

SULPHUR ISOTOPE RATIOS IN WATER, AIR, SOIL AND VEGETATION NEAR TEEPEE CREEK GAS PLANT, ALBERTA

H. R. KROUSE and J. W. CASE

Physics Department, The University of Calgary, Calgary, Alberta, Canada T2N 1N4

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Abstract. Baseline data relevant to assessing environmental impact of continued operation of the Teepee Creek gas plant or other similar future industrial operations included S concentrations, pH of soil and water, and S isotope determinations. Concentrations evaluated the S loading while isotope determinations identified sources of environmental S. The industrial source was very enriched in ^{34}S ($\delta^{34}\text{S} = +24\%$) while soil and vegetation were characterized by ^{34}S depletions ($\delta^{34}\text{S}$ values as low as -20% mean value near -8%). Thus S isotope determinations provided an excellent tool for environmental assessment in the region. It was found that the following are the more significant observations:

(1) Neither the pH data nor S isotope compositions of the water or soil samples reveal measurable S loading by the industrial operation.

(2) The measured atmospheric SO_2 concentrations are well below permitted air quality standards.

(3) Data from an atmospheric sampling array revealed that the directions of highest SO_2 concentrations did not correspond to the direction of the gas processing plant nor did high concentrations relate isotopically to the emissions.

(4) In both soil and vegetation samples, increase of S concentration was identified isotopically with mineral layers in the sub-surface and not with the industrial operation.

Thus it is concluded that S in the environment surrounding the Teepee Creek gas plant was dominated by sources other than the plant emissions.

1. Introduction

Industrial processing inevitably alters the ecosystem in which it occurs. Assessment of these alterations is a research challenge.

The Peace River region of Alberta represents a highly developed agricultural area where industrial development has been relatively recent. In response to concerns of the Government, public, and private sector, and especially local farmers whose livelihood is very dependent upon soil conditions, a study was initiated to document current S concentrations in air, water, soil and vegetation in the vicinity of the Teepee Creek gas plant, northeast of Grande Prairie, Alberta.

The Teepee Creek gas plant is a relatively small pollution source which began operations in 1976. It has a maximum daily emission rate of 2.6 Tonnes day^{-1} . The stack is 50 m high with an ID of 762 mm. The effluent gas has a temperature of 538 C and an efflux velocity of 24 m s^{-1} . Given representative atmospheric conditions the effective stack height is 72 m. For category C stability conditions the downwind maximum ground level concentration would occur at 0.74 km where the peak 30 minute concentration would be approximately 370 $\mu\text{g m}^{-3}$.

This study was also designed to generate baseline data which are desirable for assessing the environmental impact of continued operation of the Teepee Creek gas plant and other future industrial activities in the region. The basic approach involved

the determination of the S content and associated properties such as pH combined with $^{34}\text{S}/^{32}\text{S}$ abundance ratios in air, water, undisturbed soils, and dominant plant species along a gradient extending from within to beyond the probable sphere of influence of the gas plant operation. The pH and concentration measurements assessed the S loading while the isotope data were used to identify sources of the S found in the environment.

Sulphur isotope abundance variations are expressed on a $\delta^{34}\text{S}$ scale defined as

$$\delta^{34}\text{S in } \text{‰} = \left\{ \frac{[^{34}\text{S}/^{32}\text{S}]_{\text{sample}}}{[^{34}\text{S}/^{32}\text{S}]_{\text{meteorite}}} - 1 \right\} \times 100$$

where ‰ = parts per thousand or per mil and $[^{34}\text{S}/^{32}\text{S}]$ is the relative number of ^{34}S 's to ^{32}S 's. The choice of meteoritic troilite (specifically from the Canon Diablo Meteorite) as the standard arises from its consistency in isotopic composition and its proximity to the mean of the terrestrial range of δ -values. Throughout the Devonian period, the oceanic sulphate $\delta^{34}\text{S}$ value ranged from +10 to greater than +30‰. Sour gas reservoirs in the Province of Alberta is derived from ancient oceanic sulphate. In the case of shallow reservoirs, the H_2S is usually depleted in ^{34}S by about 15‰ as compared to associated anhydrite. In deeper reservoirs the S isotope composition of the H_2S is close to that of the sulphate from which it was derived. These trends have been discussed in a recent review (Krouse, 1977a). Although soils of Alberta range in $\delta^{34}\text{S}$ value from -30 to +40, values near 0 are frequently encountered (Lowe *et al.*, 1971; Hitchon and Krouse, 1972). The more negative $\delta^{34}\text{S}$ values have been associated with the Peace River region.

Thus, near a sour gas operation in the Peace River region one would expect to find SO_2 emissions with quite positive $\delta^{34}\text{S}$ values while surrounding soils and vegetation should have pre-industrial $\delta^{34}\text{S}$ values which are relatively negative. Mosses and lichens tend to acquire $\delta^{34}\text{S}$ values consistent with atmospheric S compounds while needles and leaves of trees assume $\delta^{34}\text{S}$ values intermediate between the soil and the air (Krouse, 1977b). The latter arises since needles and leaves can acquire S from the air as well as the tree's root system.

2. The Study Area

2.1. LOCATION AND SIZE

The Teepee Creek gas plant is situated approximately 30 km northeast of Grande Prairie, Alberta (55°22'N 118°24'W). The main study area (Figure 1) encompassed 550 square kilometers including portions of Townships 73 and 74, and Ranges 2 to 4, west of the 6th meridian.

