

UNIVERSITY OF CALGARY

A Multiple-Isotope Approach to Tracing Natural Gas Processing Emissions

by

Carole Erin Bradley

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF CIVIL ENGINEERING

CALGARY, ALBERTA

FEBRUARY, 2005

© Carole Erin Bradley 2005

UNIVERSITY OF CALGARY
FACULTY OF GRADUATE STUDIES

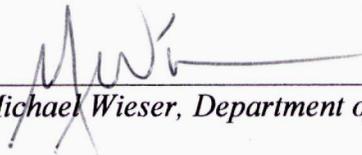
The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "A Multiple-Isotope Approach to Tracing Natural Gas Processing Emissions" submitted by Carole Erin Bradley in partial fulfilment of the requirements for the degree Master of Science.



Supervisor, Dr. Angus Chu, Department of Civil Engineering



Dr. Ann-Lise Norman, Department of Physics and Astronomy



Dr. Michael Wieser, Department of Physics and Astronomy



Dr. Ron Goodman, Department of Civil Engineering

2/17/05

Date

Abstract

This thesis explores whether emissions from natural gas processing facilities are isotopically distinct, and if so whether they can be used to identify and apportion emissions downwind. Samples were collected at source, receptor, and control sites in Alberta and British Columbia and analysed for both sulphur and boron isotopes during a series of field campaigns conducted from September 2001 to April 2003 using high-volume samplers. Sulphur dioxide (SO_2) was determined to be the most representative of a given plant at the time of sampling, while sulphate (SO_4^{2-}) appeared to be dominated by a single source, very likely a sour gas plant with SO_2 emissions on the order of $14,000 \text{ m}^3 \text{ day}^{-1}$. Isotopic fractionation as a result of SO_2 oxidation was not observed. It was possible to distinguish between sweet and sour plants and between plants in Alberta and plants in B.C., rather than from all plants individually.

Results of the receptor site samples showed some correlation between both SO_2 and SO_4^{2-} which could indicate that they were mainly emitted from the same sources, although SO_2 was much more variable than SO_4^{2-} . Atmospheric SO_4^{2-} removal may have occurred.

A method for extracting boron by allowing samples to equilibrate with ion-exchange resin was developed. The method was shown to permit the extraction of both boron and sulphate from the same particulate filter without compromising the analysis of either substance. Therefore it may be used for future sampling of boron in gaseous and particulate phases for isotope apportionment studies.

Acknowledgements

There are so very many people who deserve my thanks – my apologies to anyone that I may have missed.

First and foremost, I would like to thank my supervisors, Dr. Ann-Lise Norman and Dr. Angus Chu. I am grateful for the opportunity to have worked with you and I appreciate your guidance over the past few years.

Dr. Michael Wieser, thank you for your time and your enthusiasm, both of which you gave so freely. Thank you also to Dr. Elisabeth Dixon, who was always willing to help.

To those who do or did work in the Isotope Science Lab and the Environmental Science Lab - Jesusa, Nenita, Lili, Steve, Farzin, Dorrie, Ainslie, Tracy, Tiffany, Lindsay, Natasha, Aviv, Tyler – thank you all for the help and the camaraderie. Here's to field trips, filtering, and lab potlucks.

I very much appreciate the patience and generosity of Alan and Zu of Shell Canada, and Jeff and Colin, formerly of Williams Energy. Also, thank you very much to Bill who always came through in a crunch.

Finally, thank you to my family and friends for all of their support and encouragement.

Dedication

To Mom, Dad, and Shawn: Thank you for all of the support (emotional and otherwise), encouragement, and patience. I could not have done this without you.

Table of Contents

Approval Page.....	ii
Abstract	iii
Acknowledgements	iv
Dedication.....	v
Table of Contents.....	vi
List of Tables.....	ix
List of Figures	x
CHAPTER 1: INTRODUCTION AND BACKGROUND	1
1.1 Natural Gas	2
1.1.1 Formation	2
1.1.2 Production & Processing.....	3
1.1.3 Emissions	6
1.2 Aerosols and Atmospheric Chemistry	6
1.3 Isotopes	8
1.4 Mass Spectrometry	11
CHAPTER 2: SAMPLING & ANALYTICAL METHODS	14
2.1 Atmospheric Sampling.....	14
2.2 Sampling procedures.....	14
2.2.1 Blanks.....	17
2.3 Sampling sites.....	19
2.3.1 Control site.....	19
2.3.2 Source sites – Alberta	19
2.3.3 Source sites – British Columbia.....	20
2.3.4 Receptor site.....	21
CHAPTER 3: SULPHUR	23
3.1 Introduction	23
3.2 Sulphur Chemistry	24
3.3 Sulphur Cycle & Atmospheric Chemistry	26
3.3.1 Hydrogen sulphide.....	27
3.3.2 Sulphur dioxide.....	27
3.3.3 Sulphate.....	31
3.4 Sulphur in Natural Gas.....	31
3.5 Sulphur as an Environmental Tracer.....	33
CHAPTER 4: SULPHUR SAMPLING & ANALYSIS	35
4.1 Sulphur dioxide sampling	35
4.1.1 SO₂ filters and sampling procedures.....	35
4.1.2 Blanks.....	38
4.2 Sulphur dioxide and sulphate analysis	39
4.3 Elemental sulphur analysis.....	40

CHAPTER 5: SULPHUR RESULTS & DISCUSSION	41
5.1 Sulphur Capture & Isotopic Fractionation Tests	41
5.2 Sulphur Sources.....	47
5.2.1 Control Site	48
5.2.2 Alberta.....	50
5.2.2.1 <i>SO₂</i>	51
5.2.2.2 <i>SO₄²⁻</i>	54
5.2.2.3 <i>Solid sulphur</i>	56
5.2.2.4 <i>Discussion of emission sources</i>	58
5.2.2.5 <i>Source characterisation</i>	64
5.2.2.6 <i>Source apportionment</i>	66
5.2.3 British Columbia.....	67
5.2.3.1 <i>SO₂</i>	67
5.2.3.2 <i>Solid sulphur</i>	69
5.2.3.3 <i>Discussion of emission sources</i>	70
5.2.3.4 <i>Source apportionment</i>	71
5.2.4 Receptor Site	71
5.2.4.1 <i>Concentration measurements</i>	72
5.2.4.2 <i>$\delta^{34}\text{S}$ measurements</i>	77
5.2.4.3 <i>Discussion of receptor site samples</i>	82
5.2.4.4 <i>Source apportionment</i>	84
5.2.5 Discussion	87
CHAPTER 6: BORON.....	90
6.1 Introduction	90
6.2 Boron chemistry.....	91
6.3 Boron in the atmosphere.....	93
6.4 Boron in fossil fuels.....	96
6.5 Boron as an environmental tracer	98
CHAPTER 7: BORON SAMPLING & ANALYSIS.....	101
7.1 Introduction	101
7.2 Boron-specific sampling concerns.....	101
7.3 Sample Preparation.....	102
7.4 Boron extraction and concentration	103
7.4.1 <i>Resin preparation</i>	104
7.4.2 <i>Sample loading and boron extraction</i>	105
7.4.3 <i>Boron elution</i>	106
7.5 Boron isotope analysis.....	106
7.6 Sample Contamination.....	107
7.6.1 <i>Microwave digestion</i>	109
7.7 Volatilization	111
7.8 Boron Concentration Determination	112

CHAPTER 8: BORON RESULTS & DISCUSSION.....	116
8.1 Boron Method Tests	116
8.1.2 Boron recovery.....	116
8.1.2.1 Resin preparation	116
8.1.2.2 Sample loading and boron extraction	118
8.1.2.3 Boron elution.....	120
8.1.3 Multiple-isotope analysis effects	122
8.1.3.1 Effect of boron extraction on sulphur recovery and isotope analysis .	122
8.1.3.2 Effect of sulphur on boron recovery.....	124
8.1.4 Contamination	125
8.1.4.1 Microwave digestion.....	125
8.2 Boron Samples	127
8.2.1 Boron concentration.....	127
8.2.2 $\delta^{11}\text{B}$ measurements.....	128
8.2.3 Discussion	129
CHAPTER 9: MULTIPLE-ISOTOPE DISCUSSION	131
CHAPTER 10: CONCLUSIONS & RECOMMENDATIONS.....	133
APPENDIX A: SAMPLE LOG.....	138
APPENDIX B: CONTROL SITE MAPS.....	142
REFERENCES	145

List of Tables

Table 3.1 – Major contributors to global atmospheric sulphur budget in 1980	26
Table 5.1 - Sulphur capture and isotopic fractionation test results	43
Table 5.2 – Gas volume processed and % H ₂ S at each Alberta plant	51
Table 5.3 - Average $\Delta\delta^{34}\text{S}_{\text{SO42-}-\text{SO2}}$	58
Table 5.4 - Average $\Delta\delta^{34}\text{S}_{\text{S8-SO42-}}$	59
Table 5.5 – Apportionment of SO ₄ ²⁻ emissions to plants measured and plant 3	61
Table 5.6 – Gas volume processed and % H ₂ S at each B.C. plant	67
Table 5.7 – Source apportionment of SO ₂ measured at receptor site (February 26 – October 25, 2002)	86
Table 6.1 – Main boron species by pH.....	92
Table 7.1 – Microwave digestion, part I.....	110
Table 7.2 – Microwave digestion, part II	110
Table 8.1 – Conditioning rinse method tests	118
Table 8.2 – Extraction time tests	119
Table 8.3 – Resin rinse tests	120
Table 8.4 – Volatility tests.....	121
Table 8.5 – Boron elution tests	121
Table 8.6 – Sulphur recovery and isotope fractionation tests.....	123
Table 8.7 – Boron recovery tests	124
Table 8.8 – Microwave digestion tests	126
Table 8.9 – Boron content of field blanks and samples.....	128
Table 8.10 – $\delta^{11}\text{B}$ values of field blanks and samples	129
Table 9.1 – B / SO ₂ for selected samples	131

List of Figures

Figure 1.1 – Increase of ground temperature with depth.....	3
Figure 2.1a – High-volume air sampler measuring emissions downwind of a gas plant in Alberta	15
Figure 2.1b – High-volume air sampler filter pack	16
Figure 2.2 – Sampling sites in Alberta	20
Figure 2.3 – Sampling sites in British Columbia.....	21
Figure 4.1 – Apparatus to test SO ₂ capture efficiency and sulphur isotope fractionation. (a) Determination of $\delta^{34}\text{S}$ of SO ₂ . (b) Determination of capture efficiency and fractionation of cellulose filters.....	38
Figure 5.1 - $\delta^{34}\text{S}$ of each filter over the range of flow rates	44
Figure 5.2 – Sulphur recovery as a function of flow rate	45
Figure 5.3a - Sulphur concentration of control site samples over sampling period	49
Figure 5.3b - $\delta^{34}\text{S}$ of control site samples over sampling period	50
Figure 5.4a – Concentration of sulphur in SO ₂ emissions at gas plants in Alberta.....	52
Figure 5.4b - $\delta^{34}\text{S}$ values of SO ₂ emissions at gas plants in Alberta	53
Figure 5.4c – Concentration of sulphur in SO ₄ ²⁻ emissions at gas plants in Alberta.....	55
Figure 5.4d - $\delta^{34}\text{S}$ values of SO ₄ ²⁻ emissions at gas plants in Alberta.....	56
Figure 5.4e - $\delta^{34}\text{S}$ values of solid sulphur from gas plants in Alberta.....	57
Figure 5.5a - $\delta^{34}\text{S}$ values of sulphate and solid sulphur from gas plants in Alberta.....	59
Figure 5.5b - $\Delta\delta^{34}\text{S}_{\text{S8-SO4}2-}$ versus inlet H ₂ S.....	62
Figure 5.5c - $\Delta\delta^{34}\text{S}_{\text{S8-SO4}2-}$ versus sulphur recovery	63
Figure 5.5d - $\Delta\delta^{34}\text{S}_{\text{S8-SO4}2-}$ versus inlet gas volume	63
Figure 5.6 - $\delta^{34}\text{S}$ versus inverse sulphur concentration	66
Figure 5.7a- Concentration of sulphur in SO ₂ emissions at gas plants in B.C.	68
Figure 5.7b - $\delta^{34}\text{S}$ values of SO ₂ emissions at gas plants in B.C.....	69
Figure 5.7c - $\delta^{34}\text{S}$ values of solid sulphur from gas plants in B.C.	70
Figure 5.8a – Sulphur concentration of receptor site samples over sampling period.....	72
Figure 5.8b – SO ₂ vs. SO ₄ ²⁻ concentration (February 26 to October 25, 2002)	73
Figure 5.8c –Sulphur concentration of receptor site samples versus average temperature (February 26 - October 25, 2002).....	74
Figure 5.8d –Sulphur concentration of receptor site samples versus relative humidity (February 26 to October 25, 2002)	75
Figure 5.8e –Sulphur concentration of receptor site samples as a function of wind direction (February 26 - October 25, 2002).....	76
Figure 5.8f –Sulphur concentration of receptor site samples as a function of wind speed (February 26 - October 25, 2002).....	77
Figure 5.9a – $\delta^{34}\text{S}$ of receptor site samples over sampling period	78
Figure 5.9b – $\delta^{34}\text{S}$ of receptor site samples versus temperature (February 26 - October 25, 2002).....	79
Figure 5.9c – $\delta^{34}\text{S}$ of receptor site samples versus relative humidity (February 26 - October 25, 2002)	81
Figure 5.9d – $\delta^{34}\text{S}$ of receptor site samples versus average wind speed	82

Figure 5.10 - $\Delta\delta^{34}\text{S}_{\text{SO}_4\text{-SO}_2}$ of receptor site samples	83
Figure 5.11 - $\Delta\delta^{34}\text{S}_{\text{SO}_4\text{-SO}_2}$ versus average temperature (Feb 26 to Sep 12, 2002).....	83
Figure 5.12 - $\Delta\delta^{34}\text{S}_{\text{SO}_4\text{-SO}_2}$ versus $\text{SO}_2 \delta^{34}\text{S}$	84

CHAPTER 1: INTRODUCTION AND BACKGROUND

Alberta, one of Canada's western provinces, is rich in fossil fuels, and the natural gas industry is a key contributor to the province's strong economy. Gas wells and processing plants may be found throughout much of Alberta, along with all of the problems that accompany such operations. Foremost among environmental and public concerns is the emission of large amounts of gaseous pollutants as a result of planned and / or emergency flaring, sulphur incineration, and in the course of normal operation.

Much of the natural gas and associated pollutants emitted to the atmosphere during production and processing is already well-documented and reported to Alberta Environment (AEnv) and / or the Alberta Energy and Utilities Board (AEUB). However, in light of the possible ratification of the Kyoto Protocol and the degrandfathering of Alberta's sour gas plants, it is apparent that regulations and reporting will only become more stringent. Therefore, it is of particular importance that the industry continually improves the management of emissions and that the tools to do so become accordingly more sophisticated.

Since many gas plants often contribute to the same air shed, it is not possible to conclusively determine the sources, amounts, and characteristics of pollution from a particular processing facility using traditional methods. However, multiple isotope studies have successfully characterized atmospheric sulphur and lead isotope ratios in China (Mukai *et al.*, 2001), and both sulphur and carbon isotopes have been used to distinguish the origins of crude oil imports in Germany (Becker and Hirner, 1998).

In this thesis, samples were collected at natural gas processing plants and receptor and control sites in Alberta and British Columbia, Canada and analysed for both sulphur

and boron isotopes. We will explore whether emissions are sufficiently distinct isotopically, and if so whether isotopic compositions can be used to identify and apportion emissions downwind. Potentially, the results of this study could lead to improved dispersion modeling validation, pollution tracking, and regulatory control. Furthermore, a method such as this could easily be adapted to include other industries, in particular refining and coal-fired power plants.

1.1 Natural Gas

Natural gas consists primarily of methane (CH_4), with smaller fractions of increasingly heavier hydrocarbons as well as carbon dioxide (CO_2), hydrogen sulphide (H_2S), and various contaminants including carbonyl sulphide (COS), carbon disulphide (CS_2), and mercaptans (RSH). The gas is considered to be sour if it is composed of 1% or more H_2S , although a well or gas processing facility is defined as sour if the gas contains more than 0.001% H_2S (Petroleum Communication Foundation, 2000). Otherwise, the gas is sweet.

1.1.1 Formation

It is widely held that fossil fuels – solid, liquid, and gaseous – have organic origins. Microscopic plants and animals were deposited on the bottom of ancient seas, where they accumulated in layers that became buried deeper and deeper and were gradually converted into hydrocarbons as a result of increased pressures and temperatures, as well as chemical and bacterial processes (Petroleum Resources Communication Foundation, 1989).

Aerobic and anaerobic bacterial action destroyed the organic matter in the upper 12 metres (m) of sediment, but ceased below that depth (Link, 1982). It has been shown that temperatures required to produce oil occur between 1,500 and 6,100 m, while temperatures below 6,100 m generally produce gas. Above 1,500 m, the crust is too cool to generate either oil or gas (Link, 1982). As shown in figure 1.1, the average temperature of the earth increases between 15 and 30 °C for every 1,000 m of depth, although locally the gradient may vary (Canadian Geothermal Energy Association, 2005).

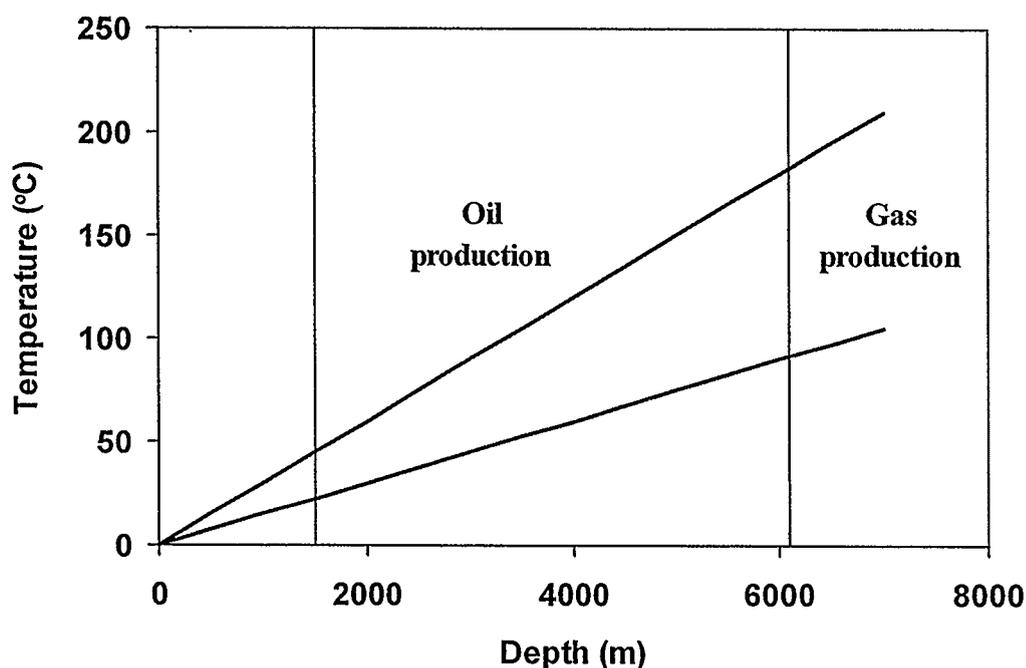


Figure 1.1 – Increase of ground temperature with depth

1.1.2 Production & Processing

Natural gas is extracted from reservoirs through wells, which are connected to processing plants through a network of pipelines. Depending on the size, age, and characteristics of the field, as well as the distance from the plant, there may be one or

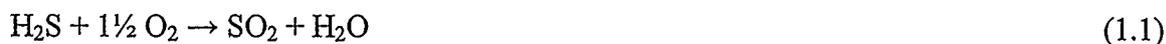
more compressor stations that are used to boost gas pressure for transport as well as to help recover gas from the well.

In a typical plant, raw gas enters as a mixture of gas and liquid. The pressure of the gas is reduced when it enters a vessel known as a separator, which causes the liquids to condense and separate from the gas. The liquids are sold as condensate, while the gas is dehydrated and sweetened.

Sweetening, the process of removing acid gas (CO_2 and H_2S) from the gas stream, may be accomplished through liquid chemical solvents (regenerative and non-regenerative), physical solvents, chemical / physical solvents, solid gas treating processes (chemical and physical), membrane processes, and direct conversion processes (Holub and Sheilan, 2000). Although the choice of method depends on many factors such as regulatory requirements and the volume and composition of gas to be processed, the most common process in use in gas processing plants in Alberta involves methyldiethanolamine (MDEA), which is a regenerative liquid chemical solvent that removes acid gas through a reversible chemical reaction. MDEA is attractive for its ability to selectively remove H_2S from a stream containing both H_2S and CO_2 ; almost complete H_2S removal is achieved while CO_2 content is optimized for sale. It is capable of partially removing other sulphur species such as mercaptans and COS, although a physical solvent better accomplishes this. The products of the sweetening process are sweetened natural gas and an acid gas stream.

The acid gas stream may be flared directly or incinerated at temperatures ranging from 400 to 800 °C, or sent to a sulphur recovery unit. Sulphur recovery typically takes place through the Claus process, where one third of the H_2S in the acid gas is combusted

to SO₂ (reaction 1.1) that is then catalytically reacted with the remainder of the H₂S to produce liquid sulphur (reaction 1.2).



However, this process removes no more than 96 - 97% of the sulphur (Gas Processors Suppliers Association, 1998), and therefore it is generally necessary to further treat the Claus process tail gas. At the very least, it should be incinerated to convert all sulphur species to SO₂, but there are also several tail gas clean-up processes. These processes consist of:

1. continuing the Claus reaction to produce more sulphur,
2. converting all of the sulphur species in the tail gas to SO₂ and recovering the SO₂ for further processing,
3. converting all of the sulphur species in the tail gas to H₂S and recycling the gas to the Claus process, or
4. converting all of the sulphur species in the tail gas to H₂S and directly oxidising the H₂S to sulphur (Gas Processors Suppliers Association, 1998).

Liquid sulphur must be degassed to remove any remaining H₂S. This is accomplished by sparging the liquid sulphur with air or steam or by the addition of a catalyst that will break down H₂S. Any H₂S which is released by the sulphur is recycled to the tail gas cleanup or sulphur removal processes. Finally, it is pumped to either a tank truck or railroad car, to a storage block, or to a sulphur-forming facility.

Although the sweetened gas stream is ready to leave the plant as sales gas, some plants further process the gas in order to remove ethane and heavier hydrocarbons from

the gas. This is typically accomplished by reducing the pressure to chill the gas and condense out liquids, sending the gas to one or more distillation columns to remove the desired components, and then recompressing the gas to the appropriate sales gas pressure (typically 5,500 kPa in Alberta, although this depends upon the pipeline operating pressure).

1.1.3 Emissions

Emissions from gas processing can occur at the well site, en route to the plant, or at the plant itself. Flaring, sulphur incineration, fugitive emissions (e.g. passing valves, leaking flanges) and direct release to the atmosphere are the main sources of emissions. If fugitive emissions and releases occur upstream of gas sweetening or during a plant upset, it is possible that H₂S will be released directly to the atmosphere. Sulphur emitted from incineration is assumed to be virtually 100% sulphur dioxide (SO₂) (Alberta Energy and Utilities Board, 2002) due to the high combustion temperatures that are required for complete destruction of all sulphur species and regulated by AEnv and the AEUB. However, the sulphur emitted from flaring is assumed to be about 98% SO₂, with the remaining 2% H₂S (Alberta Energy and Utilities Board, 2002), although in most cases acid gas flaring only occurs during a process upset.

1.2 Aerosols and Atmospheric Chemistry

Aerosols are defined as relatively stable suspensions of fine liquid and / or solid particles in a gas, which is the atmosphere. They can exist either in the troposphere or the stratosphere, although the material that reaches the stratosphere is mainly limited to volcanic effluvia (Prospero *et al.*, 1983). Aerosols are removed from the atmosphere by

either dry deposition, where particles settle or impact on surfaces (land or water), or wet removal, as rainout and washout.

Whitby (1978) identified three groups of particles: fine particles, which are further broken down into accumulation range and transient or Aitken nuclei range, and coarse particles. As a group, fine particles have diameters less than 2.5 μm : accumulation range particles have diameters between about 0.08 and 2.5 μm and Aitken nuclei particles have diameters between 0.01 and 0.08 μm . Coarse particles have diameters greater than about 2.5 μm . With the advent of improved technology, a fourth particle group has been identified: ultrafine particles are generally defined as having diameters less than 0.01 μm (Finlayson-Pitts and Pitts, 2000).

Fine and coarse particles differ both chemically and physically, and as a result they are formed, transformed, and removed differently with no chance of transformation between the two modes (Prospero *et al.*, 1983). Coarse particles are produced by mechanical processes such as wind-blown dust, sea spray, and plant fragments (Whitby, 1978) and may only be airborne for a few hundred kilometres or so. However, fine particles are mainly formed by gas-to-particle conversion, which can occur through:

1. homogeneous, homomolecular nucleation,
2. homogeneous, heteromolecular nucleation,
3. heterogeneous, heteromolecular condensation (Prospero *et al.*, 1983).

The first two processes involve formation of a new particle, while the third concerns growth of an existing particle. Two other possible pathways for gas-to-particle conversion are the direct reaction of gases with either particles on the surface or in the interior of liquid particles, or catalytic particles (e.g. soot, metals, etc.) within aerosols

(Prospero *et al.*, 1983). Aitken nuclei, of which combustion is a major source, have atmospheric lifetimes that may only last minutes; they will be incorporated into particles in the accumulation mode fairly quickly due to the chemical reactivity and physical mobility of these particles (Prospero *et al.*, 1983).

Once particles have formed, they can act as cloud condensation nuclei (CCN), initiating and enhancing cloud droplet nucleation which changes the optical characteristics of clouds as well as their frequency and duration. Since most clouds undergo a cycle of formation and evaporation many times before forming precipitation, stable particles such as sulphate may pass into and out of clouds as many as 10 times before raining out (Prospero *et al.*, 1983).

Oxidants are a key component of aerosol growth. The most important oxidants in the atmosphere are the hydroxyl radical (OH), ozone (O₃), and hydrogen peroxide (H₂O₂), where both OH and H₂O₂ are photochemical by-products of O₃ (Thompson, 1992). As a result, gas to particle conversion, or aerosol growth through oxidation and condensation onto an existing particle, will often exhibit a diurnal pattern. Furthermore, the difference between the residence time of a particle in the accumulation mode in the troposphere – about 1 week – as compared to the residence time in the stratosphere – months to years – is mainly due to the availability of both water vapour and oxidants (Prospero *et al.*, 1983).

1.3 Isotopes

Any element has a fixed number of protons, but the number of neutrons may vary. This leads to different atomic masses within the same element, and each is known as an

isotope of that element. The isotope composition of a sample (x) is expressed as a ratio of the isotope abundances compared to that of a known standard, in per mil (‰):

$$\delta_x = (R_x / R_{\text{standard}} - 1) \times 1000 \quad (1.1)$$

Isotopes of an element vary in abundance, or fractionate, due to biological, chemical, and physical processes. Fundamentally, isotopic fractionation occurs due to differences in mass. These mass differences lead to differences in molecular energy. Typically, the vibrational, rotational, and translational energies are the only ones considered, and the vibrational energy term is the most important for almost all elements.

By treating the chemical bond between two molecules as a simple harmonic oscillator (SHO), it may be shown that the vibrational frequency is inversely proportional to the square root of the masses:

$$\nu = 1 / 2\pi (k / \mu)^{1/2} \quad (1.2)$$

where ν is the vibrational frequency, k is the spring constant, and μ is the reduced mass $[m_1 m_2 / (m_1 + m_2)]$.

The solution of the Schrödinger equation for a SHO gives:

$$\epsilon_{\text{SHO}} = (1/2 + n) h\nu \quad (1.3)$$

where ϵ_{SHO} is the vibrational energy, n is the energy level, and h is Planck's constant.

The important result of equation 1.3 is that at the lowest energy level ($n = 0$), the value of ϵ_{SHO} is $h\nu/2$ and not 0. This energy is known as the zero point energy (ZPE), and it exists even at absolute zero.

Equations 1.2 and 1.3 show that substitution of a heavy isotope for a light isotope will decrease the vibrational frequency of the molecule and therefore the ZPE as well.

The reduction in ZPE energy means that any substance will have an affinity to

incorporate the heavier isotope due to the resultant reduction in energy of the substance. Furthermore, the heavy isotope will be preferentially incorporated into the substance that will show the greatest reduction in energy due to the substitution.

Substances that incorporate the lighter isotope of an element will have higher vibrational frequencies and higher ZPE compared to the substance with the heavier isotope. The bonds in molecules with higher ZPE are more easily broken.

Stable isotopes undergo equilibrium and non-equilibrium fractionations, the magnitudes of which may range from tenths to tens of ‰. Equilibrium effects occur in chemically equilibrated systems. These effects are best expressed in terms of an isotope exchange reaction, where isotopes are transferred between two phases or molecular species that have a common element. Consider, for example, the main isotope exchange reaction of boron between tetrahedral borate anions ($\text{B}(\text{OH})_4^-$) and trigonal borate complexes ($\text{B}(\text{OH})_3$):



Reaction 1.3 shows that $\text{B}(\text{OH})_4^-$ is relatively enriched in ^{10}B while $\text{B}(\text{OH})_3$ is relatively enriched in ^{11}B (Kakihana *et al.*, 1977; Spivack and Edmond, 1987; Palmer and Swihart, 1996).

Non-equilibrium fractionations may be fast, incomplete, and / or unidirectional. Translation energies may influence non-equilibrium fractionations in addition to vibrational energies. For example, fractionation due to both diffusion and evaporation occurs because molecules enriched in the lightest isotopes have faster translational velocities and will therefore preferentially escape through an orifice or break through a liquid surface. Kinetic isotope effects are primarily due to the difference in energy

required to break the bonds of molecules composed of different isotopes. As previously discussed, bonds in molecules with higher vibrational frequencies and high ZPE will be broken more easily than those in molecules with lower vibrational frequencies and ZPE. Finally, metabolic fractionation effects are due to both equilibrium and non-equilibrium processes.

1.4 Mass Spectrometry

Mass spectrometers are the most commonly used instruments for the determination of atomic weights and chemical and isotopic abundances of elements. A mass spectrometer separates a given sample into a group of components with differing masses. Although there are various designs, the majority of isotope ratio mass spectrometers (IRMS) are based on a design from the 1940s by Alfred Nier.

There are three main parts to a mass spectrometer: a source that produces ions from either solid or gaseous samples, an analyser that separates ions, and a detector that collects and quantifies the ions. Various types of mass spectrometers differ principally on the type of source or the analyser.

Regardless of the source type, the sample must be introduced into the mass spectrometer in a form that may be ionised inside a high-vacuum chamber. In the case of gaseous samples, the gas enters the source and the molecules are bombarded by electrons which results in positively-charged ions. Solid samples are deposited onto a filament which is inserted into the source and heated until the element is volatilised. This is known as thermal ionisation, and it may result in either positive or negative ions according to the design of the instrument.

The positive or negative ions are accelerated by a high-voltage field created by charged plates and focused into a narrow beam by collimating plates and lenses.

The ion beam next enters the analyser, where strong electric and / or magnetic fields resolve the ions into distinct beams; in the case of IRMS, magnetic fields are used. All ions exiting the source region within the beam have kinetic energy (K_e) as follows:

$$K_e = qV = mv^2 / 2 \quad (1.4)$$

where q : charge of the ionized particle

V : potential drop across the high voltage source,

m : mass of the particle, and

v : velocity of the particle.

Therefore, ions with the same mass and charge have the same velocity, while ions with different masses differ in velocity. The force (F) that acts on the ions is described by:

$$\vec{F} = q\vec{E} + q \vec{v} \times \vec{B} \quad (1.5)$$

where E : electric force, and

B : magnetic force.

The electric and magnetic fields resolve the ions into distinct beams by deflecting them from a straight-line path. Ions with large masses - heavy isotopes - are deflected less than ions with small masses – light isotopes.

As previously stated, IRMS use a magnetic analyser to separate ions on the basis of mass to charge. This is known as momentum focusing, and it is the most common configuration. Other instruments use electric or a combination of electric and magnetic fields to separate ions. In all of these configurations, undesirable components are separated from the ion beams as long as these particles have different masses than those

being measured. However, it is possible to generate ions from the sample that differ chemically, yet have the same mass as the particles being measured. This condition is known as isobaric interference, and if it is detected the results of the analysis must be corrected. Isobaric interference may be detected by varying the electric or magnetic field to scan other masses for fragmentation patterns that differ from those expected for the compound of interest.

Finally, the distinct ion beams, which have been separated by their mass to charge ratios, are directed into collectors such as Faraday cups or electron multipliers, which are essentially metallic cups behind slit plates. The beam is quantified by measuring the current generated when the ion imparts a charge to the conducting surface. There may be either one collector, which requires the distinct ion beams to be directed into the collector one at a time by varying the high voltage or magnetic field, or multiple collectors which do not require the electric or magnetic field to be varied.

The result of mass spectrometer analysis is to quantify the relative amounts of heavy and light isotopes of the molecules of interest. In a gas source mass spectrometer, a reference material is analysed in order to calibrate the instrument. However, this is not possible when using a solid source and so known standard materials must be analysed several times during the course of sample analysis.

CHAPTER 2: SAMPLING & ANALYTICAL METHODS

2.1 Atmospheric Sampling

The atmospheric sampling program was designed to characterize emissions from gas plants using sulphur and boron isotopes, and to determine whether these emissions could be identified and apportioned at a site downwind. In order to detect spatial variations in the $\delta^{34}\text{S}$ and $\delta^{11}\text{B}$ values of natural gas, plants were sampled in both Alberta and British Columbia. All of these plants varied widely in size, age, and inlet H_2S content. The receptor site selected was downwind of all Alberta plants chosen for this study and the control site was upwind. The possibility of temporal variation in the $\delta^{34}\text{S}$ and $\delta^{11}\text{B}$ values of emissions was addressed by sampling most sites at least two times and as many as four times, with the exception of the receptor site which was sampled at least once a month over a year.

A complete sample log may be found in Appendix A.

2.2 Sampling procedures

Gaseous and particulate samples were collected using Sierra Miscu high-volume air samplers fitted with two filters, as shown in Figures 2.1a and b. The top filter was quartz-fibre (Whatman Grade QM-A, 20.3 cm x 25.4 cm), pore size 0.8 μm , which collected aerosol sulphate and boron. The bottom filter was cellulose fibre (S & S Biopath Inc. #410, 20.3 cm x 25.4 cm), treated with potassium carbonate (K_2CO_3) and glycerol, which collected SO_2 . Elemental sulphur samples were collected where possible.

The quartz-fibre filters, always handled with polyethylene gloves in order to minimize contamination, were folded in half after sampling and wrapped in aluminum

foil. All filters were stored in individual sealed plastic bags before and after samples were taken and refrigerated until they were analysed. Elemental sulphur was poured into Styrofoam cups if collected as liquid, and all sulphur samples were stored in sealed plastic bags.

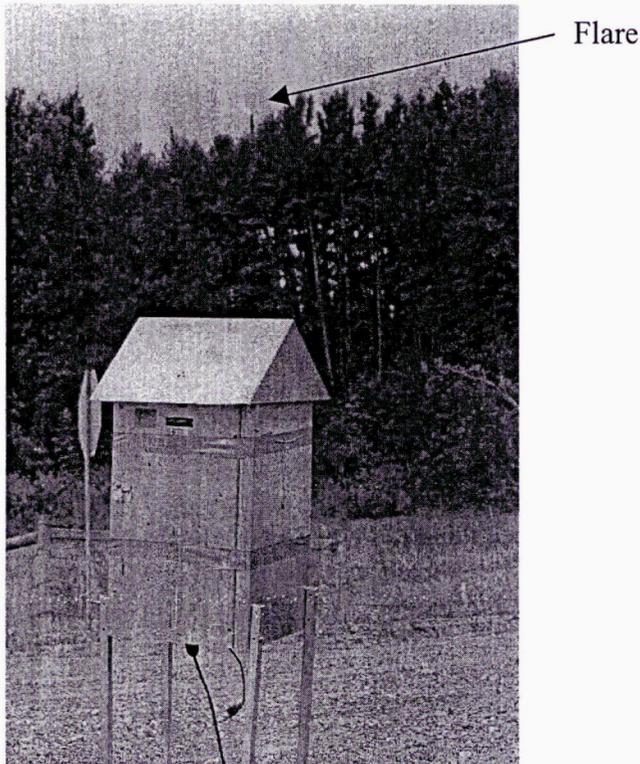


Figure 2.1a – High-volume air sampler measuring emissions downwind of a gas plant in Alberta

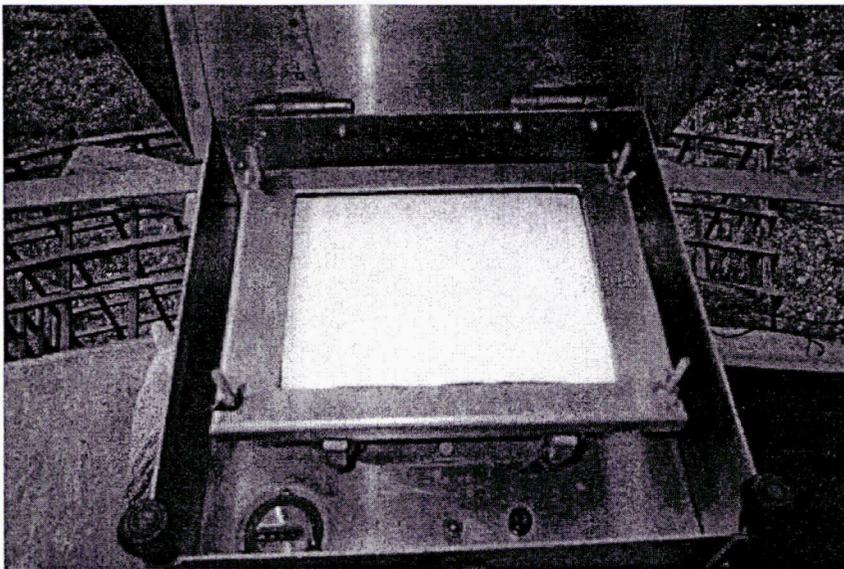


Figure 2.1b – High-volume air sampler filter pack

Two different types of high-volume air sampler were used depending on the sampling site. Where power was available at the site, a high-volume air sampler powered by a standard 120 volt AC power source was used. At sites where power was not available, a high-volume sampler configured to run on 24 volt DC power provided by two 12-volt batteries was used. Flow rates were measured at the beginning and end of each sampling period using a high volume sampler portable calibration unit (Kurz Instruments).

The flow decline of the 24 volt DC sampler resulting from the discharge of the two 12 volt batteries was tested using the calibration unit. Flow was measured and recorded every five minutes, and the following equation fit the plotted data very well ($r^2 = 0.92$):

$$\text{Flow} = -0.00003t^3 + 0.0042t^2 - 0.2334t + 23.413 \quad (2.1)$$

where t is time elapsed, in minutes. Equation 2.1 may be integrated to determine the total volume of air that has been drawn through the filters. However, it was not possible to use equation 2.1 for any of these samples as various previously-used batteries were used in

addition to the two batteries tested and beginning and ending flows did not match the flow curve.

For certain samples, the high-volume sampler was directionally controlled by a weather station (Peet Bros Company, Inc.) Every 60 seconds, the weather station communicated wind speed, wind direction, humidity, and temperature to a portable computer which was programmed to turn the sampler on when it detected that the wind was blowing from somewhere within the desired sampling sector at a speed greater than 1 km/h, with humidity less than 99%. Temperature was recorded but not used in controlling the sampler.

2.2.1 *Blanks*

It is important to minimize contamination in any sampling program, but it is particularly important to do so in atmospheric work as samples are typically very small. Contamination may be introduced during travel to and from sampling sites or during the laboratory analysis procedure. At the site itself, contamination is due to the background contribution from the area.

Filters exposed to each of the potential contaminant sources are known as blanks, and they make it possible to determine if and where contamination is introduced. Once it has been detected, it is then possible to either alter the procedure that led to the contamination or remove the effect of it from the sample. Samples were corrected for blank contribution by the following:

$$\delta^{34}\text{S}_{\text{corrected}} = (\delta^{34}\text{S}_{\text{uncorrected}} \cdot S_{\text{total}} - \delta^{34}\text{S}_{\text{blank}} \cdot S_{\text{blank}}) / (S_{\text{total}} - S_{\text{blank}}) \quad (2.2)$$

where S is the amount of sulphur measured in each case. Each of the blanks – travel, field, and lab – is described and discussed in the following sections.

