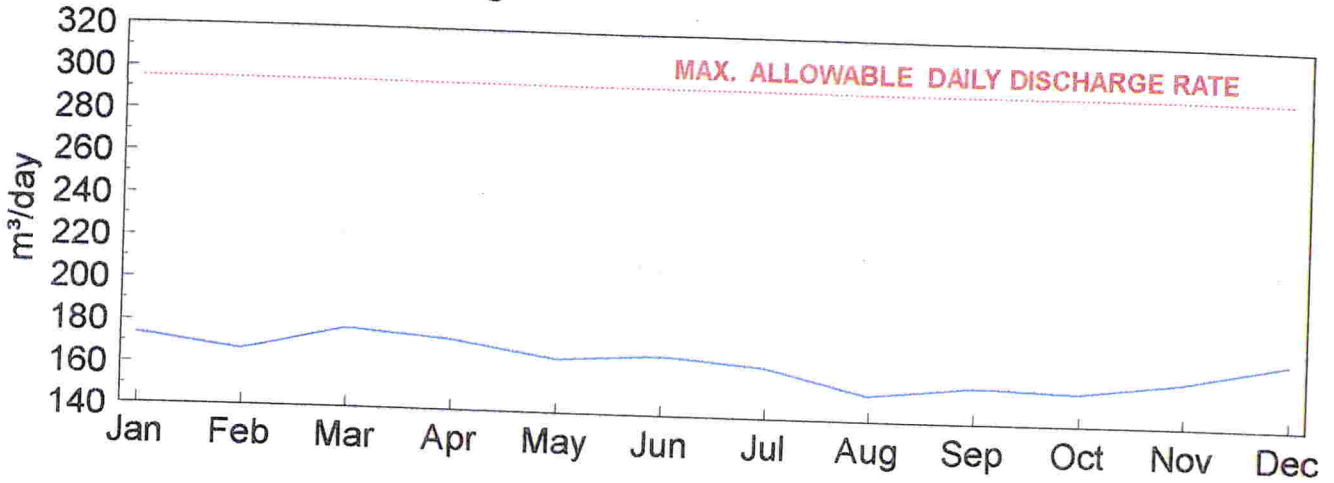
The catchment of the South drain is the metal storage yard, the southern side of Potrooms and the Metal Product's roof and cooling water systems. Because of this catchment's proximity to Potrooms any stormwater runoff will contain fluorides from fugitive dusts and gaseous discharges. In the past this has been diluted by significant volumes of fresh water from Metal Products cooling water system. There is now very little overflow from this cooling water system entering the South drain. This has reduced the flow in this drain to the point where there is, at times, no discharge during periods of dry weather. This lack of flow meant that in August 1993 discharge samples

could only be collected on two occasions. The August result and the apparent upward trend in the discharge fluoride concentration should therefore be interpreted as a measure of the reduction in overall volume discharged, not an increase in the mass of fluoride being discharged. This is supported by the lack of a similar trend in the receiving waters fluoride concentration. This issue is also being reviewed by the company's consultant. Page 50