2.2. PHYSIOGRAPHY AND SOILS

The soils of the study area are derived from glaciolacustrine materials, ranging from clays and silts to sand. The soils tend to solonchic chernozems throughout the study

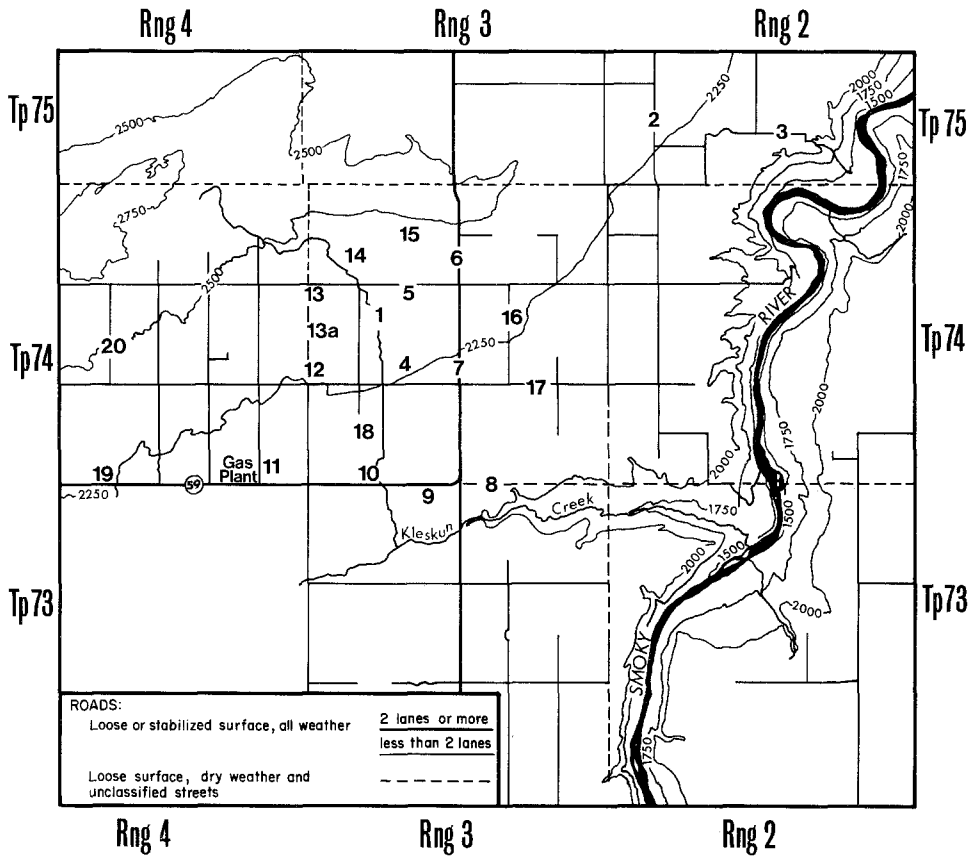


Fig. 1. Sampling locations for vegetation and soil in the study area.

area, although the better drained sites on hills or on fill have luvisolic soil profiles.

The topography of the study area consisted of a gently undulating slope from the Bad Hills. The area has several steep-sided, water channels cut by glacial meltwater. Some of these valleys are dry while others are occupied by streams much too small to have cut the channels. Low local relief results in poor drainage with water evaporation loss exceeding runoff loss in the summer and causing high salt concentrations in some upper soil layers. There are no permanent large bodies of water in the study area although there are a few alkaline sloughs.

2.3. VEGETATION

The vegetation of the area is transitional between the Peace River *Agropyron-Stipa* grasslands and the boreal forest. Portions of the dominant native plant community are still intact, and the one examined in this study, is the poplar association. The aspen (*Populus tremuloides*) dominates pure deciduous stands. It thrives over a wide range of edaphic conditions and may dominate in situations ideal for other species such as

balsam poplar (*Populus balsamifera*). Brome grass (*Bromus inermis*), an escaped cultivar, also thrives in the polar association and was also examined in this study.

2.4. CLIMATE

The climate is predominantly influenced by arctic and subarctic air masses blowing in from the north-northwest during the summer. Mild, dry air masses occasionally provide warm drying winds from the west (Longley, 1967; Powell and MacIver, 1977).

3. Materials and Methods

3.1. SAMPLING OF PRODUCTION WELL AND STACK GASES

Natural gas production wells are the source of S which through processing at the Teepee Creek plant is emitted to the atmosphere primarily as SO_2 . Thus determination of the S isotope compositions of feeder wells and stack gases represents the first step in tracing the fate of S compounds emitted to the environment.

Samples of H_2S were collected via low pressure bleeder valves by bubbling natural gas into a 1 molar solution of cadmium acetate to precipitate bright orange-yellow CdS. The CdS precipitate was treated with hot 0.1 N AgNO_3 solution to convert to Ag_2S .

3.2. ATMOSPHERE

An array of four high volume air samplers was set up at three different locations in the study area and left running for one week. A weather vane switch control turned on a designated sampler when the wind was blowing from the north, east, south or west. Chronometers in the form of circular charts were used to record the time that each sampler was actuated.

The air being sampled passed through a fiber glass particulate filter and then through a sheet of paper treated with TEA-KOH (Brown and Krouse, 1975). The latter filter chemically bound SO_2 . The particulate filter was treated with a $\text{HCl-HI-H}_3\text{PO}_2$ reduction mixture (Thode *et al.*, 1961) in a distillation apparatus. The generated H_2S was trapped and converted to Ag_2S as described above. The chemically treated filter was washed and the washing oxidized by H_2O_2 to assure conversion of all S to sulphate. The sulphate was precipitated as BaSO_4 by the addition of 0.1 N BaCl_2 solution, then reduced using the acid mixture and converted to Ag_2S as described above.

3.3. WATER

One liter of water was collected and the pH measured in the field using a permeable glass electrode pH meter. Dissolved sulphate was precipitated by the addition of 0.1 N BaCl_2 and heated on a water bath to assure complete conversion. The bulk of water was evaporated and the BaSO_4 was converted to Ag_2S as discussed above.

3.4. SOIL

At each site, four 1 liter samples were taken of the A horizon, usually Ah or Ae, in an area of undisturbed native aspen vegetation. Horizons down to bedrock were sampled for analysis at sites 2, 5, 8 and 13.

Soil pH was determined in the laboratory by making a slurry of 25 g of soil with 50 ml of distilled water and measuring the pH with a permeable glass electrode pH meter. All readings were done in triplicate for all four samples collected at each site and the average calculated.

Soluble sulphate in all samples was extracted with a LiCl solution under ultrasonic agitation. After filtration, the residue was oxidized chemically or by Parr bomb to sulphate. Soluble sulphate was then precipitated as BaSO₄. Subsequently, it was converted to Ag₂S which was dried and weighed to determine S content.

