

VARIABILITY IN FOREST SYSTEMS AS IT RELATES  
TO ELEMENTAL SULPHUR EFFECTS

by

D.G. Maynard<sup>1</sup> and P.A. Addison<sup>2</sup>

ABSTRACT

A 5-year project was initiated in 1981 to study the effects of sour gas processing on the forest ecosystem in west-central Alberta. A biomonitoring network was established in a 30- x 30-km area surrounding the Strachan and Ram River sour gas plants. In addition, detailed studies were initiated to determine the mechanisms and magnitude of the particulate elemental sulphur ( $S^0$ ) impact on the soils and vegetation of the area. This paper reports on some of the results of this study, and the quantification of variability associated with these ecological measurements and its influence on biomonitoring.

A technique was developed to determine elemental sulphur ( $S^0$ ) in soils and to estimate  $S^0$  deposition. Deposition at sites adjacent to the gas plant was found to be considerably less than the deposition that must have occurred previously to produce the  $S^0$  concentrations present in the surface organic horizon (LFH). Significant changes in soil chemical properties and plant cover were observed at these sites impinged with heavy concentrations of  $S^0$ . However, changes at sites impinged with low concentrations of  $S^0$  ( $<5000 \mu\text{g}\cdot\text{kg}^{-1}$ ) were more difficult to assess.

Random or natural soil variability ranged from 24 to 102% on a regional basis. Spatial variability was the largest component of the partitioned variability; however, there was a significant regional component as well. For the soil parameters measured, temporal variability was generally not significant. Because of the high variability, concentration differences, in the order of 50% or greater, were needed to be considered significant. Plant cover estimates measurement error was high (20%), and changes in plant cover between sampling times would have to exceed 20% before interpretation would be possible. Growth measurements were equally variable.

Sandhu, H.S., A.H. Legge, J.I. Pringle, and S. Vance, eds. 1987. Acid forming emissions in Alberta and their ecological effects: 2nd Symposium/ Workshop Proceedings. Prep. by Research Management Division, Alberta Department of the Environment and Kananaskis Centre for Environmental Research, University of Calgary. 1986 May 12-15; Calgary, Alberta. 478 pp.

<sup>1</sup>Canadian Forestry Service, North

<sup>2</sup>Canadian Forestry Service, Ottawa

THIS FILE COPY MUST BE RETURNED

TO: INFORMATION SECTION  
NORTHERN FORESTRY CENTRE  
5320-122 STREET  
EDMONTON, ALBERTA T6H 3S5

## 1. INTRODUCTION

The Canadian Forestry Service has been involved with air pollution research in Alberta for the past 15 years. During that time, our role has been to provide both industry and provincial regulatory agencies with scientific information upon which decisions, with respect to forest management, could be made. In 1981, we initiated a project upon a request from Canterra Energy Ltd. (then Aquitaine Company of Canada) and Gulf Canada Resources Inc. into the effects of sour gas processing on the forest ecosystem. This project had two objectives:

1. To establish and describe a biomonitoring network to detect and quantify the effects of sour gas processing on forest systems in the vicinity of Ram River and Strachan gas plants; and
2. To determine the mechanisms and magnitude of particulate elemental sulphur ( $S^0$ ) impact on the soil and plant components of the forested ecosystem.

In order to accomplish these two objectives, a number of new techniques had to be developed that were sufficiently precise to give us confidence in the results. Obviously, variability in both the natural system and the measurement techniques must be quantified before one can trust any technique. It is the quantification of variability in ecological measurements and its influence on biomonitoring that is the central theme of this paper.

The area under investigation was west-central Alberta where the Ram River (largest gas plant in the province) and Strachan (10th largest) sour gas plants are located. The forests of the area are dominated by lodgepole pine with co-dominants of aspen and spruce in various locations. The soils of the area are predominantly Brunisolic and Podzolic Gray Luvisols.

The results from the initial survey and the characterization of 26 sites in the area are synthesized in Addison et al. (1984). The results of that study and the more detailed work that followed demonstrated that certain sites had been heavily impinged by elemental sulphur. The rate of deposition, however, slowed considerably between 1982 and the present. These sites had measurable differences in soil chemical properties, and the response of plants in the understory was dramatic. In 1981, trees did not show either a

growth or reproduction response even though tissue sulphur (S) content was elevated.

The question that this paper attempts to address is: What evidence is required to make the above statements, and how can we collect such data when techniques are not precise and variability in the natural ecosystem is great? We hope that, through the use of examples centred around our study into the effects of elemental sulphur on a forest, some light will be shed on the subject.

## 2. DEPOSITION

We know from the extremely high concentrations of total S in the surface organic horizon (LFH) that heavy deposition of  $S^0$  has occurred at sites adjacent to the  $S^0$  blocks. However, since  $S^0$  was a major pollutant in the forest adjacent to the sour gas plants, a direct measurement of  $S^0$  in organic surface soils was required.

The precise measurement of  $S^0$  in biological systems is difficult and few attempts have been made to carry out such assays (Roy and Trudinger 1970). None of the methods described in the literature measured  $S^0$  in soils or sediments containing high amounts of organic matter. The determination of  $S^0$  in acetone extracts, originally proposed by Hart (1961), was neither accurate nor sensitive enough for organic forest horizons, giving values about 50% too high at  $1000 \text{ mg} \cdot \text{kg}^{-1} S^0$ . The use of organic solvents, such as carbon disulphide ( $\text{CS}_2$ ), as suitable extracts was rejected since one form of  $S^0$  (fresh prills) produced at the sour gas plants was either totally or partially insoluble in  $\text{CS}_2$  after 24 h. Therefore, a method was proposed (Maynard and Addison 1985) using an acetone extract (as described by Hart 1961) and a colourimetric determination of  $S^0$  as thiocyanate following the procedure of Bartlett and Skoog (1954). Interferences due to the coloured extract gave absorbance readings equivalent to 10 to  $15 \text{ mg} \cdot \text{kg}^{-1} S^0$  in moist soils, even after blank correction. A detection limit was defined as  $100 \text{ mg} \cdot \text{kg}^{-1} S^0$ . Recoveries of added  $S^0$  varied from 90 to 104% in soils containing 100 to  $50\,000 \text{ mg} \cdot \text{kg}^{-1} S^0$ , and the precision was about  $\pm 3\%$  using 95% Confidence Limit (C.L.) as a percentage of the mean at 1000, 10 000, and  $50\,000 \text{ mg} \cdot \text{kg}^{-1}$ .