#### 4.4 COASTAL PERMIT No 90060 - SEWAGE PLANT

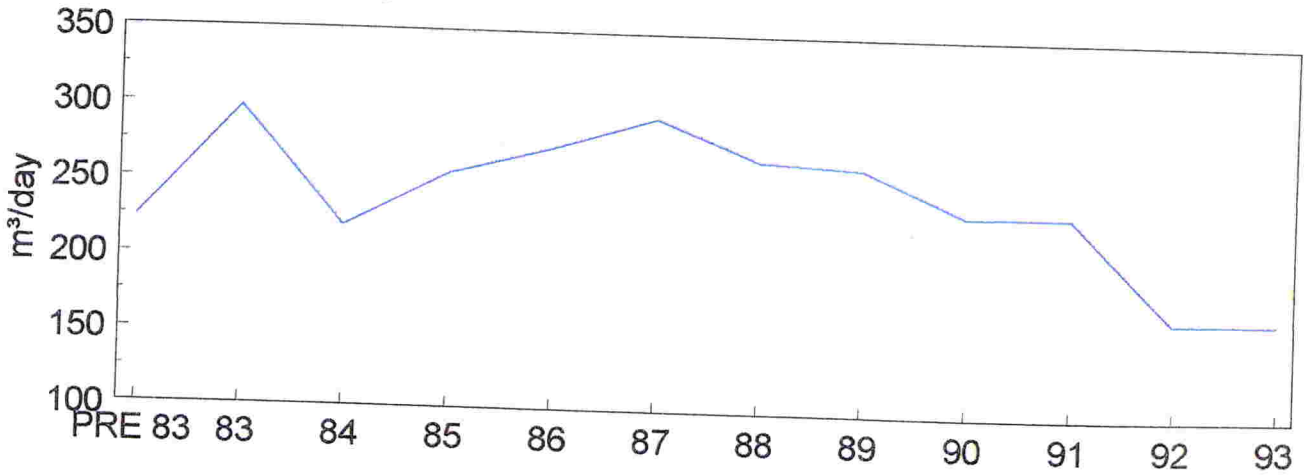
##### Flow Rates

##### 1993 Monthly Averages



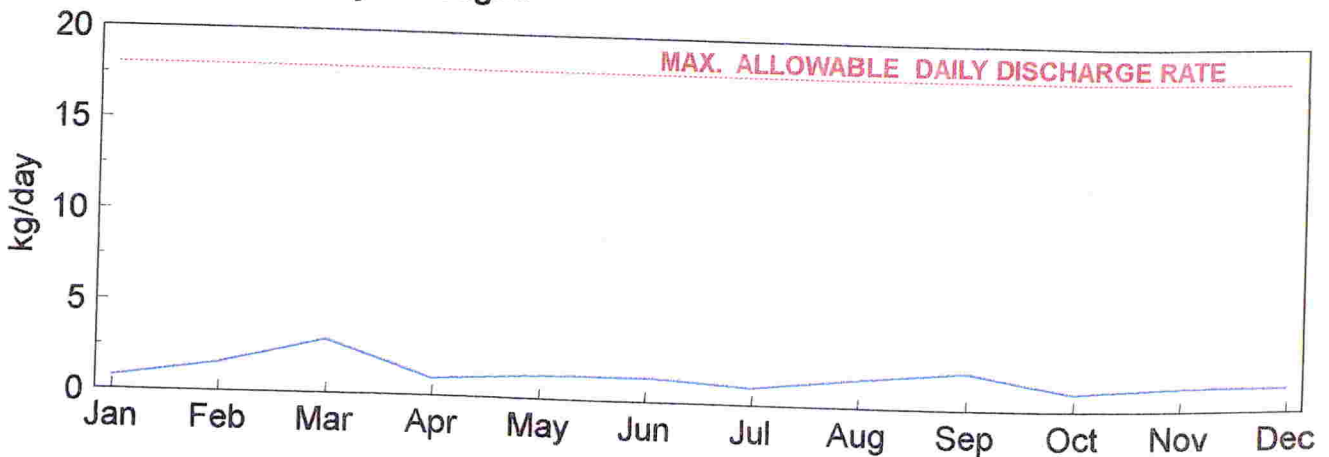
##### Flow Rates

##### Annual Averages



