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SULFUR DIOXIDE AND FOREST VEGETATION

bу

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NORTHERN FOREST RESEARCH CENTRE INFORMATION REPORT NOR -X-49 DECEMBER 1972

CANADIAN FORESTRY SERVICE ENVIRONMENT CANADA 5320 - 122 STREET EDMONTON, ALBERTA, CANADA T6H 3S5

TABLE OF CONTENTS

		Page
	ABSTRACT	1
1.	INTRODUCTION	3
2.	SULFUR REQUIREMENTS IN PLANTS	3
3.	THE INFLUENCE OF FACTORS OF THE ENVIRONMENT ON PLANT METABOLISM ON SULFUR DIOXIDE ASSIMILATION AND ON SULFUR DIOXIDE TOLERANCE LEVELS	4
4.	SYMPTOMATOLOGY OF SULFUR DIOXIDE INJURY	5
	(a) Gross visible effects	6
	(b) Microscopic effects	7
	(c) Physiological effects	8
5.	FOLIAR SULFUR CONTENT AS A DAMAGE INDEX PARAMETER	8
6.	SULFUR DIOXIDE AT THE STACK AND IN THE ENVIRONMENT	10
	(a) Controllable factors	10
	i) The efficiency and reliability of installed pollution abatement equipment	10
	ii) The rate of production	10
	iii) Numbers of gas plants per unit area	10
	iv) The rate of dispersion of stack effluent	11
	(b) Uncontrollable factors	12
	i) Emergencies	12
	ii) Weather conditions	12
7.	PROBLEMS ASSOCIATED WITH MONITORING OF ATMOSPHERIC SULFUR DIOXIDE	13
8.	THE GREEN PLANT AS A MONITORING DEVICE FOR ATMOSPHERIC SULFUR DIOXIDE	14
9.	AMBIENT AIR QUALITY STANDARDS AND THE FOREST	15
	REFERENCES	18

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ABSTRACT

Sulfur is an essential element in plant metabolism.

Sulfur is absorbed by the roots as sulfate ion, and enters the leaves as gaseous sulfur dioxide which dissolves in water to form sulfite ion. Conditions that favour good plant growth, increase the capacity of the plant to assimilate sulfur dioxide, but reduce the plant's tolerance to this gas.

Foliar symptom development resulting from sulfur dioxide fumigations are described. Since foliar sulfur levels fluctuate in healthy leaves, foliar sulfur content is not suitable as a damage index parameter.

Atmospheric sulfur dioxide levels can only be controlled at the stack. Rates of dispersion of known amounts of sulfur

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dioxide at the stack, are dependent upon uncontrollable factors of the environment. Similarly, tolerance levels of the vegetation surrounding gas plants, to sulfur dioxide fumigations, are dependent on uncontrollable factors of the environment.

Monitoring devices which show cumulative concentrations of atmospheric sulfur dioxide levels, which must be averaged to arrive at daily or hourly concentration, are of limited use. It is the maximum, not the average or cumulative concentration that must be monitored. Sulfur dioxide concentrations will fluctuate constantly at any given point in the three dimensional space occupied by forests. Hence data obtained from monitoring stations must be extrapolated with caution.

The green plant reflects the sum total effects of biotic and abiotic interacting factors of the environment. The green plant itself can therefore function as a monitoring device.

Current ground level concentration standards in Alberta allow for 1.0 ppm of atmospheric sulfur dioxide for periods not exceeding one hour, during periods of flaring. This high concentration will be lethal to all Alberta forest species.

1. INTRODUCTION

The purpose of this report is to bring to the attention of agencies concerned with atmospheric pollution control as well as gas industries, the effects of sulfur dioxide on forests. Particular emphasis is placed on the role of sulfur in green plants and also on the very close interdependence of plant metabolism, sulfur assimilation and sulfur dioxide tolerance levels. The fluctuations of foliar sulfur content in healthy vegetation are described in light of frequent use, by research workers, of foliar sulfur content as a damage index parameter. An attempt is made to clearly distinguish between controllable and uncontrollable factors that cause sulfur dioxide damage in forest vegetation.