It should be noted that in order to determine whether a blank exhibited contamination, it was necessary to have a good indication of what contamination the filter itself contributed. Several samples from each package of filters were analysed to provide a basis for comparison.

- Travel blanks:

Travel blanks, which were taken on each sampling trip, were treated identically to sample filters and stored with them. However, these blanks remained inside their plastic bags at all times. Any contamination introduced through the plastic bags during the course of the trip would have been evident from the travel blank.

- Field blanks:

At each sampling location, at least one field blank was taken. Field blanks were placed on the high-volume sampler for 1 minute without air flow through the unit, replaced in plastic bags, and were otherwise treated identically to sample filters. These blanks were in contact with the same equipment as the samples, so if any contamination was introduced by the sampling equipment, handling procedures, or background contribution it would have been evident from the field blank.

- Lab blanks:

Lab blanks were prepared in a manner identical to that of the sample filters, but they never left the lab. At least one lab blank was included in every set of sample filters analysed, and any contamination introduced by laboratory procedure would have been evident from these filters.

2.3 Sampling sites

The sampling sites and procedures used at each site are described in the following sections.

2.3.1 Control site

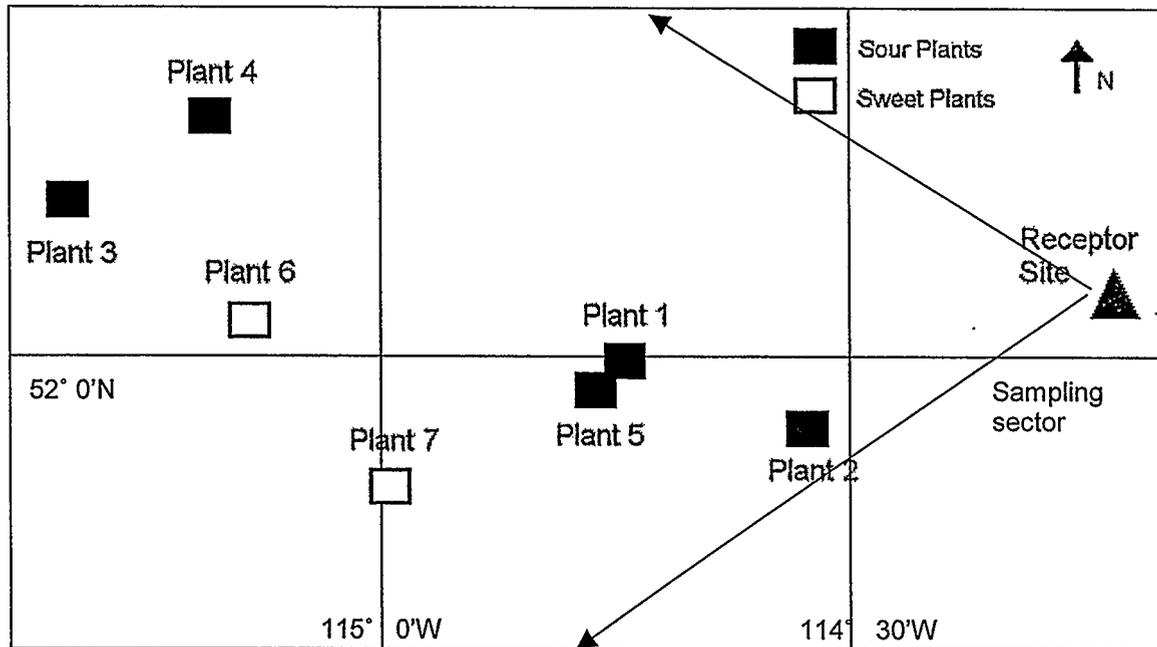
The control site was located less than 1 km south of Highway 11 and about 50 km east of Nordegg, Alberta and about 230 km southwest of Edmonton, Alberta. While there is no petroleum activity west of the site or in the immediate vicinity, there are natural gas wells with H₂S concentrations in excess of 30 % located within 55 km north of the control site and others east and south of the site (AccuMap™, 2004). Pristine air masses unaffected by industrial activity are almost impossible to find in Alberta due to the prevalence of the petroleum industry, as demonstrated by maps of the area (see Appendix B).

Two continuous 24-hour samples were taken at the control site in November 2001 and October 2002 using the AC sampler at ground level. No directional control of high-volume samplers was used at this site.

2.3.2 Source sites – Alberta

The emissions from each of seven gas plants in Alberta, shown in Figure 2.2, were sampled in July and September 2002. Further samples were taken downwind of plant 3 in December 2002 and March 2003. In all of these samples, with the exception of those taken in March 2003, the sampling system consisted of the DC high-volume sampler at ground-level with no directional control. Sampling duration ranged from one to two hours unless battery power was low. The March 2003 sample was run for one

week using the AC sampler, which was located southwest of the plant and directionally controlled with a sampling range encompassing 180° facing the plant. Solid sulphur samples were collected from the sour sites (Plants 1, 2, 3, 4, and 5).



(control site is not shown as it is almost 150 km northwest of the receptor site)

Figure 2.2 – Sampling sites in Alberta

2.3.3 Source sites – British Columbia

Emissions from each of five gas plants in B.C., shown in Figure 2.3, were sampled at least once during the period ranging from October 2001 to May 2002. Solid sulphur samples were collected from all plants except plant 8, which reinjected all acid gas produced.

All B.C. samples were collected using the DC high-volume sampler with no directional control.

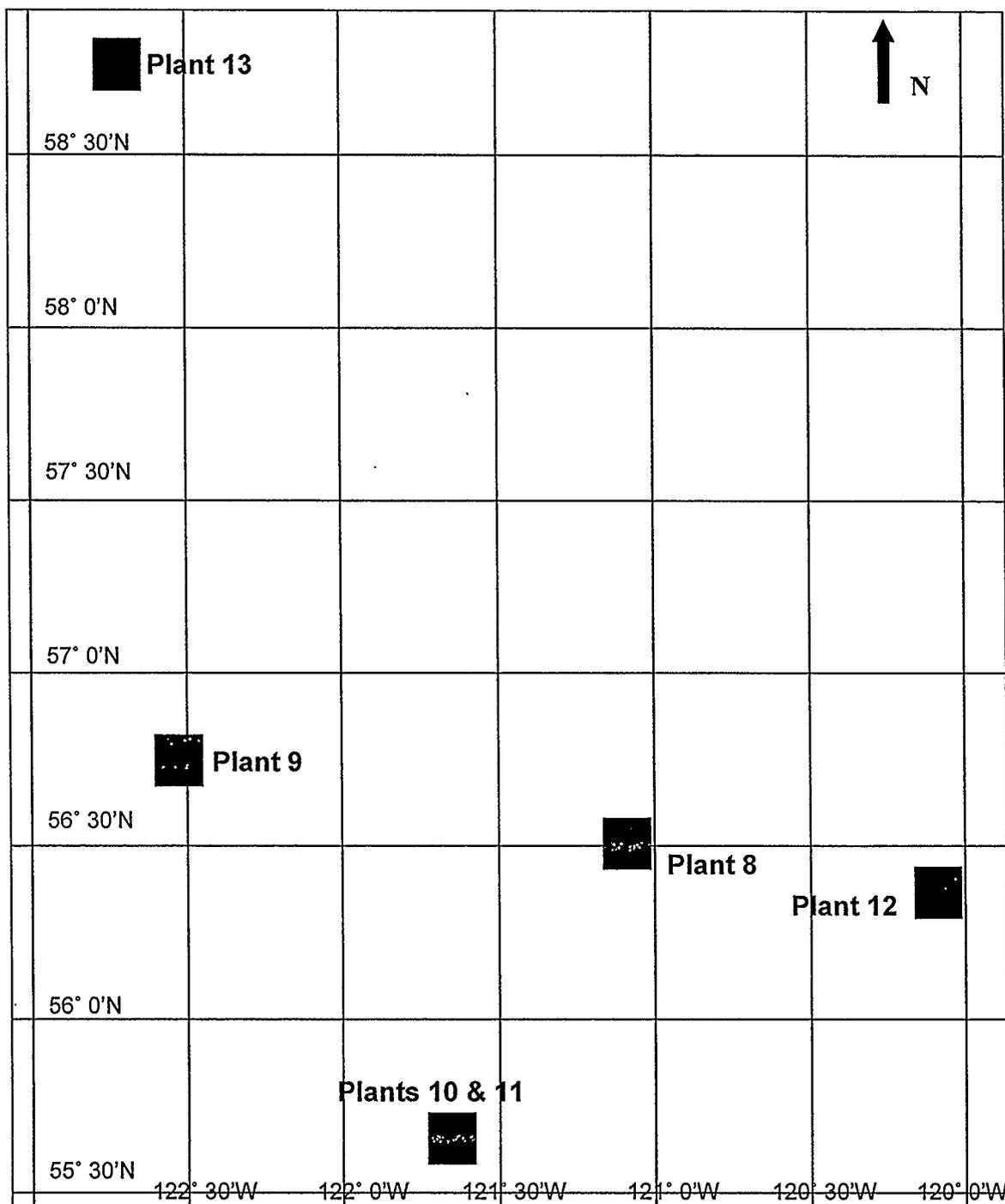


Figure 2.3 – Sampling sites in British Columbia

2.3.4 Receptor site

A sampling system was installed at the receptor site, located in central Alberta, in the summer of 2001. Samples used in this study were collected at least monthly from

September 2001 until October 2002. The AC high-volume air sampler was located about 4 m above ground-level and directionally controlled as discussed in section 2.2. The sampling sector, which was chosen to be between 235° and 302° true north, encompassed all seven gas plants in Alberta, which were all within 25 to 77 km from the receptor site. The receptor site, gas plants, and sampling sector are all shown in Figure 2.2, but the control site was not included as it is almost 150 km northwest of the receptor site.

CHAPTER 3: SULPHUR

3.1 Introduction

Sulphur is the 9th most abundant element cosmically (Goles, 1969) with Earth's mean sulphur content estimated at 10 g kg⁻¹ (Nielsen, 1991). It is found in elemental sulphur deposits in the United States, parts of Europe, Russia, Mexico, Iraq and other countries (Lien, 1991) and as a component of coal, petroleum and natural gas reservoirs, and oil sands. Furthermore, sulphur is present throughout the atmosphere, lithosphere, hydrosphere, and biosphere.

Canada's total sulphur production in 2000 was 9.8 megatonnes (Mt), 16% of the world's production. Much of this (82%) was elemental sulphur (S₈), a byproduct of the natural gas industry (Morel-à-l'Huissier, 2000). The single largest end use of sulphur is as sulphuric acid in the manufacture of phosphate-based fertilizers. Although sulphur is also used in the pulp and paper industry, in the chemical industry (for products ranging from pharmaceuticals to synthetic fibres), and various others (Morel-a-l'Huissier, 2000), it is no longer a particularly valuable commodity. The last economic peak for sulphur was in 1981 when it was worth almost \$200 US / tonne, but the price steadily decreased to \$23 US / tonne in 2000 (Buckingham and Ober, 2002).

Sulphur production is an unavoidable aspect of natural gas processing, especially in Alberta which accounts for about 85% of Canada's sour gas activity (Petroleum Communication Foundation, 2000). Anthropogenic sulphur emissions are of serious concern as they can lead to visibility reduction, acid rain, and global climate change as well as being linked both directly and indirectly to human and animal health (Alberta Environment, 2003). These concerns will be discussed further in the following sections.

3.2 Sulphur Chemistry

Sulphur has four isotopes: ^{32}S , ^{33}S , ^{34}S , and ^{36}S with abundances of 95.0%, 0.75%, 4.21%, and 0.017% respectively (MacNamara and Thode, 1950). The isotopic composition of sulphur is determined using the two most abundant isotopes, ^{32}S and ^{34}S , and expressed as $\delta^{34}\text{S}$ in per mil (‰), where

$$\delta^{34}\text{S} = \left\{ \left(\frac{{}^{34}\text{S}/{}^{32}\text{S}}{\text{sample}} / \left(\frac{{}^{34}\text{S}/{}^{32}\text{S}}{\text{standard}} \right) - 1 \right\} \times 1000 \quad (3.1)$$

The isotopic sulphur standard is Vienna Cañon Diablo Troilite (VCDT), based on troilite (FeS) from the Cañon Diablo meteorite; all sulphur isotope compositions are reported relative to VCDT which is assigned a value of 0 ‰ (Krouse and Coplen, 1997).

Substances of cosmic origin such as meteorites are primary material; that is, the isotopic composition of the meteorite should be very similar to that of Earth's sulphur at the planet's creation. In addition to meteorites, igneous and granitic intrusions and igneous rocks of primary origin all have sulphur isotope compositions close to zero (Thode, 1991) indicating that they have not undergone any significant isotopic fractionation, which would lead to a change in $^{34}\text{S} / ^{32}\text{S}$. However, most sulphur-containing substances have been subjected to processes that lead to isotopic fractionation. Sakai (1971) reported that barite from the ocean floor is the substance most enriched in ^{34}S at +87 ‰, while Austin (1970) reported that marcasite associated with petroleum is the substance most depleted in ^{34}S at -53 ‰, although Nielsen (1974) stated that volcanic exhalations can range from -65 to +95 ‰. Nonetheless, 98% of all samples analyzed at the Göttingen laboratory ranged from $\delta^{34}\text{S}$ of -40 to +40 ‰ (Nielsen, 1979).

Isotopic fractionation occurs when sulphur participates in various chemical and isotope exchange reactions throughout the lithosphere, hydrosphere, biosphere, and

atmosphere. Thermodynamically, oxidised forms of sulphur (e.g. sulphate in evaporites) tend to become enriched in ^{34}S , while reduced forms of sulphur (e.g. sedimentary sulphides) tend to become depleted in ^{34}S . This is due to the differences in ZPE as discussed in section 1.3. The extent of isotopic fractionation from one substance (e.g. sulphur dioxide) to another (e.g. sulphate) is expressed by the fractionation factor, α , as described in equation 3.2:

$$\alpha_{\text{SO}_2 - \text{SO}_4} = \left(\frac{^{34}\text{S}}{^{32}\text{S}} \right)_{\text{SO}_2} / \left(\frac{^{34}\text{S}}{^{32}\text{S}} \right)_{\text{SO}_4} \quad (3.2)$$

The largest isotopic fractionations tend to occur in sulphur that has participated in the biological sulphur cycle. Photosynthetic / photolithotropic sulphur bacteria oxidise reduced forms of sulphur, while 'sulphate respirers' reduce sulphate to sulphide in anaerobic ecosystems in the presence of organic matter (Thode, 1991). Biologically, sulphate undergoes two types of reduction: assimilatory and dissimilatory. Assimilatory sulphate reduction takes place when micro-organisms and plants use sulphate to build proteins to store energy, while dissimilatory reduction takes place when some micro-organisms in anoxic environments use sulphate rather than oxygen as an electron acceptor to obtain energy directly (Berresheim *et al.*, 1995). The dissimilatory process is several orders of magnitude faster than the assimilatory process, and therefore the biological sulphur cycle is controlled by anaerobic sulphate-reducing bacteria (Thode, 1991). Assimilatory reduction results in slight fractionation with reduced sulphur ranging from +0.5 to -4.4 ‰ relative to the precursor sulphate, while the isotope effects associated with dissimilatory reduction have been shown to range from +3 to -46 ‰ (Thode, 1991).

3.3 Sulphur Cycle & Atmospheric Chemistry

The natural and anthropogenic contributors to the global atmospheric sulphur budget, calculated from data recorded for 1980, are presented in Table 3.1 on a sulphur mass basis.

Table 3.1 – Major contributors to global atmospheric sulphur budget in 1980
After Spiro *et al.* (1992)

Source	Sulphur emission (Tg S yr ⁻¹)	Contribution
Anthropogenic (fuel use and industrial activities)	77.6	76.1 %
Marine biosphere (DMS)	11.9	11.6 %
Volcanic emissions	9.6	9.2 %
Biomass burning	2.3	2.2 %
Terrestrial biosphere (principally H ₂ S and DMS)	0.91	0.9 %
Total	102.2	

The predominant forms of sulphur in the atmospheres of developed countries are SO₂ and particulate SO₄²⁻ (Garland, 1978), reflecting the major contribution of anthropogenic emissions in these areas. Indeed, Spiro *et al.* (1992) determined that anthropogenic sources contributed 84% of the total sulphur emissions in the northern hemisphere, as compared with 50% in the southern hemisphere. In an area of intensive oil and gas production and processing such as Calgary, Alberta, it is expected that emissions from these sources would dominate atmospheric sulphur and in fact Norman *et al.* (2004) found that, on average, 77% of the SO₂, 64% of the aerosol SO₄²⁻, and 55% of the precipitation SO₄²⁻ in Calgary is derived from the oil and gas industry.

Reduced sulphur compounds such as DMS and methyl mercaptans are present as well in the atmosphere, but they exist in much smaller quantities and are rapidly oxidised.

Elemental sulphur may exist in the atmosphere as sulphur dust, but as a coarse particle it will be removed rapidly. Only the atmospheric chemistry of H_2S , SO_2 , and SO_4^{2-} will be explained in greater detail since they are the key substances in this work. However, it is important to note that other sulfur-containing compounds such as DMS may be precursors of atmospheric SO_2 and SO_4^{2-} .

3.3.1 *Hydrogen sulphide*

H_2S is mainly emitted from volcanoes, sea marshes and intertidal flats, anoxic soils, and various industries, including natural gas production and processing. The lifetime of H_2S has been reported to range from about two hours in an urban area to two days in a remote unpolluted area (Robinson and Robbins, 1968) to 42 days in winter in a northern area (Bottenheim and Strausz, 1980). It is likely not deposited until it has been oxidised to SO_2 or SO_4^{2-} (Garland, 1978). Other reduced sulphur species will behave in much the same manner as they are the most chemically reactive.

Oxidation of H_2S involves either the hydroxyl radical (OH) or nitrate (NO_3), where a hydrogen atom is abstracted as below:



The HS radical then reacts with O_2 , O_3 , or NO_2 , ultimately forming SO_2 that may be further oxidised to H_2SO_4 .

3.3.2 *Sulphur dioxide*

Of the total anthropogenic sulphur that is released to the atmosphere, Berresheim *et al.* (1995) estimated that sulphate and reduced sulphur compounds each constitute 3%

while the rest (94%) is released as SO₂. Furthermore, SO₂ is produced almost exclusively from anthropogenic sources (Robinson and Robbins, 1970), although it is also a major product of the oxidation of reduced sulphur species in the atmosphere. About half of the SO₂ emitted to the atmosphere is removed by dry deposition, while the remainder is oxidised to sulphate and eventually removed in precipitation (Garland, 1978). In the case of gas plants, oxidation may take place in the plume or once SO₂ has mixed with the surrounding air, in solution, on surfaces of solids, and in the gas phase. However, the rate of oxidation depends on the presence of H₂O in the form of clouds or fogs, concentration of oxidants, and sunlight intensity (Finlayson-Pitts and Pitts, 2000). The atmospheric lifetime of SO₂ may range from 1 hour in foggy conditions (Robinson and Robbins, 1970) to 3 to 7 days in an Arctic summer or 3 to 7 weeks in an Arctic winter (Sirois and Barrie, 1999).

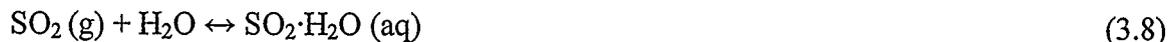
Oxidation of SO₂ to SO₄²⁻ may take place through either a homogeneous or a heterogeneous pathway. The homogeneous oxidation is a gas-phase reaction where the only significant oxidant is the hydroxyl radical, as shown below.



Sulphur isotope fractionation in the above oxidation pathway appears to be due wholly to the first of the above reactions since the next two reactions are relatively fast (Tanaka *et al.*, 1994).

The heterogeneous oxidation pathway is an aqueous dissolution, which leads to three chemical species: hydrated SO₂ (SO₂·H₂O), bisulphite ion (HSO₃⁻), and the sulphite ion

(SO_3^{2-}). The formation of HSO_3^- dominates between pH 2 to 6, the normal pH range for atmospheric droplets, while SO_3^{2-} dominates at low pH and $\text{SO}_2 \cdot \text{H}_2\text{O}$ dominates at high pH (Finlayson-Pitts and Pitts, 2000). The reactions are shown below:



All three of the above reactions are quite fast and are limited by factors such as the size of the droplet and the chemical nature of the aerosol surface. However, there is a large equilibrium fractionation associated with the first dissociation (reaction 3.9).

Egiazarov *et al.* (1971) reported a fractionation factor of 1.0165 at 25 °C, increasing with increasing temperature, which leads to the enrichment of ^{34}S in HSO_3^- relative to $\text{SO}_2 \cdot \text{H}_2\text{O}$. Reactions 3.8 and 3.10 have much smaller fractionations; Eriksen (1972b) reported a fractionation factor of 1.001 for the first reaction.

Possible oxidants, largely determined by the pH of the droplet, are O_2 , O_2 in the presence of metal catalysts (Fe^{3+} , Mn^{2+}), O_3 , H_2O_2 and organic peroxides, oxides of nitrogen (NO_x), and free radicals in clouds and fogs. Of these, H_2O_2 is expected to be the most important in clouds and fogs with $\text{pH} < 4.5$, while O_3 and the iron-catalyzed O_2 oxidation can compete at higher pH (Martin *et al.*, 1984). Overall, H_2O_2 and iron-catalyzed O_2 are the major oxidants at night, but during the day the gas-phase oxidation by OH becomes significant as it is formed by photochemical processes.

Saltzman *et al.* (1983) suggested that isotopic analysis of atmospheric SO_2 and SO_4^{2-} may be used to quantify the relative importance of each oxidation pathway. Since the atmospheric oxidations of both SO_2 and HSO_3^- are irreversible, the reactions should

demonstrate a kinetic isotope effect where the isotopically lighter molecules are preferentially oxidised and, as a result, SO_4^{2-} formed by homogeneous gas phase oxidation of SO_2 should be isotopically lighter than the precursor SO_2 . Tanaka *et al.* (1994) estimated that the resultant SO_4^{2-} would be about 9 ‰ lighter with a fractionation factor of 0.991 at 25 °C. However, Leung *et al.* (2001) determined that there may be in fact an inverse kinetic isotope effect, with a fractionation factor greater than 1.07 under atmospheric conditions leading to SO_4^{2-} that is isotopically heavier than the precursor SO_2 .

Sulphate formed by heterogeneous oxidation, which involves both kinetic and equilibrium isotopic effects, is expected to be isotopically heavier than the precursor SO_2 or HSO_3^- (Saltzman *et al.*, 1983) to a maximum of 16.5 ‰ at 25 °C (α of about 1.0165) (Eriksen, 1972a; Eriksen, 1972b).

Oxygen isotopes can also be used to determine oxidation pathways, although oxygen was not considered in this study. Much attention has recently been focused on mass-independent fractionation, where fractionation does not occur according to mass differences. Evidence of mass-independent fractionation in atmospheric processes indicates that oxygen isotopes (Savarino *et al.*, 2000; Lee *et al.*, 2002; Alexander *et al.* 2002), and possibly even sulfur isotopes (Farquhar *et al.*, 2000; Alexander *et al.*, 2003) that demonstrate the phenomenon may be used to determine oxidation pathways. The phenomenon of mass-independent fractionation may be helpful in resolving the conflicting fractionations for SO_2 oxidation described by Leung *et al.* (2001) and Tanaka *et al.* (1994).

3.3.3 Sulphate

Sulphate and methane sulphonic acid (MSA, $\text{CH}_4\text{O}_3\text{S}$) are the most stable forms of sulphur in the atmosphere and are the ultimate product of atmospheric sulphur chemistry. Since DMS is the only known precursor of MSA (Berresheim *et al.*, 1995), most sulphur species are oxidised to sulphate. Sulphate will eventually leave the atmosphere through precipitation after an atmospheric lifetime of about 5 days (Lelieveld *et al.*, 1997). However, sulphate plays a major role in the atmosphere, making up 15 - 30% of continental and 30 – 60% of marine aerosols (Whitby, 1978).

Aerosols in general, and sulphate in particular, affect both the climate and atmospheric processes. Since clouds form only in the presence of CCN, sulphate particles can affect the amount, type, and distribution of clouds, which may contribute to global climate change through the alteration of earth's radiation balance (Prospero *et al.*, 1983; Charlson *et al.*, 1991). Furthermore, aerosols can scatter and absorb light as it passes through the atmosphere, causing haziness and reduction in visibility. Finally, sulphur compounds may contribute to climate forcing in the stratosphere. The estimated global annual mean radiative forcing due to anthropogenic sulphate ranges from -0.2 to -0.8 W m^{-2} and averages about -0.4 W m^{-2} which is comparable in magnitude but opposite in sign to the radiative forcing of methane, which is about $+0.48 \text{ W m}^{-2}$ (Ramaswamy *et al.*, 2001).

3.4 Sulphur in Natural Gas

The formation of natural gas deposits was discussed previously in section 1.1.1. The majority of the sulphur in natural gas occurs as H_2S , which may vary from virtually nothing to over 90 mole percent; deposits with high amounts of H_2S often contain

elemental sulphur and polysulphides as well (Orr and Sinninghe Damsté, 1990). Natural gas with at least 2 to 3 mole percent H₂S is generally formed in carbonate reservoirs at very high temperatures, in strata associated with evaporites. Anhydrite (CaSO₄) in the evaporites combines with water to provide a source of sulphate, which is then reduced to H₂S by bacteria at reservoir temperatures below 60 °C and by thermochemical sulphate reduction (TSR) with organic matter as the reducing agent at temperatures above 80 °C (Orr, 1974). A third possibility is the TSR of sulphate by light hydrocarbon gases in some environments, as evidenced by the carbon isotope composition of the gases (Krouse *et al.*, 1988).

Low temperature shallow reservoirs are characterized by both low concentrations and low $\delta^{34}\text{S}$ values of H₂S. The isotopically light sulphur reflects the predominance of biological processes with large associated kinetic isotope effects (Krouse, 1991).

The percentage of H₂S in natural gas increases with temperature and therefore with depth, thereby indicating that high concentrations are due to TSR (Orr, 1974). Ferrous iron from the dissolution of pyrite is a major sink for TSR sulphur if the reservoir contains associated pyritic materials; otherwise, H₂S can accumulate in high concentrations (Orr and Sinninghe Damsté, 1990). The isotopic fractionation that accompanies TSR is negligible (Orr, 1974), so H₂S formed by TSR has an isotopic composition very close to that of the associated evaporites, which in turn reflect the environment and processes of formation.

Although today's oceans have quite a constant $\delta^{34}\text{S}$ value of +20.99 ‰ (Rees, 1970), marine evaporite sulphate varies from +10 to +35 ‰, a range generally believed to reflect the actual isotopic variations of sulphate in the ancient oceans (Pilot, 1991).

Accordingly, Krouse (1991) reported that H₂S in reservoirs in western Canada have $\delta^{34}\text{S}$ values that range from +15 to +30‰. Therefore, gas plants processing gas from different reservoirs or at least from different depths may be expected to emit sulphur with unique isotope compositions.

3.5 Sulphur as an Environmental Tracer

Sulphur isotopes have been successfully used to trace pollution through the environment in many different ways. Several studies have used sulphur isotope ratios to assess the contribution and impact of known sulphur emitters, such as a coal-fired power plant in Spain (Querol *et al.*, 2000), coal-fired power plants in the northeastern United States (Newman *et al.*, 1975), and volcanoes in Japan (Kasasaku *et al.*, 1999).

Meanwhile, others have apportioned atmospheric sulphur to various natural and anthropogenic sources (Krouse and Grinenko, 1991; Norman *et al.*, 1999).

Several studies have been carried out to determine the impact of gas processing plants in Alberta. Krouse and Case (1981) studied the air, water, soil, and vegetation around the Teepee Creek Gas Plant in the Peace River region. The isotopic composition of the H₂S in the gas at the base of the incinerator stack, about +24 ‰, was found to be very similar to that of the inlet gas and therefore it was expected that the $\delta^{34}\text{S}$ of SO₂ emitted from the plant should also be similar. However, using the isotope compositions and concentrations of SO₂ and SO₄²⁻ collected by an array of high volume samplers, the authors were able to show that the sulphur in the surrounding ecosystem was dominated by sources unrelated to the plant.

A similar study was performed by Krouse *et al.* (1984) at the West Whitecourt Gas Plant. Again, a directionally-controlled array of high volume samplers was used to

determine that the $\delta^{34}\text{S}$ of sulphur emissions was about +22 ‰, close to that of the inlet gas. As expected due to the high sulphur recovery (97.8 ‰), elemental sulphur was also found to be isotopically similar to the inlet gas, ranging from +22.1 to 24.1 ‰. It was suggested that differences between the average $\delta^{34}\text{S}$ values of sulphur emissions and solid sulphur may be due to slight fractionations during the sulphur recovery and tail gas cleanup processes. Furthermore, differences within the $\delta^{34}\text{S}$ values of sulphur emissions could be attributed to varying contributions from the flare and incinerator stacks, since the former could potentially burn gas from upstream of the sulphur recovery unit. Ultimately, it was confirmed that the plant was the major contributor of sulphur to the surrounding ecosystem, although the isotopic composition of aerosol sulphate was significantly different and may have been due to another source.

Mukai *et al.* (2001) used a multiple-isotope approach to determine the contributors to atmospheric sulphur and lead at several Chinese urban sites. The isotopic composition of both sulphur and lead identified coal combustion as the major source in some areas. However, they encountered problems in other regions where other unknown industrial contributions were present or where lead isotope ratios in coal and oil were indistinguishable.

CHAPTER 4: SULPHUR SAMPLING & ANALYSIS

The preparation and analysis of atmospheric sulphur samples as well as the difficulties encountered in SO₂ sampling are described in the following sections.

4.1 Sulphur dioxide sampling

It was discovered that the SO₂ samples collected downwind of gas plants often contained less sulphur than the travel, field, and / or lab blanks. In order to resolve the problem, two main aspects of atmospheric SO₂ sampling were examined:

1. the capture efficiency of the SO₂ filters and sampling procedures, and any possible sulphur isotope fractionation as a result of efficiencies less than 100%, and
2. contamination introduced by travel, background contribution at the sampling site, or by the filters themselves.

Interestingly, the problem of small samples collected using high volume samplers has been experienced by others (Krouse *et al.*, 1984), although no solution was suggested.

4.1.1 SO₂ filters and sampling procedures

Huygen (1963) developed a method for collecting SO₂ by drawing air through impregnated Whatman no. 1 cellulose filter paper. The filters were prepared by soaking them in the impregnating solution, squeezing out the excess, and drying them in an oven at 110°C. Various solutions were tested in order to find one that was highly efficient at both absorbing and stabilising gaseous SO₂, thereby preventing oxidation. Upon discovering that sodium hydroxide (NaOH) was highly efficient at collecting and retaining gaseous SO₂, a variety of potassium salts were tested since they are more

hygroscopic than the sodium salts. Glycerol was added to the solution since it stabilizes the SO₂ and is hygroscopic, although triethanolamine (TEA) was found to be preferable in some instances.

After testing various combinations of potassium salts and glycerol or TEA, Huygen (1963) determined that the two best combinations were 20% potassium hydroxide (KOH) with 10% glycerol and 20% KOH with 10% triethanolamine (TEA), with capture efficiencies of 96% and 98% respectively at 25% relative humidity. However, in order to obtain the best results, he recommended the following:

1. relative humidity $\geq 30\%$,
2. SO₂ concentration $\leq 10 \text{ mg/m}^3$,
3. total quantity of SO₂ collected \leq the equivalent of 10% of the alkali content of the filter,
4. linear velocity of the air drawn through the filters $\leq 15 \text{ cm/s}$.

Huygen's recommendations were quite restrictive, but Forrest and Newman (1973), who developed a method specifically for sampling and analysing atmospheric sulphur compounds in order to trace pollutant sulphur in stack gases using sulphur isotopes, were able to achieve sampling efficiencies greater than 95% when operating in conditions more severe than recommended as long as sample sizes were less than 50 mg SO₂. They used high-volume air samplers with linear velocities of about 65 cm/s in areas of higher SO₂ concentration. It was noted that humidity, or perhaps the absolute moisture content of the atmosphere, was the most important factor affecting the loss of SO₂ (Forrest and Newman, 1973).

In this study, filters used for SO₂ collection were impregnated with 30% potassium carbonate (K₂CO₃) and glycerol, a solution found to be almost as efficient as KOH and glycerol (95% as compared with 96%) (Huygen, 1963). They were prepared similarly to the method of Huygen (1963), with the impregnating solution poured over the filters, excess solution squeezed out with a roller, and then the filters were dried in an oven at 100 °C until they were yellow and resembled parchment. It was important not to leave the filters in the oven too long as alkali attacks cellulose (Forrest and Newman, 1973).

The following tests were performed in the lab in order to determine the capture efficiency and possibility of sulphur isotope fractionation:

- Characterisation of SO₂ gas:

A gas cylinder containing 276 mg m⁻³ (102 ppm) SO₂ was tested at the beginning and end of the experiments due to concern that the δ³⁴S composition may change as pressure decreased. This was accomplished by directing the gas through a flowmeter, and then a particulate filter in an aluminum holder (Gelman, 47 mm) in order to remove any contaminants, and finally bubbling it through an impinger containing 30% H₂O₂. The impinger also contained 5 ml of barium chloride (BaCl₂) in the first test in order to precipitate the sulphur as BaSO₄, making it visually possible to determine when enough sulphur for analysis had been collected. The apparatus for these tests is shown in Figure 4.1(a).

- Flow rate tests:

The apparatus described above was reconfigured to add two cellulose filters in polycarbonate filter holders (Gelman, 47 mm) after the particulate filter. A beaker containing 30% H₂O₂ was again placed after the filters in order to capture

any filter breakthrough. Flow rates were varied to determine whether sulphur capture and / or isotope fractionation varied accordingly. The cellulose filters and aqueous SO_4^{2-} were then prepared and analysed as described in section 4.2.

Figure 4.1(b) shows the configuration of the apparatus for these tests.

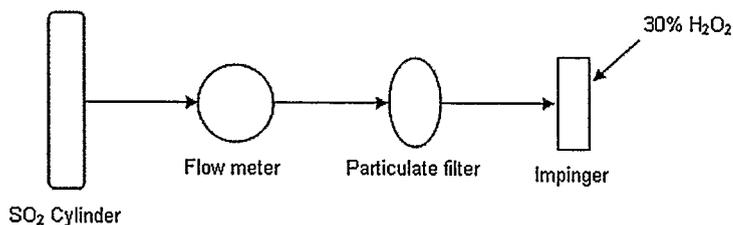


Figure 4.1a

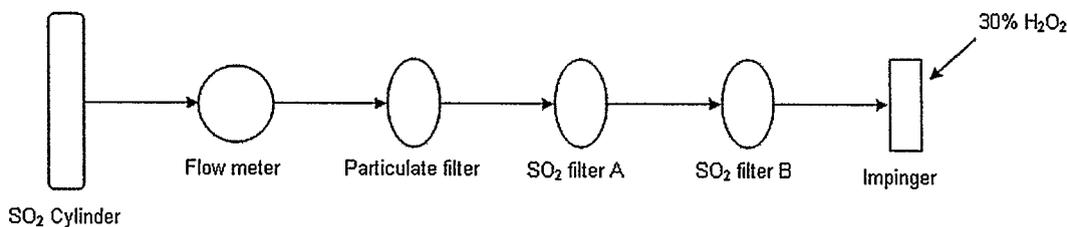


Figure 4.1b

Figure 4.1 – Apparatus to test SO_2 capture efficiency and sulphur isotope fractionation. (a) Determination of $\delta^{34}\text{S}$ of SO_2 . (b) Determination of capture efficiency and fractionation of cellulose filters.

4.1.2 Blanks

The possibility of blank contamination by diffusion through the plastic bags used to store filters during trips to and from sampling sites was tested. Unused filters were sealed in plastic bags in the normal manner, and then sealed within another plastic bag filled with air containing 102 ppm SO_2 gas. The filters were left in this manner for several days, and then prepared for analysis. No evidence of contamination was found.

Field blanks were also compared to the filter blanks. Although the sulphur content of some blanks initially seemed high, these values were not found to be statistically significant (*t*-test, $p < 0.05$).

These results indicated that the seemingly large amounts of sulphur found in field and travel blanks were in fact statistically the same as the amount of sulphur introduced by the filter itself. It was then decided to attempt to reduce the amount of sulphur contributed by the blank in order to be able to analyse small samples.

Forrest and Newman (1973), who used a 20% KOH – 10% TEA impregnating solution, determined that more sulphur was extracted after KOH impregnation than could be removed by water alone. Therefore, they pretreated the filters with 20% KOH (no TEA), dried them and rinsed them with distilled water, dried them again, and finally treated them with the impregnating solution and dried them for the last time. Using this process, it was possible to reduce the sulphur blank to about 0.1 mg as SO₂ (Forrest and Newman, 1973).

In this work, the sulphur blank of the filter was reduced by first rinsing the filters with distilled de-ionized water and drying them in an oven at 100 °C. Once the filters were dry, they were prepared by impregnation with 30% K₂CO₃ and glycerol and dried in an oven at 100 °C until parchment yellow. The sulphur blank of the filter batch tested was reduced from 0.4 mg to 0.06 mg by this procedure.

4.2 Sulphur dioxide and sulphate analysis

Both the cellulose and half of the quartz-fibre filters were prepared for analysis in a similar manner. The filters were torn into small pieces and placed into a 600 ml Pyrex beaker, with 200 mL of distilled de-ionized water poured over. In the case of the treated

cellulose filters, 2 ml of 30% H₂O₂ was added in order to convert SO₂ to SO₄²⁻. The beakers were then placed into an ultrasonic bath for 30 minutes. The contents of the beaker were vacuum-filtered through a 0.45 µm Millipore filter in order to remove the filter pieces and any other insoluble contaminants. Trapping tests, described in section 4.1.1, and the boron extraction procedure, which will be discussed in sections 7.3 and 7.4, produced solutions containing SO₄²⁻ and therefore the steps above were bypassed.

At this stage, when sulphur was present as SO₄²⁻ in solution, about 10 ml was removed. It was filtered with a 0.2 µm filter (Acrodisc syringe filter, 25 mm), and the concentration was determined using ion chromatography (IC). Since the IC only became available midway through the study, the SO₄²⁻ concentration from most of the SO₂ filters was not determined in this manner.

For all samples 5 ml of 10% BaCl₂ was added to the solution in order to convert the SO₄²⁻ to BaSO₄. Environmental grade hydrochloric acid (HCl) was added in 1 ml increments until the pH was less than 3 in order to dissolve any carbonates. The volume of the solution was reduced to less than 50 ml on a hot plate and then filtered through a 0.45 µm Nucleopore filter. The filter, on which the BaSO₄ was deposited, was dried and ashed at 800 °C for 90 minutes. Finally, the BaSO₄ was packed into tin cups in quantities ranging from 50 – 300 micrograms (µg), which were analyzed using a VG Prism mass spectrometer.

4.3 Elemental sulphur analysis

Elemental sulphur was ground with silver and baked in a 100 °C oven, uncovered, until black (about 1 hour) in order to form silver sulphide (Ag₂S). The Ag₂S was then packed into tin cups and analysed using the VG Prism mass spectrometer.

CHAPTER 5: SULPHUR RESULTS & DISCUSSION

5.1 Sulphur Capture & Isotopic Fractionation Tests

The impetus to test the sulphur capture and isotopic fractionation of the treated cellulose filters used to sample SO₂ came from the problem of small SO₂ sample sizes, as discussed in section 4.1. With the exception of Huygen (1963), who tested the capture efficiencies of several different filter impregnation solutions, little information was found concerning the capture efficiencies and sulphur isotope fractionation effects of K₂CO₃ / glycerol treated cellulose filter paper in SO₂ sampling. Therefore, the following set of experiments was performed:

- Characterisation of SO₂ gas:

The $\delta^{34}\text{S}$ composition of a gas cylinder containing 276 mg m⁻³ (102 ppm) SO₂ was determined by bubbling the gas through an impinger which contained 30% H₂O₂, thereby converting the SO₂ to SO₄²⁻. This test was performed at the beginning and at the end of the experiments because the cylinder was almost empty, raising concern that the $\delta^{34}\text{S}$ of the SO₂ might change over the duration of the tests. Huygen (1963) found the SO₂ collection efficiency of an impinger to be 96% regardless of humidity, using the method of West and Gaeke (1956) where SO₂ is bubbled through 0.1 M sodium tetrachloromercurate (II) (Na₂HgCl₄). This collection efficiency was used to determine the total amount of sulphur upon which recovery efficiencies were based, as shown in equation 5.1.