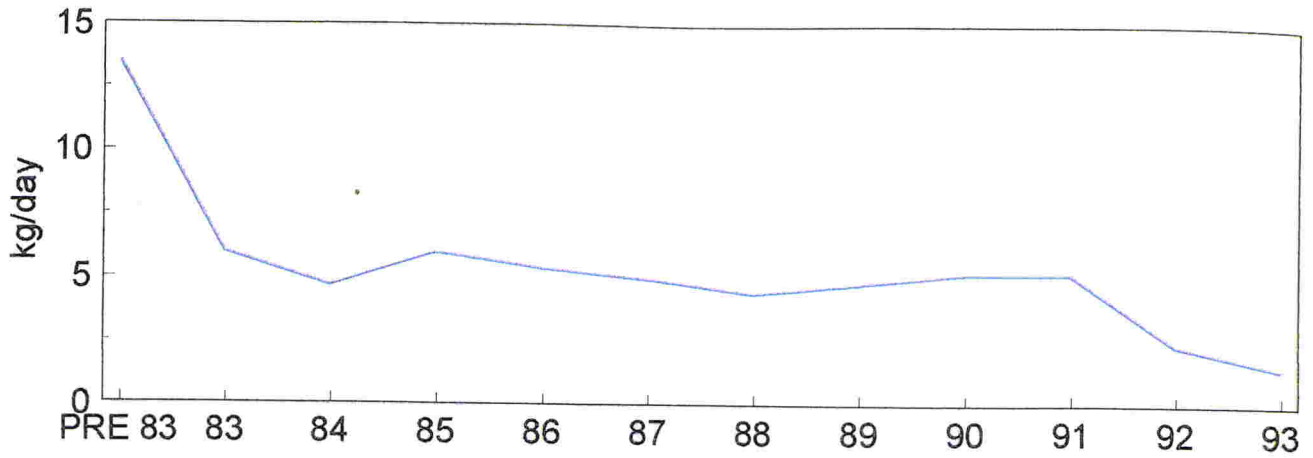
##### BOD Discharges

##### 1993 Monthly Averages

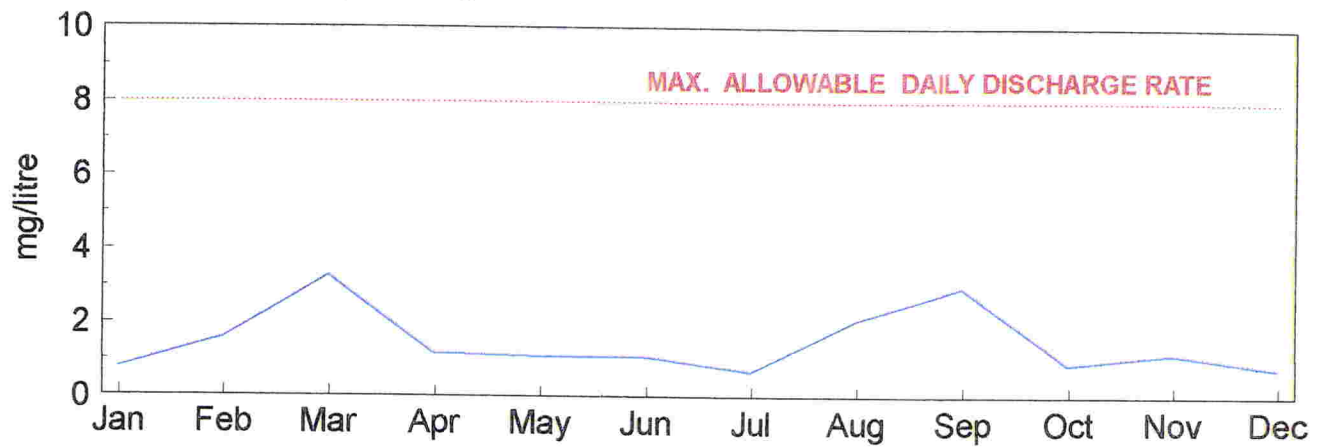




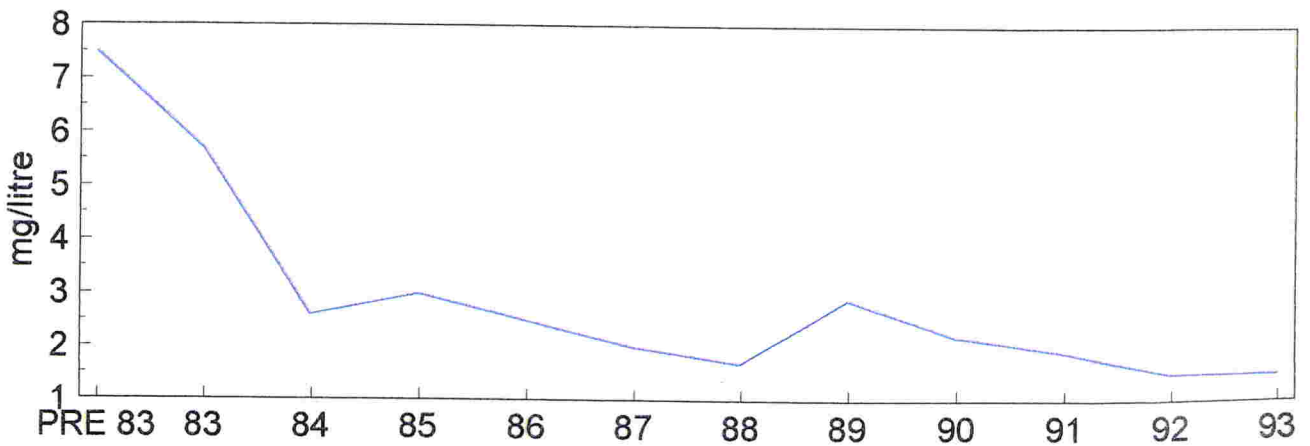
**BOD Discharges**  
**Annual Averages**