With this method, we were able to determine whether a site had been impinged with  $S^0$  in excess of  $100 \text{ mg}\cdot\text{kg}^{-1}$  with a high degree of confidence. Elemental sulphur is not normally present in surface aerobic soils (Freney and Williams 1983), and the presence of any  $S^0$  in the LFH indicated deposition of  $S^0$  had occurred. Total S concentrations, on the other hand, ranged from 900 to  $1500 \text{ mg}\cdot\text{kg}^{-1}$  in the LFH horizons of this region (Addison et al. 1984), and increases in the order of  $500 \text{ mg}\cdot\text{kg}^{-1}$  would be required (see discussion below) to be 90% confident that significant deposition ( $p < 0.05$ ) had occurred. For sites heavily impinged with  $S^0$  deposition, either total S or  $S^0$  measurements would be suitable. However, despite total S measurements being more precise than  $S^0$  determinations (Hogan and Maynard 1984), increases in the total S concentration, owing to  $S^0$  deposition amounting to  $< 500 \text{ mg}\cdot\text{kg}^{-1}$  S, could not be detected on a regional basis (see discussion below).

In the introduction, it was suggested that the majority of the deposition had occurred prior to the initiation of our study in 1981. During June to October 1982 and April to October 1983, deposition of  $S^0$  to the soil surface was measured at three sites, 50, 200, and 500 m from the  $S^0$  block at Strachan. Ten replicates of a  $132\text{-cm}^2$  plastic container with a terry-towel fabric were placed at the soil surface. The towelling was used to provide a rough surface to prevent the  $S^0$  from moving, and also it provided a material that, when extracted, did not produce any colour interferences to the  $S^0$  method. The material was changed every 2 wk and the towelling extracted with acetone and  $S^0$  determined as discussed above. The method could detect  $1 \text{ mg}\cdot\text{L}^{-1}$  of  $S^0$  in solution equivalent to a detection limit in kilograms per hectare of  $0.08 \text{ kg}\cdot\text{ha}^{-1} S^0$ . Ten replicates were measured at each site for each sampling.

The  $S^0$  deposited over the two growing seasons (1982 and 1983) accounted for  $< 10\%$  of the total  $S^0$  in the LFH. An example of the deposition rate compared to the  $S^0$  in the LFH horizon during one deposition period, July 1982, is given in Table 1. The  $S^0$  deposited during July 1982 accounted for  $< 2\%$  of the total  $S^0$  in the LFH at the most heavily contaminated site. Deposition at the site 500 m from the  $S^0$  source was  $1.3 \text{ kg}\cdot\text{ha}^{-1}$  (equivalent to approximately  $40 \text{ mg}\cdot\text{kg}^{-1}$ ), and would not be detectable in the soil by either total S or  $S^0$  measurements. The coefficient of variation (CV) for

the  $S^0$  deposition rate was in the order of 15 to 25% per sampling period. Most of this error was associated with the particulate deposition through the canopy and was not related to the technique.

Deposition rates in the same order of magnitude as July 1982 were observed throughout the 2 years that deposition was monitored. This indicated that the deposition rates of  $S^0$ , that resulted in the extremely high S concentrations of the LFH adjacent to the  $S^0$  block, occurred prior to 1982 when mechanical breakup of the  $S^0$  blocks took place. Deposition of  $S^0$  was still occurring, but at a much lower rate. However, significant changes in the total or  $S^0$  concentrations of the LFH were not observed between 1982 and 1984, owing to the large variability of the sulphur measurements. In addition, the leaching of the  $SO_4^{2-}$ -S produced from the oxidation of  $S^0$  occurred at a rate in the same order of magnitude as the deposition rate (Table 1).

### 3. SOILS

The results from the initial survey and the characterization of the soils in the area surrounding the sour gas plants were presented elsewhere (Addison et al. 1984). It was found that four sites had been impinged by  $S^0$ , and that three of the four showed significant changes in certain chemical properties. These changes were obvious owing to the heavy deposition of  $S^0$ . However, where deposition of  $S^0$  or  $SO_2$  was considerably lower and the changes in soil parameters more subtle, the variability of the parameters to be measured had to be quantified before it could be determined if there were any significant changes.

The variability associated with a given soil parameter can be either analytical or random. Analytical variability is determined by the precision of the technique used and determines the magnitude of the change that can be detected. In assessing the variability of soil parameters in forest soils, the analytical variability is usually not a factor compared to the random variability. For example, the precision for the  $S^0$  determination in LFH was approximately  $\pm 3\%$ , whereas the random variability associated with the  $S^0$  concentrations in the LFH exceeded 30%.

The random variability of several soil parameters was assessed using a nested or hierarchical sampling scheme to distinguish variation

Table 1. Deposition of elemental S and leaching of S at the Strachan sour gas plant in July 1982 in relation to the total and elemental S of the LFH horizon ( $\pm$  standard deviation).

Distance from Source (m)	Deposition <sup>a</sup> of S <sup>0</sup>	Leaching <sup>b</sup> of S	Total <sup>a</sup> S	Elemental <sup>a</sup> S
(----- kg·ha <sup>-1</sup> -----)				
50	40.5 $\pm 6.1$	95 $\pm 54$	2170 $\pm 1650$	2070 $\pm 1600$
500	1.3 $\pm 0.3$	16 $\pm 7$	270 $\pm 150$	230 $\pm 110$

<sup>a</sup> n = 10

<sup>b</sup> Total S in the leachate from zero tension lysimetres below the LFH horizon (n = 5).

derived from two or more levels of subdivision of a population (Webster 1985). This approach has been used successfully in describing the variability of various parameters in forest soils (Hammond et al. 1968; Ike and Clutter 1968).