- Flow rate tests:

These tests consisted of passing the gas through a particulate pre-filter and two SO₂ filters in series, followed by the impinger. One test where only one SO₂ filter

was used was performed in order to determine whether the $\delta^{34}\text{S}$ measured from SO_4^{2-} in the impinger would reflect the effects, if any, due to one rather than two filters. Flow rates were varied from 29.0 to 153.4 ml min^{-1} .

Results of the tests are presented in Table 5.1. Sulphur recoveries were calculated as a percentage of total sulphur, which was determined through the following calculation:

$$S_{\text{Total}} = S_{\text{SO}_2 \text{ Filter 1}} + S_{\text{SO}_2 \text{ Filter 2}} + (S_{\text{SO}_4^{2-} \text{ trap}} / 0.96) \quad (5.1)$$

Total S was calculated using equation 5.1 rather than using known concentration and total volume because the actual SO_2 concentration of the cylinder was in doubt due to its age and low pressure. In addition, flow rates were difficult to maintain at a steady rate due to changing pressures in the cylinder during these experiments.

During sample preparation, the BaSO_4 solution from one test was inadvertently allowed to boil dry and as a result, the $\delta^{34}\text{S}$ value obtained from this sample was not included in calculation of the average $\delta^{34}\text{S}$ value. Furthermore, the $\delta^{34}\text{S}$ values measured in the SO_4^{2-} trap for tests at flow rates of 29.0 and 109.5 ml min^{-1} (+1.4 ‰ for both tests) were too small to be measured properly on the mass spectrometer, and so these results were discounted.

The characterisation tests at the beginning and end of the experiments gave cylinder SO_2 $\delta^{34}\text{S}$ values of -1.2 and -2.3 ‰, respectively. The difference was not found to be statistically significant (t -test, $p < 0.05$). Therefore, the $\delta^{34}\text{S}$ of SO_2 in the cylinder was taken to be the average of the two tests, -1.8 ± 0.8 ‰.

Table 5.1 - Sulphur capture and isotopic fractionation test results

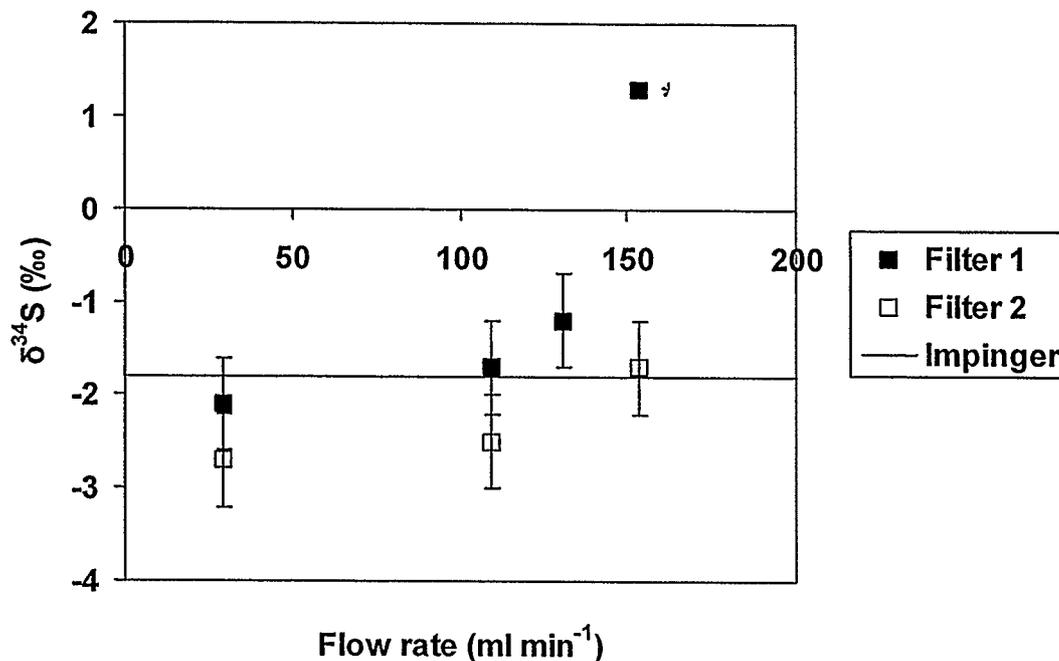
Flow (ml/ min)	SO ₂ Filter 1			SO ₂ Filter 2			SO ₄ ²⁻ trap		
	δ ³⁴ S (‰)	S (mg)	Recovery (%)	δ ³⁴ S (‰)	S (mg)	Recovery (%)	δ ³⁴ S (‰)	S (mg)	Recovery (%)
130.3							-1.2	3.73	
29.0	-2.1	0.75	81	-2.7	0.15	16	+1.4 [†]	0.02	2
109.5	-1.7	0.50	68	-2.5	0.21	29	+1.4 [†]	0.02	3
130.3	-1.2	0.48	38				-2.2	0.76	60
153.4	+1.3*	0.15	19	-1.7	0.54	67	-2.3	0.11	13
130.3							-2.3	2.56	
Avg δ ³⁴ S	-1.7 ± 0.5 ‰			-2.5 ± 0.5 ‰					

* Sample boiled dry and not included in average δ³⁴S.

† Sample below linear range on mass spectrometer (signal < 5 x 10⁻⁹).

The average δ³⁴S values for the SO₂ filters did not show any significant isotopic fractionation, although several interesting trends were apparent. Figure 5.1 shows the δ³⁴S values measured for each filter at each flow rate. It is apparent from the graph that sulphur from filter 1 was always isotopically heavier than sulphur from filter 2, although the differences were within the uncertainty of the data and were not significant (*t*-test, *p* < 0.05). Furthermore, sulphur from both filters was isotopically lightest at the lowest flow rate and increased with flow rate.

It is difficult to determine whether these trends demonstrated true phenomena. As shown in Figure 5.1, many of the isotopic differences between filter 1 and filter 2 were within the analytical uncertainty of the data. Further testing should be done to confirm these isotope effects.



* Sample boiled dry.

Figure 5.1 - $\delta^{34}\text{S}$ of each filter over the range of flow rates

The SO_2 capture efficiencies of filter 1 and filter 1 plus filter 2 are presented in Figure 5.2. Sulphur capture was highest at low flow rates and decreased as the flow rate increased, although the capture efficiency always exceeded 85% when two filters in series were used. The sample taken at a flow rate of $153.4 \text{ ml min}^{-1}$ showed a marked decrease in recovery by the first filter, although the second filter was still able to increase recovery to 86%.

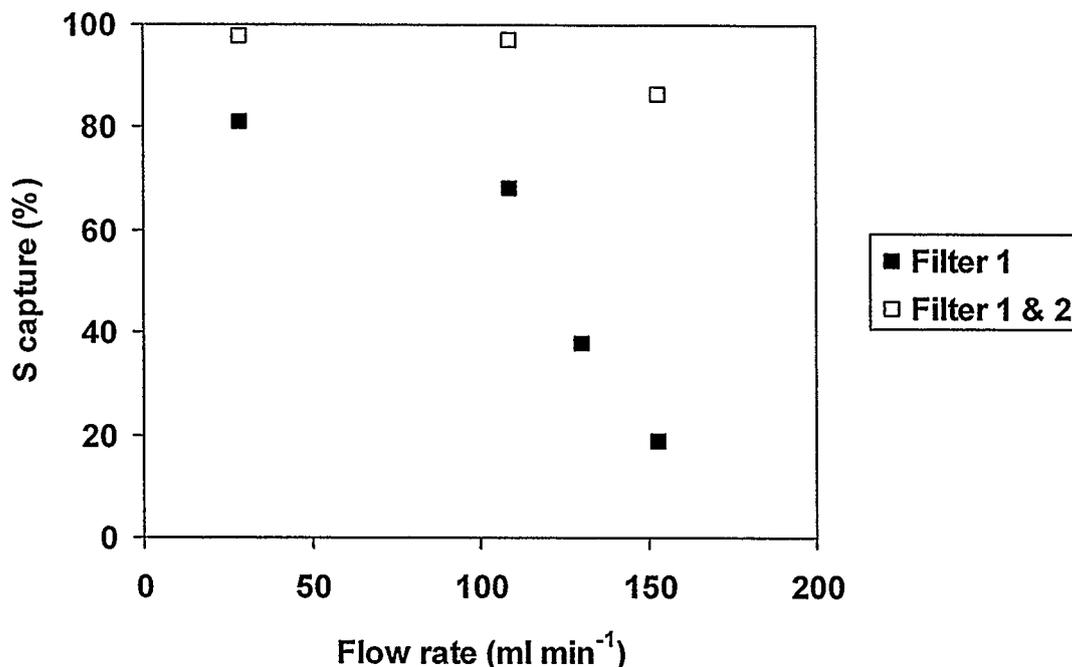


Figure 5.2 – Sulphur recovery as a function of flow rate

As discussed in section 4.1.1, Huygen (1963) recommended several operating limits for sampling SO₂ using impregnated cellulose filter paper, including:

1. relative humidity $\geq 30\%$,
2. SO₂ concentration $\leq 5,000 \mu\text{g m}^{-3}$ (3.8 ppm SO₂),
3. linear velocity of the air drawn through the filters $\leq 15 \text{ cm s}^{-1}$.

However, it was acknowledged that these limits were quite conservative. Forrest and Newman (1973) were able to achieve recoveries of 80 - 98%, using cellulose filter paper impregnated with KOH-TEA, at linear velocities of about 65 cm s^{-1} and SO₂ concentrations that did not exceed $8,000 \mu\text{g S m}^{-3}$ (6 ppm SO₂). The lowest capture efficiencies were noted both at low relative humidity ($\leq 30\%$), as cautioned by Huygen (1963), and high relative humidity ($> 80\%$) at about $22 \text{ }^\circ\text{C}$, where isotope ratios were also affected (Forrest and Newman, 1973).

The laboratory experiments here were performed using dry cylinder air, which may have affected the capture efficiencies of the SO₂ filters. Samples collected at the receptor site ranged in average relative humidity from 37% to 83%, while samples at gas plant sources and the control site were typically collected during periods of intermittent precipitation, indicating that low relative humidity was likely not a factor in the field sampling program. However, relative humidity should be monitored and the effect of precipitation on sulphur recovery tested in future source sampling programs.

The cylinder in these tests was known to have a SO₂ concentration of about 138,000 µg S m⁻³ (102 ppm SO₂), which was well above the recommended level and may have contributed to low recoveries in the capture and isotope fractionation tests. However, all field samples had quite low SO₂ concentrations: 0.1 to 0.5 µg S m⁻³ (0.1 to 0.4 ppb SO₂) at the control site, 3 to 18 µg S m⁻³ (2 to 15 ppb SO₂) in gas plant emissions, and 0.1 to 15 mg S m⁻³ (0.1 to 2 ppb SO₂) at the receptor site. Concentration of SO₂ should not have impacted field sampling collection efficiencies.

Linear flow rates ranged from 0.05 to 0.2 cm s⁻¹ for the tests, suggesting that flow did not contribute to low sulphur recoveries. However, flow rates ranged from 450 to 720 l min⁻¹ (20 to 32 cm s⁻¹) for the DC high volume air sampler, used for short term samples (e.g. plant emissions), and 1,100 to 1,450 l min⁻¹ (49 to 65 cm s⁻¹) for the AC high volume air sampler, used for long term samples (e.g. receptor site). It is entirely possible that the sample concentrations measured for this thesis are an underestimation of actual concentrations. This along with the demonstrated correlation between flow rate and SO₂ capture efficiency shown in Figure 5.2 indicate that some improvements may be

necessary for the field sampling method. In future, it is recommended that field sampling procedures include the use of two SO₂ filters in series in order to capture most of the SO₂. Further testing to validate these results and to determine capture efficiencies and isotopic fractionation effects under field conditions would be valuable.

5.2 Sulphur Sources

Gas plant emissions were sampled downwind by Sierra Miscu high volume samplers in both Alberta and B.C., and solid sulphur samples were collected where possible. The location of the plumes from each plant was determined through visual assessment of the wind direction and the location of the flare stack and/or incinerator. The sampler was then placed 500 to 2,000 m from the stack or incinerator depending on stack height which ranged from 40 to 124 m, although much of the decision about location depended upon accessibility. In some locations, it was possible to smell the plume.

A control site was chosen in order to determine the background concentration of sulphur that may be expected in the region, and a receptor site was chosen to evaluate the possibilities of apportionment of emissions measured at a site situated downwind of all Alberta plants sampled. High volume samplers were used to sample at each of these locations.

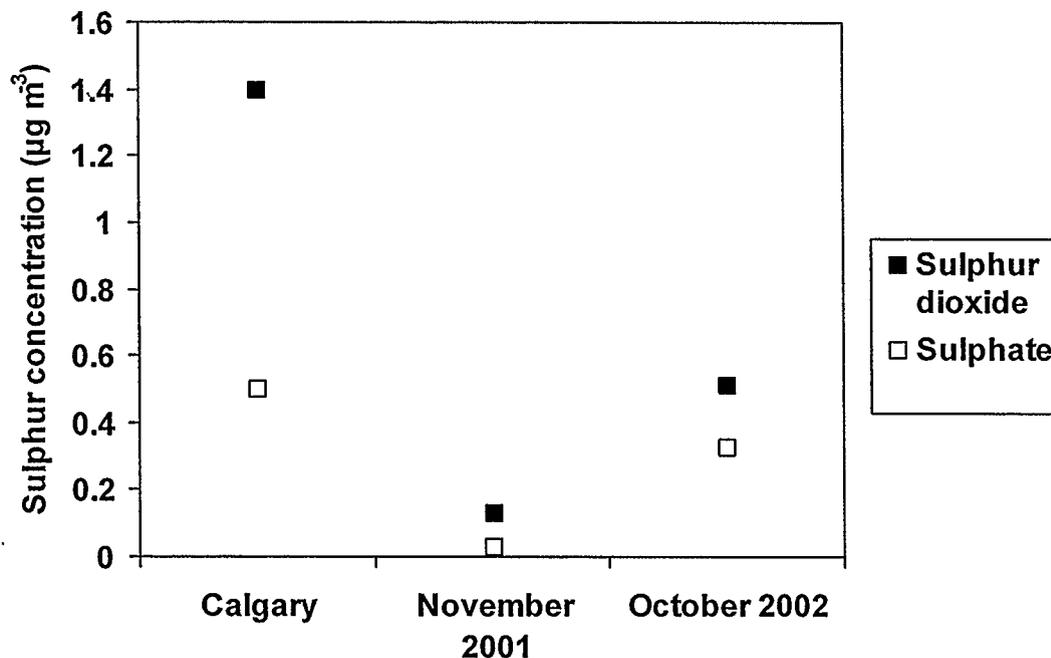
The goals of the sampling program were to determine the sulphur isotope signature of each source and to determine if significant differences in isotope composition of emissions could be used for source apportionment. A key factor was to assess whether emission isotope compositions changed over time. Results are presented in the following sections, and the complete sample log and results may be found in

Appendix A. Error bars that reflect the standard deviation of each sample are included where appropriate to reflect the uncertainty imparted by the large amount of sulphur in the lab blanks, as discussed in section 4.1.

5.2.1 Control Site

Concentrations and $\delta^{34}\text{S}$ values of both SO_2 and SO_4^{2-} measured at the control site are shown in Figures 5.3a and b. Norman *et al.* (2004), using the same sampling method, reported atmospheric SO_2 concentrations in Calgary that averaged $1.4 \pm 1.1 \mu\text{g sulphur m}^{-3}$ and SO_4^{2-} concentrations that averaged $0.5 \pm 0.4 \mu\text{g sulphur m}^{-3}$. Extreme values of $61.9 \mu\text{g sulphur m}^{-3}$ in SO_2 and $8.7 \mu\text{g sulphur m}^{-3}$ in SO_4^{2-} were measured during a peak pollution event.

The October 2002 sample had the highest sulphur concentrations of the two at $0.5 \mu\text{g sulphur m}^{-3}$ in SO_2 and $0.3 \mu\text{g sulphur m}^{-3}$ in SO_4^{2-} . On the basis of sulphur concentration alone, the control site was in fact a reasonable choice.



(Calgary results from Norman *et al.*, 2004)

Figure 5.3a - Sulphur concentration of control site samples over sampling period

However, both samples showed high $\delta^{34}\text{S}$ values for both SO_4^{2-} and SO_2 , with the October 2002 sample particularly high ($24.3 \pm 0.9\text{‰}$ and $21.9 \pm 5.5\text{‰}$, respectively). Sulphur derived from “background” was expected to be isotopically nearer to 0 ‰ for emissions from vegetation or +9 ‰ for vehicle emissions (Norman *et al.*, 2004). This suggests that, although sulphur concentrations were low, it was likely that some gas plant or well emissions were present at the time of sampling thus demonstrating the difficulty in finding an appropriate control site in Alberta unaffected by oil and gas emissions.

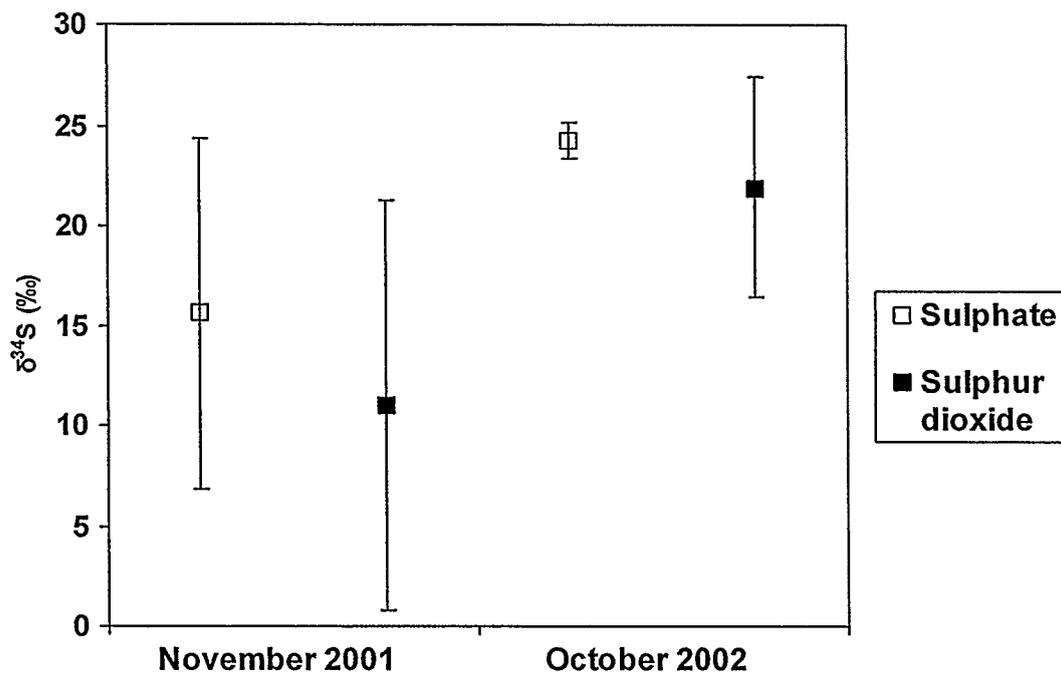


Figure 5.3b - $\delta^{34}\text{S}$ of control site samples over sampling period

5.2.2 Alberta

For each plant, the daily volume of gas processed and % H_2S are presented in Table 5.2. The $\delta^{34}\text{S}$ values and concentrations of SO_2 , SO_4^{2-} , and solid sulphur from each plant are presented in Figures 5.4a-e.

Table 5.2 – Gas volume processed and % H₂S at each Alberta plant

Plant	Gas processed (10 ³ m ³ day ⁻¹)	% H ₂ S	Sulphur recovery (%)		Sulphur emitted (10 ³ m ³ day ⁻¹)
			Actual	Required	
1	850	0.1	83.8	69.7	0.2
2	1,070	0.8	86.5	85	1.1
3	15,000	8.5	98.9	98.1	14.0
4	4,560	2.8	98.5	98.1	1.9
5	9,700	37 - 38	99.9	99.5	3.7
6	4,280	-	-	-	0.7*
7	1,310	-	-	-	0.7*

Plants 1, 6, 7 – AccuMap™, 2004

Plant 2 – Douglas, 2002

Plant 3 – Plant 3 staff, personal communication, 26 October 2004

Plant 4 – Plant 4 staff, personal communication, 28 October 2004

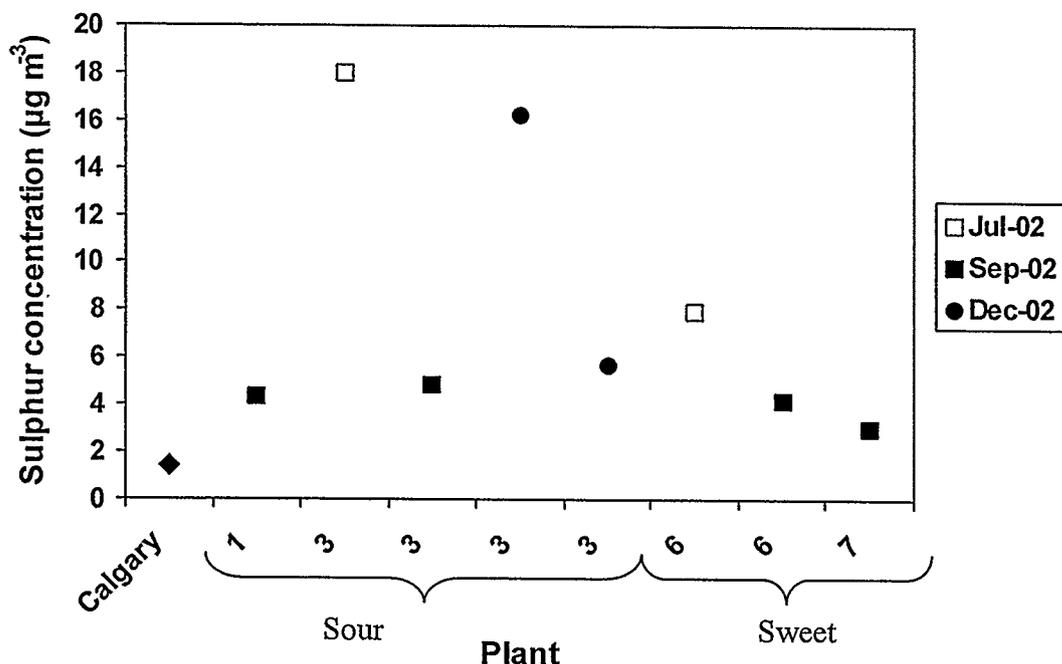
Plant 5 – Plant 5 staff, personal communication, 25 October 2004

Actual and required sulphur recoveries – Alberta Energy and Utilities Board, 2003

* Each of the sweet plants was assumed to process 0.95 tonnes of sulphur per day, which is just under the limit of 1 tonne. Once a plant processes 1 or more tonnes sulphur per day, sulphur recovery processes must be in place (Energy and Resources Conservation Board and Alberta Environment, 1988; Alberta Energy and Utilities Board, 2001).

5.2.2.1 SO₂

Figure 5.4a shows the concentration of sulphur in the SO₂ emissions. Relatively high SO₂ concentrations were measured downwind of all plants as compared with the average SO₂ concentration measured in Calgary (1.4 µg sulphur m⁻³ (Norman *et al.*, 2004)) – the lowest SO₂ concentration, measured downwind of plant 7, was still twice as great at 3.0 µg sulphur m⁻³. Certain samples had particularly high SO₂ concentrations, ranging from 5.7 to 18 µg sulphur m⁻³ at plant 3 and 8.0 µg sulphur m⁻³ at plant 6, and it is therefore likely that these samples were representative of a local sulphur source – presumably the gas plant in the area. Other potential sulphur sources will be discussed in section 5.2.4.4.



(Calgary, AB value from Norman *et al.*, 2004)

Figure 5.4a – Concentration of sulphur in SO₂ emissions at gas plants in Alberta

Sulphur isotope compositions of emissions from the plants are shown in Figure 5.4b. The maximum $\delta^{34}\text{S}$ value of SO₂ was +29.4 ‰, measured at plant 3 (sour), while the minimum was +3.0 ‰, measured at plant 7 (sweet). Emissions from plants 6 and 7, both sweet, were the lightest isotopically as expected (Krouse, 1991), averaging $+3.8 \pm 1.4$ ‰. In contrast, emissions from plant 3 had SO₂ $\delta^{34}\text{S}$ values that averaged $+21.8 \pm 7.4$ ‰, typical of sour gas emissions in Alberta which have been reported to range from +15 to +30 ‰ (Krouse, 1991). However, emissions measured downwind of plant 1, also sour, had a $\delta^{34}\text{S}$ value of +3.7 ‰.

At the time of sampling emissions downwind of plant 1, both plants 5 and 7 were upwind of the sampler. Plant 5 is a very sour plant and it is unlikely that emissions would have contributed isotopically light sulphur. However, sulphur contribution from

plant 7, where the $\delta^{34}\text{S}$ value was measured as +3.0 ‰, could explain the anomalously light $\delta^{34}\text{S}$ value of SO_2 emissions from plant 1.

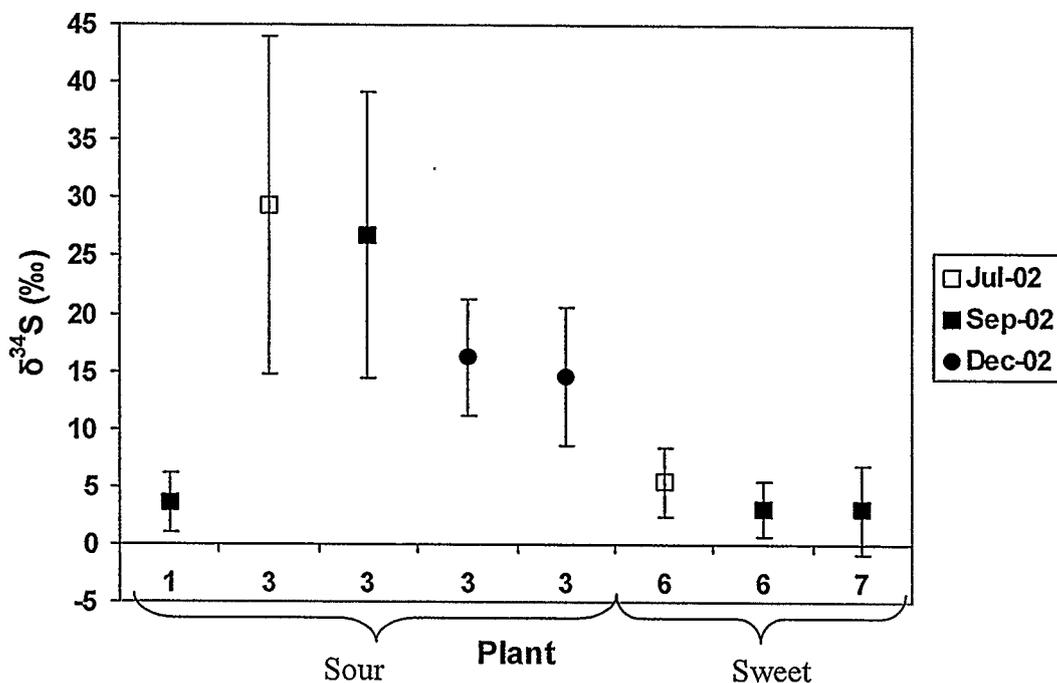


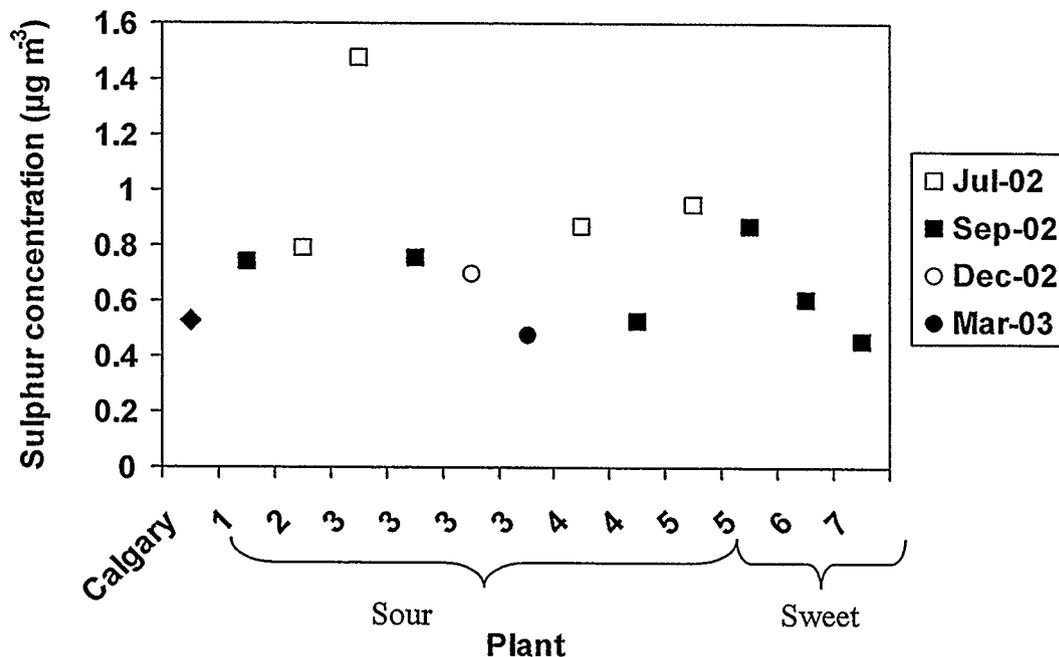
Figure 5.4b - $\delta^{34}\text{S}$ values of SO_2 emissions at gas plants in Alberta

It appears that the $\delta^{34}\text{S}$ of SO_2 emissions at plant 3 may have decreased from +29.4 ‰ in July 2002 to +14.6 ‰ in December 2002. The variation in $\delta^{34}\text{S}$ values was confirmed by the high SO_2 concentrations shown in Figure 5.4a, suggesting that the changing isotope composition may have reflected either a change in the sulphur composition of the inlet gas due to feed from different wells with lower $\delta^{34}\text{S}$ values or seasonal variability in atmospheric oxidation rates and / or pathways. Alternatively, if wind direction varied during the sampling period, emissions from other nearby gas processing plants or wells may have been captured. A final possibility is variation in the relative contributions to emissions from the flare and incinerator stacks, which could have resulted in some isotopic variation since gas combusted in the flare may have been

from a point upstream of the sulphur recovery unit. However, fractionation due to the sulphur recovery unit likely could not account for all of the differences as it is expected to be slight (Krouse *et al.*, 1984).

5.2.2.2 SO_4^{2-}

The concentration of SO_4^{2-} in emissions measured downwind of the gas plants, shown in Figure 5.4c, ranged from 0.5 to 1.5 $\mu\text{g sulphur m}^{-3}$. Considering that the average SO_4^{2-} concentration in Calgary was reported as 0.5 $\mu\text{g sulphur m}^{-3}$ (Norman *et al.*, 2004), SO_4^{2-} concentrations in emissions measured downwind of the gas plants were relatively low and not necessarily representative of emissions from the local gas plant. Relatively high SO_4^{2-} concentrations were measured in samples downwind of plants 3 (0.7 to 1.5 $\mu\text{g sulphur m}^{-3}$), 4 (0.9 $\mu\text{g sulphur m}^{-3}$), and 5 (0.9 $\mu\text{g sulphur m}^{-3}$), which were all sour.



(Calgary, AB value from Norman *et al.*, 2004)

Figure 5.4c – Concentration of sulphur in SO_4^{2-} emissions at gas plants in Alberta

As shown in Figure 5.4d, the maximum $\delta^{34}\text{S}$ value for SO_4^{2-} was +28.2 ‰, measured at plant 4 (sour), and the minimum was +13.4 ‰, measured at plant 5 (sour). Unfortunately, there were no corresponding SO_2 $\delta^{34}\text{S}$ values from either plant with which to compare because of the previously discussed problem of small SO_2 samples (section 4.1). Downwind of plants 6 and 7, the sweet plants, SO_4^{2-} was again among the lightest isotopically with $\delta^{34}\text{S}$ values averaging $+14.1 \pm 0.3$ ‰. It is interesting to note that the range of SO_4^{2-} $\delta^{34}\text{S}$ values was much smaller than that of the SO_2 $\delta^{34}\text{S}$ values, averaging $+18.5 \pm 4.0$ ‰. Furthermore, SO_4^{2-} $\delta^{34}\text{S}$ values tended to be higher than corresponding SO_2 $\delta^{34}\text{S}$ values with the exception of the July and September samples from plant 3. There was neither a decline nor an increase in SO_4^{2-} $\delta^{34}\text{S}$ values over time in emissions from plant 3 as was noted in SO_2 $\delta^{34}\text{S}$ values, suggesting several possibilities:

1. The sulphur composition of the inlet gas changed temporarily so that SO_2 $\delta^{34}\text{S}$ values changed but averaged emissions represented by SO_4^{2-} did not.
2. Seasonal variability in SO_2 oxidation rates and / or pathways did not occur.
3. Other factors masked or overwhelmed the seasonal variability and / or source signal of the SO_4^{2-} $\delta^{34}\text{S}$ values (e.g. influence of sulphur in emissions from nearby gas plants).

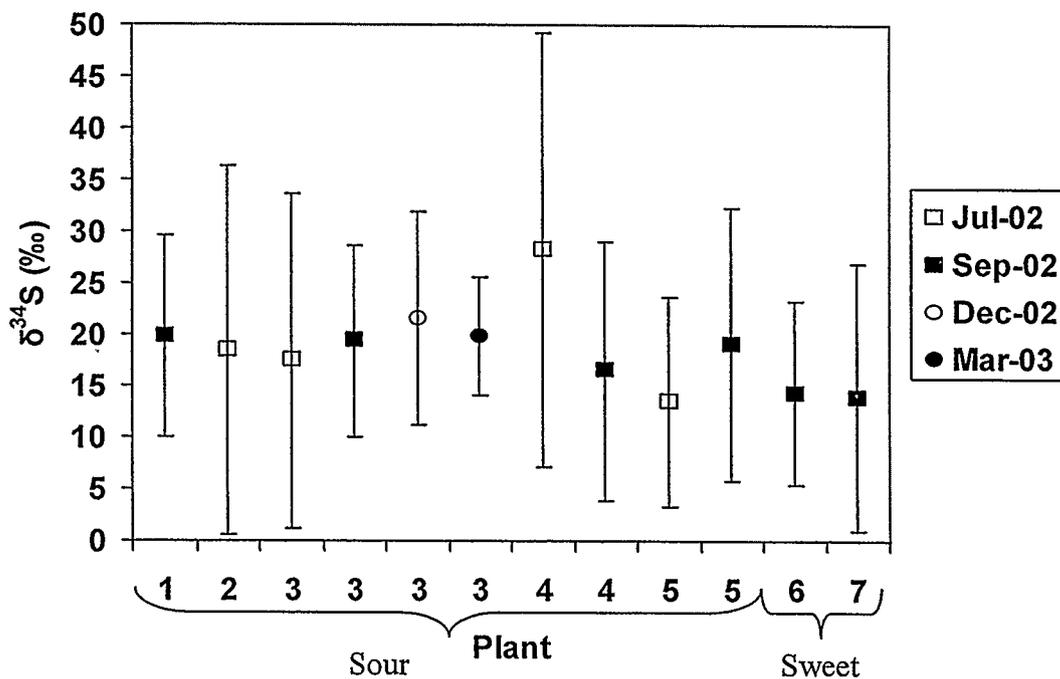
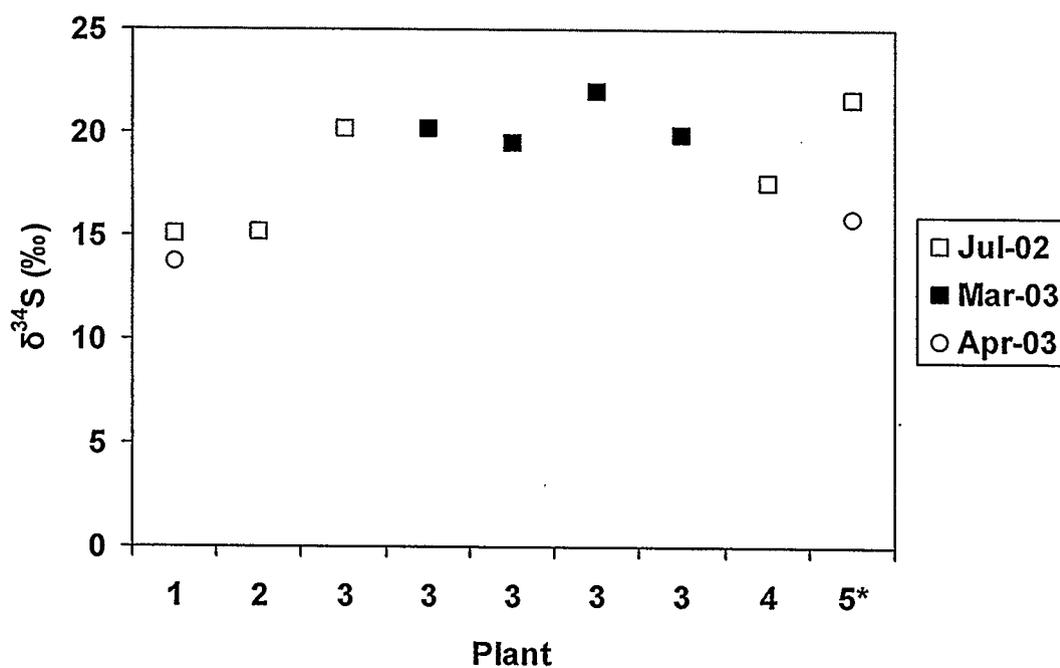


Figure 5.4d - $\delta^{34}\text{S}$ values of SO_4^{2-} emissions at gas plants in Alberta

5.2.2.3 Solid sulphur

Solid sulphur samples, shown in Figure 5.4e, ranged from a minimum $\delta^{34}\text{S}$ of +13.8 ‰ at plant 1 to a maximum of +22.0 ‰ at plant 3. Temporal and / or spatial variability tests were performed at plants 1, 3, and 5, which were all sampled on two to three different occasions from July 2002 to April 2003. Plant 1, where molten sulphur samples were collected directly from the process, didn't appear to show any significant

temporal variation with $\delta^{34}\text{S}$ averaging $14.4 \pm 0.9 \text{ ‰}$. Plant 3, where solid sulphur samples were taken at different times and from different locations on the sulphur block, showed very little temporal or spatial variation, averaging $\delta^{34}\text{S}$ of $+20.3 \pm 1.0 \text{ ‰}$. Finally, sulphur collected from the sulphur-forming plant of plant 5 did show some temporal variation, with $\delta^{34}\text{S}$ averaging $+18.8 \pm 4.1 \text{ ‰}$. However, it was later discovered that only about 80% of the sulphur collected from the forming facility was from plant 5, and the remainder was from other nearby facilities (sulphur-forming facility staff, personal communication, 4 November 2004). Solid sulphur from all plants over the sampling period averaged $+18.3 \pm 2.9 \text{ ‰}$ which was not significantly different from the average $\delta^{34}\text{S}$ value for sulphate ($+18.5 \pm 4.0 \text{ ‰}$) (*t*-test, $p < 0.05$).



* - About 80% of the sulphur sample was from plant 5.

Figure 5.4e - $\delta^{34}\text{S}$ values of solid sulphur from gas plants in Alberta

5.2.2.4 Discussion of emission sources

Table 5.3 presents the differences between the $\delta^{34}\text{S}$ values of SO_2 and SO_4^{2-} ($\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}-\text{SO}_2}$), using equation 5.2, at plants where both values could be measured.

$$\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}-\text{SO}_2} = \delta^{34}\text{S}_{\text{SO}_4^{2-}} - \delta^{34}\text{S}_{\text{SO}_2} \quad (5.2)$$

If these values were representative of sulphur emitted from the same sources, $\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}-\text{SO}_2}$ would represent the fractionation effects due to the oxidation of SO_2 to SO_4^{2-} . The results suggest that either the large differences were not related to seasonal variability or that factors such as the influence of other gas plants in the area altered the sulphur isotope compositions of samples and the SO_2 and SO_4^{2-} measured were not from the same source.