3.5. VEGETATION

Approximately 1 kg of *Populus tremuloides* leaves and *Bromus inermis* were collected at sampling sites in uncultivated aspen stands, well away from roads to eliminate interference from road dust fallout or other disturbances. The fresh plant material was packaged into air tight plastic bags. In the laboratory, the material was dried and ground, and soluble sulphate extracted with LiCl solution under agitation. The remainder was Parr bombed to sulphate. Soluble sulphate was precipitated as BaSO₄ and subsequently converted to Ag₂S to gravimetrically determine S content.

3.6. SO₂ PREPARATION AND ISOTOPIC ANALYSES

Ag₂S (up to 20 mg) was thoroughly mixed with Cu₂O (2 : 5), packed into a quartz tube of dimensions 0.5 cm × 3 cm and combusted in a vacuum system at 900°C to produce SO₂. Any H₂O in the reaction product was removed by passing the gases through a trap cooled by a dry ice-acetone slush while contaminant CO₂, because of its higher vapor pressure, was removed by vacuum distillation from a trap cooled by a n-pentane slush. The SO₂ preparation line was attached directly to a mass spectrometer built around a Micromass 602 analyser. Ion currents of mass 64 and 65 were digitally recorded and their ratio digitally printed. Corrections were made for O isotope composition at mass 66 (³²S¹⁶O¹⁸O and ³⁴S¹⁶O₂).

4. Results

4.1. STACK AND PRODUCTION WELL GASES

The δ³⁴S value of H₂S sampled at the base of the gas plant stack (i.e., prior to combustion) was +24.1. H₂S from sour gas wells of the Wabamum formation at locations 10–21–73–3 W6 and 6–32–73–3 W6 and values of +23.9 and +23.0, respectively. The sweet gas well located at the Teepee Creek gas plant site did not yield a sample sufficient for analysis. Thus we conclude that the δ³⁴S value for SO₂ emitted from the stack ranges between +23 and +24.

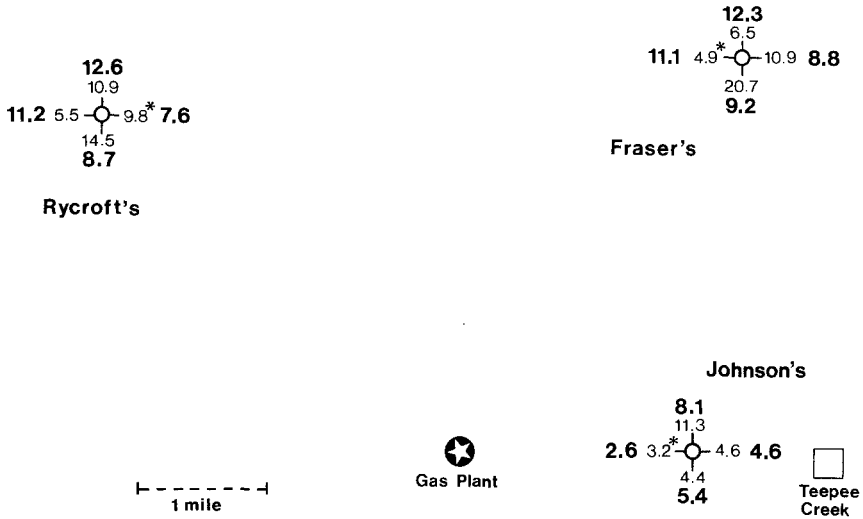


Fig. 2. High volume sampling array sites and $\delta^{34}\text{S}$ data for SO_2 and particulates. $\delta^{34}\text{S}$ values for SO_2 (large numbers) and all particulate matter (small numbers) collected at three locations shown in relation to Teepee Creek gas plant site. Values are shown separately for SO_2 and particulate matter carried by winds from the north, south, east and west. Relative abundance has been taken into consideration in calculation of average $\delta^{34}\text{S}$ values for particulate matter collected and separated by the Andersen sizing-head (*).

4.2. ATMOSPHERE

Data for air samples collected with the high volume sampling array at the Fraser, Johnson and Rycroft farms are presented in Tables I to III and Figure 2. The data are also plotted in Figure 8.

In the tables, concentrations are expressed in two ways. Relative concentration refers to the amount of material deposited on the filters and depends both on concentration in the air and the number of hours that the sampler for a specific wind direction was activated. Thus we see that the samplers which collected the most SO_2 during the periods were:

Fraser farm, South
Johnson farm, North
Rycroft farm, West

The concentration in 10^{-6} g m^{-3} is obtained by dividing the mass of the material collected by the volume of air which passed through the sampler. Since the flow was registered by a small circular chart recorder, one cannot justify stating these values beyond two significant figures. Examination of Tables I and II shows that the directions associated with highest SO_2 concentrations were

Fraser farm, North
Johnson farm, North.

TABLE I

$\delta^{34}\text{S}$ values and concentrations of SO_2 and particulates sampled at the Fraser Farm, approximately 5 km NNW of Teepee Creek, Alberta, July 31–August 6, 1978

Sampler	SO_2			Particulates			
	$\delta^{34}\text{S}$ (K)	S Concentration		$\delta^{34}\text{S}$ (K)	S Concentration		
		Relative	(10^{-6} g m^{-3})		Relative	(10^{-6} g m^{-3})	
N	+12.3	9	3.4	+ 6.5	6	2.30	
E	+ 8.8	< 1	0.2	+10.9	8	0.64	
S	+ 9.2	15	2.0	+20.7	10	1.36	
W	+11.1 ***	10	0.5	+ 5.4*	15	0.78	Top
				+ 5.7*	11	0.57	↓ 3.3
				+ 2.4*	11	0.57	
				+ 0.6*	12	0.63	Bottom

* Andersen sizer

** Facing plant

*** Filter also collected some submicron particulates

TABLE II

$\delta^{34}\text{S}$ values and concentrations of SO_2 and particulates sampled at the Johnson Farm, 1.6 km W of Teepee Creek, Alberta, Augst 7–14, 1978

Sampler	SO_2			Particulates			
	$\delta^{34}\text{S}$ (K)	S Concentration		$\delta^{34}\text{S}$ (K)	S Concentration		
		Relative	(10^{-6} g m^{-3})		Relative	(10^{-6} g m^{-3})	
N	+8.1	13	6.7	+11.3	3	1.5	
E	+4.6	5	1.0	+ 4.6	< 1	< 0.1	
S	+5.4	10	0.9	+ 4.4	5	0.45	
W**	+2.6***	8	0.2	+ 7.2*	5	0.1	Top
				+ 3.2*	11	0.25	↓ .81
				- 3.2*	7	0.16	
				- 1.9*	10	0.3	Bottom

* Andersen sizer

** Facing plant

*** Filter also collected some submicron particulates

In both cases, it is seen that the directions with highest SO_2 concentrations do not correspond to the gas processing plant.