**Suspended Solids**  
**1993 Monthly Averages**



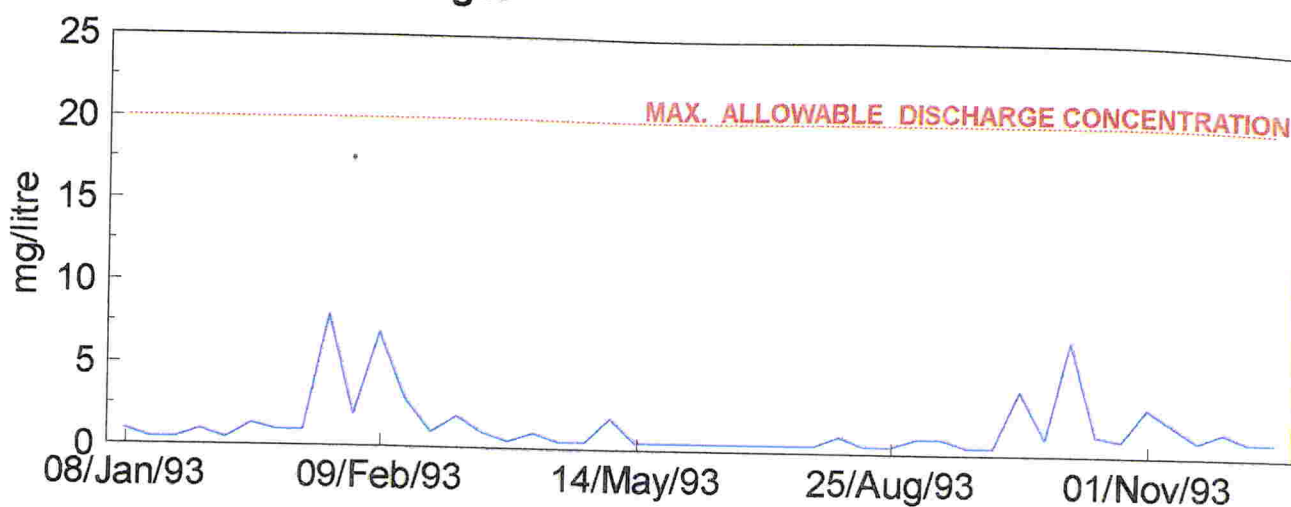
**Annual Averages**



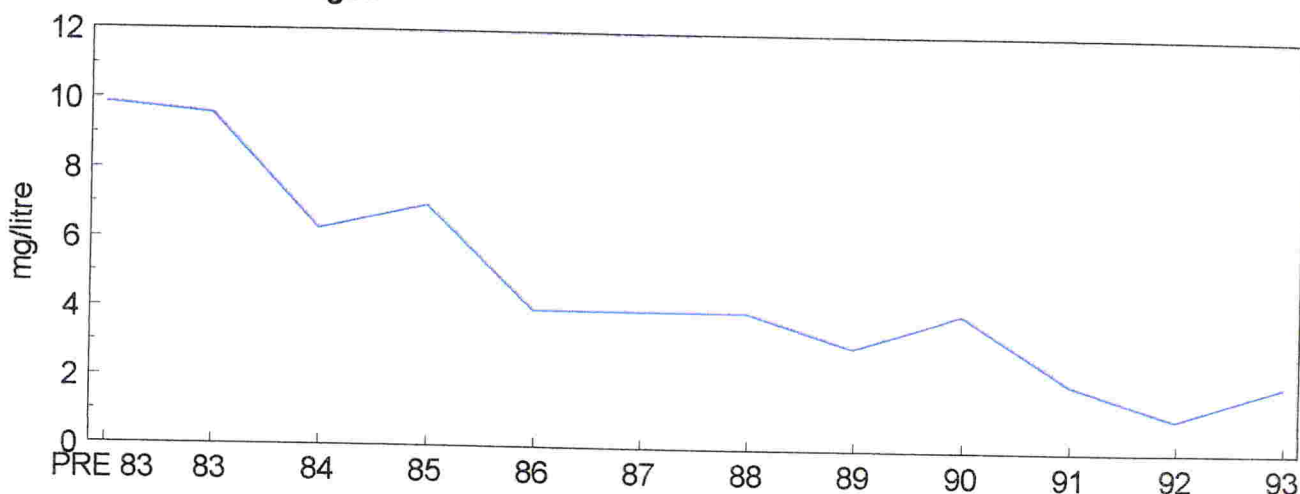
The reduction in volume and the improvements in the quality of the effluent achieved in 1992 were sustained in 1993. All permit conditions were met.