In order to determine the regional variability, the biomonitoring sites described by Addison et al. (1984) were used. In 1981, 26 sites were established in even-aged *Pinus contorta* Dougl. var. *latifolia* Engelm. stands in an area 30 x 30 km that had two sour gas processing plants at the centre (Addison et al. 1984). Site locations were based upon available air quality and airflow information, topography, logistics, and accessibility. The sites were subsequently divided into three groups: (1) sulphur-dusted; (2) sulphur gas-exposed; and (3) background. Sulphur-dusted sites had measurable ( $>100 \text{ mg} \cdot \text{kg}^{-1}$ )  $\text{S}^0$  present. The sulphation isopleth of  $0.05 \text{ mg} \cdot \text{dm}^{-2} \cdot \text{d}^{-1}$  ( $\text{SO}_3$ ) was chosen to delimit the area of gas impingement. The threshold is arbitrary and is 10% of the provincial exposure guideline.

Four sites had measurable  $\text{S}^0$  in the surface horizon and were eliminated from the variability portion of the study as significant differences in soil chemical properties had been observed (Addison et al. 1984). At each site, a 20- x 20-m plot was established with a north-south orientation. Five soil pits were dug and samples from each of the four surface horizons were collected. The samples were analyzed for pH and total Ca, Mg, K, Mn, Al, Fe, S, and P by inductively coupled plasma atomic emission spectrometry (ICP-AES) following a  $\text{HNO}_3$ ,  $\text{HClO}_4$ , and  $\text{HCl}$  digestion (Hogan and Maynard 1984). Ammonium acetate ( $\text{NH}_4\text{OAc}$ ) extractable concentrations of the above elements were also determined by ICP-AES.

A single factor analysis of variance (ANOVA), Model II (random effects), was used (Neter and Wasserman 1974). There were 22 factors (sites) with five observations (pits) per factor. Estimations of the variability of the various chemical analyses, and the proportion of the total variability of these parameters that is accounted for by differences among the plots, can be obtained by calculating an ANOVA, as shown in Table 2, for each of the measured soil variables and for each soil horizon.

To assess the temporal variability, a site, 750 m from the gas plant, was chosen. The site was sampled 13 times over 3 years (1982 to 1984), between the months of April and October. Ten replicate samples from

Table 2. A single-factor Model II ANOVA for the regional and temporal variability studies.

Source of Variation	SS	df	MS	E(MS)	F
Between sites	SSTR	$r-1$	MSTR	$s^2 + n's_t^2$	MSTR/MSE
Error (within sites)	SSE	$r(n-1)$	MSE	$s^2$	
TOTAL	SSTO	$nr-1$			



the LFH horizon were collected at each sampling time. The samples were analyzed for total and 1.0 M  $\text{NH}_4\text{Cl}$  extractable Ca, Mg, K, Mn, Al, Fe, P, and S, as described above. The site was selected because it was representative of the soils and vegetation in the area, and was thought to have a minimal amount of  $\text{S}^0$  contamination. There were, however, significant amounts of  $\text{S}^0$  present and, because of this, the S values are higher than would be expected. The Ca concentrations are not presented for this site because a portion of the site was limed in 1984.

A single factor analysis of variance, as shown in Table 2, for the regional variability was again used to partition the temporal variability. There were 13 factors (sampling dates) with 10 observations per factor.

A final experiment was carried out at three sites: (1) a site with no measurable  $\text{S}^0$ ; (2) a site with low levels of  $\text{S}^0$  (approximately  $5000 \text{ mg}\cdot\text{kg}^{-1}$ ); and (3) a heavily impacted site (approximately  $47\,000 \text{ mg}\cdot\text{kg}^{-1}$ ) adjacent to a sour gas plant. A one-time sampling was done, with 50 samples from the LFH horizon taken to assess the spatial variability and to determine the effect of  $\text{S}^0$  on the elemental concentration of the LFH horizon. Total and 1.0 M  $\text{NH}_4\text{Cl}$  extractable concentrations of Mg, K, Mn, Al, Fe, P, and S were determined, as described above, in addition to pH (5:1 water to soil ratio) and electrical conductivity (EC). Calcium was not included because two of the sites had been limed.

The regional variability of the total concentrations in the LFH horizon is given in Table 3. All the elements, except Mn, showed that regional variability was highly significant. The overall variability [as expressed by the coefficient of variation (CV)], ranged from 24 (for S) to 102% (for Mn), of which between 11 and 50% of the variance was accounted for by the variance among sites. The high overall variability associated with Mn (and to a lesser extent Fe) could possibly be related to sampling errors in separating the mineral soil from the LFH. Small amounts of mineral contamination could change the concentration of these elements. The proportion of the Mn variability, accounted for by the differences among sites, was not significant, although the overall variability for Mn was considerably higher than for any other element. The large variability of Mn within site probably obscured any regional variability.

Table 3. Regional variability of the total nutrient content in the LFH horizon.

Parameter	Mean $\pm$ std dev (CV) (mg·kg <sup>-1</sup> )	Significance <sup>a</sup>	Variance Ratio <sup>b</sup>
Ca	5050 $\pm$ 2180 (43)	*	33
Mg	1190 $\pm$ 410 (34)	*	50
K	2160 $\pm$ 530 (24)	*	29
Mn	1160 $\pm$ 1180 (102)	NS	11
Fe	3730 $\pm$ 1910 (51)	*	32
P	1080 $\pm$ 290 (27)	*	35
S	1060 $\pm$ 260 (24)	**	19

<sup>a</sup> \*, \*\*, NS = Significant at  $p < 0.001$  and 0.01 and not significant, respectively, for differences among sites.

<sup>b</sup> Ratio of the variance among sites over the total variance. This ratio measures the proportion of the total variability that is accounted for by the differences among the sites.

The regional variability of the extractable nutrients is given in Table 4. The overall variability associated with the extractable nutrients is generally higher than for the total concentrations. Similar comparisons between total and extractable nutrients in forest soils have been observed elsewhere (Grier and McColl 1971; Arp and Krause 1984). The amount of total variance accounted for among sites (regional variability), however, is generally less for the extractable concentrations than for the total concentrations.