Table 5.3 - Average $\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}-\text{SO}_2}$

Plant	$\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}-\text{SO}_2}$ (‰)	Sampling month
1	+16.1	September
3	-12.0	July
	-7.5	September
	+5.3	December
6	+11.2	September
7	+10.9	September

In contrast, Table 5.4 presents the differences between the average $\delta^{34}\text{S}$ values of SO_4^{2-} and solid sulphur ($\Delta\delta^{34}\text{S}_{\text{S}_8-\text{SO}_4^{2-}}$) at plants 1 through 5 (where solid sulphur samples were collected), using the following equation:

$$\Delta\delta^{34}\text{S}_{\text{S}_8-\text{SO}_4^{2-}} = \delta^{34}\text{S}_{\text{S}_8} - \delta^{34}\text{S}_{\text{SO}_4^{2-}} \quad (5.3)$$

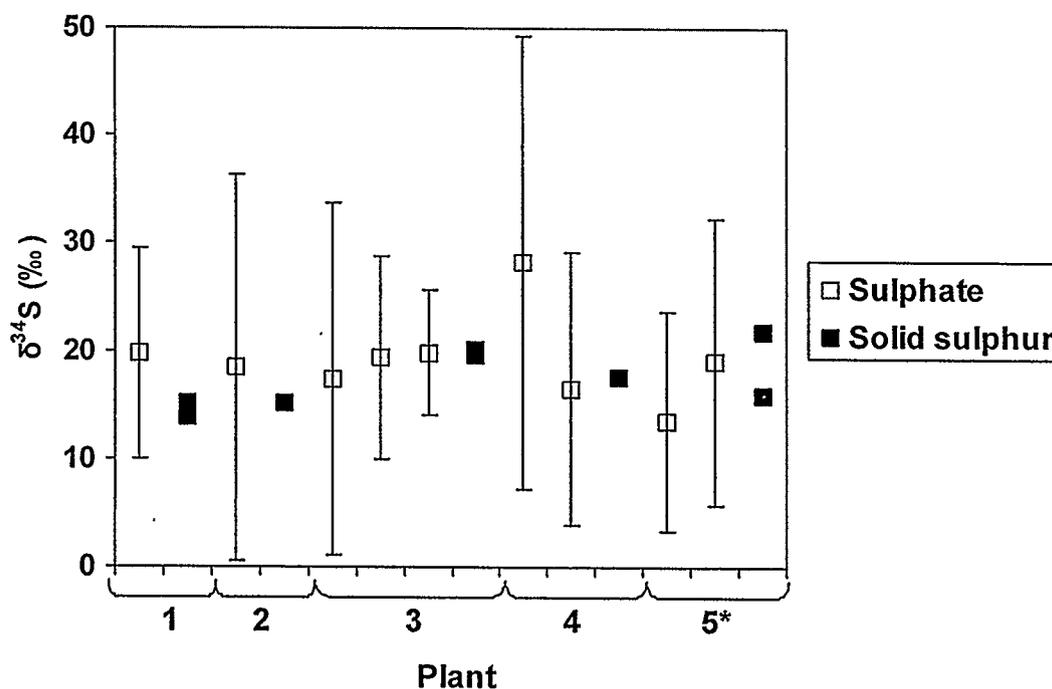
As discussed in section 3.5, the $\delta^{34}\text{S}$ value of S_8 was expected to be close to that of the inlet gas due to the high sulphur recoveries achieved at these plants. The average $\delta^{34}\text{S}$ value of SO_4^{2-} measured downwind of plant 3 ($+19.5 \pm 1.7\%$), the largest sulphur emitter of the gas plants listed in Table 5.2, and the elemental sulphur collected from plant 3 ($+20.3 \pm 1.0\%$) agreed particularly well. This leads to the question of whether the

dominant source of SO_4^{2-} in the region was oxidation of SO_2 emissions from plant 3, which would result in fairly consistent SO_4^{2-} $\delta^{34}\text{S}$ values near the average of those from plant 3. Deviations from the SO_4^{2-} $\delta^{34}\text{S}$ value of plant 3 would then be due to contributions from the emissions of nearby smaller sources with isotopically lighter sulphur as evidenced by S_8 samples collected from each sour plant (Figure 5.5a).

Table 5.4 - Average $\Delta\delta^{34}\text{S}_{\text{S}_8-\text{SO}_4^{2-}}$

Plant	$\Delta\delta^{34}\text{S}_{\text{S}_8-\text{SO}_4^{2-}}$ (‰)
1	-5.3
2	-3.2
3	+0.8
4	-4.8
5	+2.6*

* - About 80% of the sulphur sample was from plant 5.



* - About 80% of the sulphur sample was from plant 5.

Figure 5.5a - $\delta^{34}\text{S}$ values of sulphate and solid sulphur from gas plants in Alberta

Background SO_4^{2-} levels in the area may have been elevated due to plant 3 emissions and can be considered as a uniform area source as opposed to a point source.

This helps describe why the SO_2 and SO_4^{2-} $\delta^{34}\text{S}$ values for plants 6 and 7 did not

correspond. In fact, SO_4^{2-} $\delta^{34}\text{S}$ values for plants 6 and 7, and possibly 5, were less positive in keeping with contributions of SO_4^{2-} from SO_2 emitted by these facilities, assuming that no fractionation occurred during oxidation.

Krouse and Case (1981) and Krouse *et al.* (1984), in measuring emissions downwind of sour gas plants using arrays of high-volume samplers, could not find a relationship between the $\delta^{34}\text{S}$ values of SO_4^{2-} and SO_2 and concluded in both cases that the SO_4^{2-} was from an unrelated source as may be the case here. Sulphur emissions studies downwind of coal and oil-fired power plants and smelter plumes in the eastern U.S. and eastern Canada determined that typically only about 5% of the SO_2 was oxidised, and almost all of the oxidation occurred within the first few kilometers after emission. Furthermore, a significant amount of sulphate was suspected to be dropping out of the plume, which could lead to an underestimation of the extent of SO_2 oxidation (Newman *et al.*, 1975; Forrest and Newman, 1977; Newman, 1981).

If SO_4^{2-} from plant 3 SO_2 emissions was the dominant source of SO_4^{2-} in the region, it would be possible to apportion the SO_4^{2-} measured downwind of each plant to the contributions from the plant sampled and plant 3 using the following equations:

$$\delta_{\text{measured}} = \delta_{\text{plant}} f_{\text{plant}} + \delta_{\text{plant3}} f_{\text{plant3}} \quad (5.4)$$

where

$$1 = f_{\text{plant}} + f_{\text{plant3}} \quad (5.5)$$

and f_{plant} and f_{plant3} represent the fraction of total SO_4^{2-} contributed by the measured plant and plant 3, respectively. Table 5.5 presents the results of the apportionment.

Table 5.5 – Apportionment of SO_4^{2-} emissions to plants measured and plant 3

Plant	f_{plant}	$f_{\text{plant 3}}$	SO_4^{2-} concentration ($\mu\text{g S m}^{-3}$)	
			plant	plant 3
1	0.09	0.91	0.07	0.7
2	0.37	0.63	0.3	0.5
6	0.37	0.63	0.2	0.4
7	0.37	0.63	0.2	0.3

Apportionment was accomplished by assuming that the solid sulphur $\delta^{34}\text{S}$ values were most representative of sulphur processed in plants 1, 2, and 3, as discussed previously (section 3.5). Since plants 6 and 7 were sweet and therefore did not recover sulphur, the SO_2 $\delta^{34}\text{S}$ values were taken to be the most representative of emissions from these plants. Indeed, the $\delta^{34}\text{S}$ values of SO_2 appeared to be the most indicative of the emissions of any plant at that point in time, reflecting individual sources and events, and are likely most important in short-term sampling programs that aim to distinguish local emissions. Plant 4 was omitted from the apportionment as the SO_4^{2-} $\delta^{34}\text{S}$ values were higher than those of plant 3 in one case, and lower than the solid sulphur $\delta^{34}\text{S}$ value in the other. However, plant 3 was never upwind of plant 4 during sampling and as a result wouldn't have been expected to contribute to SO_4^{2-} in emissions measured downwind of plant 4. Plant 5 was omitted since the solid sulphur samples were in fact a blend of sulphur from several nearby plants.

Table 5.5 shows that SO_4^{2-} from plant 3 was a significant contributor to the emissions measured downwind of plants 1, 2, 6, and 7. However, it should be noted that the above calculations assumed that little to no fractionation occurred during gas processing and oxidation of SO_2 to SO_4^{2-} . If fractionation during processing was an important factor, relationships between SO_2 , SO_4^{2-} and S_8 should be apparent. The

following Figures 5.5b to d show the average $\Delta\delta^{34}\text{S}_{\text{S8-SO42-}}$ as a function of inlet H_2S composition, sulphur recovery, and inlet gas volume. Since the level of sulphur recovery required increases with increasing inlet sulphur volumes, these properties are all related. An r^2 value has been included in Figures 5.5b to d and in many others that follow. This value has been included as an indication of whether a correlation may exist, and values of 0.25 and greater are considered to suggest the possibility of such.

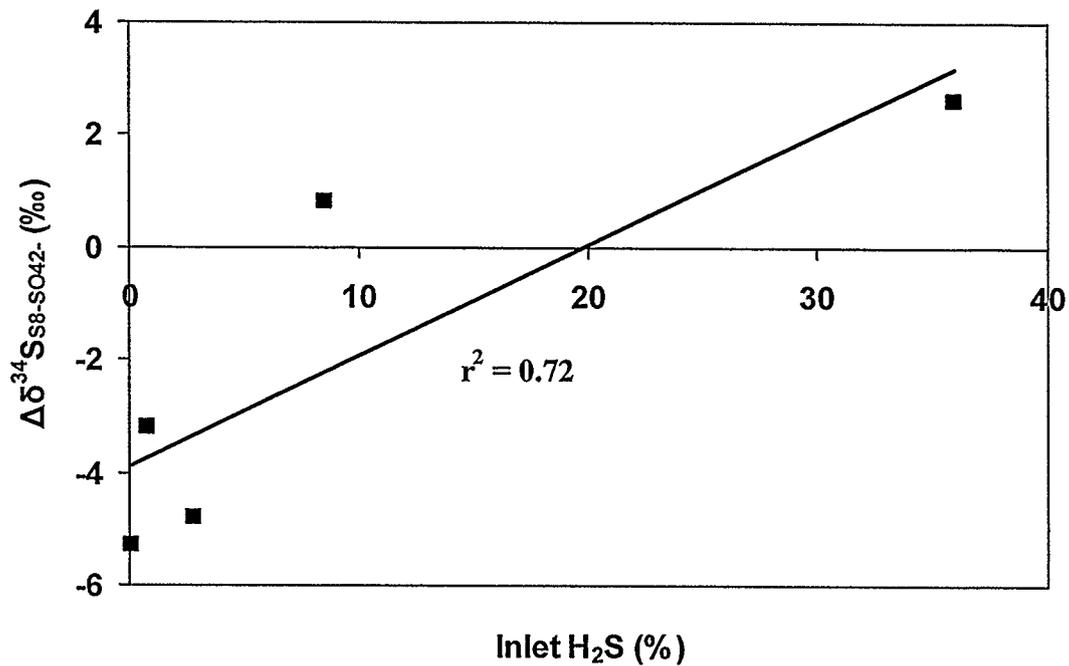


Figure 5.5b - $\Delta\delta^{34}\text{S}_{\text{S8-SO42-}}$ versus inlet H_2S

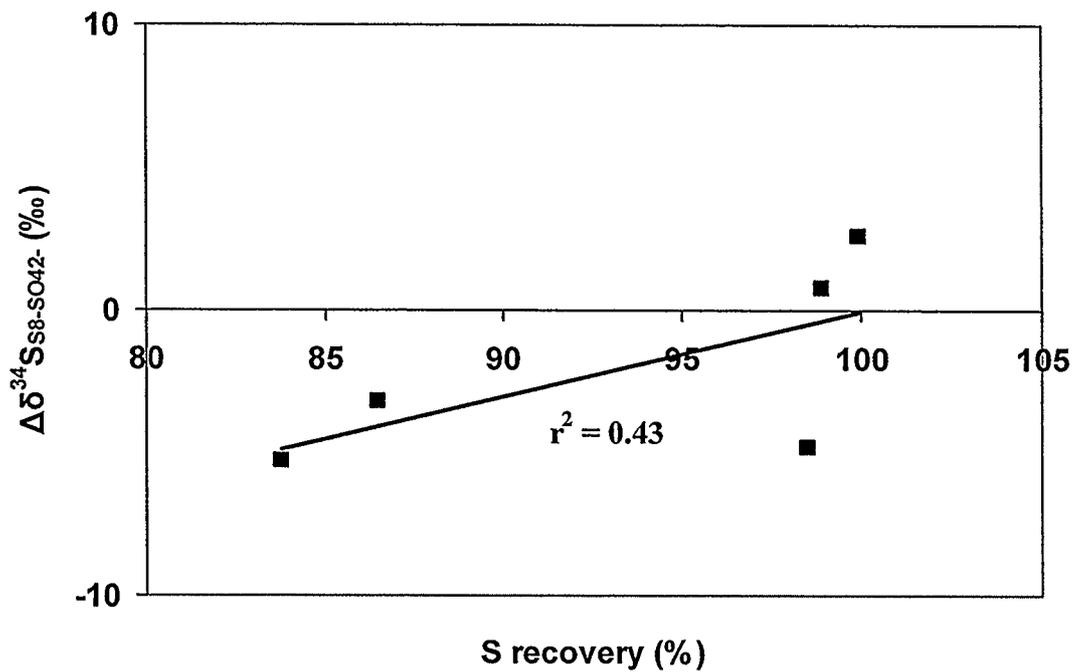


Figure 5.5c - $\Delta\delta^{34}\text{S}_{\text{S8-SO42-}}$ versus sulphur recovery

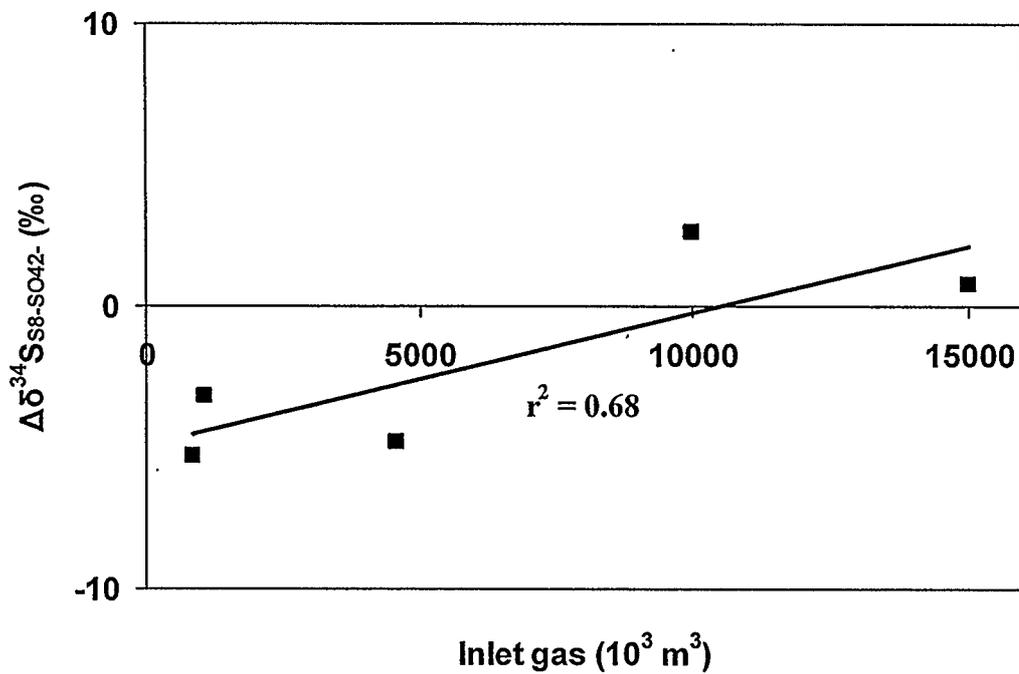


Figure 5.5d - $\Delta\delta^{34}\text{S}_{\text{S8-SO42-}}$ versus inlet gas volume

Figures 5.5 b to d all show correlations with $\Delta\delta^{34}\text{S}_{\text{S}_8\text{-SO}_4^{2-}}$, which appeared to increase with increasing inlet H_2S , sulphur recovery, and inlet gas volume. Although isotopic fractionation during sulphur recovery may occur, all sour plants that process more than 10 tonnes of sulphur per day must recover at least 95.9% of that (Energy and Resources Conservation Board and Alberta Environment, 1988; Alberta Energy and Utilities Board, 2001) and as a result the effects of fractionation may not be evident in S_8 . However, it is suspected that some aspects of gas processing, particularly sulphur recovery and tail gas clean-up, may introduce isotopic fractionation. If indeed the SO_4^{2-} measured was somewhat representative of the emissions from the plants sampled, figures 5.5 b to d may suggest that at high levels of sulphur recovery, gaseous sulphur, which is ultimately burned in the incinerator, becomes depleted in ^{34}S . Plotting $\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}\text{-SO}_2}$ against the same parameters does not yield the same sort of correlations whatsoever, instead showing two distinct groups with positive $\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}\text{-SO}_2}$ values at the small plants with low sulphur recovery and mainly negative $\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}\text{-SO}_2}$ values at plant 3, a large plant with high sulphur recovery. There is not enough data to form any conclusions, but it would be valuable to confirm whether the apparent correlation between $\Delta\delta^{34}\text{S}_{\text{S}_8\text{-SO}_4^{2-}}$ and sulphur recovery is valid. In order to do so, it would be necessary to collect molten sulphur directly from the process while concurrently sampling emissions downwind of the plant.

5.2.2.5 Source characterisation

Source characterisation is important in determining whether the sulphur isotope compositions of emissions from each plant were sufficiently distinct for source apportionment. At each location, the measured sulphur isotope compositions and sulphur

concentrations can be examined with respect to two source mixing. Source A, emissions from a given gas plant, contributes varying amounts of sulphur while source B, essentially the background contribution, is expected to have a constant sulphur concentration. Both source A and source B are assumed to have characteristic sulphur isotope compositions that did not change over time. The relationship between the two sources (A and B) and the measured sulphur isotope compositions and concentrations (C) is then described by:

$$\delta^{34}\text{S}_A [\text{S}_A] + \delta^{34}\text{S}_B [\text{S}_B] = \delta^{34}\text{S}_C [\text{S}_C] \quad (5.6)$$

where

$$[\text{S}_A] + [\text{S}_B] = [\text{S}_C] \quad (5.7)$$

Equations 5.6 and 5.7 were rearranged to give:

$$\delta^{34}\text{S}_C = (\delta^{34}\text{S}_B - \delta^{34}\text{S}_A) * [\text{S}_B] / [\text{S}_C] + \delta^{34}\text{S}_A \quad (5.8)$$

The plot of $\delta^{34}\text{S}_C$ versus $[\text{S}_C]^{-1}$ should be linear, with the sulphur isotope composition of the variable source A given by the intercept ($\delta^{34}\text{S}_A$) (Krouse *et al.*, 1984).

Isotope and concentration data from plant 3 are presented in Figure 5.6. Sulphur isotope compositions for both SO_2 and SO_4^{2-} from plant 3 are shown versus the inverse of the atmospheric sulphur concentration. While all points have large uncertainties, the SO_4^{2-} $\delta^{34}\text{S}$ values suggest plant 3 may have emissions near +17 ‰, somewhat close to the average $\delta^{34}\text{S}$ value of solid sulphur (+20.3 ‰) which is within the uncertainty of all SO_4^{2-} $\delta^{34}\text{S}$ values from plant 3. However, it is interesting to note that +17 ‰ is actually very close to the solid sulphur $\delta^{34}\text{S}$ of plant 4 (+17.6 ‰), which was upwind of plant 3 for all samples. This may indicate that SO_4^{2-} measured downwind of plant 3 was dominated by

SO_4^{2-} from plant 4, a valid possibility since the atmospheric lifetime of SO_2 can range from 1 hour to 7 weeks depending on atmospheric conditions and season.

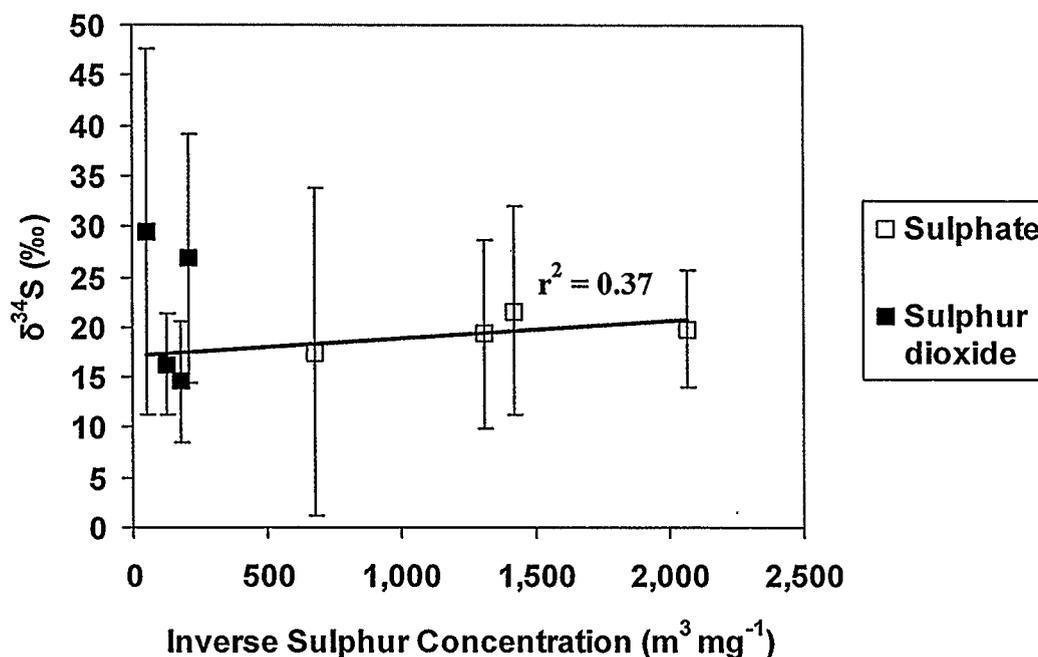


Figure 5.6 - $\delta^{34}\text{S}$ versus inverse sulphur concentration

5.2.2.6 Source apportionment

Source apportionment at a downwind receptor site using the $\delta^{34}\text{S}$ values of SO_2 and / or SO_4^{2-} emissions may be possible. However, apportionment of all seven plants and apportionment between sour plants is not possible using sulphur isotopes alone. On the basis of SO_2 $\delta^{34}\text{S}$ values, two distinct groups were apparent: emissions from plants 6 and 7, both sweet, averaged $+3.8 \pm 1.4$ ‰, while emissions from plant 3, a sour plant, averaged $+21.8 \pm 7.4$ ‰. In contrast, the $\delta^{34}\text{S}$ values of SO_4^{2-} seemed to represent a uniform area source dominated by the emissions of plant 3, and may be valuable in distinguishing emissions from one gas processing region from another. Alternatively,

SO_4^{2-} $\delta^{34}\text{S}$ values could be used in studies examining natural and anthropogenic sulphur contributions.

5.2.3 British Columbia

The daily volume of gas processed and % H_2S at each plant in B.C. are presented in Table 5.6. The $\delta^{34}\text{S}$ values and concentrations of SO_2 and solid sulphur from each plant are presented in Figures 5.7a-c.

Table 5.6 – Gas volume processed and % H_2S at each B.C. plant

Plant	Gas processed ($10^3 \text{ m}^3 \text{ day}^{-1}$)	% H_2S	% Recovery Required	Sulphur emitted ($10^3 \text{ m}^3 \text{ day}^{-1}$)
8	2,490	5	100	0
9	730	1.2	95	0.4
10	15,780	10.7	95	84.7
11	-	-	-	-
12	1,380	0.75	-	10.4
13	21,430	1.1	95	11.8

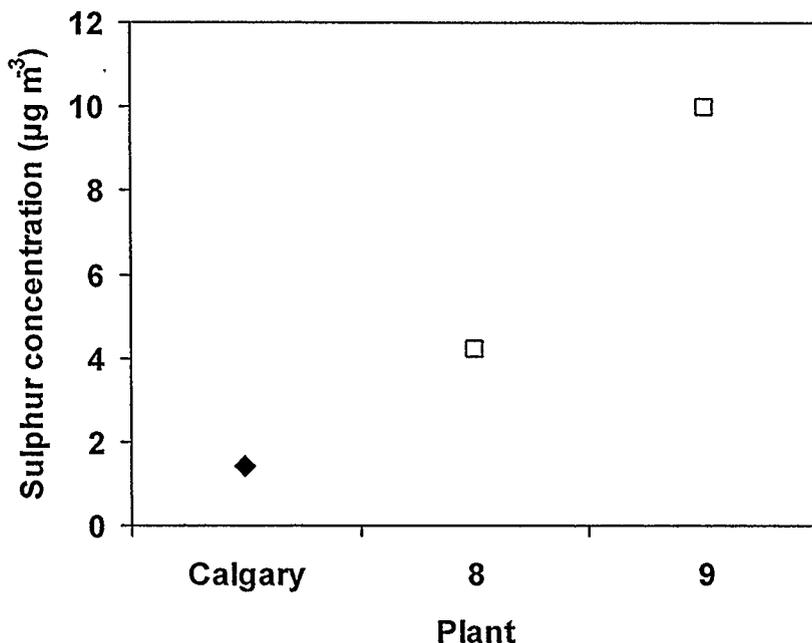
Plants 8, 9, 10 - AccuMap[™], 2004

Plant 8 % H_2S – B.C. Oil and Gas Commission, personal communication, 15 November 2004

Plant 12 – Plant 12 staff, personal communication, 17 November 2001

5.2.3.1 SO_2

The concentration of SO_2 in plant emissions was quite high, ranging from 3 to 7 times the concentration of SO_2 in Calgary ($1.4 \mu\text{g m}^{-3}$ (Norman *et al.*, 2004)). The results confirm that the samples were likely representative of SO_2 emissions from the gas plant in the area.



(Calgary, AB value from Norman *et al.*, 2004)

Figure 5.7a- Concentration of sulphur in SO_2 emissions at gas plants in B.C.

The $\delta^{34}\text{S}$ values of SO_2 , presented in Figure 5.7b, again have very large uncertainties. Although both plants sampled were sour, $\delta^{34}\text{S}$ values ranged from +2.4 to +9.3 ‰. Emissions from plant 9 had the highest SO_2 concentration ($10 \mu\text{g S m}^{-3}$) and the highest $\delta^{34}\text{S}$ value (+9.3 ‰), which was very similar to gasoline and diesel fuel (+8.9 and +9.9 ‰, respectively) and vehicle emissions in Calgary (+9 ‰) (Norman *et al.*, 2004). Emissions from plant 8, where all acid gas produced was reinjected, had a low $\delta^{34}\text{S}$ value of +2.4 ‰ yet a high SO_2 concentration of $4.2 \mu\text{g S m}^{-3}$. This suggests the influence of some other source, which will be further discussed.

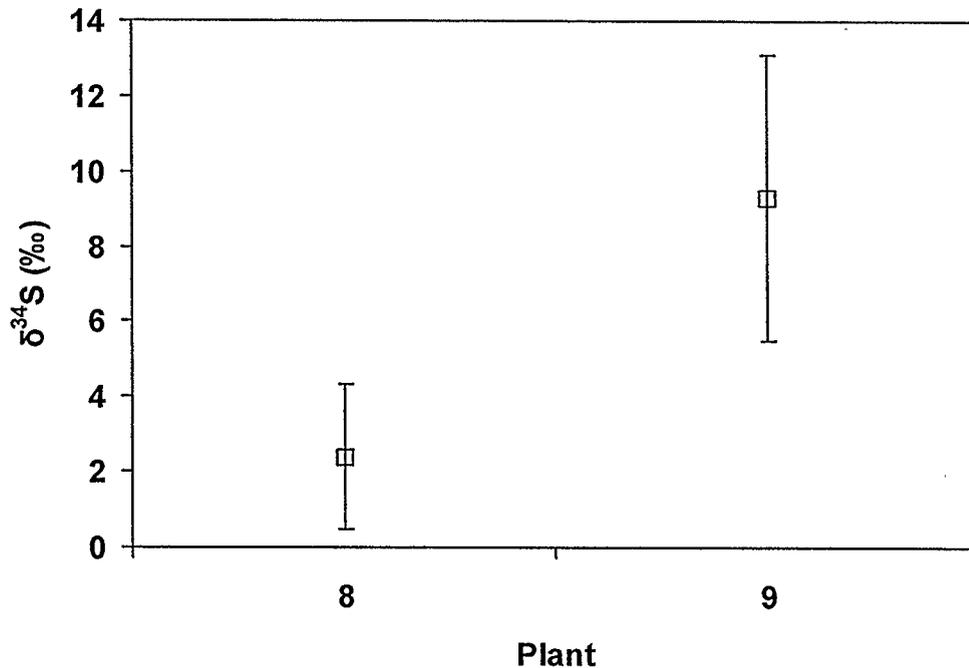


Figure 5.7b - $\delta^{34}\text{S}$ values of SO_2 emissions at gas plants in B.C.

The SO_2 sample measured downwind of plant 10, the largest sulphur emitter listed in Table 5.6, had about the same amount of sulphur and the same $\delta^{34}\text{S}$ value as SO_2 filter blanks. Plant 10 was situated at the top of a mountain with a town in the valley directly north. Although the vegetation encircling the plant demonstrated signs of sulphur stress such as yellowed needles and stunted growth, it is possible that the sampling location – directly beside the plant at the top of the mountain – was too close. In order to better assess the sulphur isotope signature of emissions from this plant, future sampling should take place in the valley as emissions will likely settle there, especially at night.

5.2.3.2 Solid sulphur

The sulfur isotope compositions of solid sulphur samples are presented in Figure 5.7c. Sulphur from plants in B.C. had an average $\delta^{34}\text{S}$ value of $+13.4 \pm 2.0$ ‰. Solid

sulphur from plant 10 was actually the combined product of sulphur from several different plants in the area. Furthermore, plants 10 and 11 were processing the same sulphur – plant 10, with a $\delta^{34}\text{S}$ value of +11.6 ‰, was in fact the gas plant, while plant 11, with a $\delta^{34}\text{S}$ value of +12.1 ‰, was the sulphur-forming operation. No significant isotope fractionation as a result of the sulphur degassing processes discussed in section 1.1.2 was detected between the two plants (t -test, $p < 0.05$).

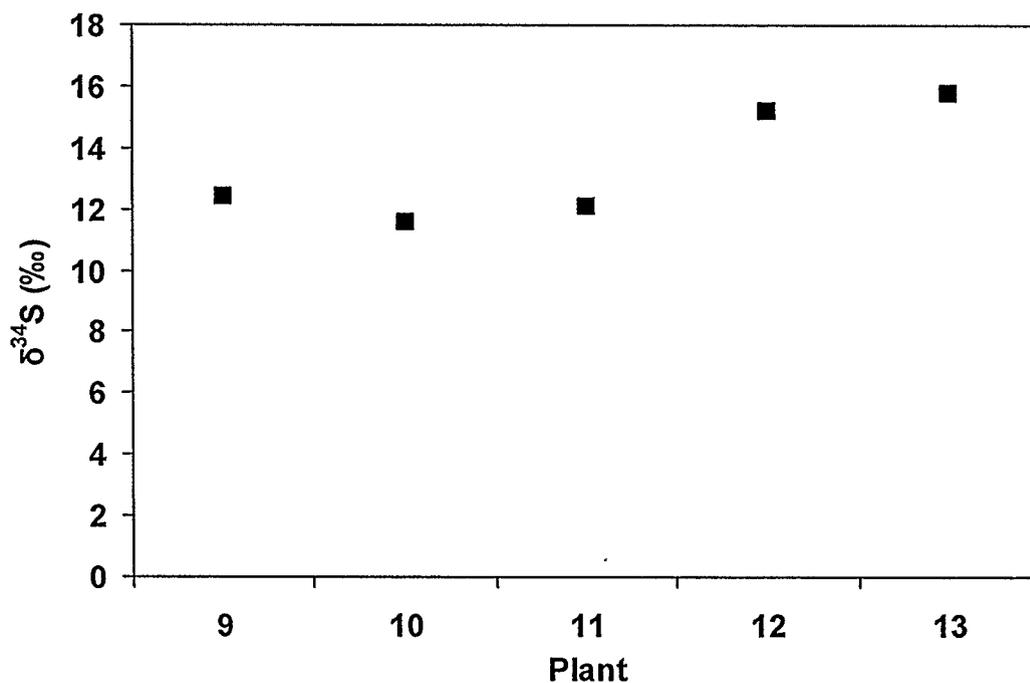


Figure 5.7c - $\delta^{34}\text{S}$ values of solid sulphur from gas plants in B.C.

5.2.3.3 Discussion of emission sources

An interesting phenomenon was noted at plant 8, where all acid gas produced was reinjected. At +2.4 ‰, the $\delta^{34}\text{S}$ value of the SO_2 sample appeared to be much lighter isotopically than expected for a sour plant or the many sour wells in the area, yet the SO_2 concentration ($4.2 \mu\text{g S m}^{-3}$) was higher than both the control site ($0.5 \mu\text{g S m}^{-3}$) and

Calgary ($1.4 \mu\text{g S m}^{-3}$) (Norman *et al.*, 2004) and therefore too high to be considered background contribution.

It has long been established that vegetation will emit H_2S after exposure to SO_2 gas or sulphate and bisulphite solutions, and in fact many species will emit H_2S as a product of photosynthesis (Winner *et al.*, 1981). Foliar sulphur will have $\delta^{34}\text{S}$ values that are much higher than any available sulphur sources (Krouse *et al.*, 1991), but the $\delta^{34}\text{S}$ of emitted H_2S can be lighter than the sulphate source by as much as 9.7 ‰ and lighter than the bisulphite source by as much as 16.8 ‰. These fractionation patterns are independent of the oxidation state of atmospheric sulphur (Winner *et al.*, 1981) and may have contributed to the sample collected downwind of plant 8.

5.2.3.4 Source apportionment

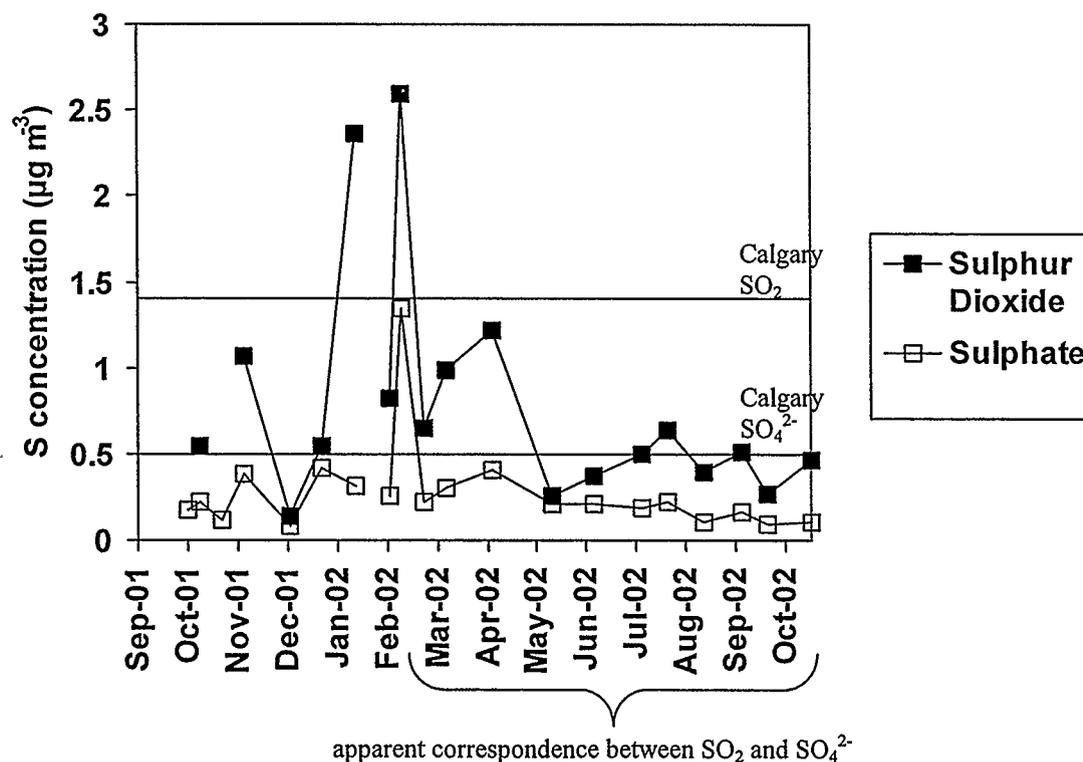
Solid sulphur from gas plants in B.C., with an average $\delta^{34}\text{S}$ value of $+13.4 \pm 2.0$ ‰, appeared to be lighter than sulphur from plants in Alberta, with an average $\delta^{34}\text{S}$ value of $+18.3 \pm 2.9$ ‰. These results suggest that source apportionment between plants in Alberta and plants in B.C. may be a possibility, although further work should be done to explore the range of $\delta^{34}\text{S}$ values measured downwind of gas plants in B.C.

5.2.4 Receptor Site

The SO_2 and SO_4^{2-} concentrations and $\delta^{34}\text{S}$ values measured during the approximately month-long samples taken at the receptor site are shown in Figures 5.8a-f and 5.9a-d.

5.2.4.1 Concentration measurements

As shown in Figure 5.8a, all concentrations were lower than those measured in Calgary with the exception of two SO₂ samples and one SO₄²⁻ sample. Such a result is to be expected because the receptor site was at least 25 km downwind of all seven Alberta gas plants sampled and in a rural area rather than a city or an industrial area. The three samples with high concentrations were measured in January and February 2002, and may have been due to flaring from a nearby well or battery. There is a lot of drilling activity in the region bounded by the seven gas plants and the receptor site, and many wells in the area were likely flaring due to testing during the period of June 2001 to October 2002 (Accumap™, 2004).



(Calgary, AB values after Norman *et al.*, 2004)

Figure 5.8a – Sulphur concentration of receptor site samples over sampling period

The period from the end of February, 2002 until the end of the sampling program in October 2002, demonstrated some relationship between SO_2 and SO_4^{2-} concentrations as shown in Figure 5.8b. This suggests that either the air sampled was well mixed or that the bulk of the SO_2 and SO_4^{2-} sampled was emitted by the same source or sources.

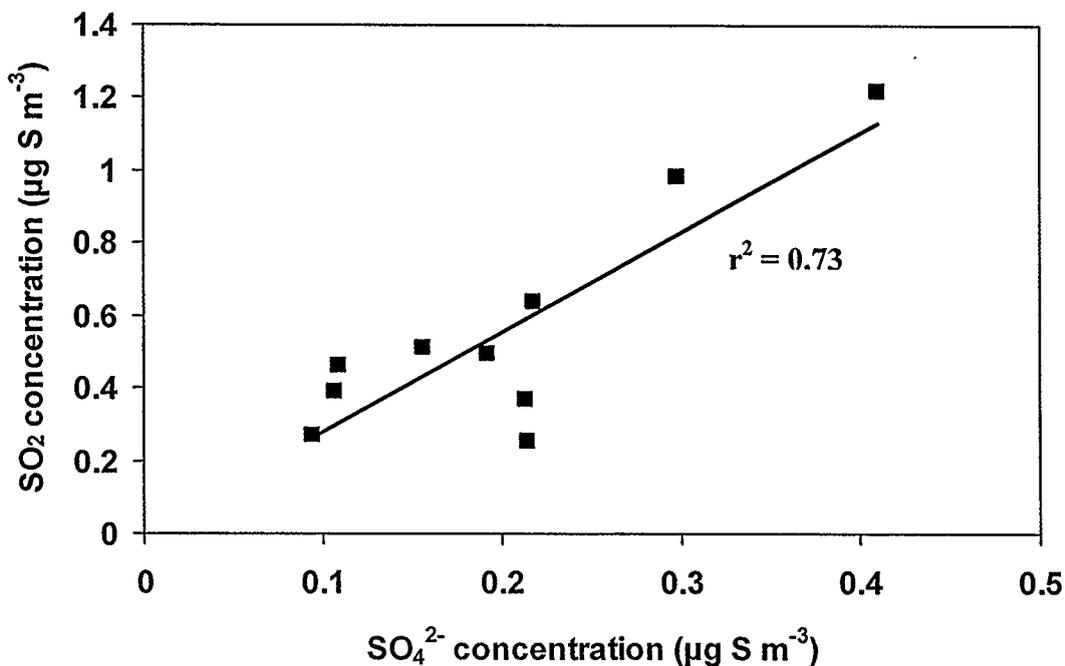


Figure 5.8b – SO_2 vs. SO_4^{2-} concentration (February 26 to October 25, 2002)

Over the period discussed above (February to October 2002), several other relationships became apparent. Figure 5.8c shows that both SO_2 and SO_4^{2-} concentrations decreased as temperature increased, again suggesting that the majority of both substances were emitted from the same source or sources and that perhaps the source itself varied seasonally. However, gas processed in plants will not vary seasonally and therefore the volume of emissions from the plants should not vary either. Staff at plants will take warm weather as an opportunity to shut the plant down in order to perform maintenance work and install new equipment, although it is unlikely that this wholly accounts for

seasonal variation. Other potential contributors to sulphur measured at the receptor site will be discussed further.