**4.5 COASTAL PERMIT No 90061 -  
SPENT CATHODE LEACHATE**

**4.5.1 Discharge Free Cyanide Concentrations  
All 1993 Discharges**

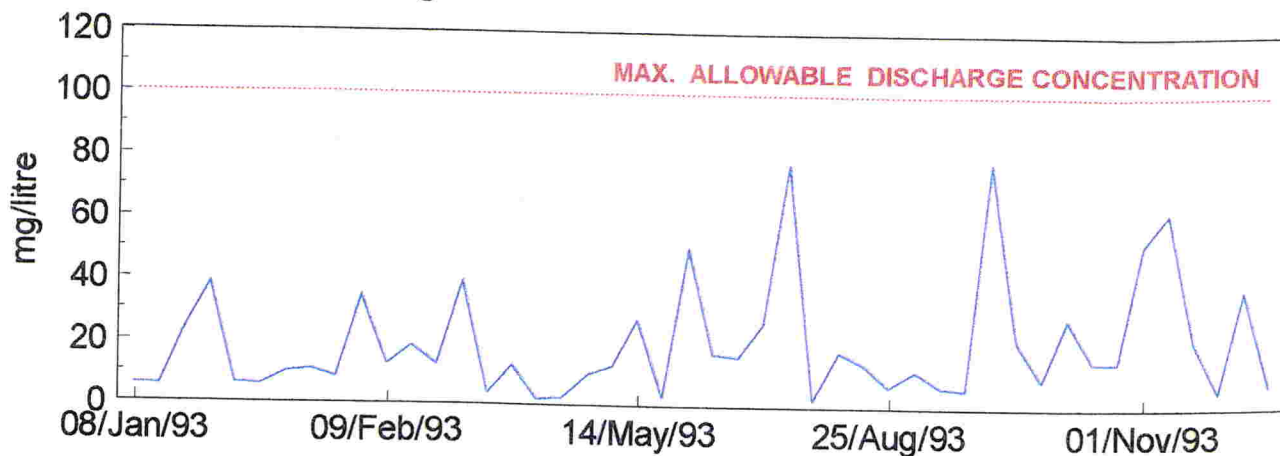


**Annual Averages**



The treatment of Spent Cathode Leachate (SCL) continues to produce an effluent with a very low concentration of free cyanide. Work was undertaken during 1993 to refine this treatment process. The object of this work was to produce the same quality of effluent but reduce the amount of chlorine producing reagent used. This work continues.