The minimum difference required to show significance ( $p < 0.01$ , 0.05, and 0.10 at 80 and 90% certainty) between two sites, for total S and Mn concentrations in the LFH, are given in Tables 5 and 6, respectively. The differences were calculated according to Sokal and Rohlf (1981) from the data of the regional study (22 plots with 5 observations per plot). A typical level of significance for a field study might be considered  $p < 0.05$  with 90% certainty. A minimum difference of  $540 \text{ mg} \cdot \text{kg}^{-1}$  S would be needed for that difference between two sites to be significant at the 0.05 level with 90% certainty, approximately a 50% change in S. For Mn, a difference of  $2450 \text{ mg} \cdot \text{kg}^{-1}$ , or a 211% change, would be required for the difference to be significant at the same level and certainty. The other elements would require a difference between 50 and 200% of the mean to be significant.

The temporal variability of the total elements in the LFH horizon is given in Table 7. This site was contaminated with approximately  $5000 \text{ mg} \cdot \text{kg}^{-1}$   $\text{S}^0$ ; however, with the exception of total S, the mean concentrations are similar to those for the region. The proportion of the total variability that can be accounted for by the differences among sampling times is only significant for Mn and Al. In fact, the ratio of the variance among times over the total variance is  $< 10\%$  for all the elements except Mn. Therefore, it appears that, for total nutrients in the LFH, temporal variability is not a major concern. Similarly, for the extractable nutrients (Table 8), temporal variability is only significant for two elements (9 and 12%, for P and Mg, respectively) other than S. Extractable S was a special case because the site was impinged by  $\text{S}^0$  and oxidation of  $\text{S}^0$  to  $\text{SO}_4^{2-}$  -S had occurred. This resulted in significant ( $p < 0.05$ ) temporal fluctuations of extractable S; however, the changes are directly attributable to the deposition of  $\text{S}^0$  and its subsequent oxidation. In contrast, to the temporal

Table 4. Regional variability of the 1.0 M  $\text{NH}_4\text{OAc}$  extractable nutrient content in the LFH horizon.

Parameter	Mean $\pm$ std dev (CV) ( $\text{mg}\cdot\text{kg}^{-1}$ )	Significance <sup>a</sup>	Variance Ratio <sup>b</sup>
Ca	4810 $\pm$ 2600 (54)	*	18
Mg	600 $\pm$ 240 (40)	**	38
K	980 $\pm$ 400 (41)	NS	7
Mn	310 $\pm$ 220 (71)	*	22
Al	150 $\pm$ 130 (87)	**	50
Fe	13 $\pm$ 16 (123)	NS	8
S	170 $\pm$ 66 (39)	NS	8

<sup>a</sup> \*, \*\*, NS = Significant at  $p < 0.01$  and  $0.001$  and not significant, respectively, for differences among sites.

<sup>b</sup> Ratio of the variance among sites over the total variance. This ratio measures the proportion of the total variability that is accounted for by the differences among the sites.

Table 5. Minimum differences for the total S of the LFH required to be significant between two sites.<sup>a</sup>

Level of Significance	90% Certainty			80% Certainty		
	0.01	0.05	0.10	0.01	0.05	0.10
Samples per Plot (n)	((----- mg·kg <sup>-1</sup> -----))					
2	1080	880	790	960	760	670
5	640	540	490	570	470	410
10	450	380	340	400	330	290
20	320	270	240	280	230	200

<sup>a</sup> In all cases, it is assumed that the number of plots is 22, according to the regional variability study. Mean S concentration in LFH from the regional variability study was  $1060 \pm 260 \text{ mg} \cdot \text{kg}^{-1}$ .

Table 6. Minimum differences for the total Mn of the LFH required to be significant between two sites.<sup>a</sup>

Level of Significance	90% Certainty			80% Certainty		
	0.01	0.05	0.10	0.01	0.05	0.10
Samples per Plot (n)	(----- mg·kg <sup>-1</sup> -----)					
2	4900	4020	3590	4350	3470	3040
5	2920	2450	2210	2590	2120	1870
10	2040	1710	1540	1800	1480	1310
20	1440	1210	1090	1280	1050	930

a In all cases, it is assumed that the number of plots is 22, according to the regional variability study. Mean Mn concentration in LFH from the regional variability study was  $1160 \pm 1180 \text{ mg} \cdot \text{kg}^{-1}$ .

Table 7. Temporal variability of the total elements in the LFH horizon.

Parameter	Mean $\pm$ std dev (CV) (mg·kg <sup>-1</sup> )	Significance <sup>a</sup>	Variance Ratio <sup>b</sup>
Mg	875 $\pm$ 310 (35)	NS	2
K	1930 $\pm$ 616 (32)	NS	6
Mn	1080 $\pm$ 680 (63)	*	13
Al	5630 $\pm$ 2750 (49)	**	9
Fe	2920 $\pm$ 1490 (51)	NS	6
P	1040 $\pm$ 205 (20)	NS	0
S	6940 $\pm$ 3420 (49)	NS	0

a \*, \*\*, NS = Significant at  $p < 0.05$  and  $0.01$  and not significant, respectively, for differences among sites.

b Ratio of the variance among sites over the total variance. This ratio measures the proportion of the total variability that is accounted for by the differences among the sites.

Table 8. Temporal variability of the 1.0 M  $\text{NH}_4\text{Cl}$  extractable nutrients in the LFH horizon.

Parameter	Mean $\pm$ std dev (CV) ( $\text{mg}\cdot\text{kg}^{-1}$ )			Significance <sup>a</sup>	Variance Ratio <sup>b</sup>
Mg	280	$\pm$ 113	(40)	*	12
K	1050	$\pm$ 436	(41)	NS	1
Mn	282	$\pm$ 186	(66)	NS	0
Al	71.5	$\pm$ 132	(182)	NS	0
Fe	6.7	$\pm$ 5.7	(85)	NS	0
P	111	$\pm$ 63	(57)	*	9
S	525	$\pm$ 369	(71)	**	17

a \*, \*\*, NS = Significant at  $p < 0.05$  and  $0.01$ , and not significant, respectively, for differences among sites.

b Ratio of the variance among sites over the total variance. This ratio measures the proportion of the total variability that is accounted for by the differences among the sites.



variability results of this study, Palmer et al. (1985) found that temporal variability was a very significant component of the overall variability of pH in several Alberta soils. The reasons for the differences in temporal variabilities between these studies are unknown, but it clearly demonstrates the need to evaluate the variability for each soil factor on the soils to be monitored.