It is also seen that the directions corresponding to the highest particulate concentrations are also the same as those for the highest SO_2 concentrations. However, there

TABLE III

$\delta^{34}\text{S}$ values and concentrations of atmospheric SO_2 and particulates sampled at the Rycroft Farm, 11 km NW of Teepee Creek, Alberta, August 15–24, 1978

Sampler	SO_2		Particulates		
	$\delta^{34}\text{S}$ (K)	S Concentration Relative	$\delta^{34}\text{S}$ (K)	S Concentration Relative	
N	+12.6	6	+10.9	4	Top ↓ Bottom
E	+ 7.6	< 1	+ 7.2*	8	
**			+ 6.4*	5	
			+11.9*	9	
S	+ 8.7	3	+12.2*	8	
W	+11.2	8	+ 5.5	4	

* Andersen sizer

** Facing gas plant

is not a consistent relationship between SO_2 and particulate concentrations or between their isotope compositions.

SO_2 data obtained at the Rycroft and Fraser farms (Figure 2) show a remarkable consistency with $\delta^{34}\text{S}$ values decreasing in the direction N, W, S to E at both locations. The overall $\delta^{34}\text{S}$ range for SO_2 at these locations is fairly narrow, +7.6 to +12.6. The data for the particulates are not quite as consistent but the south and west winds bear the highest and lowest $\delta^{34}\text{S}$ values respectively at both locations. The $\delta^{34}\text{S}$ range is also larger, +5.4 to +20.7.

In contrast, $\delta^{34}\text{S}$ values at the Johnson farm situated between the gas plant and Teepee Creek are much lower than at the other two sites. The highest $\delta^{34}\text{S}$ value is also associated with the north wind.

Data from the Andersen sizer also show variations in $\delta^{34}\text{S}$ values with the aerodynamic size of the particles. The size diameters in going from the top to the bottom filters are > 7, 3.3 to 7.7, 2 to 3.3 and 1.1 to 2.0 μm , respectively. Greater variations in $\delta^{34}\text{S}$ values with location and wind direction are seen in the smaller size fractions; this seems reasonable since they can be carried in from further distances. The lower $\delta^{34}\text{S}$ values found for SO_2 and particulates at Johnson farm are also encountered in the Andersen sizer. In particular, the only negative $\delta^{34}\text{S}$ value found for atmospheric particulates were in the 2 to 3.3 and 1.1 to 2.0 μm fractions at this location.

Thus, we conclude that the atmospheric SO_2 and particulates are generally enriched in ^{34}S , but well below the $\delta^{34}\text{S}$ value of +24 associated with the stack emissions. High S concentrations are not identified with the stack emissions. A number of sources are responsible for the atmospheric S-containing particles.

Finally, it is seen that the measured atmospheric concentrations are well below those permitted by the ambient air quality standards for Alberta (30 $\mu\text{g SO}_2 \text{ m}^{-3}$) (Clean Air Regulations, A.R. 218/75).

TABLE IV
pH, sulphur concentration and $\delta^{34}\text{S}$ data for surface and well waters near the Teepee
Creek Gas Plant, Peace River Region, Alberta, October, 1978

		pH	Sulphur (ppm)	$\delta^{34}\text{S}$
W ₁	surface	6.8	< 1	NE
W ₂	surface	7.5	1	NE
W ₃	surface	8.0	1	NE
W ₄	surface	6.8	1	NE
W ₅	surface	6.85	1	NE
W ₆	dugout	9.6	45.3	- 3.3
W ₇	dugout	8.7	1	NE
W ₈	gas plant water well	8.0	6.05	+ 11.4
W ₉	Teepee Creek well	7.9	36.87	+ 12.8
W ₁₀	Little Smoky River	6.4	9.36	+ 7.9
W ₁₁	Bezanson well	6.9	28.6	- 11.9

NE – not enough S collected for S isotope analysis

4.3. WATER

Data for the water samples are presented in Table IV. The pH values range from slightly acidic (6.4) to basic (9.6). There is an absence of low pH values that could be associated with SO_2 loading of the hydrosphere. With the exception of one dugout and Little Smoky River, surface waters tended to have sulphate concentrations of < 1 ppm S. Wells tended to have much higher sulphate concentrations than surface waters. With the exception of the Teepee Creek well, higher sulphate concentrations tend to be associated with lower $\delta^{34}\text{S}$ values. There is not a simple correlation between the pH and concentrations of $\delta^{34}\text{S}$ values. Thus the $\delta^{34}\text{S}$ data show no evidence of industrial loading of the hydrosphere and identify a subsurface source characterized by negative $\delta^{34}\text{S}$ values. The positive $\delta^{34}\text{S}$ value for the well at Teepee Creek might be related to a carbonate layer in agreement with findings in the soil study.

4.4. pH VALUES OF SOIL

All of the Ah and Ae soil horizons sampled are acidic to some degree (Table V). The average pH of the Ah horizons is 6.25 and the average pH of the Ae horizons is 6.03. The standard errors of the mean pH values for the Ah and Ae horizons are 0.069 and 0.191 pH units, respectively. This indicates that the soil pH of the Ah and Ae horizons are relatively consistent throughout the study area. There is no evidence that the pH of these surface soil horizons have been depressed as a result of soil acidification resulting from SO_2 emissions originating at the Teepee Creek gas plant.