2. SULFUR REQUIREMENTS IN PLANTS

Sulfur is an essential element in plant metabolism, and in many structural components of plants. Sulfur is usually absorbed by the roots as sulfate ion, but may also enter the leaves as gaseous sulfur dioxide, or dissolved in water as sulfurous acid (Syratt, W.J. et al 1968). Most sulfur atoms undergo valency changes from +6 to -2 prior to incorporation into organic form in a process called "assimilatory reduction". However, many active organic sulfur compounds are found in the +6 valency state, as sulfate. In the reduced state of -2, sulfur is an important constituent of all proteins, structural as well as metabolic, as part of the molecular structure of the amino acids cystein, cystine and methionine. For protein synthesis alone, sulfur is required in rather large amounts. Sulfur is found in the vitamins thiamin and biotin. It is also the major element in the backbone of ferredoxin, a sulfur-iron-protein complex which functions in the electron transfer system in photosynthetic reactions, and in nitrate and nitrate reduction (Mahler and Cordes 1966).

Green plants possess complex enzyme systems to reduce and assimilate both atmospheric sulfur dioxide and sulfate ion in aqueous solution. In healthy leaves sulfur contents should range from 500 - 14,000 ppm by dry weight (0.5 - 14 mg per gm of dry weight) depending on species (Treshow 1970). Concentrations below 250 ppm are considered critical, and give rise to deficiency symptoms, and to the substitution of selenium for sulfur in sulfur aminoacid and protein synthesis (Treshow 1970).

3. THE INFLUENCE OF FACTORS OF THE ENVIRONMENT ON PLANT METABOLISM, ON SULFUR DIOXIDE ASSIMILATION AND ON SULFUR DIOXIDE TOLERANCE LEVELS

Sulfur dioxide is readily assimilated by green plants, provided a threshold rate of gas application is not exceeded. This threshold rate is not a fixed value, but depends on fluctuating sulfur dioxide tolerance levels of plants. Any combination of at least twelve environmental factors induces fluctuations in sulfur dioxide tolerance levels. These same environmental factors induce fluctuations in rates of plant metabolism and sulfur assimilation (Linzon 1971). In general, there exists an inverse relationship between the rate of plant metabolism and sulfur dioxide tolerance levels, whereas fluctuations in rate of plant metabolism and sulfur assimilation are in phase in the presence of atmospheric sulfur dioxide. In other words, conditions that favour good plant growth, increase the capacity of the plant to assimilate sulfur dioxide, but reduce the plant's tolerance to this gas.

None of the environmental factors that influence sulfur dioxide tolerance levels can be controlled in unmanaged forests. Sulfur dioxide tolerance levels are low under the following conditions:

high light intensity both before and during fumigation.
 (Davies 1969, Rohmeder et al 1965)

- 2. high temperature (Daines 1969)
- 3. daylight (Daines 1969)
- 4. growing season (Daines 1969)
- 5. high relative humidity (Syratt et al 1968, Thomas et al 1956, Daines 1969).
- 6. water on leaves (Costonis 1971)
- 7. high soil moisture (Daines 1969)
- 8. old plants (Daines 1969)
- 9. low vigour due to insects or diseases
- 10. low nutrition levels (Faller et al 1970, Enderlein et al 1967)
- 11. susceptible species (Scheffer et al 1955, Dreisinger et al 1970)
- 12. genetic factors within species (Boertitz 1964, Boertitz et al 1969, Dochinger 1968)

Several workers developed mathematical formulae to calculate threshold rates in terms of gas concentrations and durations of exposure to symptom development. Their assumptions were that all the above environmental factors were constant.

4. SYMPTOMATOLOGY OF SULFUR DIOXIDE INJURY

Fumigation of trees with sulfur dioxide, generally induces typical changes which results in altered leaf function, colour and form. These may, over several days or weeks, result in changes in growth and development.