Temperature data was only available until September 12, 2002 due to some problems with the weather data files, but only three samples were omitted from the analysis as a result.

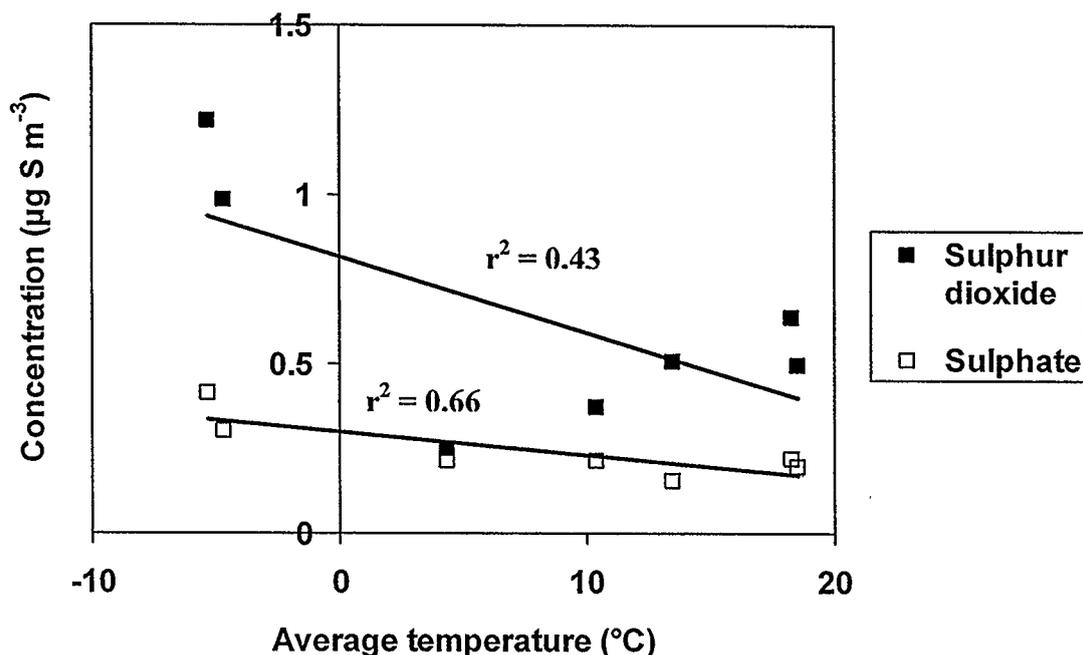


Figure 5.8c –Sulphur concentration of receptor site samples versus average temperature (February 26 - October 25, 2002)

The correlation between relative humidity and SO_2 and SO_4^{2-} concentrations is shown in Figure 5.8d. The relationship was more apparent between relative humidity and SO_2 concentrations, which may in fact be due to the effect of relative humidity on SO_2 filter collection efficiency as discussed in section 4.1.1. However, the average relative humidity is in fact a function of temperature and the amount of water vapour present, so the relationship shown in Figure 5.8d may reflect that as well. The slope of the possible correlation between relative humidity and SO_4^{2-} concentrations is quite moderate, in fact

almost horizontal, indicating that the amount of water vapour had no apparent effect on the oxidation of SO_2 to SO_4^{2-} .

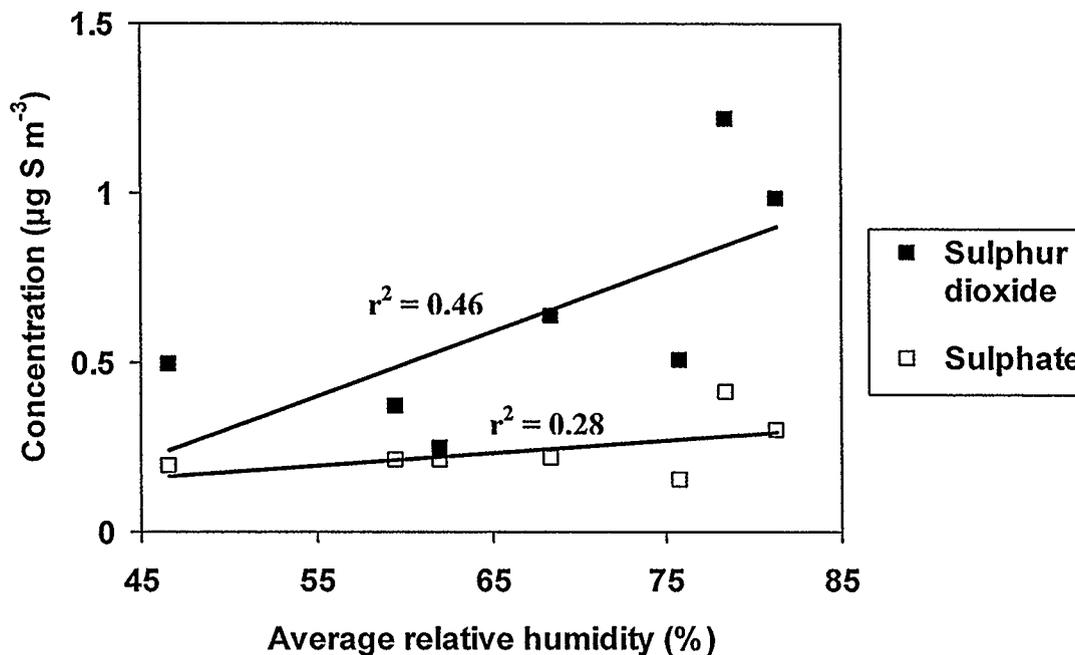


Figure 5.8d – Sulphur concentration of receptor site samples versus relative humidity (February 26 to October 25, 2002)

Figures 5.8e and f show some correlation between SO_4^{2-} concentration and both wind direction and wind speed but none between SO_2 concentration and wind speed. There was no relationship between the average wind directions and wind speeds measured. The highest and lowest SO_2 and SO_4^{2-} concentrations were measured when the wind direction averaged about 279° , which corresponded to plant 6, a sweet plant with no sulphur recovery processes. However, wind direction is not necessarily a good indicator of source emissions at scales greater than a few kilometres because of synoptic scale motions of the atmosphere.

The concentration of SO_4^{2-} appeared to increase, albeit very slightly, with an increase in wind speed. If SO_2 and SO_4^{2-} were emitted from one source, more SO_4^{2-}

could be expected at low wind speeds due to the increased time for SO_2 oxidation, although this might not be the case if SO_4^{2-} is deposited near the plant at low wind speeds or turbulent diffusion keeps SO_4^{2-} aloft longer. These results suggest that SO_4^{2-} in the region was in fact dominated by a uniform area source rather than a point source, and that the SO_2 concentrations, which varied widely, probably reflected individual source events.

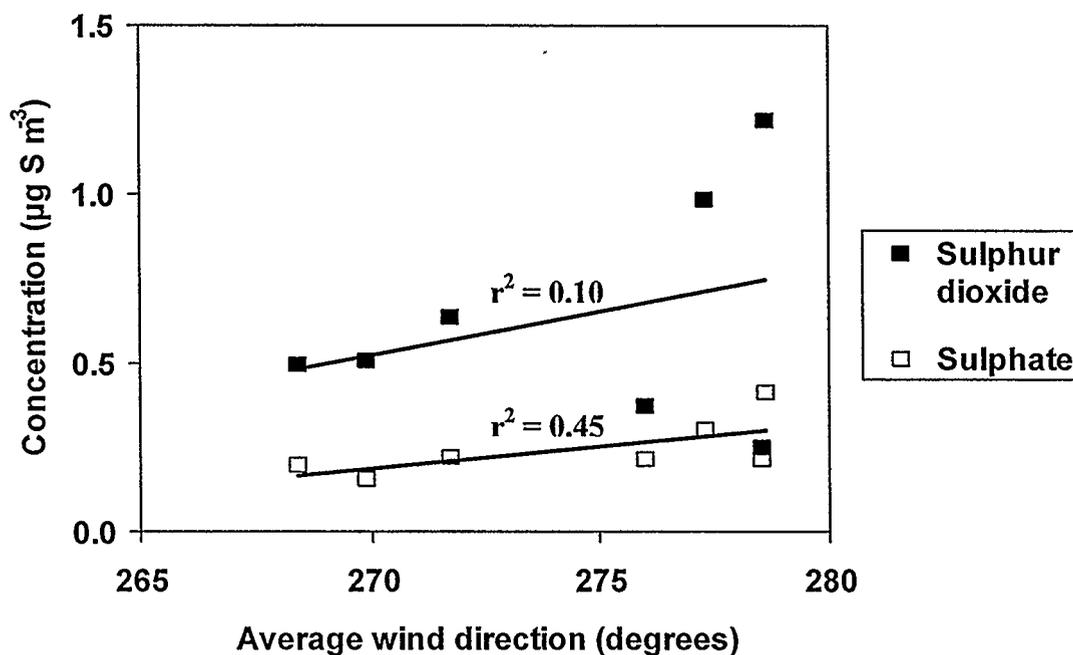


Figure 5.8e – Sulphur concentration of receptor site samples as a function of wind direction (February 26 - October 25, 2002)

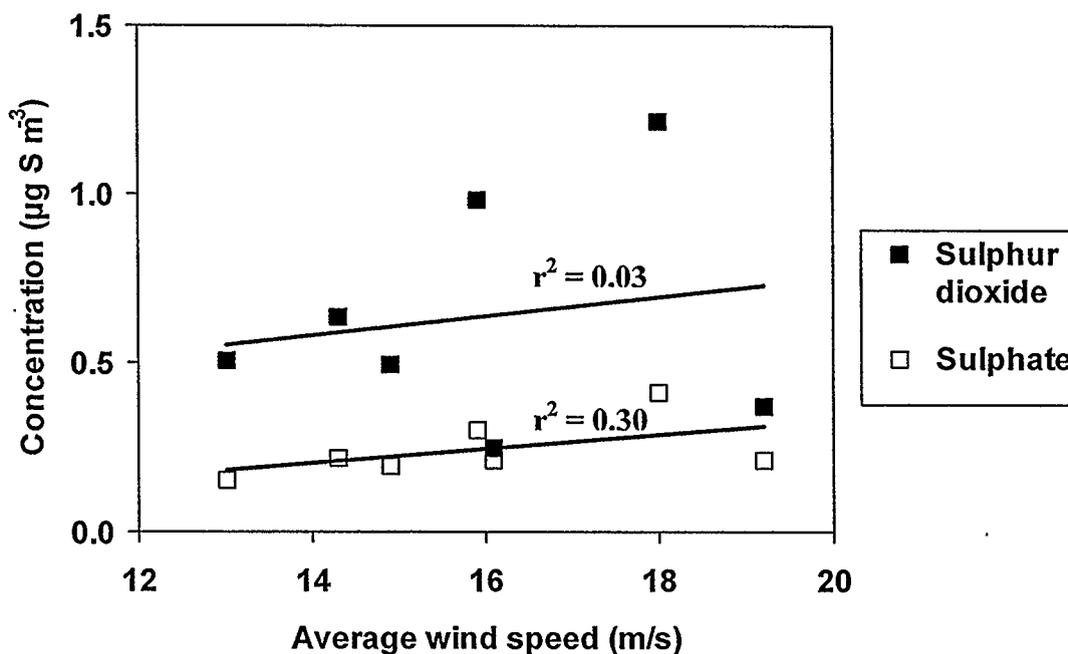


Figure 5.8f – Sulphur concentration of receptor site samples as a function of wind speed (February 26 - October 25, 2002)

5.2.4.2 $\delta^{34}\text{S}$ measurements

Sulphur isotope values for the receptor site are shown in Figure 5.9a. From September 2001 until the end of February 2002, these values showed no relationship between SO_2 and SO_4^{2-} . The SO_2 $\delta^{34}\text{S}$ values of samples collected in October 2001 and February 2002 were higher than those measured in emissions downwind of any of the plants, and these may have been due to other facilities upwind of the plants sampled. The apparently unrelated SO_4^{2-} $\delta^{34}\text{S}$ values may have been due to flaring from a nearby well or a battery, preferentially producing SO_4^{2-} unrelated to SO_2 from large gas processing plants. However, as discussed in section 5.2.4.1, there appeared to be some relationship between the $\delta^{34}\text{S}$ values of SO_2 and SO_4^{2-} from the end of February 2002 until the end of the sampling program in October 2002. SO_2 and SO_4^{2-} $\delta^{34}\text{S}$ values appeared to track each other, with SO_2 $\delta^{34}\text{S}$ values averaging about 4‰ heavier than SO_4^{2-} $\delta^{34}\text{S}$ values. While

the 4‰ difference between the $\delta^{34}\text{S}$ values of SO_2 and SO_4^{2-} was within the uncertainty of the data at most points, it may be due in part to fractionation effects resulting from SO_2 oxidation or to differences in background contribution.

Interesting samples were collected while large forest fires were burning in the Fort MacMurray area in northeastern Alberta in June 2002. Smoke from these fires was evident throughout most of southern Alberta and this was reflected by the low SO_4^{2-} $\delta^{34}\text{S}$ values as expected for contributions from the isotopically light biomass in the region (Krouse and Case, 1981). Further, Figure 5.8a shows that SO_2 concentrations were quite low over this period, but SO_4^{2-} concentrations did not increase relative to other periods suggesting that there is very little contribution to the atmospheric sulphur load in the region studied due to forest fires even when they are extensive and smoke is present.

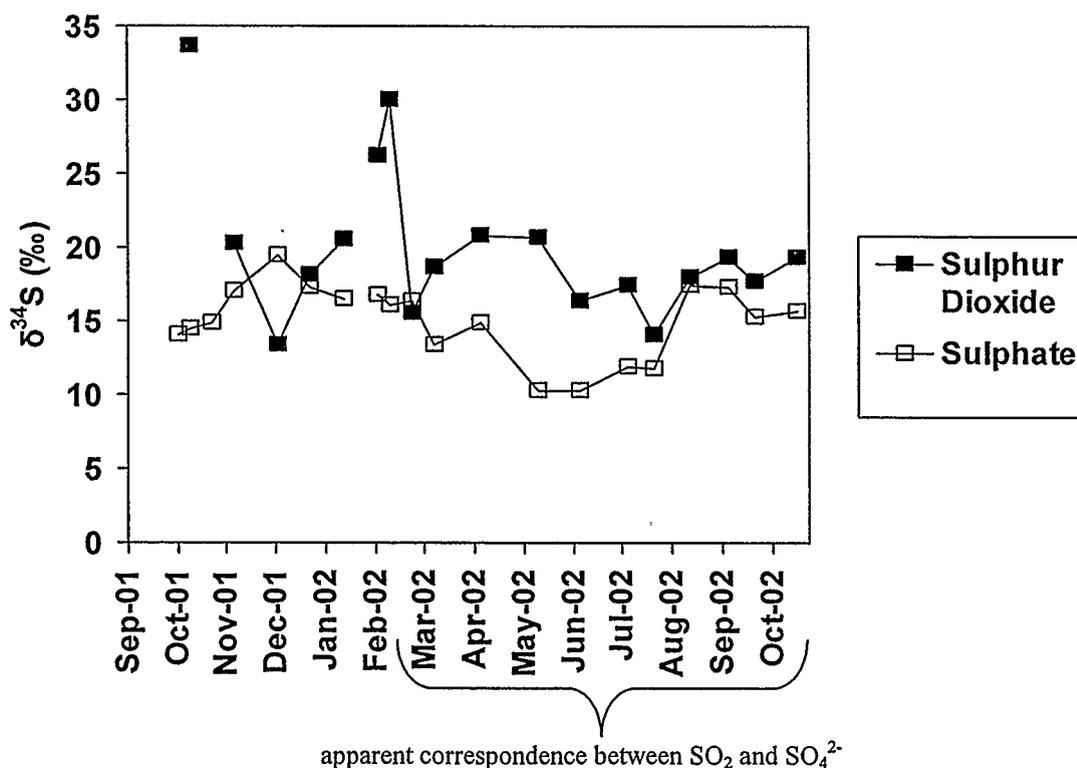


Figure 5.9a – $\delta^{34}\text{S}$ of receptor site samples over sampling period

Other possible relationships over the period that appeared to show trends in $\delta^{34}\text{S}$ values (end of February 2002 until October, 2002) are presented in Figures 5.9b - d. Figure 5.9b shows the $\delta^{34}\text{S}$ values of SO_2 and SO_4^{2-} against average temperature. While there was no correlation between SO_4^{2-} $\delta^{34}\text{S}$ values and temperature, SO_2 $\delta^{34}\text{S}$ values appeared to decrease as temperature increased. The highest SO_2 $\delta^{34}\text{S}$ values, which at almost +21 ‰ were similar to the average SO_2 $\delta^{34}\text{S}$ value of +22 ‰ of emissions downwind of plant 3 and very similar to the average solid sulphur $\delta^{34}\text{S}$ value of +20.3 ‰ from plant 3, were measured when the temperature was coldest. Figure 5.8c showed the same correlation between SO_2 concentrations and temperature.

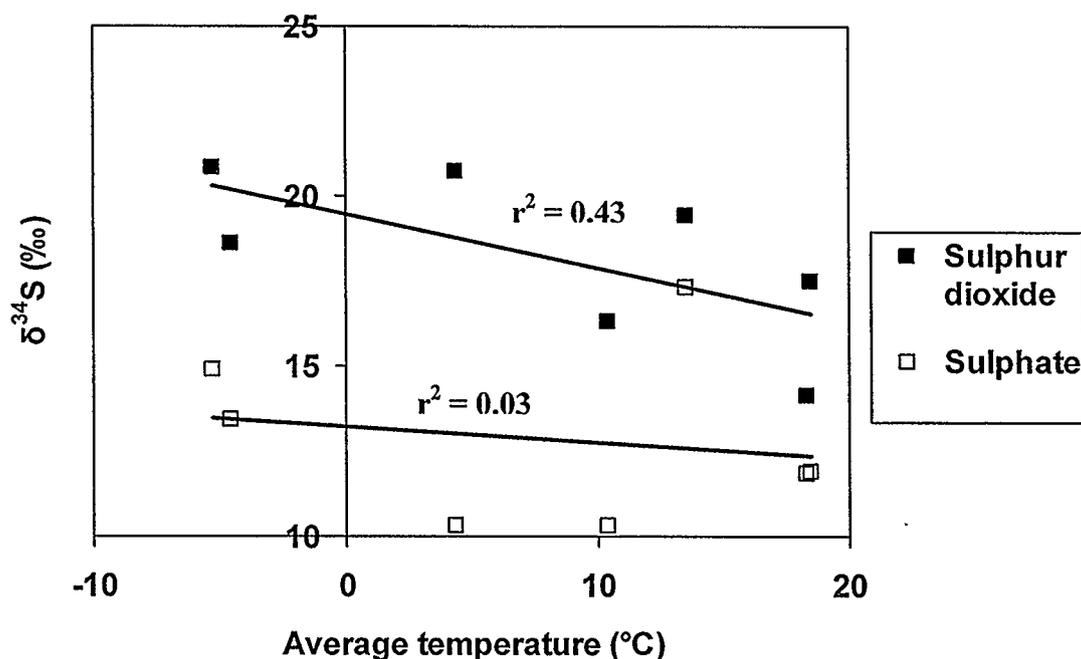


Figure 5.9b – $\delta^{34}\text{S}$ of receptor site samples versus temperature (February 26 - October 25, 2002)

Figure 5.9c shows SO_2 and SO_4^{2-} $\delta^{34}\text{S}$ values plotted against relative humidity. There was no correlation between the SO_2 $\delta^{34}\text{S}$ values and relative humidity despite the relationship between SO_2 $\delta^{34}\text{S}$ values and temperature shown in Figure 5.9b. This

implies that no isotope fractionation occurred through SO₂ trapping on treated cellulose filters and / or oxidation of SO₂ to SO₄²⁻ with increased water vapour as suggested by Saltzman *et al.* (1983). If the postulate by Saltzman *et al.* (1983), that isotope fractionation must occur in heterogeneous SO₂ oxidation, is accepted, then the effect of relative humidity on SO₂ concentrations shown in Figure 5.8d may have in fact been due to the dependence of SO₂ filter collection efficiency on relative humidity that was discussed in section 4.1.1.

Conversely, SO₄²⁻ δ³⁴S values and concentrations both increased with increasing relative humidity (Figures 5.9c and 5.8d, respectively) while showing no relationship to average temperature (Figure 5.9b). The change in SO₄²⁻ concentrations and δ³⁴S values with relative humidity could suggest an increase in heterogeneous phase oxidation due to an increase in the aqueous phase, potentially leading to heavier SO₄²⁻ δ³⁴S values (Saltzman *et al.*, 1983; Mukai *et al.*, 2001). However, SO₂ concentration also increased with relative humidity (Figure 5.8d), in fact much more dramatically than SO₄²⁻ concentration which would not be expected in a closed system. Potentially, SO₂ oxidation to SO₄²⁻ increased with increasing relative humidity and was accompanied by removal of the resultant SO₄²⁻. Interestingly, SO₄²⁻ δ³⁴S seemed to increase quite significantly with increasing relative humidity and in fact approached the SO₂ δ³⁴S values, suggesting the possibility that fractionation decreased as relative humidity increased. It should be noted that Newman *et al.* (1975), sampling plumes downwind of an oil-fired power plant, did not find any dependency of oxidation on relative humidity, although plumes of oil-fired power plants contain high concentrations of particulate matter as compared to natural gas combustion which could present difficulties in

separating the effects of heterogeneous oxidation in high particulate concentrations from those occurring solely in the aqueous phase.

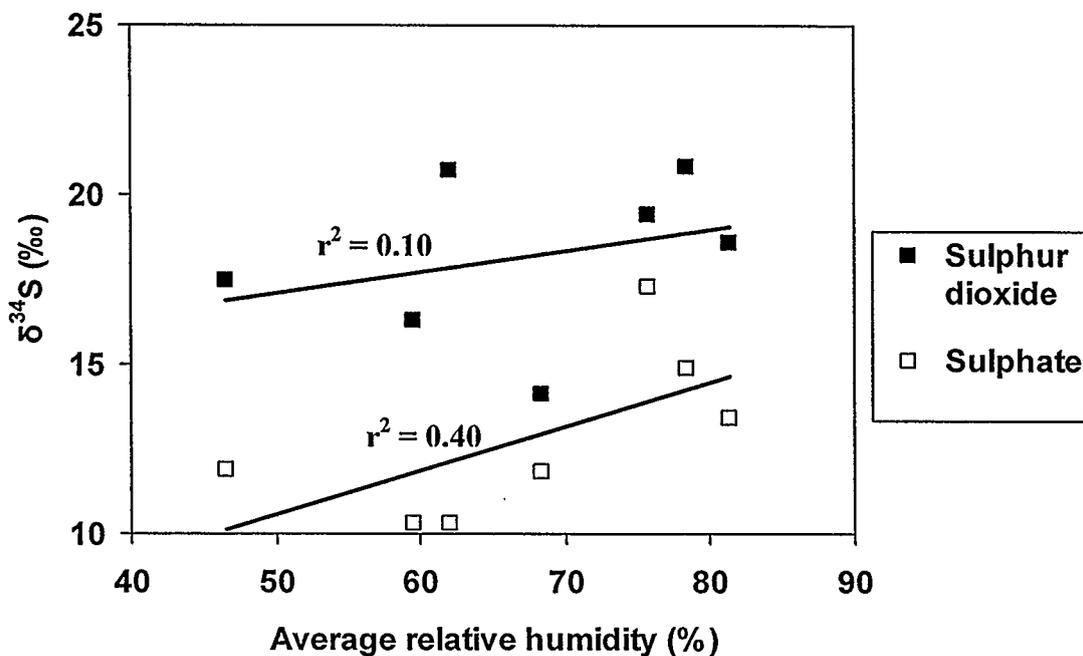


Figure 5.9c – $\delta^{34}\text{S}$ of receptor site samples versus relative humidity (February 26 - October 25, 2002)

As shown in Figure 5.9d, SO_4^{2-} $\delta^{34}\text{S}$ values over the entire sampling period seemed to decrease as the average wind speed increased, while SO_2 showed no relationship. This could have been due to some upwind source, possibly even some of the gas processing facilities in northeastern B.C. Emissions measured downwind of plant 9 had a SO_2 $\delta^{34}\text{S}$ value of +9 ‰, while solid sulphur collected from plant 10 had a $\delta^{34}\text{S}$ value of +12 ‰. There was no correlation between wind speed and wind direction.

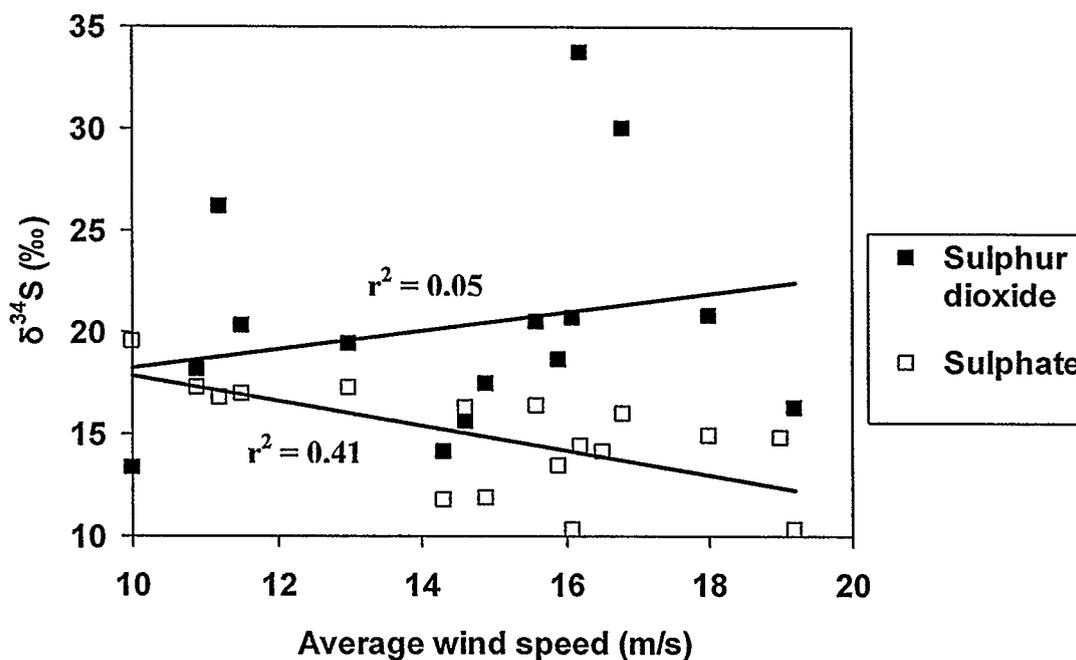


Figure 5.9d – $\delta^{34}\text{S}$ of receptor site samples versus average wind speed

5.2.4.3 Discussion of receptor site samples

In order to determine the possibility and extent of isotope fractionation between SO_2 and SO_4^{2-} , the $\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}-\text{SO}_2}$ over the sampling period was calculated using equation 5.2 and is shown over time in Figure 5.10. As discussed in sections 5.2.4.1 and 5.2.4.2, the $\delta^{34}\text{S}$ values and concentrations of SO_2 and SO_4^{2-} seemed to be related from February 26, 2002 until the end of the sampling program in October, 2002. Figure 5.11 shows some relationship between the $\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}-\text{SO}_2}$ values, which were negative over that period, and the average temperature.

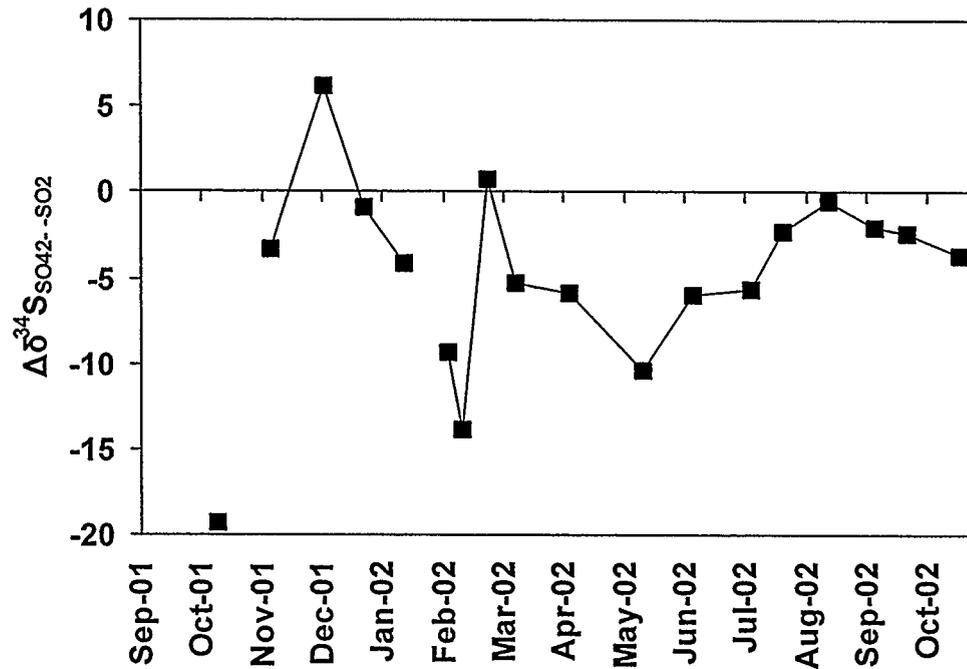


Figure 5.10 - $\Delta\delta^{34}\text{S}_{\text{SO42--SO2}}$ of receptor site samples

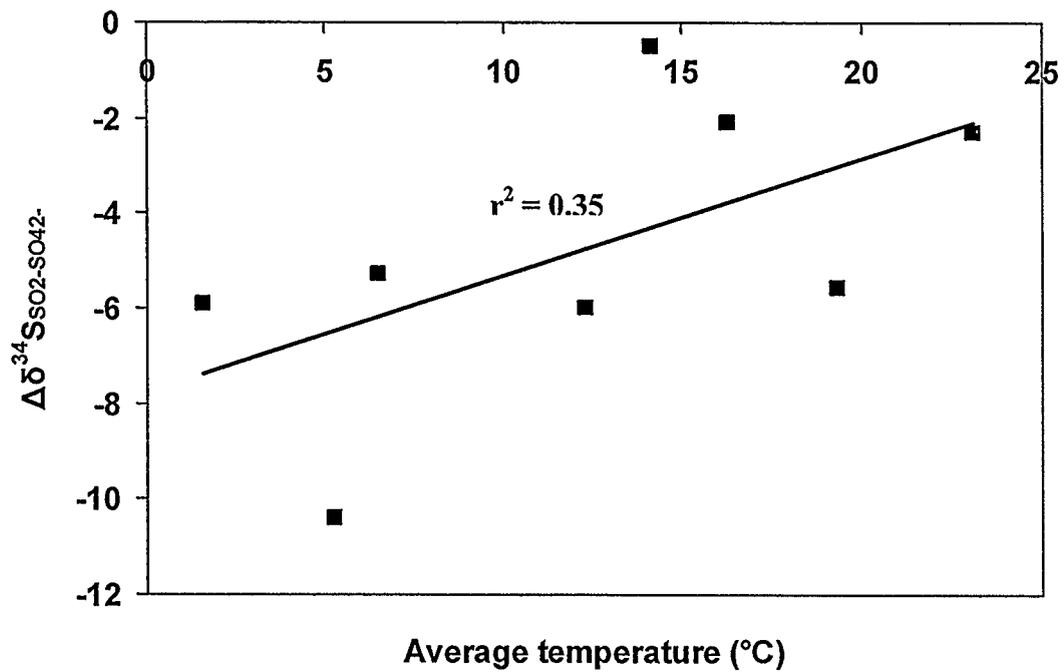


Figure 5.11 - $\Delta\delta^{34}\text{C}_{\text{SO42--SO2}}$ versus average temperature (Feb 26 to Sep 12, 2002)

As evidenced by the plot of $\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}-\text{SO}_2}$ against $\text{SO}_2 \delta^{34}\text{S}$ shown in Figure 5.12, the change in $\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}-\text{SO}_2}$ was almost entirely due to $\text{SO}_2 \delta^{34}\text{S}$ while $\text{SO}_4^{2-} \delta^{34}\text{S}$ changed very little. Again, this suggests that SO_4^{2-} was most representative of emissions from the region rather than individual sources and / or events which seemed best represented by SO_2 . However, the apparent trend between SO_2 and SO_4^{2-} suggests that at the receptor site, SO_4^{2-} originating from the same source as the SO_2 was present in great enough quantities to influence the $\delta^{34}\text{S}$ and track the increases and decreases in $\text{SO}_2 \delta^{34}\text{S}$. As a result, it may be difficult to determine whether $\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}-\text{SO}_2}$ was due to fractionation effects or to the influence of other sources.

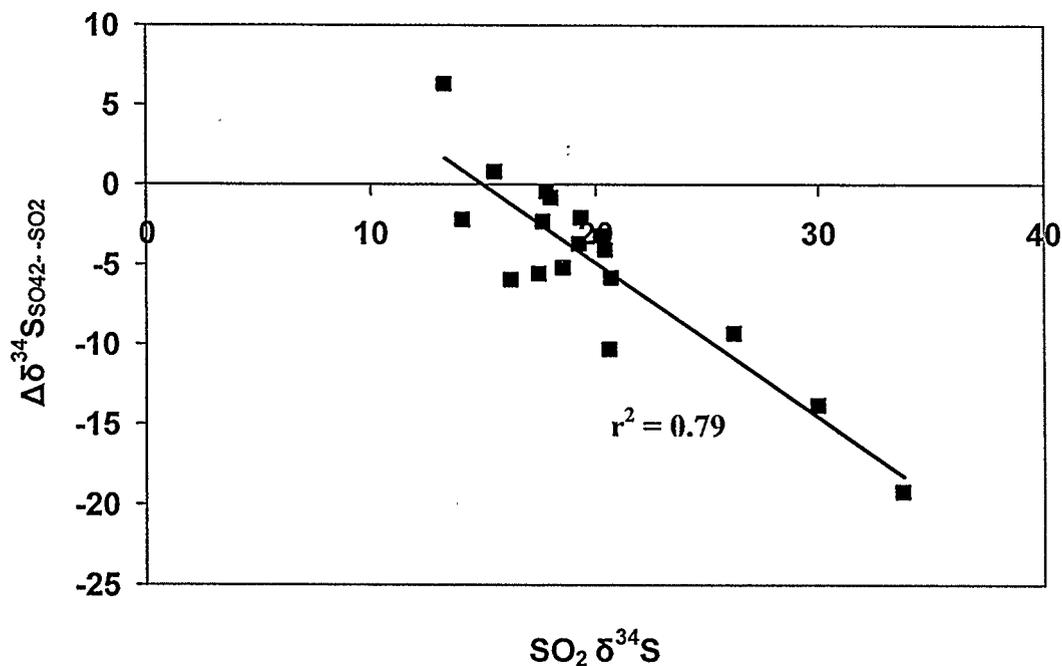


Figure 5.12 – $\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}-\text{SO}_2}$ versus $\text{SO}_2 \delta^{34}\text{S}$

5.2.4.4 Source apportionment

As discussed in section 5.2.2.6, source apportionment is probably best attempted using the average $\delta^{34}\text{S}$ values of SO_2 of sweet plants (+3.8 ‰) and sour plants (+21.8 ‰).

Other sulphur sources considered were vehicle emissions, wood burning, and home heating.

The region bounded by the seven gas plants and the receptor site is primarily rural and dominated by farmland. As an estimate, it was assumed that there were 25,000 homes and 50,000 vehicles in the region. The average natural gas usage per home per year in Alberta is 137 GJ (ENMAX, 2004), and according to pipeline specifications, salable natural gas must have a heating value of at least 36 MJ m^{-3} and contain no more than 115 mg m^{-3} total sulphur (NOVA Gas Transmission Ltd., 2004). Therefore, assuming all sulphur is emitted as SO_2 , the total contribution from homes in the region was 11 tonnes SO_2 per year.

Vegetation contains about 0.25% sulphur by dry weight (Krouse *et al.*, 1991). Assuming that each of those 25,000 homes burned one cord of wood per year and all cords of wood had the same density and weighed about 1150 kg (U.S. Department of Energy, 2004), the total sulphur contribution from wood burning was about 72 tonnes per year. Since wood burning releases high particulate volumes, it was assumed that about half of the sulphur was SO_2 and half was SO_4^{2-} , reducing the total amount of SO_2 released by burning wood to 36 tonnes per year.

Finally, it was assumed that each of the 50,000 vehicles traveled $10,000 \text{ km yr}^{-1}$, achieving an average mileage of about 10 litres per 100 km, and that the average sulphur content of both gasoline and diesel was 0.008%. Again assuming that half of the sulphur was emitted as SO_2 , the total contribution from vehicles was 2 tonnes SO_2 per year.

Although it was not known what amount of sulphur may have been emitted by the two sweet plants, it was assumed that each was just under the one tonne / day limit,

emitting 0.95 tonnes per day. Therefore, the sweet plants emitted 694 tonnes SO₂ per year. The total amount of sulphur which may have been emitted from the five sour plants was 10,349 tonnes per year. In light of these volumes, it was obvious that neither vehicle emissions nor wood burning nor home heating was significant in terms of SO₂ emitted or in terms of the δ³⁴S values.

Therefore, emissions at the receptor site were apportioned using the following equation:

$$\delta_{\text{measured}} = \delta_{\text{sweet}} f_{\text{sweet}} + \delta_{\text{sour}} f_{\text{sour}} \quad (5.9)$$

where

$$1 = f_{\text{sweet}} + f_{\text{sour}} \quad (5.10)$$

and f_{sweet} and f_{sour} represented the fraction of total SO₂ contributed by the sweet and sour plants, respectively. The SO₂ δ³⁴S values of the sweet and sour plants were taken to be +3.8 ‰ and +21.8 ‰, respectively, as discussed in section 5.2.2.1. The results of the apportionment are presented in Table 5.7.

Table 5.7 – Source apportionment of SO₂ measured at receptor site (February 26 – October 25, 2002)

Sampling period	f_{sweet}	f_{sour}	SO ₂ concentration (µg S m ⁻³)	
			sweet plants	sour plants
Feb 26 – Mar 12/02	0.18	0.82	0.17	0.81
Mar 12 – Apr 9/02	0.06	0.94	0.07	1.15
Apr 23 – May 16/02	0.06	0.94	0.02	0.23
May 16 – Jun 11/02	0.30	0.70	0.11	0.26
Jun 11 – Jul 11/02	0.24	0.76	0.12	0.38
Jul 11 – Jul 27/02	0.43	0.57	0.27	0.36
Jul 27 – Aug 19/02	0.22	0.78	0.08	0.30
Aug 19 – Sep 12/02	0.14	0.86	0.07	0.44
Sep 12 – 28/02	0.23	0.77	0.06	0.21
Sep 28 – Oct 25/02	0.14	0.86	0.06	0.40
Average	0.20 ± 0.11	0.80 ± 0.11	0.10 ± 0.07	0.45 ± 0.30

The calculations above assumed that no isotope fractionation occurred during oxidation of SO₂. It is apparent from Table 5.7 that emissions from sour gas plants dominated SO₂ measured at the receptor site, although the concentration of emissions from sweet gas plants was surprisingly high in some periods.

