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ATMOSPHERIC SULFUR DIOXIDE AND FOLIAR SULFUR CONTENT.

Northern Forest Research Centre Environment Canada Edmonton

ATMOSPHERIC SULFUR DIOXIDE AND FOLIAR SULFUR CONTENT by A. A. Loman*

1. Introduction

The purpose of this report is to bring to the attention of the agencies concerned with atmospheric pollution control as well as industries, suffic the role of sulfur in vegetation, foliar/content as a measure of damage by sulfur dioxide, and the practicality of exact determinations of admissable sulfur dioxide levels in the air, to prevent damage to forest trees.

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, cystime 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 nitrite reduction (Mahler and Cordes 1966).

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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 - 14000 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. Foliar sulfur contents as a measure of damage by sulfur dioxide

Many attempts have been made in this century to relate total sulfur levels in plant tissue, to damage caused by sulfur dioxide fumigations. In the forest, five variable factors must be considered which are interdependent: 1. fluctuations in rates of plant metabolism; 2. fluctuations in rates of sulfur assimilation; 3. fluctuations in sensitivities to sulfur dioxide; 4. fluctuations in sulfur contents in healthy plants; and 5. fluctuations in concentrations of atmospheric sulfur dioxide.

Sulfur dioxide is readily assimilated by green plants, provided a critical rate of gas application is not exceeded. This critical rate, or threshold rate, is not a fixed value, but depends on fluctuating sulfur dioxide sensitivities of plants. Any combination of at least <u>ten</u> environmental factors induces fluctuations in sulfur dioxide sensitivity (Daines 1969, Rohmeder et al 1965). These same environmental factors induce fluctuations in rates of plant metabolism and sulfur assimilation. In general, the fluctuations in rate of plant metabolism and sulfur dioxide sensitivity are in phase, whereas fluctuations in rate of sulfur assimilation depend, of

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course, also on the presence of atmospheric sulfur dioxide. The important thing to remember is that none of these environmental factors can be controlled in unmanaged forests:

1. light intensity, both before and during fumigation

2. temperature

3. time of day

4. season of year

5. relative humidity

6. presence or absence of water on leaves

7. soil moisture and texture

8. plant species

9. plant age

10. nutrition

11. genetic factors

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

Gas concentrations can be controlled at the factory stack. However, a steady flow of known sulfur dioxide emissions at the stack is dispersed by the following uncontrollable, and highly variable weather conditions:

1. windspeed

2. wind direction

3. presence or absence of temperature inversions

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4. presence or absence of precipitation

5. characteristics of surrounding topography.

Sulfur dioxide concentrations will therefore fluctuate from minimal to maximal at random locations, for random periods of time, in the forests surrounding the emission source. These uncontrollable, random, fluctuations in gas concentrations, locations, and durations of exposure are superimposed on uncontrollable fluctuations in sulfur dioxide sensitivities. It is therefore clear that although precise information of the threshold rate of sulfur dioxide applications to a given species can be obtained in the greenhouse or growth chamber, such information has no practical value in the field.

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 (June 1970) found that sulfur levels continue to fluctuate in the green photosynthesizing tissue of partially killed needles, whereas sulfur levels remained 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

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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 April-May 1970, Fujiwara 1968).

It is clear that foliar sulfur contents can not 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 cooperative 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 vininity of sour gas plants for 3 to 5 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 popular continued to fluctuate upwards (Ullman 1967). From a biological point of view, the fluctuations in foliar sulfur levels in pine and spruce after 3 to 5 years exposure to sulfur dioxide may be ascribed to

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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 lethal level for the main tree species.

4. The practicality of exact determinations of admissable sulfur dioxide levels in the air, to prevent damage to trees

From the previous two sections it is clear that steady atmospheric sulfur dioxide concentrations may be lethal during one combination, and quite harmless during a different combination of uncontrollable environmental factors. Secondly, a steady emission of known levels of sulfur dioxide at the stack will be dispersed in a random fashion, depending on uncontrollable weather conditions, resulting in random sulfur dioxide concentrations for random periods of exposure in random locations in the vicinity of the emission source.

are uncontrollable.

5. Alternatives and recommendations

The alternatives to using quantitative parameters are the use of qualitative, biological parameters. It is known that the sensitivity to

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sulfur dioxide differs between species. It is possible to select the most sensitive genera and species as indicators of sulfur dioxide damage. This qualitative type of measurement may take the form of a continuous record of the relative abundance of species in the vicinity of emission sources. Lichens are particularly suitable for this type of measurement. Another alternative is the continuous monitoring of symptom development on very susceptible species other than lichens. Such species can be selected experimentally.

A special combination of topography and climate may determine a prevailing wind direction. In such a case the locations of exposure areas to sulfur dioxide are less randomized, and are known as "impingement areas". It is important to identify possible "impingement areas" as soon after plant operations commence as possible.

To the plant engineer, the real usefulness of information obtained from graphs showing a general decline in the abundance of species of lichens is, that it signals the time to make value judgements such as: "Is it more important to continue production at the present level and risk the gradual disappearance of the surrounding vegetation, or do we continue to increase our pollution control efficiency at great cost, or do we reduce our production".

It is recommended that the plant engineer aim for as great a flexibility as possible in rates of emission of sulfur dioxide from the stack. Particular care must be taken to minimize stack emission during those periods in biological activity in which the vegetation is most susceptible. The following information has already be distributed, but will be given again:

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- 1. AVOID EXCESSIVE STACK EMISSIONS IN THE GROWING SEASON (MAY-OCTOBER) DURING THE FOLLOWING PERIODS:
 - i) Period of spring growth (May to mid-July)
 - ii) Daylight
 - iii) High Relative Humidity
 - iv) Rainfall or drizzle ...
 - v) Windspeed below 15 mph AT THE STACK

2. IN THE GROWING SEASON (MAY-OCTOBER) SENSITIVITY TO SULFUR DIOXIDE IS MINIMAL DURING THE FOLLOWING PERIODS:

- i) Darkness
- ii) Low Relative Humidity
- iii) Drought
- iv) Low temperatures
- v) Windspeed in excess of 15 mph AT THE STACK

3. RESISTANCE TO SULFUR DIOXIDE WILL BE MAXIMAL DURING THE DORMANT PERIOD IN WINTER (NOVEMBER-APRIL)

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