Together, these changes constitute a complex of symptoms, and their study is termed symptomatology.

A great variety of factors can affect the rate and extent of symptom expression and many factors may independently produce some of these symptoms, making positive diagnosis complex and dependent on wide knowledge. Furthermore,

under some conditions, changes may take place that in themselves are not damaging, but predispose the tree to damage from other causes occurring either simultaneously or subsequently.

(a) Gross visible effects

As sulfur dioxide enters the needles of conifers or the leaves of broad leaved trees, it dissolves in water and forms sulfurous acid. As described earlier, if the rate of entry is very low, the sulfur can be metabolized in a normal way and no symptoms develop. If sulfur in excess of the tree's requirements enters slowly, it eventually causes a slowly-developing (chronic)* injury, characterized visibly by a general chlorotic (yellow) appearance.

If, however, sulfur dioxide enters too rapidly, the tree's systems for coping with sulfur are overwhelmed and acute damage occurs. Affected leaves first appear water-soaked and straw coloured, the symptoms generally beginning at the tips of needles of conifers or the margin of broad leaved trees. In conifer needles, symptoms proceed towards the point of attachment, whereas in broad leaved trees, the intercostal leaf areas are affected shortly after the marginal areas. The affected areas soon dry out and gradually become reddish brown and brittle (necrotic or dead). Commonly, symptoms are more severe on the side of the tree facing towards the emission source.

Repeated fumigations may injure previously unaffected portions of partially damaged needles, resulting in a banded appearance of the necrotic portions. Severe fumigation will also affect the veinal areas of leaves of broad leaved trees. Trees are killed by severe fumigations when not only

^{*}chronic and acute relate to the morbidity status of the tree and not to disease stages.

the leaves but also next year's buds are killed.

The gradual appearance of chronic symptoms as a result of continuous, low-level exposure, may be parallelled by intermittent sub-acute fumigations of shorter duration. Both of these have the effect of shortening needle life and needle retention, although not as markedly as acute fumigations. Unaffected needles are normally retained for three to five years. In areas of continuing fumigation, retention is reduced to one to two years (Boertitz 1964, Boertitz 1969). This reduces tree growth and results in diminished terminal growth, shorter twigs and internodes, smaller needles, and in narrower growth rings; these can act as aids for diagnosis and measurement of injury.

Sub-acute fumigations, during the period of needle expansion, may similarly retard growth of that year's needles. The result is that twigs bear needles of variable lengths. This is called the "big-little needle" symptom, and is quite common in areas subjected to sulfur dioxide emissions.

In broad leaved trees, chronic injury results in chlorosis of leaf tissues in small flecks, mottled, or diffuse, and finally in a general yellowing of the entire leaf (Dochinger 1971).

(b) Microscopic effects

Damaged needles commonly show dead or necrotic brown zones, a transition zone of yellowish to reddish colour, and a zone of green, apparently unaffected tissue. Sulfur dioxide does not produce "hidden damage" in green plant tissue (Katz 1949). However, internal tissue changes that have diagnostic value are evident in the transition zones of affected needles. Changes occur in the undifferentiated parenchyma cells as a result of fumigation with sulfur dioxide (C.C. Gordon, personal communication).

(c) Physiological effects

Sulfur dioxide fumigations have temporary effects on the relative concentrations of intermediary metabolites including non-sulfur containing compounds. As was mentioned earlier, however, there is to date no evidence of hidden sulfur dioxide damage in green tissue. The development of visible symptoms such as the yellowing of foliage, is associated with the breakdown of chlorophyll molecules and accessory pigments such as carotene and xanthophylls. (Mamaev et al 1969).