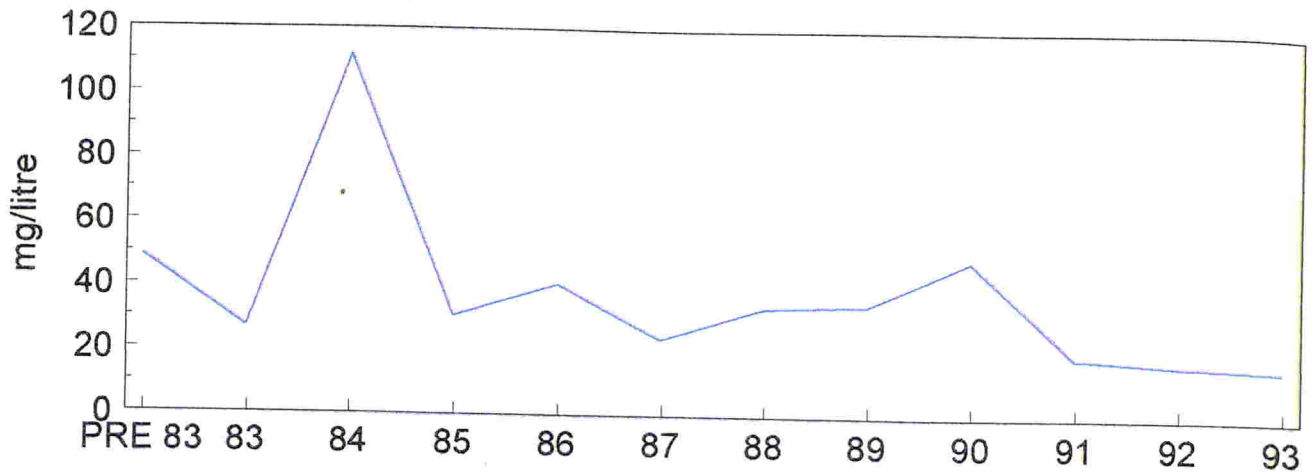
**4.5.2 Discharge Suspended Solids Concentrations  
All 1993 Discharges**