Bnt horizons which are zones of organic matter and clay enrichment in which the ratio of exchangeable Ca to Na is 10 or less, consistently had pH values below 7. Again, this is not correlated with the proximity of the gas plant, but rather to the acidic nature of the organic material and the presence of salts typical of solonchic soils. The pH values of Bnt horizons sampled at sites 13A, 2 and 5 were 5.8, 5.3, and 6.7,

TABLE V
pH Data for Soil Specimens

Site	Horizon	pH
1	Ah	6.10
2	Ae	6.61
	Bnt	5.27
	Csa	5.90
3	Ah	6.10
4	Ah	6.12
5	Ah	6.40
	Bnt	6.70
	Csak	6.17
6	Ae	6.55
7	Ah	6.06
8	Ah	6.13
	Ae	5.77
	Bt	6.37
	Ck	7.0
9	Ah	6.56
11	Ah	6.24
12	Ah	5.91
	Ae	6.37
13a	Ap	6.47
	Bnt	5.77
	IICk	7.4
14	Ah	6.05
15	Ae	6.55
16	Ae	5.38
17	Ah	5.56
19	Ah	6.60
20	Ah	6.61

respectively. The pH of the Bnt horizon at site 5 is higher than the others sampled because of the presence of an accumulation of carbonate with salts beneath it. A similar Bt horizon sampled at site 8 had a pH of 6.4; this higher value was also due to a relative abundance of exchangeable Ca.

C horizons sampled were usually high in carbonate, as indicated by visible effervescence when HCl was added. Ck (carbonate enriched) horizons at sites 8 and 13A had near neutral pH values of 7.0 and 7.4 respectively. The pH of the Csa (salt enriched) horizon at site 5 was lower (6.2) because of salt enrichment and the absence of detectable carbonates.

Table VI summarizes the soil S concentrations and $\delta^{34}\text{S}$ data. The soils were first extracted with LiCl solution to maximize sulphate recovery. The remainder was oxidized by Parr bombing or chemical oxidation. There was evidence that chemical oxidation was sometimes incomplete since elemental S formed in the cadmium acetate solution trap during the subsequent chemical reduction process. This is believed due

TABLE VI

Sulphur concentrations and $\delta^{34}\text{S}$ values for soils near Teepee Creek gas plant, Peace River Region of Alberta, July 1978

Site	Horizon	S Concentration (ppm)			$\delta^{34}\text{S}$		
		LiCl extr	Parr bomb	Chem oxid	LiCl extr	Parr bomb	Chem oxid
1	Ah		250			-15.1	
2	Ae	4	80		-6.9	-10.5	
	Bnt	30			-10.0		
	Csa	230			-19.1		
3	Ah	< 0.5	130	110	+18.0	-17.7	-18.5
4	Ah		460	100		-16.1	-17.6
5	Ah	< 0.5	250	52	-9.4	-13.5	-15.5
	Bnt	VH			-19.8		
	Csak	VH			-18.6		
6	Ae			VL			+ 1.9
7	Ah	2	410	52	-12.3	-17.1	-19.2
8	Ah	3	90	77	2.6	-11.5	-14.6
	Bt	2			-6.5		
	Ck	< 0.5			+15.3		
9	Ah	< 0.5	52		8.6	-4.9	
11	Ah	11	480	120	0.5	-12.7	-15.6
12	Ah	4	120		0.03	-6.6	
13	Ae	1	90		NE	-4.7	
13a	Ap	< 0.5			-13.9		
	Ae	< 0.5			-13.9		
	Bnt	< 0.5			-14.8		
14	Ah	6	930	90	4.8	-13.8	-15.0
15	Ae	7	120		-1.3	3.4	
16	Ae	2	52		NE	-5.8	
17	Ae		160			-13.5	
18	Ah						
19	Ah		130	52		-6.9	-9.4
20	Ah	2	140	80	-1.9	-10.0	-11.6

to release of SO_2 which reacted with H_2S to produce the elemental S. The SO_2 could arise from acidification of sulphite in the digested soil, hence indicating incomplete oxidation to sulphate. It is concluded that Parr bombing is superior.

As might be expected, the Ae horizons tend to have lower S concentrations than the Ah horizons. The horizons with the highest sulphate contents are the Bnt, Csa, and Csak horizon which have associated salt accumulations. These salts, which are usually concentrated below 50 cm are very rich in S, much of which is soluble.

Examination of $\delta^{34}\text{S}$ values in the Ah and Ae horizons throughout the study area reveals no apparent trends with respect to the location of the gas plant, $\delta^{34}\text{S}$ values of the Ah horizons were consistently negative (Table VI), ranging from -4.9 to -17.1. In one case, Site 3, the LiCl extract had a positive $\delta^{34}\text{S}$ value (+18.0). This corres-

ponds to about 0.3% of the total sulphur and in no way appears to be related to the industrial emissions.

$\delta^{34}\text{S}$ values of the Ae horizons tended to have values less negative than the Ah horizons, and at site 15 the $\delta^{34}\text{S}$ of the Ae horizon was +3.4 for the Parr bombed sample. The LiCl extraction results (Table VI) indicate that the soluble S present had a $\delta^{34}\text{S}$ value of -1.3; thus an insoluble ^{34}S rich S source of unknown type exists in the soil at site 15.

Sulphur isotope compositions of lower soil horizons were investigated using LiCl extraction only and the $\delta^{34}\text{S}$ values were found to range from -4.2 to -19.8. One exception was deeply buried carbonate rich bedrock (Ck) at site 8 which had a $\delta^{34}\text{S}$ value of +15.3.

Thus soluble salts in the soil horizons have negative $\delta^{34}\text{S}$ values. Carbonates, on the other hand have positive values. Insoluble S released from Ah, Ae, and presumably other horizons by Parr bombing or chemical oxidation usually has negative $\delta^{34}\text{S}$ values. Soluble S extracted from these horizons by LiCl extraction occasionally has slightly positive $\delta^{34}\text{S}$ values.