5.2.5 Discussion

Seasonal variability is expected to manifest itself in two ways. First, the oxidation rate of SO₂ is expected to decrease with temperature, which leads to higher SO₂ and lower SO₄²⁻ concentrations in the winter and vice versa in the summer (Saltzman *et al.*, 1983; Mukai *et al.*, 2001). Second, heterogeneous oxidation is expected to dominate during the winter, leading to SO₄²⁻ which is isotopically heavier than the precursor SO₂, while homogeneous oxidation dominates during the summer, leading to SO₄²⁻ which is isotopically lighter than the precursor SO₂ (Saltzman *et al.*, 1983; Novak *et al.*, 2001). The seasonal variation in oxidation pathway may be due to the increasing solubility of SO₂ with decreasing temperatures and decreased photochemical production of gaseous oxidants during the winter (Saltzman *et al.*, 1983). However, this may not be applicable in Alberta, where relative humidity is much higher during the summer than during the winter and winter days tend to be bright and sunny.

Mukai *et al.* (2001), who studied sulphur and lead isotope ratios to determine sources of atmospheric pollution, found that the fractionation between SO₂ and SO₄²⁻ was high in the winter with $\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}-\text{SO}_2}$ of 0 to +6 ‰ and low in summer with $\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}-\text{SO}_2}$ of -1 to +3‰ as expected. The $\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}-\text{SO}_2}$ measured at the control site was +4.6 ‰ in November 2001 and +2.4 ‰ in October 2002, with SO₄²⁻ heavier than SO₂ in both cases, although the concentration of SO₂ was greater than SO₄²⁻ in both cases. These

samples were taken at almost the same time of year (November 20, 2001 and October 25, 2002), which could certainly be considered winter, and the results seem in accordance with those of Mukai *et al.* (2001). It would be interesting to determine what seasonal variations, if any, are demonstrated by the $\delta^{34}\text{S}$ values of SO_2 and SO_4^{2-} at the control site and whether the results are in agreement with the findings of Mukai *et al.* (2001).

As discussed in section 5.2.2.4, SO_2 and most of the SO_4^{2-} measured in emissions downwind of gas plants in Alberta did not appear to be emitted from the same sources. Table 5.4 showed no seasonal relationship in $\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}-\text{SO}_2}$, and SO_2 concentrations were always much higher than SO_4^{2-} concentrations regardless of the time of year as would be expected from emissions measured in the immediate vicinity of a gas plant with suspected upwind contributors. Since SO_4^{2-} from SO_2 emitted by plant 3 appeared to dominate SO_4^{2-} throughout the region, it would be difficult to distinguish seasonal variation in oxidation pathways and / or rates regardless of whether or not it occurred.

At the receptor site, the $\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}-\text{SO}_2}$ of the samples was almost always negative. The $\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}-\text{SO}_2}$ did appear to increase with temperature over the period with coincident trends in SO_2 and SO_4^{2-} , which was contrary to the results of Mukai *et al.* (2001). Figure 5.12 further showed that changes in $\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}-\text{SO}_2}$ were almost wholly due to SO_2 $\delta^{34}\text{S}$ values while SO_4^{2-} values changed very little. These results do not seem to support the fractionation patterns proposed by Saltzman *et al.* (1983) or Mukai *et al.* (2001), especially in light of the sampling period where SO_2 and SO_4^{2-} $\delta^{34}\text{S}$ values and concentrations appeared to be related. The work of Leung *et al.* (2001), who questioned the results of others (Tanaka *et al.*, 1994) by calculating that homogenous fractionation should also result in SO_4^{2-} that is isotopically heavier than the precursor SO_2 , also cannot

explain the results from the receptor site samples. Interestingly, Norman *et al.* (2004) did not find any evidence of fractionation in the oxidation of SO_2 to SO_4^{2-} which may have been the case in this study as well.

It is likely that assigning a relative importance to each of the SO_2 oxidation pathways based solely on the sulphur isotope composition may be too simplistic. From the results of sections 5.2.4.1 and 5.2.4.2, it appears that other factors such as the possibility of SO_4^{2-} removal may play an important role. It would be valuable to confirm the actual sources and oxidation effects of SO_2 and SO_4^{2-} , but to do this effectively a radial sampling array would be necessary, preferably using size-fractionation to determine oxidation within Aitken nuclei versus accumulation modes. In addition, the oxygen isotope signature of SO_2 and SO_4^{2-} could aid in determining oxidation pathways.

CHAPTER 6: BORON

6.1 Introduction

Earth's crust is the source of many trace elements including boron (B), which averages 15 ppm and ranks 27th in abundance in the crust (Anovitz and Grew, 1996). Various geological and geochemical processes have established boron as a constituent of the lithosphere, hydrosphere, biosphere, and atmosphere. Notably, in low concentrations it is an essential nutrient for both plants and animals and therefore may be found in fossil fuels.

Commercially, boron is most valuable in the form of borate ($\text{B}(\text{OH})_4^-$) deposits, the largest of which are found in California, Turkey, and Russia (Davis, 1972). These are mined to produce sodium perborate (NaBO_3), a bleaching agent in detergents and cleaners, and borosilicate glass, amongst other products. In addition, boron enriched in the lighter isotope (^{10}B) is used as neutron-absorbing material in nuclear reactors and for neutron therapy in the treatment of certain cancers (Massey and Kane, 1972; Kakihana *et al.*, 1977). Environmentally, phytotoxicity from boron, although much less prevalent than boron deficiency, can occur and is primarily due to anthropogenic sources such as irrigation water, surface mining wastes, fly ash, industrial chemicals, sewage, and excessive application of boron-rich fertilizers (Nable *et al.*, 1997).

Although boron was well known in the ancient world and first isolated as an element in 1808, today there are still large gaps in the knowledge of boron chemistry and geochemistry. Much of this deficiency is likely attributable to the analytical challenges in measuring boron isotope abundances accurately, which include the difficulties inherent in extracting boron from complex matrices and in preventing sample contamination.

However, the largest obstacles to precise and accurate measurements may well be the lack of measurement intercalibration between laboratories and the need for appropriate working standards for various types of materials (Aggarwal and Palmer, 1995; Tonarini *et al.*, 2003; Gonfiantini *et al.*, 2003).

6.2 Boron chemistry

Boron, the fifth element, has two isotopes: ^{10}B and ^{11}B with abundances of 19.8% and 80.2%, respectively, in naturally occurring boron (Kakihana *et al.*, 1977). Isotopic abundance variations for boron are expressed as $\delta^{11}\text{B}$ in per mil (‰), where

$$\delta^{11}\text{B} = \left\{ \left(\frac{^{11}\text{B}/^{10}\text{B}}{\text{sample}} / \left(\frac{^{11}\text{B}/^{10}\text{B}}{\text{standard}} \right) - 1 \right\} \times 1000 \quad (6.1)$$

The standard reference materials (SRM) are boric acids ($\text{B}(\text{OH})_3$), certified by the National Bureau of Standards (NBS). Normal isotopic abundance is represented by NBS 951, with $19.827 \pm 0.013 \%$ ^{10}B and $80.137 \pm 0.013 \%$ ^{11}B and $^{11}\text{B}/^{10}\text{B}$ of 4.04362 ± 0.00137 (Catanzaro *et al.*, 1970). NBS 952 is highly enriched in ^{10}B which makes it useful both as a standard for nuclear studies, where boron enriched in ^{10}B is necessary, and as an isotopic spike in isotope dilution mass spectrometry which will be further discussed in section 7.8. The isotopic abundance of ^{10}B in NBS 952 is $94.949 \pm 0.005 \%$, ^{11}B is $5.051 \pm 0.005 \%$, and $^{11}\text{B}/^{10}\text{B}$ is 0.053199 ± 0.000032 (Catanzaro *et al.*, 1970).

Boron mainly occurs in soluble, oxidised forms as either tetrahedral borate anions ($\text{B}(\text{OH})_4^-$) or trigonal borate complexes ($\text{B}(\text{OH})_3$) (Kakihana *et al.*, 1977; Palmer and Swihart, 1996). The form of boron is dependent on pH as shown in Table 6.1.

Table 6.1 – Main boron species by pH

(after Kakihana *et al.*, 1977)

pH	Boron species
< 6	B(OH) ₃
7 – 8	B(OH) ₃ , B ₃ O ₃ (OH) ₄ ⁻
8 – 9	B(OH) ₃ , B ₃ O ₃ (OH) ₄ ⁻ , B(OH) ₄ ⁻
9 – 10	B(OH) ₃ , B ₃ O ₃ (OH) ₄ ⁻ , B(OH) ₄ ⁻ , B ₃ O ₃ (OH) ₅ ²⁻
> 10	B(OH) ₄ ⁻

Isotopic fractionation in aqueous solution is primarily due to differences in the inter-atomic vibrational energy and symmetry between B(OH)₄⁻, which is relatively enriched in ¹⁰B, and B(OH)₃, which is enriched in ¹¹B (Kakihana *et al.*, 1977; Spivack and Edmond, 1987; Palmer and Swihart, 1996). The main boron isotope exchange reaction is shown below.



The fractionation factor, α , is described in equation 6.3:

$$\alpha_{\text{boric acid} - \text{borate anion}} = (^{11}\text{B}/^{10}\text{B})_{\text{boric acid}} / (^{11}\text{B}/^{10}\text{B})_{\text{borate anion}} \quad (6.3)$$

Kakihana *et al.* (1977) calculated equilibrium constants of 1.0206 at 0 °C and 1.0194 at 25 °C. In isotope exchange reactions where substances are reacting on a 1:1 mole basis such as reaction 6.2, the equilibrium constant is the same as the fractionation factor, and therefore it is apparent that fractionation is slightly influenced by temperature and is larger at low temperatures.

Another phenomenon responsible for boron isotope fractionation occurs during adsorption, where ¹⁰B is preferentially incorporated into the adsorbed phase, leaving ¹¹B enriched in the aqueous phase. It is thought that this may be due to the tetrahedral coordination of B(OH)₄⁻ (Spivack *et al.*, 1987; Palmer *et al.*, 1987). This mechanism explains why the $\delta^{11}\text{B}$ of seawater, with a global average of +39.5 ‰ (Spivack and

Edmond, 1987), is so much heavier than that of most terrestrial boron, which typically ranges from -30 to +22 ‰ (Chaussidon and Albarède, 1992). Since clays (Palmer *et al.*, 1987; Williams *et al.*, 2001a; Williams *et al.*, 2001b) and carbonates (Sen *et al.*, 1994) have a stronger adsorption affinity for B(OH)_4^- than for B(OH)_3 due to vibrational energy and coordination symmetry, the isotopic fractionation resulting from adsorption is dependent on the distribution of boron species in the aqueous phase, which is dependent on pH.

In addition to the preceding discussions concerning the effects of pH, temperature, and boron species on isotope fractionation, the large mass difference between the two isotopes and the high mobility of boron (Taylor and McLennan, 1995) leads to a range of isotopic values that spans almost 130 ‰ for all known natural boron-containing substances. Isotopically, the lightest known substance was recently reported to be a sample of coal from Wyoming with a $\delta^{11}\text{B}$ value of -70 ‰ (Williams and Hervig, 2004). Water from Australian salt lakes and brines from the Dead Sea are the heaviest substances, with $\delta^{11}\text{B}$ values as high as +59 ‰ (Vengosh *et al.*, 1991a; Vengosh *et al.*, 1991b).

6.3 Boron in the atmosphere

Boron exists in the atmosphere in both gaseous and particulate forms, although particulate boron contributes less than 10% to total atmospheric boron (Fogg *et al.*, 1983; Fogg and Duce, 1985). According to laboratory work and thermodynamic calculations, gaseous boron is expected to be mainly B(OH)_3 (Fogg *et al.*, 1983), although this has not yet been proven. Natural sources of both gaseous and particulate boron include the ocean (bubbles bursting and sea salt particles degassing), volcanic emissions, forest fires,

Earth's crust (particle weathering), and, potentially, plants (volatile emissions of boron). Anthropogenic activity contributes to atmospheric boron through the combustion of coal, agricultural burning, combustion of petroleum products and wood, refuse incineration, and mineral production (Fogg and Duce, 1985).

While Anderson *et al.* (1994) attributed 65 to 85% of atmospheric boron to marine sources, Nishimura and Tanaka (1972) suggested that the sea was a sink rather than a source of boron. This issue will not be resolved without better understanding of boron isotope fractionation during vapourisation from sea-salt particles (Miyata *et al.*, 2000). Anderson *et al.* (1994) further attributed 7 to 18% of atmospheric boron to anthropogenic contributions with the balance attributed to volcanic activity, which is in agreement with Fogg and Duce (1985) who determined that natural sources contributed about ten times the amount of anthropogenic sources. The most significant anthropogenic sources were determined to be coal combustion and agricultural burning, based on known and estimated global boron emissions from the various sources (Fogg and Duce, 1985; Anderson *et al.*, 1994).

The tropospheric residence time of boron was calculated to be 19 to 36 days for gaseous boron and 2 to 6 days for particulate boron (Fogg and Duce, 1985). Using updated boron source estimates and tropospheric burdens, Anderson *et al.* (1994) refined these to 5 to 27 days and 3 days, respectively. Boron is removed from the atmosphere by deposition of gaseous boron to sea and land, rain removal, and dry deposition of particulate boron.

Using filter sampling systems and rainwater collection, total (gaseous and particulate) atmospheric boron concentrations have been reported at continental suburban

sites in the vicinity of coal-fired power plants (10 to 26 ng B m⁻³), coastal areas (7 to 85 ng B m⁻³), remote marine sites (1 to 25 ng B m⁻³), and direct emissions from coal-fired power plants in Washington, D.C., USA (29 to 162 μg B m⁻³) (Anderson *et al.*, 1994). Fogg and Rahn (1984) reported total boron concentration from emissions at two coal-fired power plants in West Virginia, USA, which ranged from 700 to 5000 μg B m⁻³ – far greater concentrations than those reported above by Anderson *et al.* (1994), although there was a difference in plant size. Gómez *et al.* (2004) reported boron concentrations in the vicinity of a ceramic industrial area in Spain ranging from 6 to 173 ng m⁻³, with an average of 65 ng m⁻³.

Much work still needs to be done to fully understand boron's atmospheric chemical cycle (Fogg and Duce, 1985). Several authors have reported interesting phenomena that have yet to be definitively explained. For example, Fogg and Duce (1985) noted that boron concentration was the same in both rainwater and the corresponding aerosol samples for all sampling locations, suggesting that particulate boron may control boron in rain despite far greater concentrations of gaseous atmospheric boron. More recently, Miyata *et al.* (2000) reported δ¹¹B values of marine atmospheres and precipitation around Japan ranging from as low as -12.8 to 5.1 ‰, much lower than those of rainwater collected over the North Pacific, which ranged from 18.9 to 37.4‰. Only anthropogenic emissions could be expected to contribute δ¹¹B values on the order of -12.8‰, yet boron concentration was not correspondingly higher as might be expected in the vicinity of, say, coal combustion. Therefore, the authors proposed that the negative δ¹¹B values may be due to isotopic fractionation during evaporation (Miyata *et al.*, 2000).

6.4 Boron in fossil fuels

In low concentrations, boron is an essential nutrient to both plants and animals. It was therefore present in the organic material that was converted into fossil fuels with time, pressure, and heat, and is expected to be present in such deposits today. Boron is a known component of coal, but very little information exists concerning boron in oil and natural gas.

The boron content of coal ranges from 5 to 400 ppm (Goodarzi and Swaine, 1993), although coal with 2455 ppm has been reported (Goodarzi and Swaine, 1994). Boron composition in coal is determined by the depositional environment and subsequent interactions, possibly with groundwater.

Williams and Hervig (2004) measured a variety of coal and kerogen samples and found that all had negative boron isotope compositions spanning a wide range from -1.1 to -70 ‰ - the lightest value ever reported for a terrestrial material. The authors suggested that the isotopically light boron was due to isotopic fractionation during coalification since the organic source material should have isotopic compositions similar to that of crustal materials (Williams and Hervig, 2004), i.e. -15 to 0 ‰ (Chaussidon and Albarède, 1992).

Boron content in oil has been measured up to 70 ppm for oils from Russia (Gulyayeva *et al.*, 1966), although oil from the Gulf of Mexico was found to contain boron only in ppb levels (Williams *et al.*, 2001c). The boron isotope composition of oil from the Gulf of Mexico showed variation between the deepest reservoir (+5 ‰) and the shallowest (+17 ‰). The associated waters ranged in boron content from 8 to 85 ppm and boron isotope composition from +28 ‰ (deepest) to +37 ‰ (shallowest) (Williams *et*

al., 2001c). The concentration of boron in associated waters as compared to oil is likely due to boron's mobility during such processes as weathering, diagenesis, and hydrothermal alteration (Taylor and McLennan, 1995), leading to partitioning into fluid phases.

It has been suggested that isotopically light boron is released from organic matter during the generation of dry gas, likely into the pore waters of the reservoir (Williams *et al.*, 2001c). However, the pore waters also contain oil and gas, and it is possible that ^{11}B is fractionated preferentially into a gas phase (Palmer and Sturchio, 1990; Palmer and Swihart, 1996), although there is no information on possible fractionation between water and gaseous organic compounds. Leeman *et al.* (1992) found an isotopic fractionation of about 3 ‰ between water and vapour at 150 °C, which suggests that larger fractionations between these two phases may be apparent at temperatures below 150 °C. However, that work focused solely on $\text{B}(\text{OH})_3$. Further exploration of this fractionation would be valuable.

Williams *et al.* (2001c) reported that the highest $\delta^{11}\text{B}$ values were found where gas reservoirs were located, and suggested that the boron isotope variation and content of pore water may be correlated with the gas/oil ratios in each reservoir.

The evidence suggests that boron should be found within natural gas, and the boron isotope composition should differ between and possibly even within reservoirs. Gnyp *et al.* (1983), in measuring trace elements in sour gas incinerator stacks, were not able to detect boron, although they were not able to measure quantities smaller than 0.05 ppm. However, only particulate samples were taken whereas most boron will likely be found in gaseous samples (Fogg *et al.*, 1983; Fogg and Duce, 1985). Further work is

needed to confirm the existence and isotope composition of boron in natural gas reservoirs, oil reservoirs, and emissions from natural gas processing plants.

6.5 Boron as an environmental tracer

Boron has been used to identify the specific sources of pollutants in both the atmosphere and groundwater in several studies. Gladney *et al.* (1978) determined that 30 to 70% of the boron in coal volatilizes on combustion, allowing a substantial amount to exit the stack with the flue gas and an equally substantial amount to remain in the solid waste product known as fly ash. As a result, both the atmospheric emissions and the fly ash leachate have been measured and used as tracers. This property also allows for comprehensive evaluation of air pollution control technologies.

Davidson and Bassett (1993) successfully traced the plumes of fly ash leachate through groundwater, a technique they found to be extremely sensitive as long as the $\delta^{11}\text{B}$ of the leachate was substantially different from that of the area's groundwater. In their suite of samples, they found that the $\delta^{11}\text{B}$ of the fly ash leachate ranged from -19.2 to +15.8 ‰, while groundwater from several different areas of the United States varied from +1.8 to +31.2 ‰. Eisenhut and Heumann (1997) were able to identify landfill seepage as the source of groundwater contamination in South-East Bavaria. They determined that the uncontaminated groundwater in the area had a $\delta^{11}\text{B}$ of +46.6 ‰, showing both that the isotopic composition of groundwater may vary considerably depending on the geochemical source and that it is likely to be distinguishable from anthropogenic contribution since detergents are likely to be the main anthropogenic contaminant emanating from landfills. Eisenhut *et al.* (1996) measured $\delta^{11}\text{B}$ of various washing powders, noting that the range was about -3 to +3 ‰ and as such similar to the sodium

perborate used in washing powder production (+3.1‰). This study was also able to distinguish the source of groundwater contamination in Israel as sewage (Eisenhut *et al.*, 1996). Hogan and Blum (2003) used boron and lithium isotopes as groundwater tracers, but noted that the isotopic fractionation during adsorption onto clay minerals as discussed in section 6.2 could limit boron's use. Several more studies were able to contribute the various contributors to a given groundwater stream, including natural contributions (Bassett *et al.*, 1995; Barth, 1998; Barth, 2000).

Several studies have measured boron isotopes and concentrations in order to determine the relative contributions of various natural and anthropogenic sources to atmospheric boron (Fogg *et al.*, 1983; Fogg and Duce, 1985; Anderson *et al.*, 1994; Miyata *et al.*, 2000). However, few studies have actually measured boron concentration or $\delta^{11}\text{B}$ in order to trace anthropogenic emissions through the atmosphere, a deficiency which is likely due to the well-documented difficulties of boron analysis as discussed in section 6.1. While Fogg and Rahn (1984) only determined boron concentrations when sampling both ambient air and coal-fired power plant stacks, their work is possibly the best example of the uses of boron as an atmospheric environmental tracer. Since the B / S ratio in coal is known to be about 6000 times greater than in oil (Bertine and Goldberg, 1971), the authors measured the B / SO₂ ratio as it is therefore a unique marker and an effective tracer of sulphate from areas of coal combustion. In West Virginia, B / SO₂ ratios measured in stack gas varied from 0.28 to 1.1×10^{-3} , while B / SO₂ ratios in the Midwest ranged from 0.5 to 100×10^{-3} , although the majority of values were in the range of 0.5 to 5×10^{-3} . As the expected contribution from coal combustion decreased, B / SO₂ ratios increased (Fogg and Rahn, 1984). However, Goodarzi and Swaine (1993)

determined that while power plant emissions were the major contributor to boron within a 2 km radius of the plant, soil / rock particles became the major sources outside that radius.

CHAPTER 7: BORON SAMPLING & ANALYSIS

7.1 Introduction

As discussed in section 6.5, boron isotopes have been used successfully in tracing groundwater contamination. However, the analysis of boron isotopes from atmospheric filtering is a much more unique application, and therefore the analysis method was developed and tested as described below.

The method was primarily developed in order to extract boron from filters without affecting the $\delta^{34}\text{S}$ analysis of SO_4^{2-} . Since only half of each particulate filter was available for both SO_4^{2-} and boron analyses, it was particularly important to recover as much material as possible from samples already expected to be small, which is an unavoidable aspect of air sampling. Other goals included creating a reasonably quick analysis procedure and avoiding contamination introduced by the analysis procedure.

7.2 Boron-specific sampling concerns

Fogg *et al.* (1983) used a procedure very similar to that described above (section 2.1.1) in sampling atmospheric boron, although 47 mm filters and filter holders were used rather than high-volume air samplers. Untreated Nucleopore filters with 0.4 μm pore size were used to collect particulate samples, while Whatman no. 41 cellulose filters were impregnated with 0.5 M potassium hydroxide (KOH) and used to collect gaseous samples. However, the authors advised against the use of glycerol in impregnating the cellulose filters as it forms a volatile compound with boron, thereby lowering boron recoveries during analysis. Under laboratory conditions, the impregnated cellulose filters were found to be 95% efficient in trapping gaseous boron and greater than 70% efficient

in field tests. No trapping efficiencies were reported for the particulate filters, which may be due to the discovery of some trapping of gaseous boron by these filters, potentially giving a false sample that is 100% too high (Fogg *et al.*, 1983).

Only particulate samples were analyzed for the purposes of this experiment. It was originally thought that boron would more likely be present in aerosols than as a gas, although it was later discovered that less than 10% of atmospheric boron exists in the particulate form (Fogg *et al.*, 1983; Fogg and Duce, 1985). However, had gaseous samples also been analysed, the glycerol which is used along with K_2CO_3 in impregnating the cellulose fibre filters may have presented some problems.

Other atmospheric boron studies have used different methods, such as a five-stage filter holder employed for both ambient and stack samples (Kitto *et al.*, 1988; Anderson *et al.*, 1994) or the dry ice / ethanol cold traps used by Nishimura and Tanaka (1972) and Miyata *et al.* (2000) in ambient air sampling. However, the method chosen for this study is similar to that of (Fogg *et al.* 1983) and it also has the benefit of relative simplicity.

7.3 Sample Preparation

All boron sample processing was performed in a clean room to prevent contamination. New, acid-rinsed polypropylene containers and polyethylene pipette tips were used, and Pyrex was avoided for all sample work.

The quartz-fibre filters were ripped into very small pieces and placed into 50 ml centrifuge tubes that were then filled with Millipore Milli-Q water. Fogg *et al.* (1983) also leached Nucleopore filters in deionized distilled water, but acidified impregnated cellulose filter leachates in order to neutralize the KOH and recover all of the boron. The tubes were typically agitated for at least one hour, after which the filter pieces were

removed and placed into a second 50 ml centrifuge tube. A small portion of the liquid sample (5 to 10 ml) was removed and placed into a 15 ml centrifuge tube for boron and sulphate concentration analysis.

7.4 Boron extraction and concentration

Ion exchange was used to extract the boron sample from aqueous solution and concentrate it for analysis. Amberlite IRA743, a weakly basic anion exchange resin with an affinity for borate ions, binds boron by forming a borate polyol complex that can be broken down by strong acids. The theoretical boron binding capacity of the resin is about 5.7 mg B per ml resin (Sah and Brown, 1997).

As discussed in section 1.4.2, ^{10}B is preferentially incorporated into borate ($\text{B}(\text{OH})_4^-$) while ^{11}B is preferentially incorporated into boric acid ($\text{B}(\text{OH})_3$) (Kakihana *et al.*, 1977; Spivack and Edmond, 1987; Palmer and Swihart, 1996). The form of boron depends on pH: at pH less than 6, all boron will be in the form of $\text{B}(\text{OH})_3$, while at pH greater than 10, all boron will be in the form of $\text{B}(\text{OH})_4^-$ (Kakihana *et al.*, 1977).

Therefore, the key to extracting all of the boron with Amberlite IRA743 resin was to maintain the pH above 10.

The possibility of boron isotope fractionation as a result of the use of ion exchange resin has been discussed (Sah and Brown, 1998), but several papers have reported that no fractionation took place during their experiments (Hemming and Hanson, 1992; Aggarwal and Palmer, 1995; Eisenhut *et al.*, 1996), presumably because they were able to achieve 100% recovery. It is likely that isotopic fractionation will not occur as long as the pH is not allowed to drop below 10, meaning that some $\text{B}(\text{OH})_4^-$ is unabsorbed (Aggarwal and Palmer, 1995). Neither Leeman *et al.* (1991), who adjusted solutions to a

pH to 8, nor Davidson and Bassett (1993), who adjusted pH to 5 or more, nor Hemming and Hanson (1994), who adjusted solutions to a pH of 8.2, reported any isotope fractionation, but there must have been unabsorbed boron which remained in the solution. Davidson and Bassett (1993) specifically stated that isotopic fractionation was not noted as long as the capacity of the resin was not exceeded.

Many studies have used ion exchange resin and similar techniques for water and soil samples (e.g. Davidson and Bassett, 1993; Bassett *et al.*, 1995; Eisenhut *et al.*, 1996; Eisenhut and Heumann, 1997). Hemming and Hanson (1994) achieved 100% boron recovery using an ion exchange technique very similar to that described below, although a peristaltic pump was used to draw the sample through the ion exchange resin (Wieser *et al.*, 2001). The method described below was developed to address the difficulty in extracting samples from large filters with concentrations that could be very low by allowing samples to equilibrate with the ion exchange resin.

The three main stages of the ion exchange are described in detail below. These procedures were subjected to much testing in order to improve boron recovery, and the results of the tests are presented in section 8.1.2. Further, the entire boron extraction method was tested to ensure that it didn't compromise the $\delta^{34}\text{S}$ analysis of SO_4^{2-} and that the presence of SO_4^{2-} didn't compromise the $\delta^{11}\text{B}$ analysis of boron, and the results of these tests may be found in section 8.1.3.

7.4.1 Resin preparation

Prior to use, the resin was prepared by rinsing with MilliQ water to remove any contaminants. Fresh resin was used for all samples in this study, although following the full preparation method should be sufficient to regenerate the resin and remove any

contaminants or remaining boron. Next, the resin was conditioned with 0.5 M hydrochloric acid (HCl) followed by 0.3 M ammonium hydroxide (NH₄OH). The resin was rinsed with MilliQ water after each conditioning step in order to remove all traces of NH₄OH and other contaminants that could interfere with ionization and hence affect the stability and sensitivity of the measurement (Aggarwal and Palmer, 1995). Other studies have reported slightly different methods of preparing the resin for use, although all intend to achieve the same result. For example, Aggarwal and Palmer (1995) used the same method as described above with 2 M HCl and 3 M NH₄OH for conditioning, while Davidson and Bassett (1993) used 0.1 M nitric acid (HNO₃) and 0.2 M sodium hydroxide (NaOH) and performed the conditioning twice. However, Hemming and Hanson (1994) found that the strength of the reagents made little difference to boron recovery and therefore used 0.1 M HCl and 0.3 M NH₄OH in the same method as described above in order to reduce potential resin decomposition by overly strong reagents.

7.4.2 *Sample loading and boron extraction*

As discussed previously (section 6.2), boron is present in one of two main species (B(OH)₃ or B(OH)₄⁻) depending on pH. Since the ion exchange resin has an affinity for B(OH)₄⁻, the pH of the sample must be above 10 to ensure that most boron is in the form of borate ions. Therefore, 12 M NH₄OH was added to the remaining liquid sample to make it basic. At least 0.1 ml of prepared resin was then added to each liquid sample. The sample was agitated with the resin for at least one hour, after which it was removed and stored with the filter pieces in the second 50 ml centrifuge tube for sulphur isotope analysis. Similar to the methods of both Hemming and Hanson (1994) and Aggarwal and Palmer (1995), the resin was briefly rinsed with MilliQ water and then with 0.3 M

NH₄OH in order to ensure that the pH remained above 10 and the B(OH)₄⁻ remained in the resin. A second rinse with MilliQ water ensured that all NH₄OH was removed.

7.4.3 Boron elution

The boron was eluted from the resin using HCl. Several different acid strengths (0.5 M, 1 M, 2 M, 3 M, and 4 M) and methods (1 rinse of 1.5 ml or 3 rinses of 0.5 ml each) were tested to determine the best method for optimum boron recovery. Again, various studies used a range of different acid strengths from 0.1 M (Hemming and Hanson, 1994) to 2 M (Aggarwal and Palmer, 1995).

After the addition of HCl to the resin, the resin and HCl were agitated for at least one hour. The amount of time necessary for each agitating step was tested, with times ranging from 1 to 4 hours. The HCl was evaporated to dryness in a clean room under a heat lamp (Hemming and Hanson, 1994).

7.5 Boron isotope analysis

Boron isotope ratios were determined using negative thermal ionization mass spectrometry (NTIMS), a technique developed by both Duchateau and De Bièvre (1983) and Zeininger and Heumann (1983). In this method, data is collected at mass 42 (¹⁰B¹⁶O₂⁻) and 43 (¹¹B¹⁶O₂⁻). Both the accuracy, which is the degree to which data is consistent with true or accepted values, and the precision, which is the reproducibility of the data, of the measurement may decrease as compared to the more widely used positive thermal ionization mass spectrometry (PTIMS). However, there are several advantages to using NTIMS: the analytical sensitivity is increased by a factor of 50 and ion emission is less sensitive to impurities as compared to PTIMS. As a result, samples of nanogram

and sub-nanogram size may be analyzed, making this method ideal for environmental work (Duchateau and De Bièvre, 1983).

Once the samples were evaporated, an activator was added to both resolubilize the sample and to increase the ion intensity. Simple salts such as $\text{La}(\text{NO}_3)_3$ have often been used as activators (Heumann and Zeininger, 1985; Duchateau and De Bièvre, 1983), but there is evidence that they cause a steep fractionation trend over time (Hemming and Hanson, 1994). Barium hydroxide ($\text{Ba}(\text{OH})_3$) has been demonstrated to be suitable and was used in this study (Eisenhut *et al.*, 1996). Samples were deposited onto rhenium filaments, heated to dryness by applying a current of 1 A to the filament, and further heated at 2 A until the filament glowed slightly red, similar to the technique employed by Duchateau and De Bièvre (1983). Prepared filaments were then inserted into the NTIMS for analysis at a vacuum of 2 to 4×10^{-7} mbar. The specifics of the configuration and operation of this particular mass spectrometer are described in previous work (Wieser, 1998).

7.6 Sample Contamination

It is very important to purify the boron samples when using NTIMS in order to eliminate isobaric interference, allow full ionization of boron species, maintain a good vacuum in the mass spectrometer, and remove contaminants that could interfere with ionization during analysis (Aggarwal and Palmer, 1995). While contaminants such as iron, calcium, and magnesium may precipitate and interfere with boron ionization (Aggarwal and Palmer, 1995), organic carbon is both the most serious contaminant and potentially the hardest to remove.

In addition to any organic contamination that may exist in the sample itself, it has been suggested that the decomposition of the resin may be a source of organics (Hemming and Hanson, 1994; Aggarwal and Palmer, 1995; Eisenhut *et al.*, 1996; Sah and Brown, 1998), which may in turn lead to isobaric interference. Several authors have identified isobaric interference as a potential concern (e.g. Hemming and Hanson, 1992; Aggarwal and Palmer, 1995; Sah and Brown, 1998). At mass 42 ($^{10}\text{B}^{16}\text{O}^{16}\text{O}^-$), possible interference is caused by $^{12}\text{C}^{14}\text{N}^{16}\text{O}^-$ which will decrease $^{11}\text{B}/^{10}\text{B}$, while $^{12}\text{C}^{15}\text{N}^{16}\text{O}^-$ and $^{13}\text{C}^{14}\text{N}^{16}\text{O}^-$ interfere at mass 43 ($^{11}\text{B}^{16}\text{O}^{16}\text{O}^-$) increasing $^{11}\text{B}/^{10}\text{B}$ (Hemming and Hanson, 1992). Hemming and Hanson (1992) suggested monitoring mass 26 ($^{12}\text{C}^{14}\text{N}^-$) and recording the peak height so that $^{11}\text{B}/^{10}\text{B}$ may be corrected, since there is a correlation of approximately 1:3 between the peak height of mass 26 and the calculated intensity of mass 42. However, others have found no evidence of CNO- interference (Bassett, 1990; Eisenhut *et al.*, 1996; Hogan and Blum, 2003).

Contamination was found to be a problem with the majority of the samples taken for the purposes of this study. Many of the filters were gray in colour, and the resulting solutions were also gray and cloudy with particulate material. The contaminating substances interfered with the NTIMS analysis by causing the pressure in the instrument to increase, making it impossible to continue with analysis in some cases and casting doubt on the results in other cases. Since many of the samples were obviously dirty, it was concluded that the contamination was likely due to some sort of organic substance.

Several methods have been suggested to purify boron samples prior to NTIMS analysis. Hemming and Hanson (1992) removed organics from powdered samples by placing them in an ultrasonic bath first with a 30% H_2O_2 solution and then distilled

deionised water. This method removed most visible insoluble organics, and any remaining organics were removed by centrifugation. However, soluble organic contamination, such as that from ion exchange resin, is very difficult to remove. Hemming and Hanson (1994) suggested ultrafiltration, which consists of forcing the sample through a filter by centrifugation, while Aggarwal and Palmer (1995) suggested irradiating the samples with ultraviolet light for up to 24 hours. Microwave digestion was tested for this study, in a method described in the following section.

However, a new method where boron is sublimated from an organic-rich substance sounds promising as it is apparently possible to obtain 100% recovery and even when there is loss of boron isotopic fractionation does not occur (Gaillardet *et al.*, 2001). Briefly, the microsublimation technique developed by Gaillardet *et al.* (2001) involves heating a boron-containing sample in a beaker attached to a condenser tube, condensing the evaporated boron, and then proceeding to concentrate the boron using an ion exchange resin such as Amberlite IRA743.

Other contaminants may be removed by following the boron-specific resin with additional purification methods. For instance, a non-specific cation or anion resin used after the boron-specific resin would remove ions in the sample, while methyl borate distillation (adding methanol to the sample, distilling it and then evaporating to dryness) is particularly effective at removing silica (Aggarwal and Palmer, 1995).

7.6.1 Microwave digestion

Microwave digestion has often been used to digest an organic matrix in which boron is present (Vanderpool and Johnson, 1992; Evans and Krähenbühl, 1994; Wieser *et al.*, 2001).

The sample was first transferred into a Teflon bomb with 0.25 ml concentrated nitric acid (HNO₃), allowed to stand for 15 minutes, and then 1 ml hydrogen peroxide (H₂O₂) was added. The bomb was placed into a microwave and subjected to the following procedure:

Table 7.1 – Microwave digestion, part I

Power Level	Time
Low	2 minutes
Wait	2 minutes
Medium-Low	5 minutes
Wait	3 minutes
Medium	5 minutes
Medium-Low	15 minutes

The Teflon bomb was then cooled in an ice bath for 30 minutes to allow any vapourised material to condense before adding a further 0.5 ml H₂O₂ and returning it to the microwave for:

Table 7.2 – Microwave digestion, part II

Power Level	Time
Medium	5 minutes
Medium-Low	15 minutes

The sample was again allowed to cool, and once cool 1 ml of concentrated NH₄OH was added. The sample was evaporated to dryness under infrared heat lamps, and then dissolved in 1 ml of concentrated NH₄OH. The supernatant was separated by centrifugation and removed. At this point, the boron extraction and concentration method described above could be used, ensuring the pH is at least 10 and adding conditioned resin to the sample.

This method was tested to ensure that neither fractionation nor significant loss of material occurred for sulphate in solution with boron. Results are presented in section 8.1.4.

7.7 Volatilization

Boron's volatility in acidic solutions has long been known (Feldman, 1961). In HCl, boron may form boron chloride gas (BCl_3) which has a boiling point of 12.5°C , meaning that boron can easily evaporate from solution even at room temperature (Ishikawa and Nakamura, 1990). Evaporation can lead to isotopic fractionation since the vapour will be enriched in ^{11}B , while the residue will be enriched in ^{10}B . This phenomenon has been identified as a concern particularly when using concentrated HCl (about 6 M) (Ishikawa and Nakamura, 1990; Xiao *et al.*, 1997). However, dilute HCl (0.1 M) appears to actually minimise isotopic fractionation as compared to boron in water, although boron is still lost, and Hemming and Hanson (1992) reported no loss of boron when using 1 M HCl. No isotopic fractionation will occur if all boron is volatilized as one species, which may be the case in dilute acid. If the pH is about 1, boron exists predominantly as $\text{B}(\text{OH})_3$ in the solution (Xiao *et al.*, 1997). Mannitol is often used to prevent both loss during and after evaporation and isotopic fractionation (e.g. Feldman, 1961; Ishikawa and Nakamura, 1990; Aggarwal and Palmer, 1995; Xiao *et al.*, 1997), although it was not used in this study. The possibility of boron volatility was tested, and the results are found in section 8.1.2.3.

7.8 Boron Concentration Determination

Boron concentration was determined using a technique known as isotope dilution mass spectrometry (IDMS). In order to use IDMS to determine concentration, the element to be analysed must have two stable or long-lived radioactive isotopes. In this case, both ^{10}B and ^{11}B are stable and there are no long-lived radioactive isotopes. An exactly known quantity of “spike”, enriched in the isotope with the lower natural abundance, was added to the sample. In this case, the spike was NBS-952, the Standard Reference Material enriched to $\sim 95\%$ in ^{10}B (Catanzaro *et al.*, 1970). Once the sample and the spike were fully mixed and equilibrated, the isotope abundance ratio of the mixture was fixed and subsequent loss of material would not affect the measurement; this property is one of the main advantages of IDMS and makes it ideal for trace analysis work such as atmospheric sampling. The sample ratio was then measured using the NTIMS and the concentration of boron in the sample may be determined.