## 4.5.2 Discharge Suspended Solids Concentrations

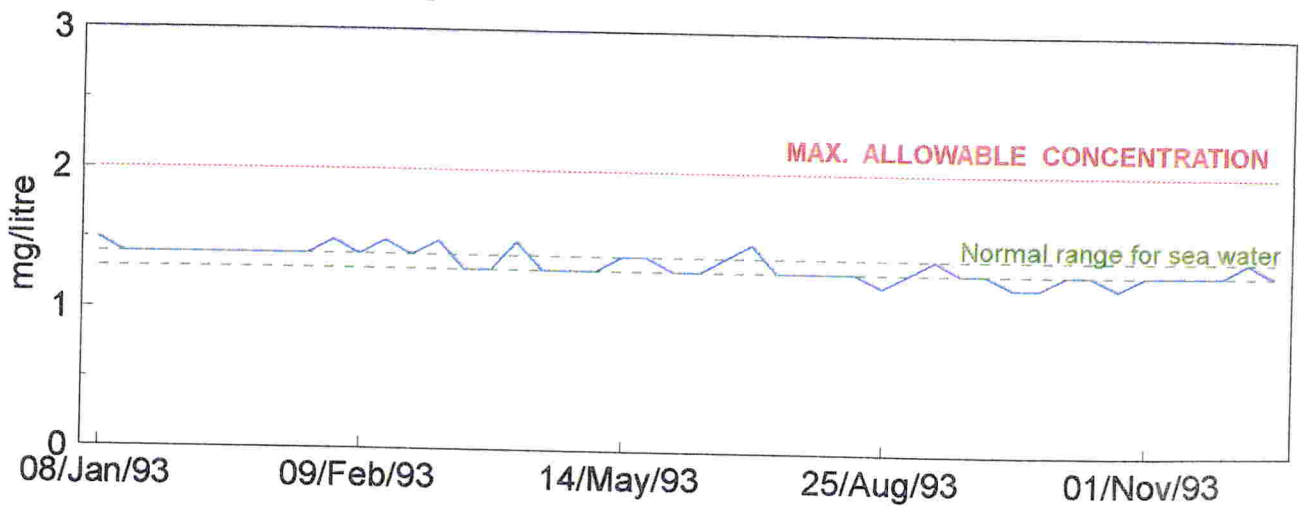
### Annual Averages



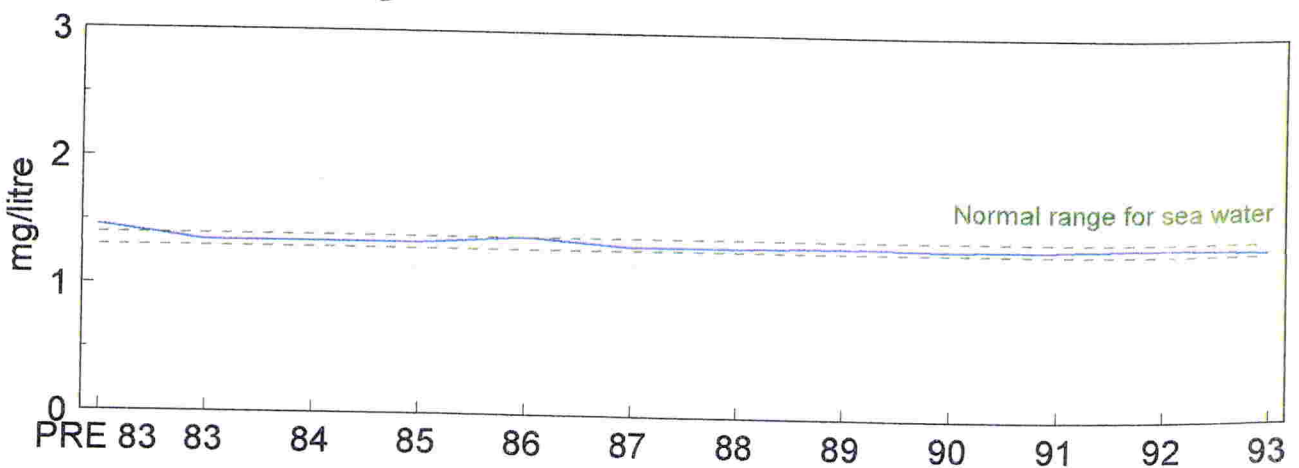
The reduced volume of leachate generated since the capping of the existing pad meant there were only 46 discharges during 1993. This compares with 90 in 1992 and 127 in 1991. Compliance with all permit conditions pertaining to the quality and quantity of the discharge was maintained for all 1993 discharges.

