Possible new toxicant indicated in

SEVERE AIR POLLUTION EPISODE IN SOUTH COAST BASIN

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THE PHOTOCHEMICAL air pollution episode that occurred between November 8 and 11, 1973, in the south coast air basin of California, was unusual because the accompanying weather conditions and the resulting injury to vegetation did not fit into the pattern normally associated with attacks of ozone and peroxy acetyl nitrate (PAN). The injury to leafy vegetables was worse than usual, considering the concentration of phytotoxicants measured.

Severe injury was observed on vegetable crops in the coastal plain of Los Angeles and Orange counties, and less severe injury was observed in the inland valleys of San Bernardino and Riverside counties. Injury, particularly on leaf lettuce, also occurred in the agricultural areas on the plateau southeast of Riverside, near Moreno.

Staff members from Agricultural Commissioners' offices in the four counties sharing the south coast basin, and representatives from the Air Pollution Program of the State Department of Food and Agriculture surveyed the area to estimate the extent of the damage. Mature Boston leaf lettuce in Orange County was reported to be unmarketable after the pollutant attack. In Los Angeles and San Bernardino counties, injury was heavy, but with extensive trimming much of it could be marketed. Immature lettuce throughout the basin was severely injured, but prospects of full recovery were good if no further attacks occurred. Other crops severely injured were romaine lettuce, Swiss chard, endive, parsley, and beets.

In general, the symptoms were of the type attributed to PAN, but the overall syndrome differed sufficiently to make it apparent that the incident was unique. On Boston lettuce the injury was confined largely to 1- to 3-inch bands around the exposed leaf margins on leaves of all ages. The effect was primarily leaf collapse or "burn," which ultimately turned brown and covered the entire head. Normally PAN injury is confined to leaf tissue of a precise age or stage of growth and consequently develops on only a few leaves following a single exposure. But in this incident, large areas of leaves on Swiss chard and other plants collapsed, and injury symptoms developed which were not attributable to ozone or PAN. In most areas the injury was far more severe than that produced previously from comparable concentrations of total oxidant and PAN.

Oxidant concentrations

Concentrations of oxidants differed markedly from one region to another. On November 10, at the University of California's Riverside monitoring station, the highest total oxidant reading was 0.17 ppm, sufficient to cause light plant injury. At the South Coast Field Station in Orange County, the highest reading of 0.47 ppm was considered severe. During the same period, PAN maximum at U.C. Riverside was recorded at 16 ppb, sufficient for light plant injury, while at Garden Grove the highest reading was 30 ppb. PAN concentrations remained above 7 ppb for 40 continuous hours from 1:00 a.m. on November 9 to 5:00 p.m. on November 10. Photochemical oxidants rarely survive through the night, and such a long period of elevated levels has not been reported previously.

On November 9, 10 and 11, after the PAN peak, the automated electron capture chromatograph (PAN-alyzer) recorded another peak which coincided with the retention time for peroxypropionyl nitrate (PPN). This was strong evidence that toxic levels of PPN, a homologue of PAN, were present. The PAN-alyzer was not calibrated for accurate measurement of PPN, but comparison with an instrument at U.C. Riverside which has previously been calibrated for PPN indicated that a maximum concentration of about 8.5 ppb was reached and persisted for about three hours. On November 10, estimated concentrations exceeding 4 ppb were recorded continuously for 16 hours; and during the three days, concentrations of about 4 ppb were recorded for a total of 32 hours. Traces of PPN have been detected at U.C. Riverside, but measurable levels have not been recorded.

Phytotoxicity of synthesized PPN has been tested on several occasions by exposing seedlings of petunia, barley, tomato, bean and other plants to PPN under controlled conditions. In all instances PPN was from seven to ten times more toxic than PAN under comparable conditions.

The unusual response of plants to the recent smog attack has stimulated speculation about the possibility of an unidentified new phytotoxicant. This is a distinct possibility, but many other factors must also be considered in evaluating the episode. In Orange County, where the most severe injury occurred, the smog contained a mixture of PAN, PPN, and ozone. Elevated levels of toxicants persisted continuously for up to 40 hours.