The first step in the use of IDMS was to accurately determine the concentration of boron in the spike solution used. The spike solution was prepared from powdered H_3BO_3 , and the concentration was known as accurately and precisely as possible by preparing gravimetric solutions. A solution containing NBS-951, the boron standard, in a known concentration was also used. The spike solution was calibrated by preparing several samples containing precisely weighed amounts of both the NBS-951 and NBS-952 solutions and allowing them to equilibrate. Aliquots of these samples were evaporated and loaded on filaments in the normal manner, and the isotope ratios were measured using the NTIMS. The concentration of the spike was then determined through the following equation:

$$C_{spike} = \left[\frac{R\left(\frac{11}{10}\right)_{standard} - R\left(\frac{11}{10}\right)_{mixture}}{R\left(\frac{11}{10}\right)_{mixture} - R\left(\frac{11}{10}\right)_{spike}} \right] \cdot \left[\frac{atom\%^{10}B_{standard}}{atom\%^{10}B_{spike}} \right] \cdot \frac{M_{spike}}{M_{standard}} \cdot \frac{w}{m} \cdot C_{standard} \quad (7.1)$$

where $atom\%^{10}B$ is the abundance of ^{10}B in the solution, M is the atomic mass of boron in the solution, and w and m are the masses of the spike and standard solutions, respectively.

The ratios in the first term were measured on the NTIMS. Thus, any biases affecting the measurement of the spike, mixture, and non-spiked sample cancel out in the calculation and the result was free from analytical biases arising from the isotope ratio measurements. $R\left(\frac{11}{10}\right)_{standard}$ was known to be 4.025 ± 0.002 from repeated laboratory tests, w and m were measured during sample preparation, and $R\left(\frac{11}{10}\right)_{mixture}$ was determined by analysis using the NTIMS. Using this procedure, the concentration of boron in the spike solution was determined to be $4.182 \pm 0.036 \mu\text{g B g}^{-1}$.

Once the spike was calibrated, IDMS was then used to determine the concentration of boron in samples. Precisely weighed amounts of the calibrated spike solution were added to weighed samples, which were dissolved in HCl used to elute boron from the resin. After the spike and sample solutions have equilibrated, they were evaporated and loaded on filaments in the normal manner, and the isotope ratios were measured using the NTIMS. The concentration of the sample was then determined through the following equation, which was simply a rearrangement of equation 7.1:

$$C_{sample} = \left[\frac{R\left(\frac{11}{10}\right)_{spike} - R\left(\frac{11}{10}\right)_{mixture}}{R\left(\frac{11}{10}\right)_{mixture} - R\left(\frac{11}{10}\right)_{sample}} \right] \cdot \left[\frac{atom\%^{10}B_{spike}}{atom\%^{10}B_{sample}} \right] \cdot \frac{M_{sample}}{M_{spike}} \cdot \frac{w}{m} \cdot C_{spike} \quad (7.2)$$

Ideally, the sample would also be measured without the addition of spike in order to determine $R\left(\frac{11}{10}\right)_{sample}$, which will give the most accurate results. However, when it was

not possible to measure both the concentration and the isotope ratio of a sample, a mean terrestrial value for the isotope abundance ratio of the sample could be used since the magnitude of the error that was introduced was small due to both the mass and liquid measurement uncertainties and the relatively narrow range of boron isotope ratios. As an example, a sample of coal with the most depleted $\delta^{11}\text{B}$ value measured (-70 ‰) (Williams and Hervig, 2004) would have an isotope ratio of about 3.75. Conversely, water from Australian salt lakes and brines from the Dead Sea with the most enriched $\delta^{11}\text{B}$ values measured (+59 ‰) (Vengosh *et al.*, 1991a; Vengosh *et al.*, 1991b) would have isotope ratios of about 4.27. The difference between the isotope ratios of the most extreme $\delta^{11}\text{B}$ values measured is only about 12%.

The IDMS procedure may be used in determining the recovery of a known amount of boron during some sample extraction procedure, or to determine the concentration of boron in an unknown sample. For the purposes of developing and testing the boron extraction and concentration method, IDMS was used to verify boron concentration at various steps in the procedure and to determine recoveries. In the analysis of actual particulate filter samples, the spike was added directly to the HCl after elution from the ion exchange resin and before evaporation.

IDMS is an extremely powerful method in the quantification of trace elements because it is a more direct and physical measurement than most classical chemical measurements (De Bièvre, 1990). All of the isotope ratios used in equations 7.1 and 7.2 are measured, which means that any analytical bias will be present in every measurement and will in fact cancel itself out, as long as all measurements are performed under the same analytical conditions. Heumann (1992) referred to the use of the stable or long-

lived radioactive isotope as a spike as the “most ideal form of internal standardization in analytical chemistry”. The power of IDMS is such that it is used for calibrating other methods and certifying standard reference materials (De Bièvre *et al.*, 1988), and Rokop *et al.* (1990) was able to analyse amounts of technetium from 1 nanogram (ng) to less than 1 femtogram (fg) (6×10^6 atoms) using NTI-IDMS.

CHAPTER 8: BORON RESULTS & DISCUSSION

8.1 Boron Method Tests

A new boron method was developed in order to extract boron from a particulate filter paper without compromising the analysis of SO_4^{2-} . The method, described in sections 7.3 and 7.4, allows samples to equilibrate with ion-exchange resin beads. Various tests, described in the following sections, were performed in order to verify that the method was able to recover an acceptable amount of boron from samples. In all of the following tests, NBS-951, the boron standard, was used as the boron sample. Where it was necessary to determine boron concentration, NBS-952, the boron spike, was added to the sample.

8.1.2 Boron recovery

In the initial stages of developing the boron method, concentration measurements revealed that only about half of the boron was being recovered. Boron recovery could be affected by any of the 3 main steps in the method:

1. Resin preparation
2. Sample loading and boron extraction
3. Boron elution.

Therefore, each step was tested to determine where the loss of boron occurred.

8.1.2.1 Resin preparation

Boron recovery could be affected by the preparation of the resin if:

- the resin was previously used and not properly rinsed,

- the conditioning step was not adequate in preparing the resin, or
- some contaminants or conditioning solutions were not completely removed and affected NTIMS analysis by interfering with fractionation (Aggarwal and Palmer, 1995).

All resin used in this work was fresh, so contamination from previous samples was not an issue. However, the conditioning step was tested to determine whether it might have an effect on boron recovery. All conditioning rinses tested followed the same procedure, with resin shaken for about one minute with several ml of each of the following, consecutively:

- MilliQ water,
- HCl,
- MilliQ water,
- NH_4OH , and
- MilliQ water.

Conditioning was tested using varying acid strengths and 0.3 M NH_4OH . The strength of NH_4OH was not varied, but the MilliQ water was tested after the final rinse and found to have a pH of about 8.5. Twelve hours later, the pH had not changed. This was taken to be an acceptable pH for resin preparation, and therefore 0.3 M NH_4OH was used for all conditioning.

Hemming and Hanson (1994) found that the strength of the acid and base used in conditioning made little difference and thus opted for weak versions of each (0.1 M HCl and 0.3 M NH_4OH) in order to avoid breaking down the resin, which could lead to

fractionation of the ion beam during analysis with NTIMS (Aggarwal and Palmer, 1995).

A range of acid strengths was tested, and results are presented in Table 8.1.

Table 8.1 – Conditioning rinse method tests

HCl strength (M)	Boron recovered (%)
0.5	51.0
	50.8
	64.5
	50.0
	58.0
	52.2
1.0	50.6
1.5	32.6
2.0	32.9
2.5	37.1
3.0	54.7

The results shown in Table 8.1 show that the acid strength used during conditioning did not seem to affect boron recovery. Therefore, 0.5 M was used for conditioning as it was used in samples with some of the highest recoveries (50 – 65%), and it was least likely to contribute to resin decomposition.

8.1.2.2 Sample loading and boron extraction

Boron recovery could be affected by this step if:

- the pH of the sample was not above 10,
- the resin was not in contact with the sample for an adequate amount of time, or
- the final rinse step allowed the loss of boron.

The first two points concern the extraction of boron from the sample. In order to address these, all samples were first carefully checked before loading to ensure that the pH was above 10. Next, a series of samples were left in contact with the resin for varying amounts of time, as shown in Table 8.2, and then processed and measured on the NTIMS

in order to determine recovery. The amount of boron remaining in the solution that was in contact with the resin was also measured for some of the samples.

Table 8.2 – Extraction time tests

Extraction time (h)	Boron recovered (%)	Boron remaining in solution (%)
1	51.0	0.6
5	50.8	0.4
5	58.0	
5	52.2	
25	64.5	
25	50.0	0.6

Table 8.2 shows that the amount of time allowed for extraction had no effect on the ultimate boron recovery. However, the amount of boron remaining in solution was less than 1% in all cases, indicating that the resin extracted boron very effectively.

The final rinse, which is intended to remove any excess solution or contaminants and keep the pH above 10, was tested to determine whether it could affect recovery. Three different approaches were tested for the final rinse step:

- 1 minute rinse with each of MilliQ water, 0.3 M NH_4OH , and MilliQ water,
- 1 minute rinse with 0.3 M NH_4OH , two 15 second rinses with MilliQ water, and
- no rinse.

In some of the samples, pH was tested during the rinses. Results are presented in Table 8.3.

Table 8.3 – Resin rinse tests

Rinse method	pH (after each rinse)	Boron recovered (%)
1 min. MQ H ₂ O	8.5	51.0
1 min. 0.3 M NH ₄ OH	>10	50.8
1 min. MQ H ₂ O	8.5	64.5
		58.0
1 min. 0.3 M NH ₄ OH	>10	52.2
15 sec. MQ H ₂ O	9	
15 sec. MQ H ₂ O	8	
No rinse		50.0

Table 8.3 shows that the rinse method also did not affect ultimate boron recovery. However, in the rinse steps the pH did appear to decrease to a potentially problematic level. The rinse procedure decided upon was a combination of the first two methods which allowed the pH to remain at about 10: the resin was rinsed very quickly with MilliQ water, for about one minute with 0.3 M NH₄OH, and again very quickly with MilliQ water. Since omitting the rinse did not increase boron recovery, the step was retained in the procedure since it removes some of the potential contaminants that could interfere with analysis on the NTIMS.

8.1.2.3 Boron elution

The previous sections established that neither the resin preparation nor the boron extraction steps influence the ultimate boron recovery. Furthermore, it was verified that >99% of the boron in the sample solution was extracted by the resin. Therefore, the poor boron recoveries must have been due to some aspect of boron elution. The two major factors that could impact recovery are:

- HCl strength, and
- elution method (i.e. one rinse of 1.5 ml HCl or three separate rinses of 0.5 ml HCl each).

As discussed in section 7.7, boron is known to be volatile in acidic solutions.

Therefore, before determining the best acid strength for recovery volatility was tested at both 1 and 3 M HCl. Possible loss of boron during evaporation was tested by evaporating samples of NBS-951. After evaporation, NBS-952 (spike) was added to the dried sample and evaporated. The results of these tests are shown in Table 8.4.

Table 8.4 – Volatility tests

HCl strength (M)	Boron recovered (%)
1.0	92.8
3.0	90.2

Table 8.4 shows very little difference between 1.0 M and 3.0 M HCl. Even at 3.0 M HCl, 90% of the boron was recovered, demonstrating that volatility is likely not a concern.

Having established an allowable range for acid strength, the elution procedure was next tested to determine both the optimum HCl strength as well as the best elution method. The tests and results are presented in Table 8.5.

Table 8.5 – Boron elution tests

HCl strength (M)	HCl volume (ml)	Boron recovered (%)
1.0	0.5	50.6
	0.5	69.3
	0.5	79.0
1.5	1.5	32.6
2.0	1.5	32.9
2.5	1.5	37.1
3.0	0.5	54.7
	0.5	77.1
	0.5	87.8

It is evident from Table 8.5 that 3 separate rinses of 0.5 ml each give the best boron recoveries. The highest recovery (88%) was achieved with 3.0 M HCl. The standard ISL procedure, where the sample is drawn through a column of resin using a peristaltic pump, was tested for comparison; these tests in conjunction with ISL experience give a range of 80 – 95% recovery. Therefore, boron recovery from three rinses of 3.0 M HCl is comparable to the conventional method. As discussed in section 7.4, the conventional method was prohibitively slow due to large sample volumes.

8.1.3 Multiple-isotope analysis effects

One difficulty inherent in atmospheric sampling is that samples are typically very small. This sampling program was structured so that only half of each particulate filter was available for the analysis of both SO_4^{2-} and boron, necessitating the development of a method that could extract boron from a sample without affecting the recoveries and isotope analyses of either sulphur or boron. The following sections describe the tests that were performed to verify that the analysis of both sulphur and boron is possible using this boron extraction method.

8.1.3.1 Effect of boron extraction on sulphur recovery and isotope analysis

The boron extraction method could potentially affect the recovery and $\delta^{34}\text{S}$ analysis of SO_4^{2-} through sulphur absorption by the resin or loss otherwise during the preparation. Solutions containing both NBS-951 and varying amounts of potassium sulphate (K_2SO_4) were subjected to the boron extraction procedure. The sulphur recoveries and $\delta^{34}\text{S}$ values are presented in Table 8.6.

There were some logistical difficulties encountered in attempting to prepare the 6 ppm sample. In order to have enough sulphur in the sample for isotope analysis, it was necessary to split the sample into three separate 50 ml tubes for boron extraction and recombine them for sulphur analysis. By splitting the sample into three, there was only 0.2 mg of SO_4^{2-} in each tube rather than almost 0.7 mg. This may have contributed to the poor sulphur recovery and ultimately to a sample that was too small for sulphur isotope analysis.

Table 8.6 – Sulphur recovery and isotope fractionation tests

SO_4^{2-} (pre-extraction)		SO_4^{2-} (post-extraction)	
Concentration (ppm)	$\delta^{34}\text{S}$ (‰)	Recovery (% S)	$\delta^{34}\text{S}$ (‰)
99	19.3	41.1	19.3
		31.5	-
48	19.3	39.2	19.1
		49.1	18.3
		42.1	17.9
6	18.9	27.2	-
Average	19.2 ± 0.2	Average	18.7 ± 0.7

Sulphur recovery varied from 27% at 6 ppm SO_4^{2-} to 49% at 48 ppm SO_4^{2-} . The average $\delta^{34}\text{S}$ value of all samples (18.7 ± 0.7 ‰) was compared to the average $\delta^{34}\text{S}$ value of all solutions (19.2 ± 0.2 ‰), and no evidence of significant isotope fractionation was found (*t*-test, $p < 0.05$).

The results of the sulphur recovery and isotope fractionation tests show that there was no isotope fractionation despite significant loss of sulphur. As a result, it was decided that a small portion of the filter leachate (5 - 10 ml) would be removed before the solution was made basic, thereby avoiding contact with the resin. This portion would be analysed for SO_4^{2-} concentration using the IC. Therefore, it was possible to accurately

determine both the concentration and the $\delta^{34}\text{S}$ value of SO_4^{2-} using the boron extraction method for most samples.

8.1.3.2 Effect of sulphur on boron recovery

If the loss of sulphur as determined in section 8.1.3.1 was due to absorption by the resin or if the sulphur was present during analysis using the NTIMS, boron recovery and/or isotope analysis may be affected. As above, solutions containing both NBS-951 and varying amounts of potassium sulphate (K_2SO_4) were subjected to the boron extraction procedure. The HCl strength used in the boron elution step was varied, and elution was accomplished through three HCl rinses as described in section 8.1.2.3. The boron recoveries are presented in Table 8.7.

Table 8.7 – Boron recovery tests

SO_4^{2-} Concentration (ppm)	HCl strength (elution) M	Recovery (% B)
99	2.0	84.9
	3.0	85.3
48	1.0	74.6
6	3.0	64.6
	3.0	72.0

Boron recovery ranged from 65% at 6 ppm SO_4^{2-} and 3.0 M HCl to 85% at 99 ppm SO_4^{2-} and 3.0 M HCl. It is possible that the logistical difficulties in preparing a 6 ppm SO_4^{2-} sample as described in section 8.1.3.1 led to the low boron recoveries, since the amount of boron in each of three tubes would be very small. Otherwise, the presence of SO_4^{2-} did not seem to affect boron recovery.

8.1.4 Contamination

As discussed in section 7.6, the presence of contaminants in samples may cause difficulty in maintaining vacuum in the NTIMS, interfere with ionization of boron species and cause isobaric interference (Aggarwal and Palmer, 1995). Most samples taken for the purposes of this study showed contamination, and it was assumed that some sort of organic substance was the cause. The contaminating substance led to analytical problems, in some cases making it impossible to analyse the sample. Although the decomposition of the resin is suspected to contribute to contamination (Hemming and Hanson, 1994; Aggarwal and Palmer, 1995; Eisenhut *et al.*, 1996; Sah and Brown, 1998), the contamination exhibited by these samples was most likely introduced during sampling.

Microwave digestion, used to break down organic matter so that it may be separated from the boron sample (Vanderpool and Johnson, 1992; Evans and Krähenbühl, 1994; Wieser *et al.*, 2001), was tested for this study.

8.1.4.1 Microwave digestion

The microwave digestion procedure was tested to ensure that it caused neither significant loss of sulphur nor sulphur isotope fractionation. Samples containing the boron standard (NBS-951) and varying amounts of a sodium sulphate (Na_2SO_4) solution were subjected to either microwave digestion only (MD), or microwave digestion followed by boron extraction (MD - BE). Results of these tests are presented in Table 8.8.

Table 8.8 – Microwave digestion tests

Procedure	SO ₄ ²⁻		B	
	S recovery (%)	δ ³⁴ S (‰)	B recovery (%)	δ ¹¹ B (‰)
MD (1)	110.0	-3.7		
MD – BE (2)	74.8	-3.5		-1.1 ± 2.5
MD – BE (3)	59.9	-3.4	68.6	-12.7 ± 2.5
	Average	-3.5 ± 0.2		

The SO₄²⁻ solution was found to have a concentration of 85 ppm SO₄²⁻ and a δ³⁴S value of -3.9 ‰. The sample that was only subjected to microwave digestion appeared to recover more sulphur than was present in the original solution, suggesting that the procedure may have introduced sulphur. It is difficult to determine how sulphur may have been introduced into the sample as all solutions used were high purity or environmental grade. No significant isotope fractionation occurred for the first two procedures (*t*-test, *p* < 0.05), but the δ³⁴S value of the SO₄²⁻ sample in the third showed significant fractionation (*t*-test, *p* > 0.95). The samples that were subjected to both microwave digestion and boron extraction recovered 60 - 75% sulphur.

The sample with the lowest sulphur recovery and isotopic fractionation also had a low boron recovery (69 %) and demonstrated considerable isotope fractionation with a δ¹¹B value of -12.7 ‰ as compared to 0 ‰. It is possible that something happened during the preparation of this sample that caused loss of both sulphur and boron. The boron isotope fractionation was likely due to the loss of material since both microwave digestion and boron extraction using resin are well- established methods. It should be noted that the NTIMS was not running very well at this time, and it was not possible to analyse several of the samples that were prepared for this test.

As in section 8.1.3.1, this method will be suitable for determining SO₄²⁻ concentrations and δ³⁴S values if the portion of the filter leachate taken for IC analysis is

removed before the samples undergo microwave digestion. However, extreme care must be taken in order to avoid any losses throughout sample preparation. It is recommended that future analysis of atmospheric boron samples should test the method of Gaillardet *et al.* (2001), described in section 7.6, as it may be easier and / or more effective.

8.2 Boron Samples

Boron in emissions was measured from some of the particulate filter samples taken at Alberta gas plants and the control and receptor sites. The presence of organic contaminants in most of the samples led to analytical difficulties and as a result only a subset of samples was analysed for boron. As discussed in section 7.6, the issue of contamination was addressed through microwave digestion.

8.2.1 Boron concentration

Boron concentration was determined using isotope dilution mass spectrometry and equation 7.2. The most accurate determination of the amount of boron in the sample requires the measurement of $R\left(\frac{11}{10}\right)_{sample}$, although some samples for which that value was not available were determined by assuming that the sample was similar to the boron standard. This substitution is not expected to introduce errors that exceed mass and liquid measurement uncertainties.

There was not enough boron found in filter blanks to analyse. However, the amount of boron found in field blanks is presented in Table 8.9, along with boron concentrations at sampling sites. These samples have analytical uncertainties on the order of $\pm 5\%$.

Table 8.9 – Boron content of field blanks and samples

Location	Field blank ($\mu\text{g B}$)	Sample	
		($\mu\text{g B}$)	($\mu\text{g B} / \text{m}^3$)
Control site	3.4	3.5	2.1
Plant 3	3.4	-	-
Plant 6	18.3	5.2	79.5
Receptor site	April – May 2002	5.1	0.7
	May – June 2002	8.2	0.7
	July 2002	5.2	0.8
	October 2002	3.3	

It is interesting that most sites had field blank levels of about $3.4 \mu\text{g}$, while plant 6 had a field blank that was over five times higher. The sample at the same location also had a very high boron concentration ($79.5 \mu\text{g B} / \text{m}^3$), although the total amount of boron in the sample was lower than the field blank. The amount of boron in the control site sample was about the same as that in the field blank, while boron in the receptor site samples was about one and a half to two and a half times greater than the amount of boron in the field blank. It would be valuable to test boron migration through the plastic storage bags, as was carried out for SO_2 , described in section 4.1.2.

8.2.2 $\delta^{11}\text{B}$ measurements

The $\delta^{11}\text{B}$ values of field blanks and samples are presented in Table 8.10. It did not make sense to correct these samples for the influence of field blanks. Most of the field blanks had $\delta^{11}\text{B}$ values close to 0 ‰, while the uncorrected samples varied from +2.5 to -10.3. The uncertainty of these values, ± 2 ‰, was due to the analytical difficulties introduced by organic contamination and to the small sample sizes.

Table 8.10 – $\delta^{11}\text{B}$ values of field blanks and samples

Location	$\delta^{11}\text{B}$ (‰)	
	Field blanks (± 2 ‰)	Samples (uncorrected) (± 2 ‰)
Control site	-1.2	-6.1
Plant 3	0.7	+2.5
		-10.3
Plant 6	-0.6	-4.8
Receptor site	2.5	-
Lab blank	-	-3.5

8.2.3 Discussion

The accuracy of the boron method developed here was comparable to that of the conventional procedure performed in the same laboratory, with measured $\delta^{11}\text{B}$ values of NBS-951 about 5 ‰ lower than the published value of 4.04362 (Catanzaro *et al.*, 1970). The precision of the method itself was about ± 1 ‰, but the precision of the samples was reduced to ± 2 ‰ due to the analytical problems that resulted from sample contamination.

It is unfortunate that more samples could not be analysed since there does appear to be variation both in boron concentration as well as $\delta^{11}\text{B}$. Of particular interest are the field blank and sample at plant 6, which seemed to have a high background boron concentration.

Gómez *et al.* (2004) sampled air in the vicinity of a ceramic industrial area in Spain using a high-volume sampler fitted with cellulose membrane filters. He measured gaseous atmospheric boron that ranged from 6 to 173 ng m^{-3} and averaged 65 ng m^{-3} . Furthermore, he identified that boron concentration varied seasonally, being higher in the winter and lower in the summer. Even though particulate boron contributes less than 10% to total atmospheric boron (Fogg *et al.*, 1983; Fogg and Duce, 1985), Table 3.15 shows particulate boron concentrations that are an order of magnitude higher in some

cases than those measured by Gómez *et al.* (2004). The results in sections 8.2.1 and 8.2.2, although not as complete as desired, indicate that boron may indeed be useful for characterising and apportioning emissions.

CHAPTER 9: MULTIPLE-ISOTOPE DISCUSSION

The intent of a multiple-isotope approach to characterising and apportioning emissions was to characterise emissions using sulphur isotopes and use boron as a second means of identification. That is, if the $\delta^{34}\text{S}$ measured in emissions downwind of one plant was too close to that measured downwind of other plants to be distinguishable, the $\delta^{11}\text{B}$ value could provide a unique identifier.

It is unfortunate that contamination precluded the analysis of most of the samples because the samples that were analysed show some interesting results. There was insufficient data to attempt any multiple-isotope analysis of the results, but if boron and sulphur isotope compositions and concentrations are measured in emissions downwind of gas plants in future, the B / S ratio should be considered. Fogg and Rahn (1984) measured B / SO₂ ratios in stack gases from coal-fired power plants as that ratio provided a means of unique identification. As the expected contribution from coal combustion decreased, B / SO₂ ratios increased. Table 9.1 shows B / SO₂ values for samples where both values were collected.

Table 9.1 – B / SO₂ for selected samples

Location		B / SO ₂
Control Site		0.004
Plant 6*		0.02
Receptor Site	April - May 2002	0.003
	May - June 2002	0.002
	July 2002	0.001

* Field blank was larger than sample.

In comparison, Fogg and Rahn (1984) measured B / SO₂ ratios in coal-fired power plant stack gas in West Virginia that varied from 0.0003 to 0.001, while B / SO₂ ratios in the Midwest ranged from 0.0005 to 0.001. The values presented here suggest

that boron is present in quantities that are an order of magnitude higher than those reported by Fogg and Rahn (1984).

This analysis could help not only characterise emissions measured downwind of gas plants but may also aid in apportioning emissions downwind and determining the extent of SO₂ oxidation.

CHAPTER 10: CONCLUSIONS & RECOMMENDATIONS

The aim of this thesis was to determine whether emissions from natural gas processing plants are isotopically distinct using sulphur and boron, and if so whether they can be used to identify and apportion emissions downwind. Accordingly, sulphur and boron isotopes were measured at source, receptor, and control sites. Other aspects of this thesis included testing SO₂ filters for capture efficiency and sulphur isotope fractionation and the development of a boron extraction method for particulate samples.

The results of the sulphur recovery and isotope fractionation tests led to several key findings. No significant isotope fractionation due to the use of impregnated cellulose filters was found, although slight fractionations on the order of -0.7 ‰ may have occurred. Further testing should be done to confirm whether these isotope effects are reproducible. Furthermore, it was determined that the samples measured for this thesis may not have captured all of the SO₂ and it is therefore recommended that two SO₂ filters in series be used in future sampling programs in order to capture most of the SO₂.

Emissions measured downwind of gas plants tended to have SO₂ δ³⁴S values that changed over time, while the SO₄²⁻ δ³⁴S values did not vary much over time or between plants. These findings suggested that SO₂ δ³⁴S values were most likely representative of individual sources and events. However, aerosol SO₄²⁻ δ³⁴S values indicated that a uniform area source, likely due to SO₄²⁻ from oxidation of SO₂ emitted by plant 3, dominated the region. Therefore, SO₄²⁻ δ³⁴S values from plant 3 would be valuable in distinguishing natural gas processing emissions from other sources. No fractionation due to SO₂ oxidation was evident.

An interesting phenomenon was noted at the sour gas plants, however. The apparent fractionation between solid sulphur and SO_4^{2-} , $\Delta\delta^{34}\text{S}_{\text{S8-SO}_4^{2-}}$, appeared to increase with inlet H_2S , sulphur recovery, and inlet gas volume, yet no corresponding relationships were apparent between solid sulphur and SO_2 . This could indicate that at least some of the SO_4^{2-} measured in emissions downwind of the plants was actually emitted from the plants being sampled at that time. Sulphur recovery is likely the key factor if indeed the relationship is real since it is that process which has been suggested to have the potential for fractionation (Krouse *et al.*, 1984). It would be valuable to confirm whether this relationship actually exists.

On the basis of SO_2 $\delta^{34}\text{S}$ values, it was possible to distinguish between the emissions of sweet and sour plants, which averaged +3.8 and +21.8 ‰ respectively, rather than from all seven plants individually. However, the temporal changes in SO_2 $\delta^{34}\text{S}$ values noted at plant 3 indicate that each plant should be extensively characterized in order to determine the effects of seasonal, diurnal, and inlet gas variations. A reduced number of sampling sites would allow proper characterization of each, either through an increased number of short-term samples or by erecting a directionally-controlled sampler for long-term sampling.

It was possible to distinguish solid sulphur $\delta^{34}\text{S}$ values measured at plants in Alberta, which averaged +18 ‰, from those measured at plants in B.C., which averaged +13.4 ‰. The SO_4^{2-} $\delta^{34}\text{S}$ values from all Alberta plants also averaged about +18.3 ‰, indicating that these values could be used to distinguish between regional emissions. Therefore, an alternative to characterising individual plants within a region may be to

sample several gas plants operating in the same area and use a regional average to distinguish between the emissions from different regions.

Results of the receptor site samples showed some correlation between both SO_2 and SO_4^{2-} concentrations and $\delta^{34}\text{S}$ values over the period from the end of February until the end of the sampling program in October, 2002 which could indicate that they were mainly emitted from the same sources. The concentrations of both SO_2 and SO_4^{2-} and the $\delta^{34}\text{S}$ values of SO_2 appeared to decrease over this period as temperature increased. However, the concentrations and $\delta^{34}\text{S}$ values of both SO_2 and SO_4^{2-} showed an increase with increasing relative humidity. Since relative humidity is a function of both temperature and the amount of water vapour present, it is possible that these effects are all related to heterogeneous oxidation.

However, in a closed system, or at least one with no significant input or removal, it would be expected that if SO_2 concentration and / or $\delta^{34}\text{S}$ decreased, SO_4^{2-} concentration and / or $\delta^{34}\text{S}$ values would increase. The $\delta^{34}\text{S}$ of SO_4^{2-} could also increase and the $\delta^{34}\text{S}$ values of SO_2 decrease, depending on the dominant oxidation mechanism. It was demonstrated that gas plant emissions dominated SO_2 at the receptor site, with no other potential source large enough to have an influence, yet it could not be shown that the amount of SO_4^{2-} was increasing due to the oxidation of the SO_2 . A possible explanation for these results may be SO_4^{2-} removal after oxidation.

Over the period of where apparent trends between $\delta^{34}\text{S}$ values of SO_2 and SO_4^{2-} were evident at the receptor site, an examination of the difference between the two values, $\Delta\delta^{34}\text{S}_{\text{SO}_4^{2-}-\text{SO}_2}$, showed that almost all of the variation was due to the $\delta^{34}\text{S}$ values of SO_2 . This could indicate that SO_2 and SO_4^{2-} measured at the receptor site were emitted

by different sources despite the apparent correlation between the two, or that in fact SO_4^{2-} was removed after oxidation so that the oxidation effects could not be captured by measurements conducted at a single receptor site.

It became evident through the results measured at the receptor site that the concentrations and $\delta^{34}\text{S}$ values of both SO_2 and SO_4^{2-} could not be explained as simplistically as has been done in other studies (Saltzman *et al.*, 1983; Mukai *et al.*, 2001). Although it has been shown that potentially significant amounts of sulphate can fall out short distances away from the emission source (Newman *et al.*, 1975; Forrest and Newman, 1977; Newman, 1981), the above-mentioned studies did not appear to consider this or any other atmospheric process apart from SO_2 oxidation in their work. It is very important that the mechanisms of oxidation and associated fractionations be better understood in order to resolve these questions, but it may be necessary to use isotopes of another element such as oxygen (Savarino *et al.*, 2000; Lee *et al.*, 2002; Alexander *et al.* 2002).

A portion of this thesis involved the development of a method to extract boron from a particulate filter sample without affecting the $\delta^{34}\text{S}$ analysis of SO_4^{2-} . This method, which allowed boron to equilibrate with ion-exchange resin, was developed and tested extensively. Some problems arose during analysis of samples when contamination was discovered, and as a result very few samples could be reported. Microwave digestion, a technique already in use for removing boron from an organic matrix (Vanderpool and Johnson, 1992; Evans and Krähenbühl, 1994; Wieser *et al.*, 2001), was tested to ensure that it did not affect the $\delta^{34}\text{S}$ analysis of SO_4^{2-} . A new and apparently very effective method for the extraction of boron from other materials was developed (Gaillardet *et al.*,

2001), and should be tested for use in any future work as it may simplify the process somewhat and prevent any loss of material.

Regardless, the results show that there may in fact be some valuable information to be gained by measuring boron isotopes in sour gas emissions. It is recommended that further testing be carried out and that SO₂ filters be tested for boron as well, since particulate boron contributes less than 10% to total atmospheric boron (Fogg *et al.*, 1983; Fogg and Duce, 1985).

Ultimately, the results obtained from this work suggest that identification and apportionment of emissions downwind of sour gas plants using sulphur and boron isotopes shows potential. Furthermore, the methods developed through this thesis could easily be adapted to include the identification and apportioning of emissions from other industries.

APPENDIX A: SAMPLE LOG

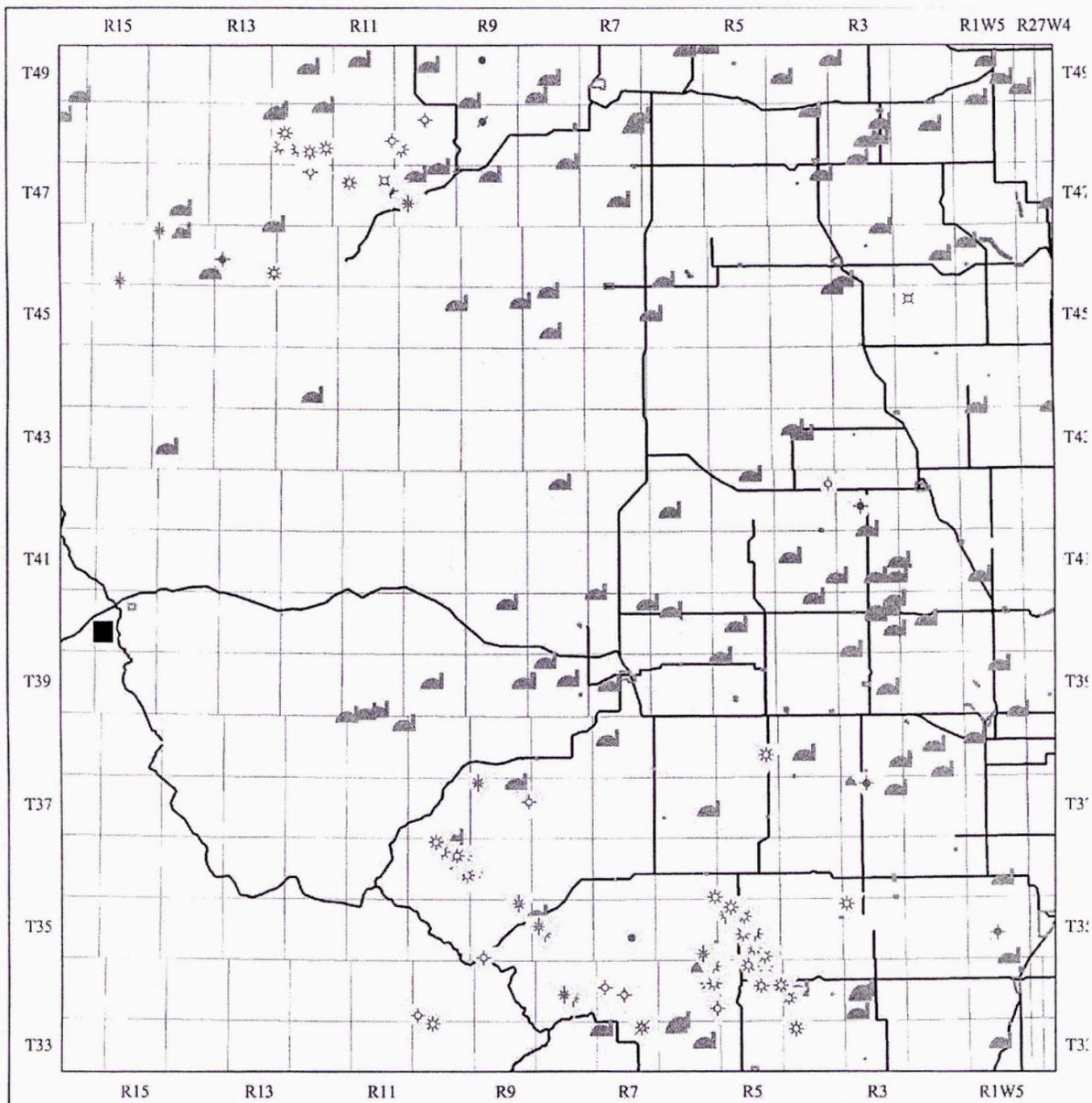
Sample	Date	Sulphur dioxide			
		Concentration ($\mu\text{g S m}^{-3}$)	$\delta^{34}\text{S}$ (‰)	Error (‰)	
Control Site	Nov 20 - 21/01	0.1	11.0	10.2	
	Oct 25 - 26/02	0.5	21.9	5.5	
Alberta	Plant 1	Sep 27/02	4.4	3.7	2.6
	Plant 3	Jul 28/02	18.0	29.4	14.6
		Sep 28/02	4.9	26.8	12.4
		Dec 1/02 (1)	8.0	16.3	5.0
		Dec 1/02 (2)	5.7	14.6	6.1
	Plant 6	Jul 27/02	8.0	5.4	3.0
		Sep 29/02	4.2	3.1	2.4
Plant 7	Sep 29/02	3.0	3.0	3.9	
B.C.	Plant 8	May 22/02	4.2	2.4	2.0
	Plant 9	May 22/02	10.0	9.2	3.8
Receptor Site	Sep 25 - Oct 2/01				
	Oct 2 - 10/01	0.6	33.7	20.4	
	Oct 10 - 23/01				
	Oct 23 - Nov 6/01	1.1	20.3	13.4	
	Nov 6 - Dec 4/01	0.1	13.3	3.1	
	Dec 4 - 24/01	0.5	18.1	7.4	
	Dec 24/01 - Jan 14/02	2.4	20.5	4.7	
	Jan 29 - Feb 5/02	0.8	26.2	12.6	
	Feb 5 - 12/02	2.6	30.0	28.5	
	Feb 12 - 26/02	0.6	15.6	3.8	
	Feb 26 - Mar 12/02	1.0	18.6	4.3	
	Mar 12 - Apr 9/02	1.2	20.8	4.7	
	Apr 23 - May 16/02	0.2	20.7	4.8	
	May 16 - Jun 11/02	0.4	16.3	3.6	
	Jun 11 - Jul 11/02	0.5	17.5	3.8	
	Jul 11 - 27/02	0.6	14.1	3.1	
	Jul 27 - Aug 19/02	0.4	17.9	4.0	
	Aug 19 - Sep 12/02	0.5	19.4	4.5	
Sep 12 - 28/02	0.3	17.7	4.1		
Sep 28 - Oct 25/02	0.5	19.3	4.3		

Sample	Date	Sulphate			
		Concentration ($\mu\text{g S m}^{-3}$)	$\delta^{34}\text{S}$ (‰)	Error (‰)	
Control Site	Nov 20 - 21/01	0.03	15.6	8.8	
	Oct 25 - 26/02	0.3	24.3	0.9	
Alberta	Plant 1	Sep 27/02	0.7	19.8	9.8
	Plant 2	Jul 26/02	0.8	18.4	17.9
	Plant 3	Jul 28/02	1.5	17.4	16.3
		Sep 28/02	0.8	19.3	9.4
		Dec 1/02 (1)	0.7	21.6	10.4
	Plant 4	Mar 30 - Apr 8/03	0.5	19.8	5.8
		Jul 28/02	0.9	28.3	21.1
	Plant 5	Sep 28/02	0.5	16.5	12.6
		Jul 26/02	0.9	13.4	10.2
	Plant 6	Sep 27/02	0.9	19.0	13.2
Sep 29/02		0.6	14.3	8.9	
Plant 7	Sep 29/02	0.5	13.9	13.0	
Receptor Site	Sep 25 - Oct 2/01	0.2	14.1	2.4	
	Oct 2 - 10/01	0.2	14.4	1.2	
	Oct 10 - 23/01	0.1	14.8	0.7	
	Oct 23 - Nov 6/01	0.4	17.0	1.5	
	Nov 6 - Dec 4/01	0.1	19.5	0.3	
	Dec 4 - 24/01	0.4	17.3	0.7	
	Dec 24/01 - Jan 14/02	0.3	16.4	0.6	
	Jan 29 - Feb 5/02	0.2	16.8	1.5	
	Feb 5 - 12/02	1.3	16.0	1.2	
	Feb 12 - 26/02	0.2	16.3	0.6	
	Feb 26 - Mar 12/02	0.3	13.4	0.2	
	Mar 12 - Apr 9/02	0.4	14.9	0.5	
	Apr 23 - May 16/02	0.2	10.3	0.4	
	May 16 - Jun 11/02	0.2	10.3	0.2	
	Jun 11 - Jul 11/02	0.2	11.9	0.1	
	Jul 11 - 27/02	0.2	11.8	0.6	
	Jul 27 - Aug 19/02	0.1	17.4	0.5	
	Aug 19 - Sep 12/02	0.2	17.3	0.4	
Sep 12 - 28/02	0.1	15.3	0.2		
Sep 28 - Oct 25/02	0.1	15.6	0.4		