The spatial variability of three sites: (1) an uncontaminated site; (2) a site with a moderate concentration of  $S^0$  in the LFH (approximately  $5000 \text{ mg} \cdot \text{kg}^{-1} S^0$ ); and (3) a heavily contaminated site (approximately  $48\,000 \text{ mg} \cdot \text{kg}^{-1} S^0$ ), was determined. The pH and electrical conductivity (EC) of the LFH horizon for the three sites are given in Table 9. Only the most heavily impinged site (Site 3) had significant decreases in pH and increases in EC in the LFH horizon compared to the unimpinged site (Site 1). The uncontaminated site and the moderately contaminated site also had similar total and extractable concentrations for Mn, Mg, K, and P (Tables 10 and 11). In general, these concentrations were similar to the regional concentrations. At Site 3 (heavily impinged site, adjacent to the sour gas plant), the total and extractable concentrations of Mg, K, P, and Mn were significantly reduced. This site was also an area of low pH (Table 9), indicating these cations and P were more readily solubilized and leached. In contrast, Fe and Al increased significantly at the most heavily impinged sites. This was probably a result of increased activity at these sites owing to their proximity to the sour gas plants. Increased activity would result in additions of mineral particulate to the LFH horizon that could increase the Fe and Al concentrations, owing to the high concentration of these elements in the mineral soils of this area.

The spatial variability of the elements measured at the heavily contaminated site was surprisingly similar to the variability observed at the other two sites, with the exception of S. As indicated earlier, the increased variability in S was related to the deposition of the particulate  $S^0$  through the canopy. Manganese was the most variable element but it also showed the largest response to  $S^0$  deposition, decreasing 20-fold to  $<50 \text{ mg} \cdot \text{kg}^{-1}$  in the LFH at the most heavily contaminated site.

The results of the deposition and soil data indicate that very high concentrations of  $S^0$  have been deposited into the forest within 500 m of the

Table 9. Spatial variability of pH and electrical conductivity ( $\text{mS}\cdot\text{cm}^{-1}$ ) of the LFH horizon at three sites.

Site ( $\text{mg}\cdot\text{kg}^{-1} \text{ S}^0$ )	pH			Conductivity		
	Mean $\pm$ std dev *		%CV	Mean $\pm$ std dev		%CV
1 (no $\text{S}^0$ )	4.3 $\pm$ 0.3	b	7	0.4 $\pm$ 0.1	a	25
2 (5 000)	4.5 $\pm$ 0.8	b	18	0.7 $\pm$ 0.2	a	28
3 (47 000)	2.5 $\pm$ 0.4	a	16	4.1 $\pm$ 1.4	b	34

One sampling in August 1984 ( $n = 50$ ).

\* Means in each column followed by the same letter do not differ significantly at  $p \leq 0.05$ .

Table 10. Spatial variability of the total nutrient concentrations ( $\text{mg}\cdot\text{kg}^{-1}$ ) of the LFH horizon at three sites.

Site	Mg	K	Mn	Al	Fe	P	S
1	838 $\pm$ 198a*	1840 $\pm$ 500b	750 $\pm$ 420b	3750 $\pm$ 1400a	2080 $\pm$ 1140a	1070 $\pm$ 173c	1 040 $\pm$ 140a
2	862 $\pm$ 294a	1780 $\pm$ 430b	1020 $\pm$ 760c	5450 $\pm$ 2480b	2790 $\pm$ 1320b	937 $\pm$ 185b	5 720 $\pm$ 1 920b
3	1040 $\pm$ 611a	1140 $\pm$ 400a	48 $\pm$ 24a	5270 $\pm$ 2290b	3340 $\pm$ 1310b	616 $\pm$ 146a	47 700 $\pm$ 14 100c

One sampling in August 1984 (n = 50).

\* Means in each column followed by the same letter do not differ significantly at  $p \leq 0.05$ .

Table 11. Spatial variability of the extractable concentrations ( $\text{mg}\cdot\text{kg}^{-1}$ ) of the LFH horizon at three sites.

Site	Mg	K	Mn	Al	Fe	P	S
1	565 $\pm$ 167c *	1460 $\pm$ 480c	572 $\pm$ 240b	80 $\pm$ 39a	9 $\pm$ 5a	138 $\pm$ 47c	97 $\pm$ 37a
2	248 $\pm$ 77b	945 $\pm$ 295b	564 $\pm$ 410b	82 $\pm$ 110a	12 $\pm$ 13a	54 $\pm$ 39b	390 $\pm$ 140b
3	327 $\pm$ 155a	184 $\pm$ 44a	30 $\pm$ 20a	108 $\pm$ 74a	143 $\pm$ 98b	26 $\pm$ 14a	3850 $\pm$ 2100c

One sampling in August 1984 (n = 50).

\* Means in each column, followed by the same letter do not differ significantly at  $p \leq 0.05$ .

two sour gas plants. Significant changes have occurred in several of the soil chemical properties measured at these sites. Total and extractable concentrations of Mg, K, Mn, and P in the LFH horizon have decreased, along with decreases in the pH and increases in the EC. Iron and aluminum concentrations tended to increase. However, changes in these soil properties at sites with low level deposition of  $\text{SO}_2$  or  $\text{S}^0$  are much more difficult to assess. At Site 2 (approximately  $5000 \text{ mg}\cdot\text{kg}^{-1} \text{ S}^0$  in the LFH horizon), moderate concentrations of  $\text{S}^0$  have been deposited for a minimum of 4 years. Significant differences in chemical properties, such as pH, Mn, and the basic cations, between Site 2 and Site 1 (unimpinged site) were not found. In a laboratory study,  $1000 \text{ mg}\cdot\text{kg}^{-1}$  of  $\text{S}^0$  was applied to LFH material and the soil incubated for 28 wk (unpublished results this laboratory). In 8 wk, the entire  $1000 \text{ mg}\cdot\text{kg}^{-1}$  of  $\text{S}^0$  had oxidized to sulphate; however, no changes in the pH or extractable cations were observed. This suggests that the LFH horizon in this area has the ability to buffer additions of acid.

