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Effects of Continuous H_2S Fumigation on Crop and Forest Plants

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■ Continuous fumigation of alfalfa (*Medicago sativa L*), Thompson seedless grapes (*Vitis vinifera*), lettuce (*Lactuca sativa*), sugar beets (*Beta vulgaris*), California buckeye (*Aesculus californica*), ponderosa pine (*Pinus ponderosa*), and Douglas fir (*Pseudotsuga menziesii*) with 3000 parts per billion (ppb) H_2S in greenhouses caused leaf lesions, defoliation, reduced growth, and death of sensitive species. Three hundred ppb caused lesser but similar effects. Sulfur accumulated in leaves depending upon dosage. Faster growing plants accumulated sulfur more rapidly. Lower levels of H_2S, 30 ppb and sometimes 100 ppb, caused significant stimulation in growth of lettuce, sugar beets, and alfalfa. The stimulation occurred at certain times of year and may be influenced by temperature and/or humidity.

Hydrogen sulfide is a malodorous gas emitted from many industrial and biological processes. It is highly toxic to man (*1*), but its effects on vegetation have received scant attention. Two high concentration short-term fumigation studies represent the major works done with this compound. McCallan et al. (*2*) fumigated 29 species of vegetation in greenhouses with 20–400 ppm H_2S for 5 h during the middle of the day. A wide difference in degree of injury was observed. No effect was seen on eight species at 400 ppm, while some plants were injured by less than 40 ppm. Young tissue was most sensitive. Increasing temperature caused a rapid increase in injury.

Benedict and Breen (*3*) fumigated 10 common weed species with a number of air pollutants including H_2S. They used 100–500 ppm for 4 h, and the fumigations were done on plants 3 and 6 weeks of age. They observed that the younger plants were more susceptible and that drier soil caused plants to show much more injury.

These short-term studies used H_2S concentrations at least one order of magnitude higher than other compounds such as SO_2, fluorides, and ozone which are normally encountered in polluted air; yet, the degrees of injury to vegetation were comparable. As a result, it has been assumed by investigators that the amounts which occur near industrial emitters or from natural sources cause minor impacts. Thus, oxidized sulfur, as SO_2, is much more toxic at high concentrations on a molar basis than H_2S, but at low levels it can overcome sulfur deficiency and serve as a fertilizer (*4–6*). No controlled studies have been done to find out what the effects of long-term, ambient levels of H_2S may be on vegetation. Because development of geothermal energy can cause emissions of considerable amounts of H_2S, the present study was designed to assess its effects on several crop and forest species which grow near sources of geothermal energy.

Procedure

Fumigations. Continuous, uniform fumigations were conducted in four greenhouses glazed with translucent corrugated fiberglass (Glassteel, Duarte, Calif.). All greenhouses were equipped with activated charcoal filters on air intake and exhaust to exclude ambient pollutants and avoid cross contamination. Temperatures were maintained within 3 °C of ambient during hot weather with evaporative coolers. During cool weather, inside and outside temperatures were the same. Hydrogen sulfide diluted with nitrogen was injected into the carbon-filtered, incoming air stream to provide the required concentrations of fumigant. H_2S was monitored with a Phillips Model 1900 H_2S analyzer.

Two fumigation procedures were employed. In the first series of experiments during 1975, alfalfa (*Medicago sativa L*), Thompson seedless grapes (*Vitis vinifera*), ponderosa pine (*Pinus ponderosa*), and California buckeye (*Aesculus californica*) were exposed to concentrations of 0, 30, 300, and 3000 parts per billion (ppb) of H_2S. Lower pollution levels (0, 30, 100, and 300 ppb) were used in the second fumigation series during 1976 which involved alfalfa, lettuce (*Lactuca sativa*), sugar beets (*Beta vulgaris*), Douglas fir (*Pseudotsuga menziesii*), and a second set of Thompson seedless grapes.

Materials. All species of plants were grown in 28-L pots except lettuce and Douglas fir which were grown in 20- and 7-L pots, respectively. A soil mix consisting of peat moss, redwood shavings, and silt (1–1–1) was used to which salts were added at the following rates, in kg/m^3 of mix: single super phosphate, 1.5; KNO_3, 0.15; K_2SO_4, 0.15; dolomitic limestone, 2.2; and oyster shell lime, 0.90. Copper, Zn, Mn, and Fe were added at 30, 30, 15, and 15 ppm, respectively. The plants were irrigated with one-half strength Hoagland's solution twice weekly. Tap water was used when additional irrigations were needed. Plant species, varieties used, and duration of treatments are summarized in Table I.