5. FOLIAR SULFUR CONTENT AS A DAMAGE INDEX PARAMETER

Foliar sulfur levels fluctuate in healthy leaves. Katz (1949) stated: "Unless the concentration and exposure to gas and other (environmental) factors are known accurately, there is no quantitative relation between the increase in sulfur levels of plant tissue and the degree of injury, because the sulfur content is subject to great variation in normal plants". Many workers in the 60's and 70's confirmed Katz's conclusions, that foliar sulfur levels are not related to damage by sulfur dioxide. Some of these are Berry, G.R. et al 1964, Viel, M.G. et al 1965, Garber, K. 1960, Wentzel, K.F. 1968 and Bjorkman, E. 1970. Guderian 1970 (b) found that sulfur levels continue to fluctuate in the green photosynthesizing tissue of partially killed needles, whereas sulfur levels remain steady in the killed portions of such needles. Guderian further reported that foliar sulfur levels decrease after cessation of fumigations, and are therefore not only dependent on rates of sulfur assimilation during fumigations, but also on frequency and duration of sulfur dioxide free periods between fumigations. Hence the timing of sampling for sulfur level determinations after exposure to sulfur dioxide becomes an additional variable factor. There is another

complicating factor. Long periods of uninterrupted exposure to very low levels of sulfur dioxide cause greater increases in foliar sulfur levels than shorter periods of exposure to higher but still sublethal levels of sulfur dioxide (Guderian 1970 (a).

It is clear that foliar sulfur contents cannot be used as a measure of damage by sulfur dioxide. However, given a steady source of sulfur dioxide emissions, as found in sour gas plants, foliar sulfur levels will be indicative of the extent of sulfur dioxide dispersion. Katz (1949) noted: "Nevertheless, such data (foliar sulfur contents) from comprehensive collections of certain sensitive plants, may be used to define the area within which the gas occurs". Today, this is indeed the only "practical" use that can be made of knowledge of foliar sulfur contents obtained from field samples.

Results of a co-operative study of the Alberta Forest Service and the Provincial Air Pollution Control Division showed that pine and spruce foliar sulfur contents fluctuated upwards in the vicinity of sour gas plants for three to five years, after which they fluctuated down again to levels found at the time the gas plants went into production, whereas foliar sulfur contents of aspen and poplar continued to fluctuate upwards (Ullman 1967). From a biological point of view, the fluctuations in foliar sulfur levels in pine and spruce after three to five years exposure to sulfur dioxide may be ascirbed to any of the uncontrollable factors of the environment which were listed above and about which we have no information. From a practical point of view, sulfur dioxide emissions near the sour gas plants investigated by these agencies have up to now obviously been below the tolerance level for the main tree species.

6. SULFUR DIOXIDE AT THE STACK AND IN THE ENVIRONMENT

(a) Controllable factors

The amount of sulfur dioxide released into the environment depends on the following factors that can be controlled:

i) The efficiency and reliability of installed pollution abatement equipment

Control of pollution at the source by means of the "Best Practicable Technology" approach, is the strategy recommended by Federal Authorities (Lucas 1971). Operating limitations of sulfur recovery units in gas plants result in 0.5 - 1 per cent below theoretical recovery rate after initial start up, and will decline further to 1.5 per cent before the catalyst is replaced because of catalyst deactivation (Klemm, 1972).

ii) The rate of production

Once the sulfur recovery efficiency of an individual gas plant is known, the rate of production is the principal controllable factor determining rates of sulfur dioxide emission from the stack.

iii) Numbers of gas plants per unit area

Potential increases in numbers of gas plants depend on the discovery of new large fields. Amounts of sulfur dioxide releases into the environment can be controlled by limiting the numbers of gas plants with known production rates and sulfur recovery efficiencies, per unit area. (Tollefson 1972). Extensive sulfur dioxide damage to forest vegetation has been associated with the mining

industry of the Sudbury region of Ontario. Sudbury is an example of too many sulfur dioxide effluent sources per unit area. There are 18 mines and 9 reduction plants, managed since 1888 by the International Nickel Company of Canada and the Falconbridge Nickel Mines. It is estimated that about two million tons of sulfur dioxide are emitted annually in the Sudbury area alone (Leblanc, Fabius et al 1972, Linzon 1971 (a)).