Spatial variability was the largest component of the overall variability; however, there was a significant regional component. For example, the regional variance of S accounted for 19% of the total variance, and the difference required to be 90% confident at the 0.05 level of significance would be reduced from  $540 \text{ mg}\cdot\text{kg}^{-1}$  (when the spatial and regional components were included) to approximately  $480 \text{ mg}\cdot\text{kg}^{-1}$  (when the regional component is removed). In contrast, temporal variability for the elements measured in this study was generally not significant.

The variabilities of the various elements observed in this study are similar to the variabilities found in LFH horizons for other forest systems (Grier and McColl 1971; Quesnel and Lavkulich 1980; Arp and Krause 1984) and do provide a general assessment of soil variability. However, it is important that the variability of a given technique or measurement should be evaluated for the soils of an area prior to the establishment of any long-term soil monitoring sites.

#### 4. PLANTS

Although visual estimates of plant cover are among the most common measurements made in plant ecology, errors in measurement are rarely quantified. Error analysis is imperative in repetitive sampling for biomonitoring

because systematic error in the measuring technique must be quantified before changes in vegetation can be determined. Although sources of error have been outlined by Cain and de Oliveira Castro (1959), Greig-Smith (1964), and Kershaw (1973), only Sykes et al. (1983) have determined the magnitude of errors when different quadrat sizes and several observers are used.

In order to determine the precision of the cover estimates, 20 randomly distributed 1- x 1-m quadrats were permanently established in a 20- x 20-m site. A visual assessment of the percentage cover of every understory species in each quadrat was performed nine times between 09 and 19 August 1982 by the same observer. No variation in the vegetation was apparent during this 11-day period. To minimize observer bias, the order in which the quadrats were examined was varied, the work was interspersed with other tasks, observer access to the data was restricted, and the observer was discouraged from discussing the project.

Consistent measurements were obtained when the observer was thoroughly familiar with the vegetation and had described several similar stands prior to initiating this experiment. Despite the attempts to have the observer not remember specifics about the plots, there is an obvious familiarity period in the repetitive measurements made over the 9-day period. The precision improved as the observer's familiarity with the vegetation increased, as is reflected in Table 12. Measurements made 1 day apart towards the end of the 9 days were 94 to 96% similar (Table 12), whereas those taken 1 day apart at the beginning of the 9 days were only 89 to 92% similar. The increase in the observer's familiarity with the vegetation was a result of improved species identification and recollection of the characteristics of certain quadrats.

The main factors that influenced the precision of observations were plant morphology, distribution of individuals, and incorrect identification of species. These errors resulted in a total uncertainty in repetitive estimations of 10%. The greatest uncertainty in cover estimates was found in those species with small mean covers. Since errors have both relative and fixed components, those species whose uncertainties were dominated by fixed errors, caused by mis-identification or distribution, had very large percent errors at low covers. A similar increase in relative error at low cover

Table 12. Sorensen's similarity indices (%) for nine repetitive site samplings of a *Pinus contorta* stand in Alberta, Canada.

---

1									
91	2								
92	93	3							
91	92	96	4						
90	93	96	94	5					
90	92	93	93	96	6				
90	92	94	93	96	95	7			
89	92	93	92	96	96	96	8		
89	93	93	94	95	97	96	96	9	

---

values has been shown for lichens (Addison 1984). Rounding errors also tend to increase the relative error in measurement at low-cover values.

When all species were considered, the similarity between sampling times did not improve with the elimination of the highly variable species. These highly variable species were normally those with the lowest covers and, since Sorenson's index weights each species by its cover, the influence of these species was minimized.

Seasonal variation in plant cover is an inherent aspect of the plant community and, therefore, it was not unexpected that cover estimations taken in the spring and autumn of the year differed from those taken in the summer. What was not expected, however, was the relatively long period of time in which cover changed very little (June to August; Table 13). This appears to be a result of the evergreen nature of the species (mosses) that dominate the cover of the lower stratum and, hence, the similarity index.

The total uncertainty in the visual estimation of plant cover in the *Pinus contorta* stand (Table 14) resulted from both measurement errors and between-year variation. Seasonal variation was minimized by sampling only in August. The total uncertainty was about 20%; 10% due to errors in sequential measurements and 10% due to between-year variation. It appears, therefore, that even if changes in plant cover between sampling times were statistically significant, they would have to exceed 20% before interpretation was possible. This systematic error in the estimation of plant cover may be a limiting factor in the utilization of plant community measurements for biomonitoring purposes.

Uncertainty in the estimation of plant cover did not, however, account for the changes in the vegetation at sites severely contaminated by elemental sulphur in this case. Shrub and herb cover and diversity decreased 98% and 76%, respectively. Decreases occurred over a 5-year period and, initially, were greater for herbs than they were for shrubs. The decline in the herbs occurred 1 year before decreases in half the shrub species (unpublished data, this laboratory). Mosses were the most sensitive species and had declined to about 1% cover from an estimated 50% cover after only 2 years of significant elemental sulphur dusting (Kennedy et al. 1985).

It is apparent, based on this study, that before a technique is used in biomonitoring, a full analysis must be carried out to determine both



Table 13. Sorensen's similarity indices (%) for the May to September 1983 site samplings of a *Pinus contorta* stand in Alberta, Canada.

---

May				
77	June			
77	92	July		
74	88	91	August	
79	81	80	86	September

---

Table 14. Sorensen's similarity indices (%) for the annual (August 1981 through 1984) site samplings of a *Pinus contorta* stand in Alberta, Canada.

---

1981

80      1982

79      87      1983

75      89      84      1984

---

the precision of the technique itself and the feasibility of using the technique, given the natural variability in the system itself. In the case of plant communities, each community will be different, and our findings can only give some general guidelines for the level of uncertainty and the seasonal variation that must be addressed before community analysis can be used as a biomonitoring technique.