Figure 3 shows a clear relationship between soil S concentrations and $\delta^{34}\text{S}$ values. As the S concentrations increase, the $\delta^{34}\text{S}$ values become increasingly negative. The lowest $\delta^{34}\text{S}$ values are associated with soils enriched by salts, sometimes in very high concentrations as with the Bnt and Csa horizons from site 5. These relationships support the contention that low (negative) $\delta^{34}\text{S}$ values of soil S are associated with salt content. If elevated soil S concentrations were related to Teepee Creek gas plant emissions, the $\delta^{34}\text{S}$ values of these soils should approach +24 with increasing concen-

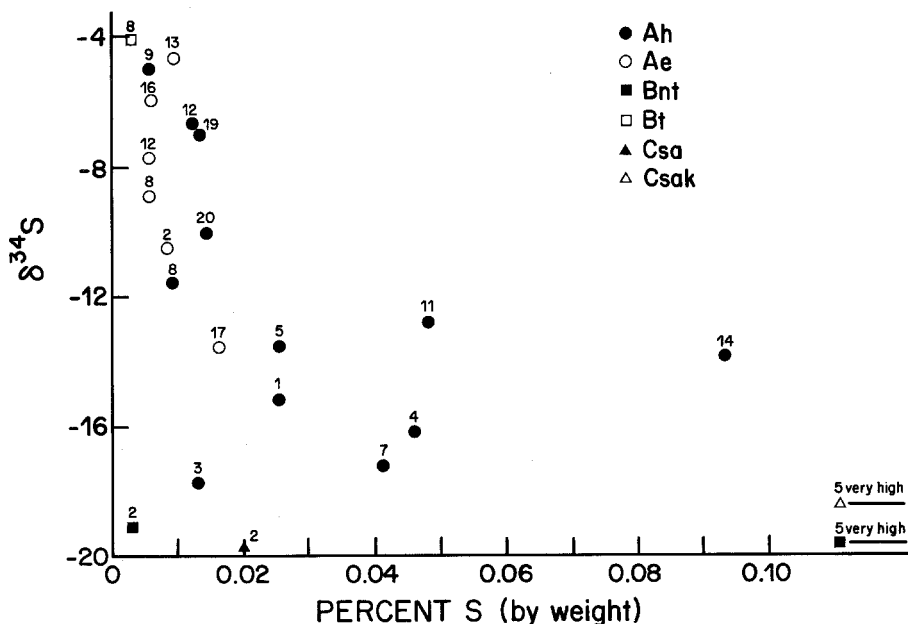


Fig. 3. Sulphur content and isotopic composition of soil horizons.

tration. Thus it is concluded that higher concentrations of S in the soil are primarily related to subsurface salt layers and there is no evidence of loading by the gas plant emissions.

4.5. VEGETATION

Lichens usually acquire $\delta^{34}\text{S}$ values close to those of atmospheric S compounds (Krouse, 1977b). This is interpreted to reflect either direct chemical interaction with atmospheric gases or solutions bearing S compounds derived from the atmosphere. In Figure 8 it is seen that the lichens examined are isotopically closer to the atmosphere than to the soil. The $\delta^{34}\text{S}$ value of +23.9 for LiCl extractable S at site 2 is close to that of the stack emissions; however, the location is not consistent with a large contribution from the stack.

TABLE VII

Sulphur concentrations and $\delta^{34}\text{S}$ values for vegetation near Teepee Creek gas plant, Peace River Region of Alberta, July 1978

Site	<i>Bromus (inermis)</i>				<i>Populus tremuloides</i>					
	LiCl ppms	Extr $\delta^{34}\text{S}$	Insol. ppms	Total ppms	LiCl ppms	Extr $\delta^{34}\text{S}$	Insol. ppms	Total ppms		
1	430	+ 5.4	430	- 7.6	860	110	- 0.8	1850	- 8.4	1960
2						120	- 3.2	2240	- 1.6	2360
3	160	- 4.6	950	- 5.6	1110	120	- 3.5	1120	- 7.7	1240
4	350	- 8.3	990	- 8.8	1340	310	-12.9	3180	-13.8	3490
5	180	-12.5	1420	-11.2	1600	40	- 3.8	2060	-11.2	2100
6	660	-10.5	1030	- 9.9	1690	60	- 5.6	2370	- 2.2	2430
7	767	-22.3	860	-12.0	1627	37	- 9.8	520	- 9.4	557
8	293	-11.2	1940	-13.4	2233	75	- 8.0	1590	-11.2	1665
9	560	- 8.2	90	-	650	92	-11.3	2620	- 7.0	2712
10	37	- 5.2	950	- 9.0	987	42	- 5.8	1810	- 8.5	1852
11	545	+ 8.2	990	- 6.3	1535	63	+ 0.5	1200	- 6.3	1263
12	605	- 5.6	1290	-11.4	1895	121	+ 6.5	2240	- 6.5	2361
13	93	- 2.2	1030	- 7.1	1123	477	- 1.9	2150	- 6.4	2627
14	292	- 6.0	1380	- 7.6	1672	21	- 1.5	1940	- 6.3	1961
15	97	- 1.3	770	- 3.2	867	90	- 1.9	1510	- 3.9	1600
16	88	- 9.8	520	- 6.2	608	42	- 1.1	1630	- 7.5	1672
17	703	-13.9	1420	-16.8	2123	193	-12.6	1720	-15.3	1913
18	464	- 8.3	820	- 5.7	1284	144	- 3.3	2020	- 6.2	2164
19	526	- 6.9	340	- 6.6	866	119	- 3.9	2370	- 5.9	2489
20	119	- 8.1	650	- 4.7	769	87	+10.9	1290	- 4.6	1377

Site	Ground Lichens				
	LiCl ppms	Extr $\delta^{34}\text{S}$	Insol. ppms	Total ppms	
2	40	+23.5	470	-6.3	510
5	13	+ 5.7	-		