All data, where replicated, were analyzed statistically by an analysis of variance and a multiple-range test (*7*).

Results

Effects of Continuous H_2S Fumigation on Alfalfa. During 1975 when fumigation levels were 0, 30, 300, and 3000 ppb H_2S, green alfalfa showed white marginal leaf lesions on mature leaves within 5 days at the highest level of H_2S. To determine yield, the plants were cut at 28–35-day intervals depending upon growth rate and development. Growth was reduced during the first growing period at both 300 and 3000 ppb H_2S with Hayden (Table II). The highest level reduced growth of Eldorado, and a trend was shown at 300 ppb. No effect on growth was caused by 30 ppb. During the subsequent

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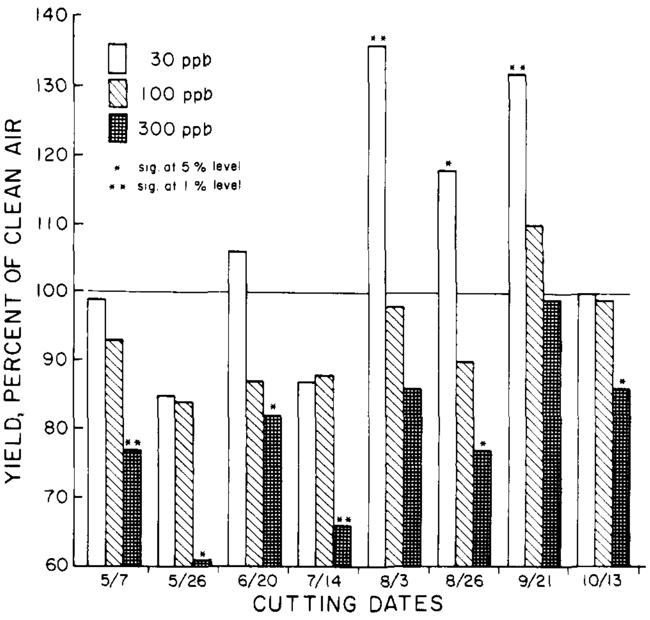

Figure 1. Effect of increasing levels of H_2S on fresh weight of alfalfa

growth period, most of the plants died at 3000 ppb, and growth was reduced in both varieties at 300 ppb. Composite single samples of dried tissue from these two cuttings were analyzed for total sulfur and showed graduated accumulation corresponding to the levels of H_2S in the different atmospheres. Third and fourth cuttings showed the same reduction in growth at 300 ppb H_2S but no statistical effect at 30 ppb.

During 1976, fumigation at 3000 ppb was discontinued, and a treatment at 100 ppb H_2S was added in an attempt to determine more precisely the amount of H_2S which caused reduced growth in this crop. Yield responses to concentration of fumigant are shown in Figure 1 where the yields at the various concentrations are expressed in percent of the yield of plants grown in charcoal filtered air. The results showed that 300 ppb H_2S caused significantly reduced yields in all cuttings except August 3 and September 21, while 100 ppb had no statistical effect on yield. The lowest level, 30 ppb, significantly increased yields in the late summer, August 3, August 26, and September 21, of 136, 118, and 132%, respectively, of the alfalfa grown in carbon-filtered air. Thus, continuous fumigation with H_2S at 3000 and 300 ppb caused foliar injury and reduced growth. At 100 ppb neither of these effects occurred, and with 30 ppb a significant growth stimulation during summer was observed.

Effects on Grapes. The immediate effect of the 3000 ppb level on grapes was similar to that seen on alfalfa in 1975. White to yellow lesions, which later turned brown, appeared on leaves. Defoliation began to occur after about 4 weeks at the highest level and within several more days almost all leaves were lost. However, the plants were not killed but continued growth of canes and put out small chlorotic leaves until the exposure was terminated. The 300 ppb level caused lesser but similar, readily observable injury. No foliar effects were seen at the 30 ppb level.