In this study, we used a lichen technique that had been tested for both its precision and its effectiveness to measure lichen response to air pollution in the Athabasca Oil Sands area (Addison 1984). Despite this earlier study that found arboreal lichens could be photographed and the cover determined for certain species groups, the technique did not appear effective in this area. It appears that a combination of the variability in lichen cover and inherent differences in the lichen habitat prevented the effective use of the technique, and no definitive statement on the effect of sour gas processing on lichen plant communities could be made. This shows clearly the importance of on-site testing of each biomonitoring technique used.

In 1981, a concerted attempt was made to determine whether the trees in the vicinity of sour gas processing had been affected by the operations. Ten trees (<10 cm DBH) were harvested at each site. Measurements were made of the height, diameter, and the length between terminal bud scale scars on the leader for the past 5 years. The top five branches (>5 years old) were collected, separated into age classes, and dried. Needle number and weight, and stem length and weight were recorded. In addition, basal disks were collected and the basal increment measured with a Digi-micrometer. A sample of 2- to 5-year cones was taken from the 10 trees. The number of seeds per cone and the viability of the seed were determined.

No pattern in either tree growth or reproduction that could be attributed to pollution was seen. The natural variability in the stands of trees was substantial and the coefficient of variation for basal area growth at all sites, for example, was about 55% (Table 15). Using the ratio of tree growth, after the gas plant started up, to tree growth, prior to start-up, reduced the coefficient of variation, but the range of values in the sulphur-dusted sites was about 30%.

Table 15. Characteristics of *Pinus contorta* at the biomonitoring sites. Values are means  $\pm$  95% confidence limits.

Site	Age (y)	Height (m)	Growth Rate			Ratio of Basal Area 1972 to 1981/1962 to 1971	Reproduction	
			Leader (cm·yr <sup>-1</sup> )	Lateral Branches (cm·yr <sup>-1</sup> )	Basal Area (1972 to 1981) (cm <sup>2</sup> ·yr <sup>-1</sup> )		Seed Production (seeds/cone)	Viability (% filled seed)
Sulphur-dusted								
1	49 ± 1	17.4 ± 1.2	27 ± 7	7.8 ± 0.7	85.8 ± 26.1	1.07 ± 0.26	22	86 ± 13
2	73 ± 4	20.3 ± 2.5	14 ± 5	5.3 ± 0.9	65.8 ± 37.7	0.97 ± 0.30	27	74 ± 15
5	75 ± 2	20.9 ± 1.2	14 ± 4	6.0 ± 0.6	64.8 ± 37.8	0.93 ± 0.31	29	86 ± 12
15	76 ± 2	20.3 ± 1.3	13 ± 3	5.3 ± 0.7	52.3 ± 22.8	1.29 ± 0.24	27	87 ± 12
Sulphur-gas exposed <sup>a</sup>								
3	104 ± 3	22.4 ± 1.4	6 ± 1	3.1 ± 0.2	43.6 ± 20.3	1.09 ± 0.37	37	87 ± 17
11	99 ± 3	24.5 ± 1.9	8 ± 2	4.2 ± 1.0	104.0 ± 44.4	1.06 ± 0.22	35	75 ± 15
12	95 ± 8	22.6 ± 1.3	5 ± 3	2.8 ± 0.4	40.2 ± 17.1	0.89 ± 0.30	15	83 ± 17
13	71 ± 5	21.6 ± 0.8	18 ± 5	6.8 ± 1.4	137.0 ± 56.6	0.93 ± 0.12	28	39 ± 31
14	78 ± 3	22.2 ± 1.4	11 ± 3	4.0 ± 0.6	66.0 ± 29.4	1.27 ± 0.35	39	75 ± 13
23	106 ± 2	17.8 ± 1.3	10 ± 2	4.3 ± 0.3	35.8 ± 16.1	0.94 ± 0.23	30	84 ± 10
All sites								
	89 ± 8	19.2 ± 1.2	11 ± 2	4.5 ± 0.6	60.6 ± 13.0	1.01 ± 0.08	29 ± 2	80 ± 5

<sup>a</sup>The sulphur gas designation refers to sites that have 7-year mean sulphation rates  $>0.05 \text{ mg} \cdot \text{dm}^{-2} \cdot \text{d}^{-1}$  ( $\text{SO}_3$ ).

5. SUMMARY

In order to adequately design a monitoring program, the objective of the study must first be defined. For example, it makes no sense, economically or otherwise, to design an elaborate soil-sampling program to provide an estimate of total S in the LFH horizon, with a high degree of precision, when the object of the program is to provide an estimate for liming. Conversely, compositing of samples may reduce the variability of the total S measurement (which is what is needed for determining the lime requirement) but prevents quantitative comparisons from one time to the next, or from one site to another.

Defining the objects of a monitoring study is only the first step in the preparation of a sampling program. A complete assessment has to be carried out to determine not only the variability of the technique, but also to determine if a given technique or measurement is feasible, given the variability. The use of the lichen technique described above is a good example. While the lichen response provided an excellent technique for use in the Fort McMurray area, the same technique provided no definitive information on the effect of sour gas processing on lichen plant communities in the Rocky Mountain House area.

When designing a long-term monitoring program to compare various parameters over time, the degree of confidence and level of significance required, plus an estimate of the resources available, must be considered. By partitioning the variability, as demonstrated above for several soil measurements, the optimum number of plots and number of replicates per plot to best estimate a given soil variable can be determined. It is important that the best possible estimate for the parameter(s) of greatest importance is determined, while sacrificing precision of the more variable but less important measurements. Again, this emphasizes the importance of testing techniques in an area prior to implementing a full-scale program.

The results of the 5-year study around the two sour gas processing plants of west-central Alberta demonstrated that  $S^0$  had adversely affected both the soils and vegetation in the areas immediately adjacent to the plants (<500 m). Current deposition rates of  $S^0$ , however, are considerably lower than the rates that must have occurred to produce the concentrations of  $S^0$  presently in the LFH horizon. From the direct measure of  $S^0$  in the LFH

horizon and by the use of lead candle data, areas of low-level  $S^0$  or  $SO_2$  deposition distant from the sour gas plants have been determined. Monitoring of the total S concentration in the LFH did not provide a very sensitive measure of  $S^0$  deposition in the area because of the natural soil variability. In addition, because of the buffering capacity in the LFH and the low rate of deposition outside the areas of heavy  $S^0$  impingement, no significant changes in pH could be detected. Other soil parameters measured and the various vegetation techniques used also showed no detectable effects outside the heavily contaminated areas. Therefore, outside of the area of heaviest  $S^0$  impingement ( $>5000 \text{ mg} \cdot \text{kg}^{-1}$ ), no detectable changes in the soils or vegetation measurements taken could be seen.

