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Introduction

This paper is intended to present our literature search about the injuries to green plants by O_3 in the air. It also is a report to describe some field experimental work in the observation of O_3 and H_2O_2 droplets applied to green plants during the extremely dry and hot summer season of 1983.

Literature Search

Recently, much has been reported about the injuries to vegetation by ozone and other air pollutants (1). According to the reports by Middleton (2) and Richardson et al. (3), ozone probably has cased more injury to vegetation than any other air pollutant in the United States. There are considerable varietal and species differences in ozone sensitivity as observed by Brennen (4) and Davis (5). Generally speaking, the characteristic of specific injuries, as well as the extent of injury are greatly influenced by the type of plant, length of exposure, concentration of ozone, and other environmental conditions such as light, relative humidity, temperature, etc.

Ozone injury lesions include pigmented lesions, upper-surface and either surface bleaching, bifacial necrosis, or chlorosis. Severe injury results in tissue collapse and necrosis, and chronic injury appears as various amounts or degrees of chlorosis. Ozone injury may also result in retarding growth and reducing yield of many species of plants.

The most common acute symptoms of ozone injury is the small stipple or flecklike necrosis lesions visible on the leaf surface. These irregular shapes of a few millimeters diameter may be dark brown to black stipple and light tan to white fleck.

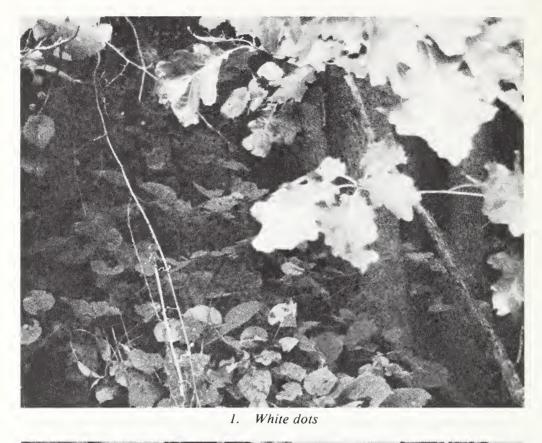
High light intensity during ozone exposure generally increases the sensitivity of the leaf tissues (6,7). Low light intensity during exposure to ozone can also cause extensive areas of the leaf to turn white or light yellow, apparently because the chlorophyll is bleached out but the tissue is not completely damaged.

Low concentrations of ozone for several hours of exposure may cause chlorosis of the oldest leaves of the plants. The chlorosis appears to be the same when leaves become senescent. Low level ozone exposure may also cause excessive development of red pigmentation, resulting in a red or purple color change of some leaves.

The location of injury with respect to the position on the leaf and the degree of maturity of leaves is frequently of significant diagnostic value. Injury is frequently limited to the upper leaf surface. When there is injury, it is usually intervenal since veins are relatively resistant to ozone and they may develop symptoms of injury only when it is severe (7). Leaves of 65-69% of their full size have been reported to be the most sensitive to ozone injuries, depending on the species.

Ozone concentrations of 0.13-0.17 ppm for 2,4,8 hours exposure time (8), 0.16-1.3 ppm for 4 hours (9), and 0.1-0.3 ppm for 4 hours (4) have been tested and reported in recent studies. All concentrations are in V/V. In fumigation experiments, 2-4 hours are usually required to cause injury to the most sensitive species (6).

Several paramaters can be used to measure ozone injury to leaves. For visible





2. Brown and white dots and sheen FIGURES: 1 & 2. Peroxide and 0_3 (?) injuries to oak (top) and grape (bottom) leaves in hot and dry weather. assessment of leaf injury, the number of injured leaves and the extent of leaf necrosis are used for making an estimate (10).

Field Experiments

Because little has been reported about the injury to green plants by hydrogen peroxide, we conducted field experiments by applying both O_3 water droplets and H_2O_2 water droplets to green plants separately for our own study of special interest (11,12). For O_3 study, we used ozonated water diluted to 0.3120 ppm water solution for spraying the droplets to various leaves by means of an air spray gun (30 liters per minute air to spray 1.0 liter O_3 water droplets per minute). For H_2O_2 water spray we used only a simple droplet spray devise using 0.5 ppm H_2O_2 water solution.