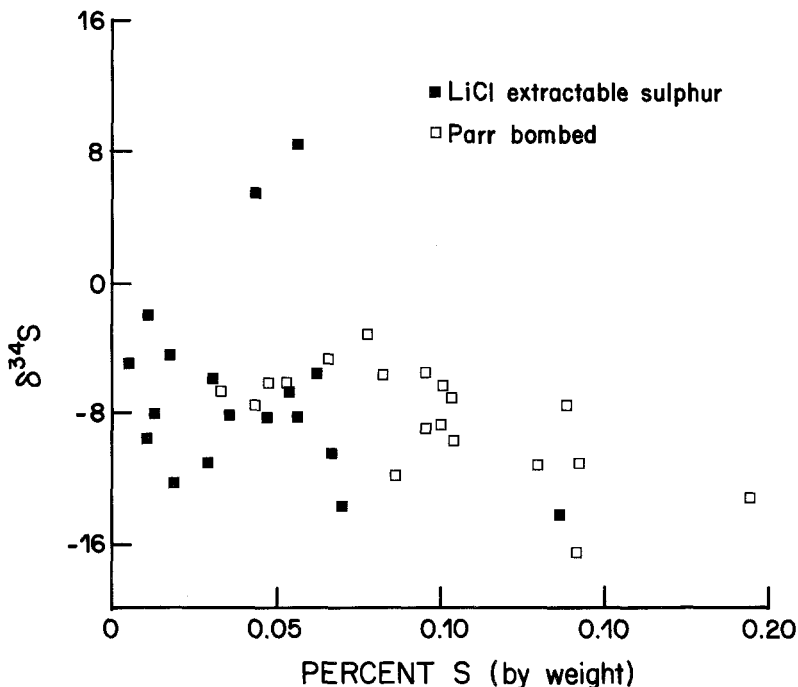


Fig. 4. Sulphur content and isotopic composition of *Bromus inermis*.

In contrast to lichens, trees and grasses have root systems, thus leaves can derive S from both the soil and the air. Soluble sulphate in aspen leaves and brome grass were found to have $\delta^{34}\text{S}$ values ranging from -15 to $+10$. These correspond to a small fraction of the S in the leaves. The fraction remaining after sulphate extraction was considerably larger (Table VII) and had a narrower $\delta^{34}\text{S}$ range from -16 to -1 . Thus a few positive $\delta^{34}\text{S}$ values are associated with the minor sulphate fraction. The concentration and $\delta^{34}\text{S}$ differences between the LiCl extractable and remaining fractions are quite evident in Figures 4 and 5. In a similar fashion to soils, Figure 4 shows that $\delta^{34}\text{S}$ values tend to decrease with increasing S concentration for brome grass. The trend is not evident with the aspen leaf data (Figure 5). However, it is seen that the higher S concentrations in aspen leaves tend to be identified with $\delta^{34}\text{S}$ values near -8 which is considerably below the value of the gas plant stack emissions ($+24$).

There is no trend of $\delta^{34}\text{S}$ values becoming more positive upon approaching the gas processing plant as would be expected if significant industrial S were being taken up by the vegetation.

The $\delta^{34}\text{S}$ value for brome grass and aspen are plotted against the $\delta^{34}\text{S}$ values for upper soil layers in Figures 6 and 7. If the vegetation derived all of its S from these layers with no isotopic selectivity, then the isotope data would plot on a line of slope 1 going through the origin. In both Figures 6 and 7 the Ae horizon tends to plot below the unity slope line while the upper Ah horizon generally plots above the line. In both cases the Ae data tend to fit closer to a straight line plot.

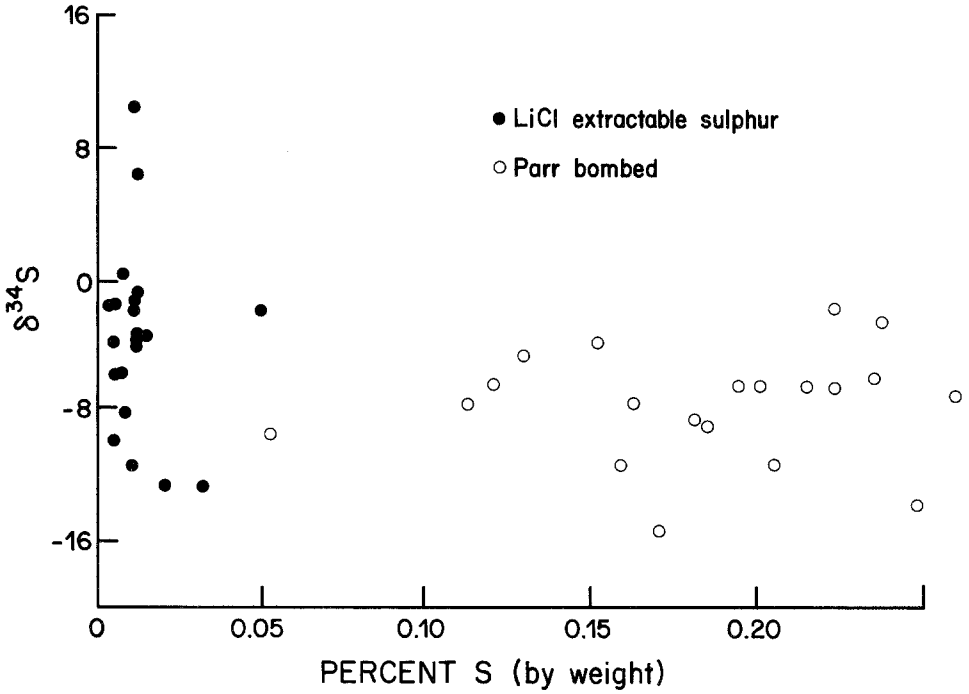


Fig. 5. Sulphur content and isotopic composition of *Populus tremuloides* leaves.

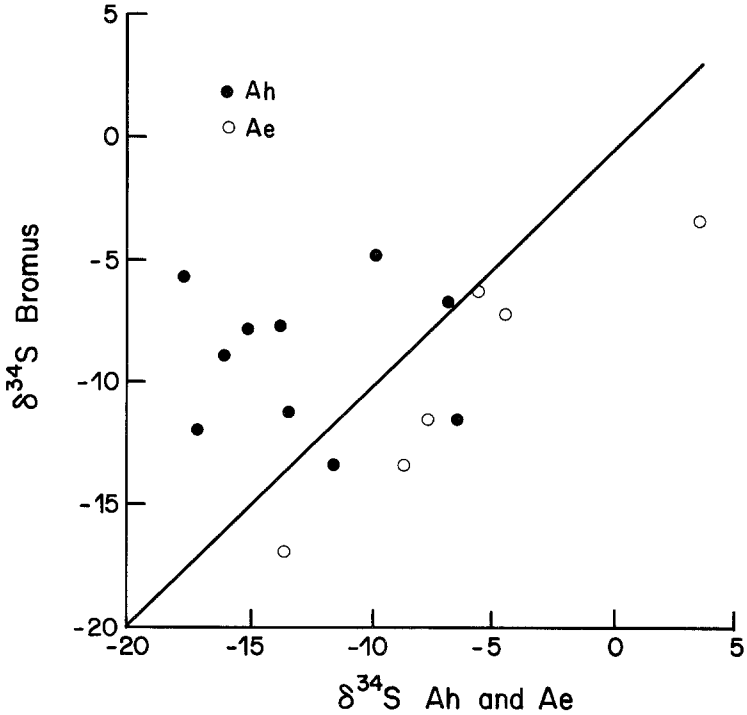


Fig. 6. $\delta^{34}\text{S}$ values for *Bromus inermis* versus $\delta^{34}\text{S}$ values for Ah and Ae soil horizons. Points along the line of unity slope would mean that all S in the plant was derived from the associated soil horizon.