## 6. REFERENCES

- Addison, P.A. 1984. Quantification of branch dwelling lichens for the detection of air pollution impact. *Lichenologist* 16:297-304.
- Addison, P.A., K.A. Kennedy, and D.G. Maynard. 1984. Effects of sour gas processing on a forest ecosystem in west-central Alberta. Information Report NOR-X-265. Edmonton: Agriculture Canada, Canadian Forestry Service, Northern Forestry Centre.
- Arp, P.A. and H.H. Krause. 1984. The forest floor: lateral variability as revealed by systematic sampling. *Can. J. of Soil Sci.* 64:423-437.
- Bartlett, J.K. and D.A. Skoog. 1954. Colorimetric determination of elemental sulfur in hydrocarbons. *Anal. Chem.* 26:1008-1011.
- Cain, S.A. and G.M. de Oliveira Castro. 1959. Manual of vegetation analysis. Harper, New York.
- Freney, J.R. and C.H. Williams. 1983. The sulfur cycle in soil. Pages 129-201 in *The global biogeochemical sulfur cycle*, eds., M.V. Ivanov and J.R. Freney. SCOPE No. 19. John Wiley and Sons, New York.
- Greig-Smith, P. 1964. Quantitative plant ecology. Butterworth, London.
- Grier, C.C. and J.G. McColl. 1971. Forest floor characteristics within a small plot of Douglas-fir in western Washington. *Soil Science Society of America Proceedings* 35:988-991.
- Hammond, L.C., W.L. Pritchett, and V. Chew. 1958. Soil sampling in relation to soil heterogeneity. *Soil Science Society of America Proceedings* 22:548-552.

- Hart, M.G.R. 1961. A turbimetric method for determining elemental sulfur. *Analyst* 86:472-475.
- Hogan, G.D. and D.G. Maynard. 1984. Sulphur analysis of environmental materials by vacuum inductively coupled plasma atomic emission spectrometry (ICP-AES). Pages 676-683 in *Proceedings of Sulphur-84, International Conference*. June 1984; Calgary, AB. The Sulphur Development Institute of Canada, Calgary.
- Ike, A.F. and J.L. Clutter. 1968. The variability of forest soils of the Georgia Blue Ridge Mountains. *Soil Science Society of America Proceedings* 32:284-288.
- Kennedy, K.A., P.A. Addison, and D.G. Maynard. 1985. Effect of particulate elemental sulphur on moss. *Envir. Poll. (Series A)* 39:71-77.
- Kershaw, K.A. 1973. *Quantitative and dynamic plant ecology*. Clowes, London.
- Maynard, D.G. and P.A. Addison. 1985. Extraction and colorimetric determination of elemental sulfur in organic horizons of forest soils. *Can. J. of Soil Sci.* 65:811-813.
- Neter, J. and W. Wasserman. 1974. *Applied linear statistical models*. Richard D. Irwin Inc., Homewood, Illinois.
- Palmer, C.J., H. Regier, and R.L. Corbet. 1985. Monitoring for soil acidification. Muskoka Conference, 1985. Poster session.
- Quesnel, H.J. and L.M. Lavkulich. 1980. Nutrient variability of forest floors near Port Hardy, British Columbia, Canada. *Can. J. of Soil Sci.* 60:565-573.
- Roy, A.B. and P.A. Trudinger. 1970. *The biochemistry of inorganic compounds of sulphur*. Cambridge University Press, Cambridge, England.
- Sokal, R.R. and R.J. Rohlf. 1981. *Biometry. The principles and practice of statistics in biological research*. Freeman, San Francisco.
- Sykes, J.M., A.D. Horrill, and M.D. Mountford. 1983. Use of visual cover assessments as quantitative estimators of some British woodland taxa. *J. of Ecol.* 71:437-450.
- Webster, R. 1985. Quantitative spatial analysis of soil in the field. *Adv. in Soil Sci.* 3:1-70.

**SECOND  
SYMPOSIUM/  
WORKSHOP  
PROCEEDINGS**



**ACID FORMING EMISSIONS  
IN ALBERTA  
AND  
THEIR ECOLOGICAL EFFECTS**

at the  
**PALLISER HOTEL  
CALGARY, ALBERTA  
MAY 12-15, 1986**

Co-sponsored by Alberta Department of the Environment,  
Canadian Petroleum Association, Energy Resources Conservation Board,  
Kananaskis Centre for Environmental Research,  
The University of Calgary



**ACID FORMING EMISSIONS IN ALBERTA**

**AND THEIR ECOLOGICAL EFFECTS**

**Proceedings of the Second Symposium/Workshop**

**Held at**

**Calgary, Alberta  
1986 May 12-15**

**Edited by**

**H.S. Sandhu  
A.H. Legge  
J.I. Pringle  
S. Vance**

**Co-sponsored by**

**Alberta Environment  
Research Management Division**

**The Canadian Petroleum Association**

**Energy Resources Conservation Board**

**The University of Calgary  
Kananaskis Centre for Environmental Research**

Copies of the Proceedings may be obtained from:

Research Management Division  
Alberta Environment  
Publications Office  
14th floor, Standard Life Centre  
10405 Jasper Avenue  
Edmonton, Alberta  
T5J 3N4

(403) 427-3946

This report may be cited as:

Sandhu, H.S., A.H. Legge, J.I. Pringle, and S. Vance, eds. 1987. Acid form emissions in Alberta and their ecological effects: 2nd Symposium/ Workshop Proceedings. Prep. by Research Management Division, Alberta Department of the Environment and Kananaskis Centre for Environmental Research, University of Calgary. 1986 May 12-15; Calgary, Alberta. 478 pp.