We began our field experiment in late July. The green plants were pin oak, soft cottonwood, and grape. During the period of study, there was no measurable rain fall and the temperature was 80 to 95 degrees F in day time and 70 to 77 degrees during the night. Some decolorization of all leaves sprayed was observed. White sheen and brown-yellow color changes were very visible (photos). Color changes were noted to have developed after 24 hours of a single spray (30 seconds exposure time to 0.3 ppm V/V O₃ in air). During the spray of O₃ water droplets, the person was totally covered with a clear plastic hood, and *no contact with any spray mist was permitted*. A breathing mask was also provided so that *no mist was inhaled*. The H₂O₂ concentration was 0.5 ppm prepared from standard 5.0% H₂O₂ solution.

Discussion

We used a simple aerosol spray device for producing the O_3 and H_2O_2 droplets on to leaves of oak, cottonwood, and grape in order to see if their possible injuries might look similar. We were also particularly interested in the environmental conditions such as temperature, sunlight, air moisture, wind velocity, and the time of contact or exposure. Unfortunately, throughout the entire length of experiment time, it was hot and bright-sunny during the day time. Practically, there was no precipitation during the entire period.

During the entire course of field experimentation and observation, we have noticed that the injuries by both 0_3 and H_2O_2 appeared to be very similar. Therefore, we wish to discuss here a little about the chemical reactions of O_3 and H_2O_2 transformations. According to the study the work performed by Rollefson and Burton (11), O_3 can be produced by O_2 and H_2O_2 through UV activation (1850 A range). In this reaction O_3 and H_2O_2 were produced. Interestingly enough, H_2O_2 was noted to be produced by green plants by the work of the senior author and many others (12,13,14). In other words, we have noted the following reactions:

$$\begin{aligned} H_2O_2 + O_2 &\stackrel{\cup V}{\rightharpoondown} H_2O + O_3, \\ O_3 + H_2O &\rightarrow H_2O_2 + O_2, \\ CO_2 + 4H_2O &\rightarrow C \bullet H_2O + 2H_2O_2 + 2H_2O, \\ 2H_2O_2 &\stackrel{-}{\rightharpoondown} 2H_2O + O_2. \end{aligned}$$

If all their findings are correct, it seems that there is a possibility that O_3 in the air might become H_2O_2 falling on to the leaf, and vice versa. Perhaps further experiments may enlighten us in the future.

Literature Cited

1. Purdue Exponent, October 19, 1983 (also Lafayette Journal and Courier), October 18, 1983.

- 2. Middleton, J. T. et al., 1950. Injury to Herbaceous Plants by Smog or Air Pollution. Plant Disease Repter., 34:245-252.
- Richardson, B. L. et al., 1968. Air Pollution with Relation to Agronomic Crops, V. Oxidant Stipple to Grape. J. Arg., 50:559-561.
- 4. Brennen, E. et al., 1969. Response of Forage Legumes to Ozone Fumigations. Phytopathology 59:1458-1459.
- 5. Davis, D. D. et al., 1981. Susceptibility of Tree and Shrub Species and Response of Black Cherry Foliage to Ozone. Plant Dis. 65 (11):904-907.
- 6. Jacobson, J. S. et al., 1970. Symposium on Recognition of Air Pollution Injury to Vegetation, APCA.
- 7. Norman, N. L., et al., 1969. Handbook of Effects Assessment, Vegetation Damage, Center for Air Environment Studies, Pennsylvania State University.
- Olszyk, D. M., et al., 1982. Evaluation of Injury to Expanded and Expanding leaves of Peas Exposed to Sulfur Dioxide and Ozone. J. Am. Soc. Hort. Sci. 107 (2):266-272.
- 9. Heggestad, H. E. et al., 1981. Differences among Coleus Cultivars to Tolerance to Ozone and Sulfur Dioxide. J. Hered 72(6):459-460.
- 10. Hans-Jurgen, S. et al., 1982. Effect of Repetitive Ozone Treatment on Bean Plant Stress Ethylene Production of Leaf Necrosis. Atm. Env. Vol. 16, No. 9:2267-2270.
- 11. Rollefson, G. K. et al., 1942. Photochemistry and the Mechanism of Chemical Reactions. Prentice Hall, N. Y.
- 12. Howe, R. H. L., "Ozone Pollution", Letter to the Editor, C and E News, Am. Chem. Society, Nov. 17, 1975.
- 13. Howe, R. H. L., "A 4-H Theory of the Photosynthesis of Green Plants", Presented at Indiana Academy of Science, Fall meeting, 1982, (and also in a report to the Great Lakes Region Meeting, American Chemical Society, 1973).
- 14. Payne, D. C. "SST an Ozone", Am. Chem. Society C and E News, August 16, 1971.