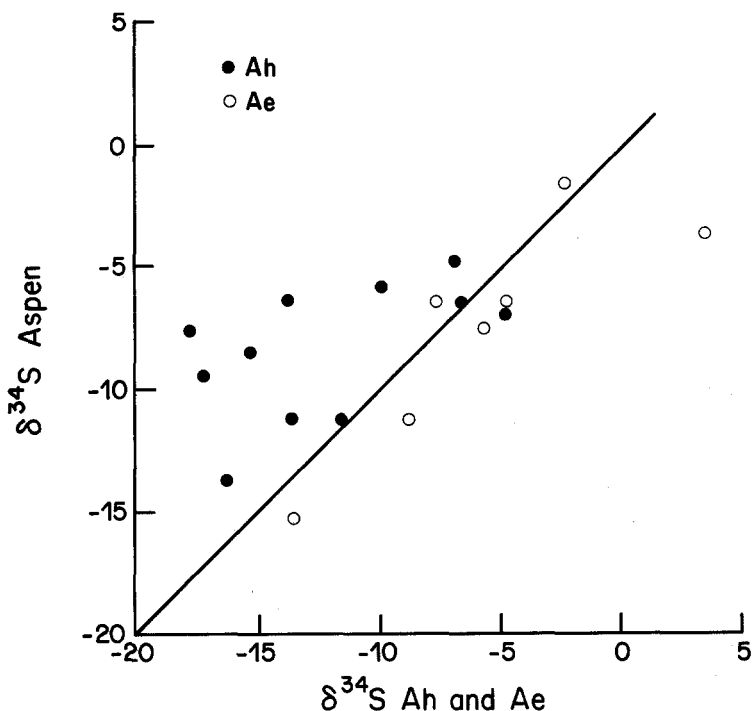


Fig. 7. $\delta^{34}\text{S}$ values for *Populus tremuloides* leaves versus $\delta^{34}\text{S}$ values for Ah and Ae soil horizons. Points along the line of unity slope would mean that all S in the plant was derived from the associated soil horizon.

Thus we conclude that the vegetation examined is not taking up significant amounts of industrial S from the atmosphere but rather has its S isotope composition determined by the soil at the interface between the Ah and Ae horizon or lower.

5. The Overall Sulphur Isotope Distribution and Conclusions

The overall S isotope distribution is shown in Figure 8. A number of sources of S compounds are immediately evident. The raw H_2S stands out as having the most positive $\delta^{34}\text{S}$ value but its contribution is too small to be seen in the surrounding soil and vegetation. The air is moderately enriched in ^{34}S but the wind-directionally controlled sampler array generally identifies the more positive values with a direction opposite to that of the industrial stack. The $\delta^{34}\text{S}$ values of the particulates do not bear a simple relation to the atmospheric SO_2 .

There are two sources of S in the soil, a salt layer characterized by $\delta^{34}\text{S}$ values around -19 and a carbonate layer identified with positive $\delta^{34}\text{S}$ values. Evidence of the latter is found occasionally in the soil profiles and in certain water wells. The soils, grass, and aspen leaves tend to have $\delta^{34}\text{S}$ distributions similar to the soil whereas if the air had contributed significant amounts of S to the vegetation, it should have

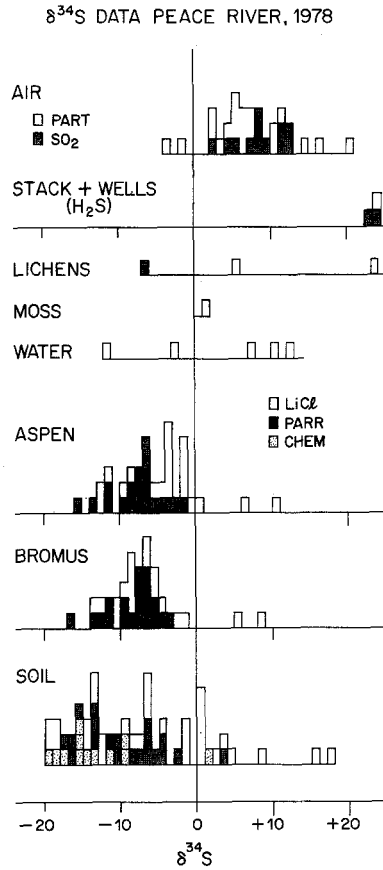


Fig. 8. Summary of $\delta^{34}\text{S}$ data in environments surrounding the Teepee Creek gas processing plant, Peace River Region, Alberta, 1978.

shifted the $\delta^{34}\text{S}$ data of the vegetation to values intermediate between the soil and the air as found in other locations (Krouse, 1977b).

Increasing S concentrations in soil horizons tend to be identified with more negative $\delta^{34}\text{S}$ values, the limit tending to about -20 . If the industrial S had been loading the soil, the trend would have been towards $+24$ with increasing S concentration. Consistent with the trend in the soil, increasing S concentration in the brome grass is identified with more negative $\delta^{34}\text{S}$ values.

Thus, it is concluded from pH concentration and isotope data that S in the environment surrounding the Teepee Creek gas plant is dominated by sources other than the plant emissions. Hence any minor effects due to the industrial operation cannot be delineated from the much larger background trends on the basis of measurements at this point in time. However, the fact that $\delta^{34}\text{S}$ value of the emissions ($+24$) is so distinct from the negative $\delta^{34}\text{S}$ values of the current surrounding environment, means that there is significant isotopic 'leverage' for monitoring the situation in the future.

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