Sample		Date	Solid Sulphur $\delta^{34}\text{S}$ (‰)
Alberta	Plant 1	Jul 26/02	13.8
		Sep 27/02	15.1
	Plant 2	Jul 26/02	15.2
	Plant 3	Jul 28/02	20.2
		Mar 30 - Apr 8/03	20.2
			19.5
			22.0
			19.9
	Plant 4	Jul 28/02	17.6
Plant 5	Jul 26/02	21.7	
	Sep 27/02	15.9	
B.C.	Plant 9	Oct 28/01	12.4
	Plant 10	Oct 29/01	11.6
	Plant 11	Oct 29/01	12.1
	Plant 12	Nov 17/01	15.2
	Plant 13	Oct 28/01	15.8

Sample	Date	Boron	
		Concentration ($\mu\text{g B m}^{-3}$)	$\delta^{11}\text{B}$ (‰)
Control Site	Oct 25 - 26/02	2.1	-6.1
Alberta	Plant 3	Sep 28/02	-
		Dec 1/02 (1)	-10.3
	Plant 6	Sep 29/02	79.5
Receptor Site	Apr 23 - May 16/02	0.7	-
	May 16 - Jun 11/02	0.7	-
	Jul 11 - 27/02	0.8	-

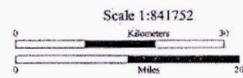
APPENDIX B: CONTROL SITE MAPS

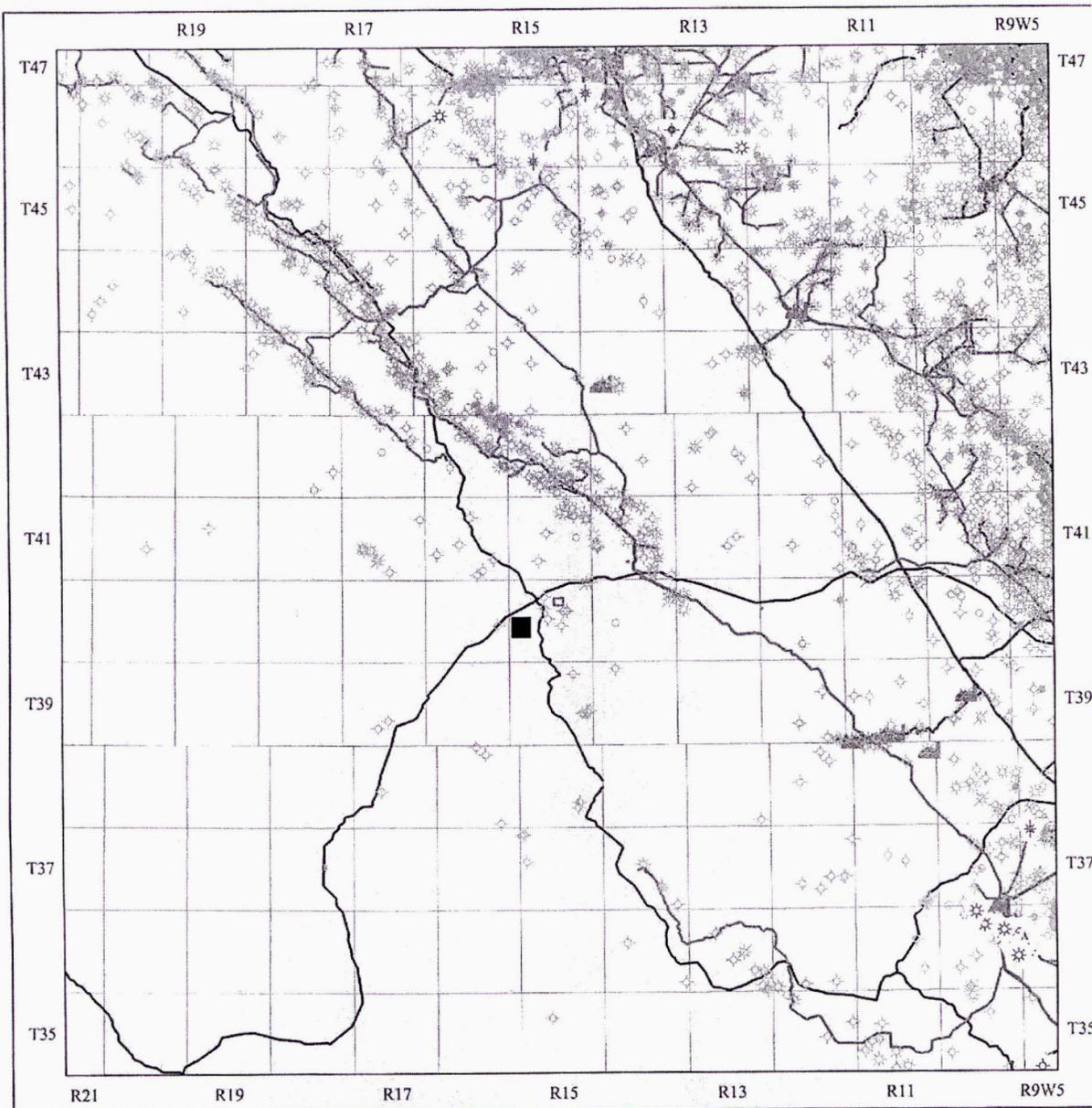


WELL LEGEND	
Bottom Hole Locations:	
○ Suspended	⊗ Service or Drain
⊗ Oil	⊗ Gas
⊗ Dry & Abandoned	⊗ Suspended Oil
⊗ Abandoned Oil	⊗ Suspended Gas
⊗ Abandoned Gas	

WELL LISTS	
⊗	+30% H2S
■	Control site

<p>Registered Company</p> <p>Created in AccuMap™ Product of HES Energy</p> <p>AccuMap Vol. 14 No. 10, Oct 13 2004 © Copyright © HES 2004</p>
--

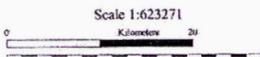




WELL LEGEND	
Bottom Hole Locations:	
○ Location	◇ Suspended
⊖ Service or Drain	⊕ Oil
⊗ Gas	⊘ Dry & Abandoned
⊗ Suspended Oil	⊘ Abandoned Oil
⊗ Suspended Gas	⊘ Abandoned Gas
⊗ Injection	

WELL LISTS	
⊗	+30% H2S
■	Control site

Registered Company	
Created in AccuMap™ Product of IHS Energy AccuMap <small>Vol. 14, No. 03, Oct 11, 2004 Copyright © 2004 IHS Energy Services Inc. (937) 770-6643</small>	



(Accumap, 2004)

REFERENCES

- AccuMap™. 2004. IHS Energy: Calgary, Alberta, Canada.
- Aggarwal, J.K. and M.R. Palmer. 1995. Boron Isotope Analysis. *Analyst* **120**: 1301 - 1307.
- Alberta Energy and Utilities Board. 2004. Available at <http://www.eub.gov.ab.ca/>. Last accessed 23 November 2004.
- Alberta Energy and Utilities Board. 2001. Interim Directive ID 2001-03: Sulphur Recovery Guidelines for the Province of Alberta. Available at <http://www.eub.gov.ab.ca/BBS/requirements/ils/ids/id2001-03.htm>. Last accessed 23 November 2004.
- Alberta Energy and Utilities Board. 2002. Draft Guide 60: Upstream Petroleum Industry Flaring, Incinerating, and Venting. Available at <http://www.eub.gov.ab.ca/bbs/products/guides/g60/g60-draft.pdf>. Last accessed 23 November 2004.
- Alberta Energy and Utilities Board. 2003. Statistical Series (ST) 101: Sulphur Recovery and Sulphur Emissions at Alberta Sour Gas Plants. First Annual Report. Available at <http://www.eub.gov.ab.ca/bbs/products/STs/st101-2003.pdf>. Last accessed 23 November 2004.
- Alberta Environment. 2004. Available at <http://www3.gov.ab.ca/env/>. Last accessed 23 November 2004.
- Alberta Environment. 2003. Sulphur Dioxide: Environmental Effects, Fate and Behaviour. Available at <http://www3.gov.ab.ca/env/air/pubs/SulphurDioxideEnvEffectsFateandBehaviour.pdf>. Last accessed 23 November 2004.
- Alexander, B., J. Savarino, N.I. Barkov, R.J. Delmas, and M.H. Thiemens. 2002. Climate driven changes in the oxidation pathways of atmospheric sulfur. *Geophysical Research Letters* **29**: 1685.
- Alexander, B., M.H. Thiemens, J. Farquhar, A.J. Kaufman, J. Savarino, and R.J. Delmas. 2003. East Antarctic ice core sulfur isotope measurements over a complete glacial-interglacial cycle. *Journal of Geophysical Research* **108 (D24)**: 4786.
- Anderson, D.L., M.E. Kitto, L. McCarthy, and W.H. Zoller. 1994. Sources and Atmospheric Distribution of Particulate and Gas-Phase Boron. *Atmospheric Environment* **28**: 1401 – 1410.

- Anovitz, L.M. and E.S. Grew. 1996. Mineralogy, Petrology and Geochemistry of Boron: An Introduction. In: Grew, E.S. and L.M. Anovitz, Eds. Boron Mineralogy, Petrology and Geochemistry. Mineralogical Society of America: Washington, D.C., USA, pp. 1 – 40.
- Austin, S.R. 1970. Some Patterns of Sulfur Isotope Distribution in Uranium Deposits. *Earth Science Bulletin* **3**: 5 - 22.
- Barth, S.R. 1998. Application of boron isotopes for tracing sources of anthropogenic contamination in groundwater. *Water Research* **32**: 685 - 690.
- Barth, S.R. 2000. Boron Isotopic Compositions of Near-Surface Fluids: A Tracer for Identification of Natural and Anthropogenic Contaminant Sources. *Water Air and Soil Pollution* **124**: 49 - 60.
- Bassett, R.L. 1990. A critical evaluation of the available measurements for the stable isotopes of boron. *Applied Geochemistry* **5**: 541 – 554.
- Bassett, R.L., P.M. Buszka, G.R. Davidson, and D. Chong-Diaz. 1995. Identification of Groundwater Solute Sources Using Boron Isotopic Composition. *Environmental Science & Technology* **29**: 2915 – 2922.
- Becker, S. and A.V. Hirner. 1998. Characterization of crude oils by carbon and sulphur isotope ratio measurements as a tool for pollution control. *Isotope in Environmental and Health Studies* **34**: 202.
- Berresheim, H., P.H. Wine, and D.D. Davis. 1995. Sulfur in the atmosphere. In: Singh, H.B., Ed. Composition, Chemistry, and Climate of the Atmosphere. Van Nostrand Reinhold: New York, USA, pp. 251 - 307.
- Bertine, K.K. and E.D. Goldberg. 1971. Fossil Fuel Combustion and the Major Sedimentary Cycle. *Science* **173**: 233 - 235.
- Bottenheim, J.W. and O.P. Strausz. 1980. Gas-Phase Chemistry of Clean Air at 55° N Latitude. *Environmental Science & Technology* **14**: 709 – 718.
- Buckingham, D.A. and J.A. Ober. 2002. Historical Statistics for Sulfur, United States Geological Survey OFR 01-006. Available at <http://minerals.usgs.gov/minerals/pubs/of01-006/sulfur.html>. Last accessed 2 August 2004.
- Canadian Geothermal Energy Association. What Is Geothermal Energy and How Can It Be Used? Available at <http://www.geothermal.ca/whatis.html#earthtemp>. Last accessed 1 February 2005.

- Catanzaro, E.J., C.E. Champion, E.L. Garner, G. Marinenko, K.M. Sappenfield, and W.R. Shields. 1970. Boric Acid; Isotopic, and Assay Standard Reference Materials. National Bureau of Standards Special Publication 260-17: Washington, D.C., USA, 60 pp.
- Charlson, R.J., J. Langner, H. Rodhe, C.B. Leovy, and S.G. Warren. 1991. Perturbation of the northern hemisphere radiative balance by backscattering from anthropogenic sulfate aerosols. *Tellus* **43AB**: 152 - 163.
- Chaussidon, M. and R. Albarède. 1992. Secular boron isotope variations in the continental crust: an ion microprobe study. *Earth and Planetary Science Letters* **108**: 229 – 241.
- Davidson, G.R. and R.L. Bassett. 1993. Application of Boron Isotopes for Identifying Contaminants such as Fly Ash Leachate in Groundwater. *Environmental Science & Technology* **27**: 172 – 176.
- Davis, W.E. 1972. National Inventory of Sources and Emissions barium, boron, copper, selenium, and zinc. SectionII. *NTIS, PB-210 677* : 44 pp.
- De Bièvre, P., J. Savory, A. Lamberty, and G. Savory. 1988. Meeting the need for reference measurements. *Fresenius Journal of Analytical Chemistry* **332**: 718 – 721.
- De Bièvre, P. 1990. Isotope dilution mass spectrometry: what can it contribute to accuracy in trace analysis? *Fresenius Journal of Analytical Chemistry* **337**: 766 – 771.
- Douglas, H., Ed. 2002. The Canada Gas Plant Directory. Volume VII. Northern Star Communications Ltd.: Calgary, Alberta, Canada.
- Duchateau, N.L. and P. De Bièvre. 1983. Boron isotopic measurements by thermal ionization mass spectrometry using the negative BO_2^- ion. *International Journal of Mass Spectrometry and Ion Processes* **54**: 289 – 297.
- Egiazarov, A.C., M. Kaviladze, M.N. Kerner, E.L. Oziashvili, A. Ebralidze, and K.E. Esakiya. 1971. Separation of sulfur isotopes by chemical exchange. *Isotopenpraxis* **7**: 379 – 383.
- Eisenhut, S. and K.G. Heumann. 1997. Identification of ground water contaminations by landfills using precise boron isotope ratio measurements with negative thermal ionization mass spectrometry. *Fresenius Journal of Analytical Chemistry* **359**: 375 – 377.

- Eisenhut, S., K.G. Heumann, and A. Vengosh. 1996. Determination of boron isotopic variations in aquatic systems with negative thermal ionization mass spectrometry as a tracer for anthropogenic influences. *Fresenius Journal of Analytical Chemistry* **354**: 903 – 909.
- Energy and Resources Conservation Board and Alberta Environment (1988). Report 88A: Sulphur Recovery Guidelines for Sour Gas Plants in Alberta. Available at <http://www.eub.gov.ab.ca/bbs/documents/reports/r88aa.pdf>. Last accessed 23 November 23, 2004.
- ENMAX. 2004. What is Natural Gas? Available at <http://www.enmax.com/Energy/Residential/ElectricityGas/What+is+Natural+Gas.htm>. Last accessed 23 November 2004.
- Eriksen, T.E. 1972a. Sulfur Isotope Effects I. The Isotopic Exchange Coefficient for the Sulfur Isotopes $^{34}\text{S} - ^{32}\text{S}$ in the System $\text{SO}_{2\text{g}} - \text{HSO}_3^-_{\text{aq}}$ at 25, 35, and 45 °C. *Acta Chemica Scandinavia* **26**: 573 – 580.
- Eriksen, T.E. 1972b. Sulfur Isotope Effects II. The Isotopic Exchange Coefficients for the Sulfur Isotopes $^{34}\text{S} - ^{32}\text{S}$ in the System $\text{SO}_{2\text{g}} - \text{Aqueous Solutions of SO}_2$. *Acta Chemica Scandinavia* **26**: 581 – 584.
- Evans, S. and U. Krähenbühl. 1994. Boron analysis in biological material: microwave digestion procedure and determination by different methods. *Fresenius' Journal of Analytical Chemistry* **349**: 454 – 459.
- Farquhar, J., J. Savarino, T.L. Jackson, and M.H. Thiemens. 2000. Evidence of atmospheric sulphur in the Martian regolith from sulphur isotopes in meteorites. *Nature* **404**: 50 – 52.
- Feldman, C. 1961. Evaporation of Boron from Acid Solutions and Residues. *Analytical Chemistry* **33**: 1916 – 1920.
- Finlayson-Pitts, B.J. and J.N. Pitts Jr. 2000. Chemistry of the Upper and Lower Atmosphere. Academic Press: San Diego, USA, pp. 294 - 348, 358.
- Fogg, T.R., R.A. Duce, and J.L. Fasching. 1983. Sampling and Determination of Boron in the Atmosphere. *Analytical Chemistry* **55**: 2179 – 2184.
- Fogg, T.R. and R.A. Duce. 1985. Boron in the troposphere: Distribution and fluxes. *Journal of Geophysical Research* **90(D2)**: 3781 – 3796.
- Fogg, T.R. and K.A. Rahn. 1984. Boron as a tracer of aerosol from combustion of coal. *Geophysical Research Letters* **9**: 854 – 857.

- Forrest, J. and L. Newman. 1973. Sampling and Analysis of Atmospheric Sulfur Compounds for Isotope Ratio Studies. *Atmospheric Environment* **7**: 561 – 573.
- Forrest, J. and L. Newman. 1977. Further studies on the oxidation of sulfur dioxide in coal-fired power plant plumes. *Atmospheric Environment* **11**: 465 - 474.
- Gaillardet, J., D. Lemarchand, C. Göpel, and G. Manhès. 2001. Evaporation and Sublimation of Boric Acid: Application for Boron Purification from Organic Rich Solutions. *Geostandards Newsletter* **25**: 67 – 75.
- Garland, J.A. 1978. Dry and Wet Removal of Sulphur From the Atmosphere. *Atmospheric Environment* **12**: 349 - 362.
- Gas Processors Suppliers Association. 1998. Engineering Data Book, Eleventh Edition. Tulsa, Oklahoma, pp. 22-10 – 12.
- Gladney, E.S., L.E. Wangen, D.B. Curtis, and E.T. Jurney. 1978. Observations of Boron Release from Coal-Fired Power Plants. *Environmental Science & Technology* **12**: 1084 – 1085.
- Gnyp, A.W., C.C. St. Pierre, D.S. Smith, and S. Viswanathan. 1983. A Trace Element Emission Study at Selected Sour Gas Plant Incinerator Stacks in The Province of Alberta, Waterton – Shell Canada Resources Limited, Pincher Creek – Gulf Oil Canada Limited. The Industrial Research Institute of the University of Windsor: Ontario, Canada, 151 pp.
- Goles, G.G. 1969. Cosmic Abundances. In: Wedepohl, K.H., Ed. Handbook of Geochemistry, Volume I. Springer-Verlag: Berlin, Germany, pp. 116 – 133.
- Gómez, E.T., T. Sanfeliu, M.M. Jordán, J. Rius, and C. de la Fuente. 2004. Geochemical characteristics of particulate matter in the atmosphere surrounding a ceramic industrialized area. *Environmental Geology* **45**: 536 - 543.
- Gonfiantini, R., S. Tonarini, M. Gröning, A. Adorni-Braccesi, A.S. Al-Ammar, M. Astner, S. Bächler, R.M. Barnes, R.L. Bassett, A. Cocherie, A. Deyhle, A. Dini, G. Ferrara, J. Gaillardet, J. Grimm, C. Guerrot, U. Krähenbühl, G. Layne, D. Lemarchand, A. Meixner, D.J. Northington, M. Pennisi, E. Reitznerová, I. Rodushkin, N. Sugiura, R. Surberg, S. Tonn, M. Wiedenbeck, S. Wunderli, Y. Xiao, and T. Zack. 2003. Intercomparison of Boron Isotope and Concentration Measurements. Part II: Evaluation of Results. *Geostandards Newsletter* **27**: 41 – 57.
- Goodarzi, F. and D.J. Swaine. 1993. Behavior of Boron in Coal During Natural and Industrial Combustion Processes. *Energy Sources – Journal of Extraction Conversion and the Environment* **15**: 609 – 622.

- Goodarzi, F. and D.J. Swaine. 1994. Paleoenvironmental and environmental implications of the boron content of coals. *Geological Survey of Canada Bulletin* **471**: 76 pp.
- Gulyayeva, L.A., V.B. Kaplun, and E.P. Shishenina. 1966. Distribution of boron among the components of petroleum. *Geochemistry International* **3**: 636 - 641.
- Hemming, N.G. and G.N. Hanson. 1992. Boron isotopic composition and concentration in modern marine carbonates. *Geochimica et Cosmochimica Acta* **56**: 537 - 543.
- Hemming, N.G. and G.N. Hanson. 1994. A procedure for the isotopic analysis of boron by negative thermal ionization mass spectrometry. *Chemical Geology* **114**: 147 - 156.
- Heumann, K.G. 1992. Isotope dilution mass spectrometry. *International Journal of Mass Spectrometry and Ion Processes* **118/119**: 575 - 592.
- Heumann, K.G. and H. Zeininger. 1985. Boron trace determination in metals and alloys by isotope dilution mass spectrometry with negative thermal ionization. *International Journal of Mass Spectrometry and Ion Processes* **67**: 237 - 252.
- Holub, P.E. and M. Shelian. 2000. Fundamentals of Gas Sweetening. In: 2000 Laurance Reid Gas Conditioning Conference. Norman, Oklahoma.
- Hogan, J.F. and J.D. Blum. 2003. Boron and lithium isotopes as groundwater tracers: a study at the Fresh Kills Landfill, Staten Island, New York, USA. *Applied Geochemistry* **18**: 615 - 627.
- Huygen, C. 1963. The Sampling of Sulfur Dioxide in Air With Impregnated Filter Paper. *Analytica Chimica Acta* **28**: 349 - 360.
- Ishikawa, T. and E. Nakamura. 1990. Suppression of Boron Volatilization from a Hydrofluoric Acid Solution Using a Boron-Mannitol Complex. *Analytical Chemistry* **62**: 2612 - 2616.
- Kakihana, H., K. Masahiro, S. Satoh, M. Nomura, and M. Okamoto. 1977. Fundamental Studies on the Ion-Exchange Separation of Boron Isotopes. *Bulletin of the Chemical Society of Japan* **50**: 158 - 163.
- Kasasaku, K., T. Minari, H. Mukai, and K. Murano. 1999. Stable Sulfur Isotope Ratios of the Gases from Mt. Sakurajima and Satsuma-Iwojima Volcanoes - Assessment of Volcanic Sulfur on Rainfall Sulfate in Kagoshima Prefecture. *Journal of Chemical Society of Japan Chemistry and Industrial Chemistry* **7**: 479 - 486.

- Kitto, M.E., D.L. Anderson, and W.H. Zoller. 1988. Simultaneous Collection of Particles and Gases Followed by Multielement Analysis Using Nuclear Techniques. *Journal of Atmospheric Chemistry* **7**: 241 – 259.
- Krouse, H.R. 1991. Sulphur isotope tracing of the fate of emissions from sour gas processing in Alberta, Canada. In: Krouse, H.R. and V.A. Grinenko, Eds. Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment, SCOPE 43. John Wiley & Sons: Chichester, England, pp. 309 – 326.
- Krouse, H.R. and J.W. Case. 1981. Sulphur Isotope Ratios in Water, Air, Soil and Vegetation Near Teepee Creek Gas Plant, Alberta. *Water, Air, and Soil Pollution* **15**: 11 – 28.
- Krouse, H.R. and T.B. Coplen. 1997. Reporting of Relative Sulfur Isotope-Ratio Data (Technical Report): Commission on Atomic Weights and Isotopic Abundances. *Pure and Applied Chemistry* **69**: 293 - 295.
- Krouse, H.R. and V.A. Grinenko. 1991. Environmental Sulphur Isotope Studies in Japan. In: Krouse, H.R. and V.A. Grinenko, Eds. Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment, SCOPE 43. John Wiley & Sons: Chichester, England, pp. 343 – 361.
- Krouse, H.R., A.H. Legge, and H.M. Brown. 1984. Sulphur Gas Emissions in the Boreal Forest: The West Whitecourt Study V. Stable Sulphur Isotopes. *Water, Air, and Soil Pollution* **22**: 321 – 347.
- Krouse, H.R., J.W.B. Stewart, and V.A. Grinenko. 1991. Pedosphere and Biosphere. In: Krouse, H.R. and V.A. Grinenko, Eds. Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment, SCOPE 43. John Wiley & Sons: Chichester, England, pp. 268 – 306.
- Krouse, H.R., C.A. Viau, L.S. Eliuk, A. Ueda, and S. Halas. 1988. Chemical and isotopic evidence of thermochemical sulphate reduction by light hydrocarbon gases in deep carbonate reservoirs. *Nature* **333**: 415 - 419.
- Lee, C.C.-W., J. Savarino, H. Cachier, and M.H. Thiemens. 2002. Sulfur (^{32}S , ^{33}S , ^{34}S , ^{36}S) and oxygen (^{16}O , ^{17}O , ^{18}O) isotopic ratios of primary sulfate produced from combustion processes. *Tellus* **54B**: 193 - 200.
- Leeman, W.P., R.D. Vocke Jr., E.S. Beary, and P.J. Paulsen. 1991. Precise boron isotopic analysis of aqueous samples: Ion exchange extraction and mass spectrometry. *Geochimica et Cosmochimica Acta* **55**: 3901 - 3907.

- Leeman, W.P., R.D. Vocke, and M.A. McKibben. 1992. Boron isotopic fractionation between coexisting vapour and liquid in natural geothermal systems. In: Kharaka, Y.K. and A.S. Maest, Eds. Proceedings of the 7th International Symposium on Water-Rock Interaction Volume 7. A.A. Balkema: Rotterdam, pp. 453 - 456.
- Lelieveld, J., G.-J. Roelofs, L. Ganzeveld, J. Feichter, and H. Rodhe. 1997. Terrestrial sources and distribution of atmospheric sulphur. *Philosophical Transactions: Biological Sciences* **352**: 149 – 157.
- Leung, F.Y., A.J. Colussi, and M.R. Hoffman. 2001. Sulfur Isotopic Fractionation in the Gas-Phase Oxidation of Sulfur Dioxide Initiated by Hydroxyl Radicals. *Journal of Physical Chemistry A* **105**: 8073 - 8076.
- Lien, A.Y. 1991. Native Elemental Sulphur Deposits. In: Krouse, H.R. and V.A. Grinenko, Eds. Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment, SCOPE 43. John Wiley & Sons: Chichester, England, pp. 91 - 95.
- Link, P.K. 1982. Basic Petroleum Geology. OGCI Publications: Tulsa, OK, USA, 235 pp.
- MacNamara, J., and H.G. Thode. 1950. Comparison of the Isotopic Constitution of Terrestrial and Meteoritic Sulfur. *The Physical Review* **78**: 307 – 308.
- Martin, L.R. 1984. Kinetic studies of sulfite oxidation in aqueous solution. In: Calvert, J.G., Ed. SO₂, NO and NO₂ Oxidation Mechanisms: Atmospheric Considerations. Butterworths: Boston, MA, USA, pp. 63 – 100.
- Massey, A.G. and J. Kane. 1972. Boron. Mills & Boon Limited: London, England, 64 pp.
- Miyata, Y., T. Tokieda, H. Amakawa, M. Uematsu, and Y. Nozaki. 2000. Boron isotope variations in the atmosphere. *Tellus Series B* **52**: 1057 – 1065.
- Morel-à-l'Huissier, P. 2000. Sulphur. Natural Resources Canada. Available at <http://www.nrcan.gc.ca/mms/cmty/content/2000/58.pdf>. Last accessed 2 August 2004.
- Mukai, H., A. Tanaka, T. Fujii, Y. Zeng, Y. Hong, J. Tang, S. Guo, H. Xue, Z. Sun, J. Zhou, D. Xue, J. Zhao, G. Zhai, J. Gu, and P. Zhai. 2001. Regional Characteristics of Sulfur and Lead Isotope Ratios in the Atmosphere at Several Chinese Urban Sites. *Environmental Science & Technology* **35**: 1064 - 1071.
- Nable, R.O., G.S. Bañuelos, and J.G. Paull. 1997. Boron toxicity. *Plant and Soil* **193**: 181 – 198.

- Newman, L. 1981. Atmospheric oxidation of sulfur dioxide: a review as viewed from power plant and smelter plume studies. *Atmospheric Environment* **15**: 2231 - 2239.
- Newman, L., J. Forrest, and B. Manowitz. 1975. The application of an isotopic ratio technique to a study of the atmospheric oxidation of sulfur dioxide in the plume from an oil-fired power plant. *Atmospheric Environment* **9**: 959 - 968.
- Nielsen, H. 1974. Isotopic composition of the major contributors to atmospheric sulphur. *Tellus* **26**: 213 - 221.
- Nielsen, H. 1979. Sulfur Isotopes. In: Jäger, E. and J.C. Hunziker, Eds. Lectures in Isotope Geology. Springer-Verlag: Berlin, Germany, pp. 283 - 312.
- Nielsen, H. 1991. Sulphur in the cosmos and the crust-mantle system. In: Krouse, H.R. and V.A. Grinenko, Eds. Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment, SCOPE 43. John Wiley & Sons: Chichester, England, pp. 65 - 67.
- Nishimura, M. and K. Tanaka. 1972. Sea Water May Not Be a Source of Boron in the Atmosphere. *Journal of Geophysical Research* **77**: 5239 - 5242.
- Norman, A.L., L.A. Barrie, D. Toom-Sauntry, A. Sirois, H.R. Krouse, S.M. Li, and S. Sharma. 1999. Sources of aerosol sulphate at Alert: Apportionment using stable isotopes. *Journal of Geophysical Research* **104 (D9)**: 11,619 - 11,631.
- Norman, A.L., H.R. Krouse, and J. McLeod. 2004. Apportionment of Pollutant S in an Urban Airshed: Calgary, Canada, a Case Study. In: Borrego, C. and S. Incecik, Eds. Air pollution modeling and its application XVI. Kluwer Academic: New York, USA, pp. 107 - 125.
- NOVA Gas Transmission Ltd. 2004. Alberta System Tariff: General Terms and Conditions. Available at http://www.transcanada.com/Alberta/info_postings/tariff/gtc.pdf. Last accessed 24 November 2004.
- Novak, M., I. Jackova, and E. Prechova. 2001. Temporal Trends in the Isotope Signature of Air-Borne Sulfur in Central Europe. *Environmental Science & Technology* **35**: 255 - 260.
- Orr, W.L. 1974. Changes in sulphur content and isotopic ratios of sulphur during petroleum maturation - study of Big Horn Basin paleozoic oils. *American Association of Petroleum Geology Bulletin* **50**: 2295 - 2318.

- Orr, W.L. and J.S. Sinninghe Damsté. 1990. Geochemistry of Sulfur in Petroleum Systems. In: Orr, W.L. and C.M. White, Eds. Geochemistry of Sulfur in Fossil Fuels. American Chemical Society: Washington, D.C., USA, pp. 2 - 29.
- Palmer, M.R., A.J. Spivack, and J.M. Edmond. 1987. Temperature and pH controls over isotopic fractionation during adsorption of boron on marine clay. *Geochimica et Cosmochimica Acta* **51**: 2319 – 2323.
- Palmer, M.R. and N.C. Sturchio. 1990. The boron isotope systematics of the Yellowstone National Park (Wyoming) hydrothermal system: A reconnaissance. *Geochimica et Cosmochimica Acta* **54**: 2811 - 2815.
- Palmer, M.R. and G.H. Swihart. 1996. Boron Isotope Geochemistry: An Overview. In: Grew, E.S. and L.M. Anovitz, Eds. Boron Mineralogy, Petrology and Geochemistry. Mineralogical Society of America: Washington, D.C., USA, pp. 709 – 744.
- Petroleum Communication Foundation. 2000. Flaring: Questions + Answers. Calgary, Alberta, Canada.
- Petroleum Resources Communication Foundation. 1989. Our Petroleum Challenge in the 1990s. Calgary, Alberta.
- Pilot, J. 1991. Sulphur and oxygen isotope composition of marine evaporite and barite strata. In: Krouse, H.R. and V.A. Grinenko, Eds. Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment, SCOPE 43. John Wiley & Sons: Chichester, England, pp. 68 - 87.
- Prospero, J.M., R.J. Charlson, V. Mohnen, R. Jaenicke, A.C. Delany, J. Moyers, W. Zoller, and K. Rahn. 1983. The Atmospheric Aerosol System: An Overview. *Reviews of Geophysics and Space Physics* **21**: 1607 – 1629.
- Querol, X., A. Alastuey, A. Chaves, B. Spiro, F. Plana, and A. Lopez-Soler. 2000. Sources of Natural and Anthropogenic Sulphur Around the Teruel Power Station, NE Spain. Inferences from sulphur isotope geochemistry. *Atmospheric Environment* **34**: 333 – 345.
- Ramaswamy, V., O. Boucher, J. Haigh, D. Hauglustaine, J. Haywood, G. Myhre, T. Nakajima, G.Y. Shi, and S. Solomon. 2001. Radiative Forcing of Climate Change. In: Houghton, J.T., Y. Ding, D.J. Griggs, M. Noguer, P.J. van der Linden, X. Dai, K. Maskell, and C.A. Johnson, Eds. Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press: Cambridge, UK, pp. 349 - 416.

- Rees, C.E. 1970. The sulphur isotope balance of the ocean: an improved model. *Earth and Planetary Science Letters* **7**: 366 – 370.
- Robinson, E. and R.C. Robbins. 1968. Sources, abundance, and fate of gaseous atmospheric pollutants. Final Report SRI Project PR-6755. American Petroleum Institute: New York, USA.
- Robinson, E. and R.C. Robbins. 1970. Gaseous Sulfur Pollutants from Urban and Natural Sources. *Journal of the Air Pollution Control Association* **20**: 233 - 235.
- Rokop, D.J., N.C. Schroeder, and K. Wolfsberg. 1990. Mass Spectrometry of Technetium at the Subpicogram Level. *Analytical Chemistry* **62**: 1271 – 1274.
- Sakai, H. 1971. Sulfur and oxygen isotopic study of barite concretions from banks in the Japan Sea off the Northeast Honshu, Japan. *Geochemical Journal* **5**: 79 - 93.
- Saltzman, E.S., G.W. Brass, and D.A. Price. 1983. The Mechanism of Sulfate Aerosol Formation: Chemical and Sulfur Isotopic Evidence. *Geophysical Research Letters* **10**: 513 – 516.
- Sah, R.N. and P.H. Brown. 1997. Techniques for boron determination and their application to the analysis of plant and soil samples. *Plant and Soil* **193**: 15 – 33.
- Sah, R.N. and P.H. Brown. 1998. Isotope Ratio Determination in Boron Analysis. *Biological Trace Element Research* **66**: 39 – 53.
- Savarino, J., C.W. Lee, and M.H. Thiemens. 2000. Laboratory oxygen isotopic study of atmospheric Sulfur (IV) oxidation: Origin of the mass independent oxygen isotopic anomaly in atmospheric sulfates and other sulfate deposits. *Journal of Geophysical Research* **105**: 29,079 – 29,088.
- Sen, S., J.F. Stebbins, N.G. Hemming, and B. Ghosh. 1994. Coordination environments of B impurities in calcite and aragonite polymorphs: A ^{11}B MAS NMR study. *American Mineralogist* **79**: 819 – 825.
- Sirois, A. and L.A. Barrie. 1999. Arctic lower tropospheric aerosol trends and composition at Alert, Canada: 1980 - 1995. *Journal of Geophysical Research* **104(D9)**: 11,599 - 11,618.
- Spivack, A.J. and J.M. Edmond. 1987. Boron isotope exchange between seawater and the oceanic crust. *Geochimica et Cosmochimica Acta* **51**: 1033 – 1043.
- Spivack, A.J., M.R. Palmer, and J.M. Edmond. 1987. The sedimentary cycle of the boron isotopes. *Geochimica et Cosmochimica Acta* **51**: 1939 – 1949.

- Spiro, P.A., D.J. Jacob, and J.A. Logan. 1992. Global Inventory of Sulfur Emissions With 1° x 1° Resolution. *Journal of Geophysical Research* **97D**: 6023 - 6036.
- Tanaka, N., D.M. Rye, Y. Xiao, and A.C. Lasaga. 1994. Use of stable sulfur isotope systematics for evaluation oxidation reaction pathways and in-cloud-scavenging of sulfur dioxide in the atmosphere. *Geophysical Research Letters* **21**: 1519 – 1522.
- Taylor, S.R. and S.M. McLennan. 1995. The geochemical evolution of the continental crust. *Reviews of Geophysics* **33**: 241 – 265.
- Thode, H.G. 1991. Sulphur Isotopes in Nature and the Environment: An Overview. In: Krouse, H.R. and V.A. Grinenko, Eds. Stable Isotopes: Natural and Anthropogenic Sulphur in the Environment, SCOPE 43. John Wiley & Sons: Chichester, England, pp. 1 - 26.
- Thompson, A.M. 1992. The Oxidizing Capacity of the Earth's Atmosphere: Probable Past and Future Changes. *Science*, **256**: 1157 - 1165.
- Tonarini, S., M. Pennisi, A. Adorni-Braccesi, A. Dini, G. Ferrara, R. Gonfiantini, M. Wiedenbeck, and M. Gröning. 2003. Intercomparison of Boron Isotope and Concentration Measurements. Part I: Selection, Preparation and Homogeneity Tests of the Intercomparison Materials. *Geostandards Newsletter* **27**: 21 – 39.
- U.S. Department of Energy. 2004. Energy Savers: Comparing Heating Fuels. Available at <http://www.eere.energy.gov/consumerinfo/factsheets/cb5.html?print>. Last accessed 23 November 2004.
- Vanderpool, R.A. and P.E. Johnson. 1992. Boron Isotope Ratios in Commercial Produce and Boron-10 Foliar and Hydroponic Enriched Plants. *Journal of Agriculture and Food Chemistry* **40**: 462 – 466.
- Vengosh, A., A.R. Chivas, M.T. McCulloch, A. Starinsky, and Y. Kolodny. 1991a. Boron isotope geochemistry of Australian salt lakes. *Geochimica et Cosmochimica Acta* **55**: 2591 – 2606.
- Vengosh, A., A. Starinsky, Y. Kolodny, and A.R. Chivas. 1991b. Boron isotope geochemistry as a tracer for the evolution of brines and associated hot springs from the Dead Sea, Israel. *Geochimica et Cosmochimica Acta* **55**: 1689 – 1695.
- West, P.W. and G.C. Gaeke. 1956. Fixation of Sulfur Dioxide as Disulfitomercurate(II) and Subsequent Colorimetric Estimation. *Analytical Chemistry* **28**: 1816 – 1819.
- Whitby, K.T. 1978. The physical characteristics of sulfur aerosols. *Atmospheric Environment* **12**: 135 – 159.

- Wieser, M.E. 1998. Stable Isotope Ratio Mass Spectrometry of Nanogram Quantities of Boron and Sulfur. Ph.D. Thesis. University of Calgary, Calgary, AB.
- Wieser, M.E., S.S. Iyer, H.R. Krouse, and M.I. Cantagallo. 2001. Variations in the boron isotope composition of *Coffea Arabica* beans. *Applied Geochemistry* **16**: 317 – 322.
- Williams, L.B. and R.L. Hervig. 2004. Boron isotope composition of coals: a potential tracer of organic contaminated fluids. *Applied Geochemistry* **19**: 1625 – 1636.
- Williams, L.B., R.L. Hervig, J.R. Holloway, and I. Hutcheon. 2001a. Boron isotope geochemistry during diagenesis. Part I. Experimental determination of fractionation during illitization of smectite. *Geochimica et Cosmochimica Acta* **65**: 1769 – 1782.
- Williams, L.B., R.L. Hervig, and I. Hutcheon. 2001b. Boron isotope geochemistry during diagenesis. Part II. Applications to organic-rich sediments. *Geochimica et Cosmochimica Acta* **65**: 1783 – 1794.
- Williams, L.B., R.L. Hervig, M.E. Wieser, and I. Hutcheon. 2001c. The influence of organic matter on the boron isotope geochemistry of the gulf coast sedimentary basin, USA. *Chemical Geology* **174**: 445 – 461.
- Winner, W.E., C.L. Smith, G.W. Koch, H.A. Mooney, J.D. Bewley, and H.R. Krouse. 1981. Rates of emission of H₂S from plants and patterns of stable sulphur isotope fractionation. *Nature* **289**: 672 - 673.
- Xiao, Y.K., R.D. Vocke Jr, G.H. Swihart, and Y. Xiao. 1997. Boron Volatilization and Its Isotope Fractionation during Evaporation of Boron Solution. *Analytical Chemistry* **69**: 5203 – 5207.
- Zeininger, H. and K.G. Heumann. 1983. Boron isotope ratio measurement by negative thermal ionization mass spectrometry. *International Journal of Mass Spectrometry and Ion Physics* **48**: 377 – 380.