Cane length was reduced at the highest H_2S level as compared to the other treatments, but less dieback occurred at 30 and 300 ppb H_2S (Table III). Total dry weight of cane was reduced to one-half with 300 ppb as compared to the control or 30 ppb, but the total length was the same statistically, showing that the H_2S caused a thin spindly growth of canes. With 3000 ppb the cane length was about one-half the control, but weight was one-fourth, showing the same effect. Composite leaf samples were analyzed for total sulfur and showed

Table I. Species and Varieties of Plants and Treatments

Plant species	Variety	Season	# Plants/ treatment	# Harvests	# Days of fumigation
Alfalfa	Eldorado	1975	32	4	28–35
Alfalfa	Hayden	1975	32	4	28–35
Alfalfa	Hayden	1976	80	8	28–35
Grapes	Thompson seedless	1975	10	1	117
Grapes	Thompson seedless	1976	5	1	145
P. pine		1975	5	1	76
Ca. buckeye		1975	5	1	117
Sugar beet	Holly hyb.	1975	15	1	134
Sugar beet	Holly hyb.	1976	15	1	123
Lettuce	Dark green Boston	1976	27	1	59
Lettuce	Dark green Boston	1976	27	1	88
Lettuce	Dark green Boston	1976	27	1	96
D. fir		1976	10	1	246

Table II. Effects of Continuous H_2S Fumigation on Growth and Sulfur Accumulation in Alfalfa[a]

		Alfalfa variety			
		Eldorado		Hayden	
	H_2S, ppb	Av dry wt/ pot, g	Total S as SO_4, %	Av dry wt/ pot, g	Total S as SO_4, %
Cutting #1	0	52 y	1.03	52 x	0.92
13 Aug 1975	30	51 y	1.23	52 x	1.36
	300	42 y	2.45	32 y	2.44
	3000	16 z	4.85	11 z	5.20
Cutting #2	0	45 y	0.94	46 y	1.00
9 Sept 1975	30	46 y	1.10	43 y	1.29
	300	31 z	3.00	28 z	3.41

[a] Values followed by different letters are different at the 1% level.

Table III. Effects of Increasing Levels of H_2S on Cane Length, Dead Length, and Dry Weight of Thompson Seedless Grapes[a]

H_2S, ppb	Total length, cm	Dead length, cm	% Dead	Total dry wt, g	Total sulfur as SO_4 in leaves, %
0	1252.9 y	191.3 z	15.5 z	145.0 x	0.78
30	1160.0 y	212.4 z	18.7 z	143.1 x	1.26
300	1090.1 y	572.1 x	53.3 x	72.5 y	3.33
3000	673.5 z	422.2 y	63.1 y	38.0 z	4.50

[a] Values followed by different letters are different at the 1% level.

Table IV. Effects of Increasing Levels of H_2S on Leaf and Cane Weights of Grapes[a]

	Leaves		Canes	
H_2S, ppb	Fr wt, g	Dry wt, g	Fr wt, g	Dry wt, g
0	265.6 a	78.6 a	267.2 a	123.8 a
30	375.6 b	97.0 a	251.8 a	115.8 ab
100	298.4 b	80.6 a	219.6 a	86.0 bc
300	260.4 a	57.0 b	152.0 b	62.8 c

[a] Values followed by different letters are different at the 5% level.

accumulations in grape leaves similar to those in alfalfa.

Significant increase of fresh leaf weight was induced with 30 and 100 ppb H_2S over the controls with the same numerical trend in dry weight (Table IV) in 1976. Fresh weight of canes was reduced significantly by 300 ppb, and dry weight with both 300 and 100 ppb. Thus, H_2S caused severe foliar injury and defoliation at 3000 and 300 ppb but was not lethal as it was to alfalfa. The stimulation in fresh weight or leaves with the lower levels of H_2S was similar to the effect observed with fresh weight of alfalfa in summer.

Effects on Ponderosa Pine. Little effect of fumigation was observed for 4–6 weeks, but later at the 3000 ppb H_2S level a progressive tip burn was observed with defoliation after 10 weeks of exposure. With 300 ppb, tip burn occurred after 8 weeks. No visible effect was caused by 30 ppb. Needle analyses showed that the pines accumulated much less sulfur than the other species, 0.96, 1.23, 1.11, and 1.65% as sulfate in plants receiving 0, 30, 300, and 3000 ppb, respectively, probably because the rate of growth is so slow.

Needle counts showed that the average number of needles remaining in the first and second whorls were statistically equal in all treatments, but in the third whorl significantly greater drop occurred in treatments receiving 300 and 3000 ppb H_2S and the fourth whorl was lost completely.

Effects on California Buckeye. The buckeye proved quite resistant to the effects of H_2S. At the 3000 ppb level, a bronzing of the leaves occurred after 4 weeks exposure with less at 300 ppb and none at the lowest level. Some defoliation occurred at the highest level after 8 weeks exposure. Total sulfur analysis of leaves showed 1.02, 2.49, 4.40, and 5.54% sulfate on a dry weight basis in plants receiving 0, 30, 300, and 3000 ppb, respectively.