iv) The rate of dispersion of stack effluent

The rate of dispersion of stack effluent cannot be controlled, but can be influenced by the proper selection of plant location and by effective stack height. Trail, British Columbia, is an example of the importance of topography on effluent dispersion. In Trail, Consolidated Mining and Smelting Company operates smelters that are situated in the Columbia Valley, which functions as an extended chimney. Stack effluents are not emitted randomly, but drift daily down the same areas. Reductions in growth rates were most pronounced in the vicinity of steady emission sources, but recovery to increased growth rates were noted in trees in the vicinity of reducing plants after the installation of pollution abatement equipment or plant closure (Katz 1939).

(b) Uncontrollable factors

i) Emergencies

Human error, mechanical failure or flaring during plant upset, may temporarily elevate sulfur dioxide concentration in the forest to above-threshold-levels. Since ground level concentration standards for flaring in Alberta (Anonymous 1970) are above the threshold level for jack pine, white spruce, trembling aspen, balsam poplar, white birch and larch, (Dreisinger et al 1970) (Table I), flaring during the growing season and in calm, humid and warm weather, may severely damage or kill well defined areas of forest vegetation. Possible synergistic effects of sulfur dioxide with other components of the effluent may be damaging.

ii) Weather conditions

Prolonged spells of severe cold may reduce sulfur recovery in gas plants by a significant amount of theoretical recovery rates and hence could constitute additional hazard.

Controlled rates of sulfur dioxide emissions at the stack are diluted in the atmosphere by the following uncontrollable and highly variable weather conditions.

- i) windspeed
- ii) wind direction
- iii) temperature inversions
- iv) relative humidity
- v) precipitation
- vi) mechanical and thermal air turbulence factors

Sulfur dioxide concentrations will therefore fluctuate from minimal, below-threshold-concentrations, to maximal, above-threshold-concentrations.

It is well established that plumes from stacks may retain their integrity for long distances during certain types of weather conditions. These plumes frequently impinge upon the ground surface at different distances from the stacks. Vegetation damage frequently results within these impingement areas which may encompass several square miles or more in area.

7. PROBLEMS ASSOCIATED WITH MONITORING OF ATMOSPHERIC SULFUR DIOXIDE

There are two basic problems in monitoring that must be understood:

- 1. In forests surrounding sulfur dioxide emission sources, sulfur dioxide concentrations will fluctuate constantly at any given point in the three dimensional space occupied by forests. In absolute terms, an atmospheric sulfur dioxide concentration is unique for a specific location, and for a specific, very short period of time. Hence data obtained from a monitoring station must be extrapolated with caution to locations outside the micro environment occupied by the monitoring device.
- 2. For the biologist, monitoring for atmospheric sulfur dioxide becomes meaningful when locations, concentrations and durations of lethal fumigations can be identified. Plants may be killed, either partly or completely when subjected to lethal concentrations of sulfur dioxide for short periods of time. Exposure cylinders will only provide information on cumulative amounts of

sulfur dioxide which can be averaged for numbers of hours or days of exposure, and are therefore of very limited use.

Monitoring devices of the continuous monitoring type are essential for meaningful surveillance. These systems entail considerable cost, and must be placed in strategic positions which take into account differences in effluent concentration with height above ground as well as the principal plume impingement areas.

8. THE GREEN PLANT AS A MONITORING DEVICE FOR ATMOSPHERIC SULFUR DIOXIDE

Sour gas plants release known and controlled amounts of sulfur dioxide from the stack. Rates of effluent dispersion and sulfur dioxide effects on vegetation are determined by the cumulative effects of large numbers of interacting variables, none of which can be controlled. However, the green plant itself reflects the sum total effects of biotic and abiotic interacting variable factors of the environment. The green plant itself can therefore function as a monitoring device, and can serve as an indicator of the state of health of forests surrounding gas plants.