Another possible explanation is that susceptibility of plant tissues may have been increased significantly by favorable weather conditions before and during the prolonged exposure. During two of the four days when severe plant injury occurred, records from Riverside and Orange counties showed a continuous overcast condition: maximum relative humidity ranged from 66% to 88%; minimum relative humidity was from about 50% to 60%. On November 11, the last day of the pollution attack, relative humidity dropped to 34% in Orange County and to 41% in Riverside. Maximum temperatures at both locations were between 70°F and 80°F, and minimum temperature ranged from the mid-40s to the mid-50s. These weather conditions are favorable for rapid growth of vegetables which suffered injury—and may have been responsible for the production of exceptionally susceptible leaf tissue.

As has been suggested, it is entirely possible that a new toxicant developed in the polluted atmosphere, perhaps in response to changes in primary pollutants being discharged. A more probable explanation of the sudden exceptionally severe symptoms may be that elevated levels of a mixture of ozone, PAN and PPN invaded the area during a period when the climate was particularly favorable for maximum plant susceptibility. It is also possible that additional compounds related to PAN and PPN may occasionally add to the toxicant complex. Controlled experiments with peroxybutyryl nitrate (PBN) have indicated it to be approximately twice as toxic as PPN. No analyses for additional compounds were made during this episode.

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Effects of spraying chemicals *on* YOUNG CITRUS TREES *for* FROST PROTECTION

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In attempts to increase the cold tolerance of young citrus trees, chemicals (including a growth retardant, three anti-transpirants and two plastics) were applied to grapefruit nursery trees that were then planted in the field. The results showed a slight but not commercially important increase in frost tolerance.

SINCE PROTECTING young trees against frost damage has always been a problem, the development of a chemical that would provide the necessary protection is desirable. Such a chemical should be easily applied, nontoxic, have no harmful residues, and have the ability to be effective for several months.

In 1955, it was reported that maleic hydrazide (MH) caused a depression in the cambial activity of grapefruit trees. Later experiments indicated that MH foliar sprays provided some frost protection by inhibiting new growth and inducing dormancy in young citrus trees, with the variability in response to MH sprays associated with relative humidity at time of application. Since the early 1960's, interest in MH for frost protection has decreased.

New chemicals tested included (1) Dimethyl Sulfoxide (DMSO), a solvent by-product of the paper industry which prevented freeze damage to living cells; (2) Decenylsuccinic acid (Decenyl), an unsaturated fatty acid which appears to protect peach, apple, and pear blossoms from freezing; (3) N^6 benzeladenine (N^6BA), a kinin which has protected antherium; and (4) a number of antitranspirants that gave ornamentals some cold protection.

Trials conducted in Florida during the winter of 1964–65 used MH, Decenyl, DMSO, N^6BA, and the antitranspirant Frost-X at various concentrations on both young Valencia and navel orange nursery trees and one-year-old Parson Brown orange trees in the field. There were slight differences in foliage damage due to freezing temperatures, but none of the treatments gave adequate protection.

Subsequently, in California during the winter of 1969–70, 14 compounds were sprayed on container-grown grapefruit nursery trees and one-year-old lemon trees in the field. Twelve of the compounds were antitranspirants and three were growth inhibitors. The three growth inhibitors were MH, the potassium salt of 6-hydroxy-3-(2H)-pyridacinone (KMH), and ethyl hydrogen 1-prophylphosphonate (NIA-10637).

Results of subjecting the grapefruit trees to temperatures as low as 20°F in a cold chamber showed no significant difference in cold protection. Temperatures in the field where the young lemon trial was located never reached freezing, but there were significant differences in growth response from the different sprays.

During the winter of 1971–72, seven treatments, with ten single tree replications, were sprayed on grapefruit nursery trees which were subsequently planted in

Photo 1. Polyurethane foam sprayed on young grapefruit tree (Treatment 4).

Photo 2. White polyester paint sprayed on young grapefruit tree (Treatment 5).