Effects on Sugar Beets. Beets were grown, harvested, and analyzed for fresh and dry weight of leaves, percent total sulfur, fresh weight of roots, and percent sugar. Results with individual beets (Table V) showed that 30 ppb H_2S stimulated fresh weight of leaves and roots 41 and 51%, respectively. A numerical trend occurred with 100 ppb, but 300 ppb inhibited these two responses significantly as compared to the stimulated growth and also reduced sugar content in roots. A nonsignificant numerical increase in dry weight of leaves was also seen at 30 and 100 ppb. The average total sulfur content as sulfate showed a regular but small accumulation in leaves and roots corresponding to treatment. Leaves had much more sulfur per unit weight than roots.

Table V. Yield of Leaves, Roots, and Sugar Content of Sugar Beets Exposed to Increasing Levels of H_2S[a]

Individual beets, leaves

H_2S, ppb	Fresh wt, g	Dry wt, g	% Sulfate
0	149.6 bc	19.8 bc	0.66
30	210.5 a	25.2 b	0.93
100	200.8 ab	23.3 b	1.33
300	127.6 c	15.2 c	1.88

Individual beets, roots

H_2S, ppb	Fresh wt, g	% Sugar	% Sulfate
0	291.3 bc	19.3 a	0.05
30	440.6 a	18.3 a	0.06
100	370.7 ab	18.2 a	0.08
300	219.6 c	15.8 b	0.12

Total, 3 beets/pot

H_2S, ppb	Leaves		Roots, fresh wt, g
	Fresh wt, g	Dry wt, g	
0	1242.0 c	126.2 c	643.4 bc
30	2037.6 a	194.0 a	881.0 ab
100	1874.8 ab	176.8 ab	1034.2 a
300	1640.8 abc	137.0 bc	502.2 c

[a] Values followed by different letters are different at the 5% level.

Table VI. Effects of Increasing Levels of H_2S on Fresh Weight, Diameter, and Sulfur Content of Dark Green Boston Head Lettuce[a]

H_2S, ppb	Fresh wt, g	Diam, cm	Sulfur as SO_4
0	104.4 x	26.9 x	0.78
30	167.7 y	29.9 y	0.82
100	97.3 x	25.5 x	1.30
300	34.7 z	19.9 z	1.77

[a] Values having different letters are different at the 1% level. Growth period 3/13/76–5/10/76.

Statistical analyses for the 1976 crop of sugar beets were done on the total of 3 beets per pot as opposed to evaluating single beets as in the first crop. These results (Table V) showed that leaf growth was stimulated significantly by both 30 and 100 ppb H_2S. Root weight was significantly greater in 100 ppb H_2S than in the control atmosphere but was statistically the same in the 30 and 300 ppb H_2S.

Beets grown in carbon-filtered air were attacked by powdery mildew and required immediate spray treatment for control. The H_2S fumigated beets showed little of the fungus indicating that the H_2S may have been acting as a fungal growth inhibitor.

Effects on Lettuce. Results with the first lettuce crop (Table VI) showed a large stimulation in growth with 30 ppb H_2S, but reduced growth at the highest level. Dried samples of the lettuce were analyzed for total sulfur and show that additional sulfur accumulated in leaves in direct relationship to the H_2S in the atmosphere. Limited organoleptic tests of flavor of lettuce from control and fumigated treatments showed no differences.

Because of the large increase in yield shown in the treatment with 30 ppb H_2S, a second crop of lettuce was grown to confirm the original observations. The crop was grown similarly, but the greenhouse temperatures were higher than before, August 12–November 8, 1976. The pronounced growth stimulation at 30 ppb observed previously was absent in this series. Reduced growth with 300 ppb H_2S, however, was observed as before.

The experiment was done a third time during a cooler period, October 20, 1976–January 4, 1977. This trial showed a statistically significant increase in fresh weight, dry weight, and head diameter with 30 and 100 ppb H_2S over the plants grown in carbon-filtered air. Reduction in fresh and dry weight occurred with 300 ppb H_2S. The magnitude of growth stimulation was less than in the original experiment. The reason for the above discrepancies in growth stimulation response is not clear. Differences in growing temperatures may be implicated.

Effects on Douglas Fir. Color of the Douglas fir foilage was not affected by 30 ppb H_2S. All needles remained bright green with no "tip burn". A slight burn was observed with 100 ppb H_2S, but 300 ppb caused very extensive foliar injury. This species showed overt injury to the pollutant more clearly than all other plants tested. Growth measurements showed that 300 ppb H_2S caused reduction in growth and dry weight but at 100 ppb these effects were insignificant.