Plant species show a wide range of sensitivity to atmospheric sulfur dioxide. Among the most sensitive species are mosses and lichens (Leblanc 1971, Leblanc 1969, Gilbert 1968).

Short-term studies of short-term sulfur dioxide effect may be conducted by transplanting lichens into polluted zones, and recording the time required for the lichens to die. Results of such studies have shown that survival times near steady emission sources are minimal, but increase with increasing distances from such sources (Kirschbaum et al 1971, Leblanc et al 1966, Schoenbeck 1968).

Short-term studies of long-term sulfur dioxide effects involve the evaluation of lichen luxuriance and numbers of species in preselected sites. Modifications of this approach include the construction of an Index of Atmospheric Purity (Leblanc, Fabius et al 1972), the construction of detailed distribution maps of selected lichen species (Skye, Erik 1968), and the construction of a qualitative sulfur dioxide air pollution scale (Hawksworth, D.L. and F. Rose 1970). The results of these and other (Smith, C.W. 1968, Barkman, J.J. 1968, Gilbert, O.L. 1968) studies consistently showed that numbers of species decrease with decreasing distance to the emission source. A few anomalies were noted, where species of lichens were found in pockets inside areas otherwise denuded of these species. Such areas were believed to be sheltered from sulfur dioxide gas due to topography and surrounding vegetation which acted as buffer zones (Gilbert, O.L. 1970).

Meaningful biological monitoring systems can be developed when the specific functions and values of forests surrounding emission sources have been determined. Criteria of injury relating to a variety of resource use allocations have been summarized (Knabe 1971, Guderian et al 1960).

9. AMBIENT AIR QUALITY STANDARDS AND THE FOREST

In Alberta, the maximum acceptable ground level concentration standards for sulfur dioxide in forested areas are as follows: (Anon 1970)

- (a) 0.30 ppm for 30 minutes
- (b) 1.0 ppm for less than one hour for a short period of emergency flaring

The ambient air quality standards for Alberta in forested areas are as follows:

- (a) 0.30 ppm for one hour
- (b) 0.10 ppm for 24 hours

Dreisinger <u>et al</u> (1970 published minimum average concentrations of sulfur dioxide in ppm at which injury occurred (Table I).

Table I

Minimum average concentrations (in ppm) at which injury occurred (Adapted from Dreisinger et al 1970). Ground Level Concentration Standards (G.L.C.S.) and Ambient Air Quality Standards (A.A.Q.S.) (Anonymous 1970).

Species	30 min	< 1 hr	1 hr	2 hrs	4 hrs	8 hrs	24 hrs
			ppm				
Trembling aspen			0.42	0.39	0.26	0.13	
Jack Pine			0.52	0.44	0.29	0.20	
White birch			0.46	0.38	0.28	0.21	
Larch			0.41	0.38	0.34	0.26	
Balsam poplar			0.82	0.65	0.45	0.26	
White spruce			0.87	0.79	0.70	0.50	
G.L.C.S.	0.30	1.0					
A.A.Q.S.			0.30				0.10
•							

A comparison of ground level concentration standards and threshold concentrations of sulfur dioxide for the species listed, all of which occur in Alberta, shows that 1.0 ppm for less than one hour, permitted during flaring, will injure Alberta forest species. All the other standards are below the threshold level of Alberta trees, but populations of the most sensitive plants, such as lichens and bryophytes will undoubtedly be killed. It has been

reported that the most sensitive species of lichens are unable to survive in areas where average annual sulfur dioxide levels are greater than 0.011 ppm, and no lichens survive in areas where annual concentrations of sulfur dioxide exceed 0.035 ppm (Gilbert 1968).

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1972. Sulfur dioxide and forest vegetation.

Information Report NOR-X-49; 22 p.; Northern Forest Research Centre, Environment Canada, Edmonton, Alberta.

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