## 4.5.3 Receiving Water Fluoride Concentrations

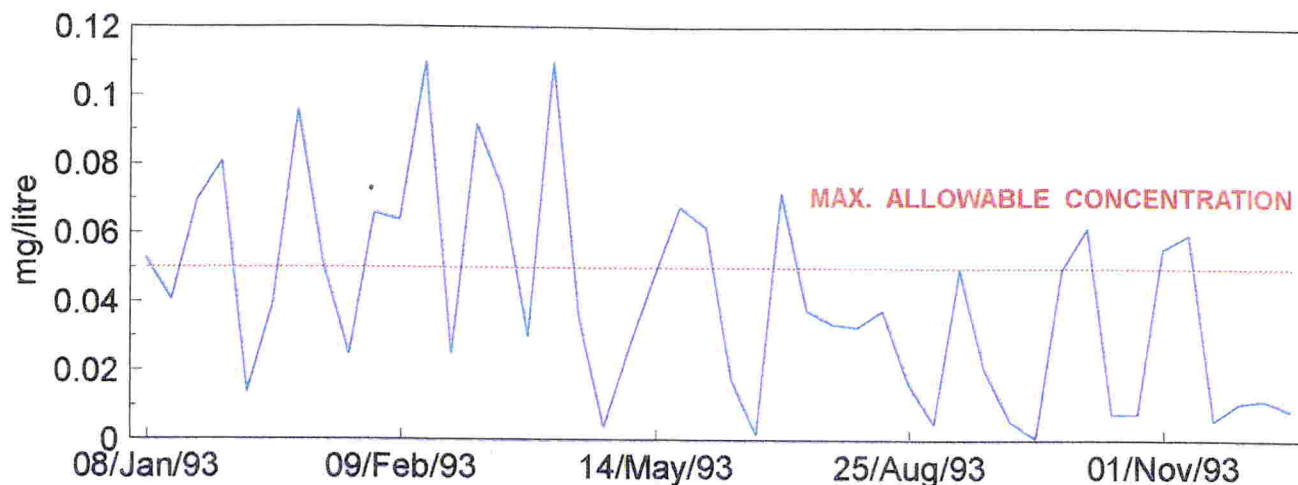
### All 1993 Discharges



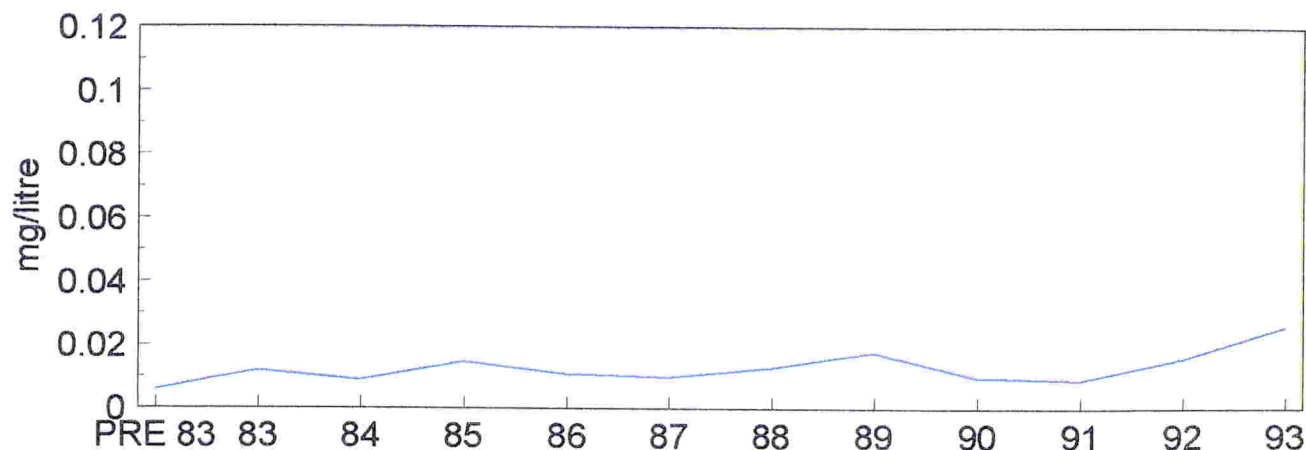
### Annual Averages



**All 1993 Discharges**



**Annual Averages**



The apparent upward trend in the 1993 annual average receiving water total cyanide is the result of a change of procedure rather than a change in the condition of the environment. A revised receiving water sampling protocol (ref. IDC report 1992) operated for the first full year. This calls for the receiving water sample to be collected shortly after low tide. This has two effects. Firstly, this is when the discharging effluent concentration in the receiving sea water is at its predicted maximum. Secondly, and more importantly, there is a groundwater discharge zone at or just below the low tide mark. Sampling at this stage of the tide ensures the concentration of this material is also at its maximum. This is considered the source of the cyanide measured and these samples serve to routinely monitor the quality of this discharge. No trends are evident.

### **5.1 Spent Cathode Leachate**

The investigation into the effects and mitigation of the leakage of spent cathode leachate into the aquifer at NZAS continued through 1993. The main components of the investigation were:

- confirming the discharge of contaminated groundwater into the sea,
- developing in situ bioremediation options, and
- developing pump and treat options.

The investigation has confirmed that contaminated groundwater is being discharged into Foveaux Strait adjacent to the Spent Cathode Pad. There are two zones of contamination, one at or just below the low tide mark and a second approximately 60 metres offshore. As expected the discharge rate relative to the movement of the sea water is small and there is rapid dilution.

Pilot scale trials of an in situ bioremediation process known as a biocurtain have shown that cyanide concentrations in the upper part of the aquifer can be reduced. Free cyanide, if present, can be reduced by 90% or greater. Complexed cyanide concentration can be reduced by up to 40%. Unfortunately it now appears that achieving these levels of reduction may require the disturbance of a strip of coastal dune in excess of 20 metres wide by 200 to 300 metres long.

A dense plume of leachate rich groundwater has been located at the bottom of the fine sand layer of the aquifer, 20 metres below ground level. This dense plume is approximately one metre thick. Trials will continue in 1994 to establish the viability of selectively removing this material for treatment prior to discharge to Foveaux Strait.

### **5.2 Diesel Leak**

The active recovery of diesel from the aquifer under the NZAS site ceased in August. At that time the rate of recovery had dropped to less than 20 litres/day. The total volume of diesel recovered from the aquifer was 523,000 litres. The diesel recovery will be restarted in February 1994 to determine if time or changed circumstances have made more free diesel available for recovery.

The installation of the bioremediation plant was completed and commissioned in June 1993. The trial area is under the metal storage yard. The trial is to determine the best means of delivering nutrients and oxygen to the naturally occurring diesel degrading bacteria. Once the most effective method has been determined the bioremediation will be expanded to include the entire area of the spill.