Discussion

These results indicate that continuous fumigation of plants with 300 or 3000 ppb H_2S causes leaf lesions, defoliation, and reduced growth, the dosage and severity of injury being correlated. Sulfur derived from H_2S accumulates in plant tissues, the amount again depending upon the degree of exposure. Rapidly growing crop plants such as grapes, alfalfa, and lettuce were injured more than slower growing California buckeye and ponderosa pine and also had a more rapid accumulation of sulfur. Douglas fir was much more sensitive than ponderosa pine to foliar injury. Sugar beets seemed to be more resistant to H_2S than the other rapidly growing crop species studied.

Use of continuous, unvarying fumigation levels for exposing plant species may be unrealistic when compared to the exposures experienced by vegetation in the field, where the vagaries of wind, convection, etc., cause varying dilution effects. However, because H_2S is relatively low in "acute" toxicity (*3*, *4*), the total dosage, i.e., time × concentration, may be more important in determining effects than short-term, higher-than-average concentration.

The pronounced stimulation of growth with alfalfa, sugar beets, and lettuce at low dosages of H_2S, i.e., 30–100 ppb, seems to be a real effect at certain times of year. The magnitude of this stimulation may be affected by environmental factors such as day length, temperature, or humidity. This response may involve a fertilizing effect despite the inclusion of soluble sulfate in the fertilizer mix in an amount usually considered adequate for maximum plant growth. A similar growth stimulating effect was observed by Thomas et al. (*4*), Faller (*5*), and Cowling and Lockyer (*6*) with low levels of SO_2. However, the response here may have been greater because H_2S had less acute toxicity or a higher threshold at which acute injury occurred.

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Laboratory Study of Liquid-Phase Controlled Volatilization Rates in Presence of Wind Waves

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■ Liquid-phase mass transfer coefficients (k_L) are determined by a novel method in which hydrocarbons are volatilized from aqueous solution in a laboratory wind wave tank. Wind velocities range from zero to 11.6 m/s with and without gentle stirring of the water to simulate undersurface turbulence. The dependence of k_L on wind speed is best correlated by the wind friction velocity and surface roughness (obtained from the air logarithmic velocity profile) combined as a roughness Reynolds Number. The results suggest that correlation or prediction of k_L is best achieved by considering three wind velocity regions: below 3 m/s where k_L is about 3 cm/h and is strongly influenced by the water body turbulence, 3 to about 10 m/s where k_L is controlled by wind induced waves, and above about 10 m/s where whitecapping may occur. Implications for predicting environmental volatilization rates are discussed.

Environmental management is increasingly assisted by models of atmospheric and aquatic systems in which the physical and biological consequences of introducing pollutants can be assessed quantitatively and in advance. In these models mass transfer between the atmosphere and water bodies is often a significant process. For example, transfer of oxygen from the atmosphere to rivers and lakes influences dissolved oxygen content. Carbon dioxide transfer from the atmosphere to oceans and lakes is a dominant mechanism for the removal of this gas from the atmosphere and in certain lakes may control the rate of eutrophication. Sulfur dioxide transfer may lead to lake acidification. Hydrocarbons and chlorinated hydrocarbons may volatilize from water bodies at relatively high rates despite their low vapor pressures (*1–4*).

The traditional approach to calculating the flux of a compound between air and water phases is to use the two-film concept (*5*) in which it is assumed that the concentrations immediately on either side of the interface are in equilibrium as can be expressed by a Henry's law constant. The interfacial concentrations can then be eliminated from the calculations, and the flux N expressed in terms of an overall mass transfer coefficient k_{OL} and the difference between the liquid concentration C_L and the liquid concentration C^* in equilibrium with the atmospheric partial pressure P,

$$N = k_{OL}(C_L - C^*) \tag{1}$$

where

$$1/k_{OL} = 1/k_L + RT/Hk_G \tag{2}$$

where $C^* = P/H$ and k_L and k_G are the liquid- and vapor-phase mass transfer coefficients, respectively, and H is the Henry's law constant. Depending on the magnitude of k_L, k_G, and H, most of the resistance to mass transfer may lie in one phase. For most hydrocarbons and chlorinated hydrocarbons which are only sparingly water soluble and have high values of H, the resistance lies in the liquid phase.

Difficulties arise in applying this simple mass transfer