

ethanol fraction, which contained 16 percent gynaminic acid, showed no HAI activity. This is in agreement with findings by Odin (4), showing that no quantitative relationship was found between the presence of Bial-positive material and the HAI of various substances. Growth-promoting activity for *L. bifidus* var. *pennsylvanicus*, however, was found in both the 50 to 60 percent and 60 to 87 percent fractions where the Bial-positive material was present.

The HAI activity of these preparations was lost on incubation with active Lee virus, active PR8 virus, and *Vibrio cholerae* filtrate (RDE). HAI activity was not lost on heating in boiling water for 10 minutes. These properties are similar to those of the Francis inhibitor of human serum.

In conclusion, it may be stated that the presence of normal hemagglutinin-inhibitor in human milk has been demonstrated.

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Chlorosis Produced by Fluorine on Citrus in Florida

A chlorotic condition of citrus trees in the Bartow area of Polk County, Fla., was noted in April 1950. This chlorotic pattern was unique in that it differed from known chloroses resulting from nutritional deficiencies or toxicities. Although certain instances of typical iron, zinc, manganese, and other deficiency symptoms could be found in this area, the most prevalent pattern resembled the pattern on citrus that results from boron toxicity. However, there was no gumming on the undersides of the affected leaves, which is always associated with boron toxicity (1).

The appearance of this chlorosis seemed to be associated with a triple-superphosphate manufacturing plant that had recently been put into operation. Qualitative tests of citrus leaf ash from affected trees indicated the presence of fluorine. Shortly after this first observation of chlorosis, additional scrubbing facilities were installed at the triple-

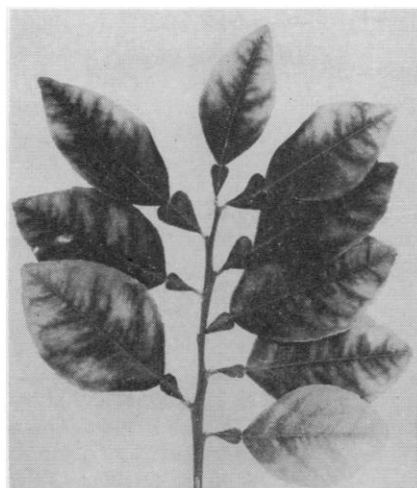


Fig. 1. Chlorosis of citrus leaves induced by fluorine.

superphosphate manufacturing plant, and the chlorotic pattern on citrus was alleviated.

However, in January 1954, several other instances of chlorosis were observed. This pattern, shown in Fig. 1, occurred in groves on several different types of soil, and under several different systems of management. As the number of new triple-superphosphate manufacturing plants in the vicinity has increased (there are seven at present), the extent of the area affected has also increased.

It is known that Florida pebble rock phosphate contains from 2 to 4 percent fluorine (2). In the production of triple-superphosphate, the rock is treated first with sulfuric acid, then with phosphoric acid, and in each treatment fluorine is released.

Analyses of citrus leaves in California (3) that had been obtained near an industrial plant indicated that up to 211 ppm of fluorine on a dry weight basis could be found in leaves from trees that were suspected of being damaged. However, no instances of chlorosis were reported. Chlorotic leaves from affected Florida groves ranged in fluorine content from 370 ppm to as low as 48 ppm. Chlorotic citrus leaves were observed up to 6 miles away from the nearest plant, but analyses of these leaves did not prove that the leaves were abnormally high in fluorine content. Thus, chlorosis was not in all cases associated with an unusually high fluorine content. It would appear that fluorine could cause leaf chlorosis, then be dissipated by translocation or otherwise lost, an observation similar to that made by others (4). Normal-appearing leaves away from the affected area contained from 12 to 30 ppm of fluorine.

Since the degree of chlorosis was not always related to the fluorine content of affected leaves, samples of an air plant,

Tillandsia usneoides, commonly called Spanish moss, growing in the affected area, were taken at varying distances from one of the triple-superphosphate manufacturing plants and analyzed. The results of these analyses (Table 1) indicated that fluorine was being released by the plant operation. The deviations from the general trend can be ascribed to the topography of the area sampled.

During the spring of 1955, sprays of aqueous HF, H_2SiF_6 , and H_3PO_4 were applied at a concentration of 0.1N to 4-year-old Ruby Red grapefruit trees located north of Lake Alfred, 20 miles away from the nearest triple-superphosphate plant. Approximately 1 lit of solution was applied per tree, per spray application. After the application of seven sprays during a 2-month period, a chlorotic leaf pattern appeared that was identical to the pattern observed in the affected area. This pattern occurred with both the HF and H_2SiF_6 sprays and was confined to the growth produced during the period of spraying. It appeared that the growth that was about three-fourths matured was the most susceptible to the fluorine injury. A similar observation was made in the area affected by the triple-superphosphate plants.

A small amount of leaf burn resulted from the H_3PO_4 spray, but no pattern appeared. Sulfuric acid sprays were not used because it had been previously noted that chlorotic leaf symptoms were present near one plant that produced defluorinated phosphate rock but did not operate a sulfuric acid plant.

It has been observed by others (5) that gaseous fluorine compounds are more toxic to many species of vegetation than are equivalent concentrations of sulfur dioxide and also that the greatest accumulation usually occurs at the tips or margins of leaves. This results in an inhibition of photosynthesis or degradation of chlorophyll. The reason chlorosis develops in Florida and not in California may be the result of differences in climatic conditions, primarily the higher

Table 1. Fluorine content of Spanish moss.

Distance from manufacturing plant (mi)	F (ppm)
0.20	9400*
1.5	688
2.5	688
3.5	888
4.0	132
5.0	110
6.0	60
7.0	100
20.0	100

* This sample was taken within 400 yards of the plant. It is likely that part of the fluorine present was in the form of rock and triple-superphosphate dust.

humidity under which leaves develop in Florida.

From the evidence obtained, it appears conclusive that the unique chlorotic leaf pattern on citrus that appears in association with triple-superphosphate manufacturing plants is the result of the fluorine evolved in the process of manufacture (6).

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Photochemical Reactions of Nitrogen Dioxide and Hydrocarbons in Air

The principal chemical characteristic of Los Angeles smog is the presence of relatively high oxidant concentrations. The nature and genesis of the oxidant have been the subject of intense study during the past several years. Haagen-Smit and coworkers (1, 2) have investigated the photochemical reactions of a series of synthetic mixtures of nitrogen dioxide and hydrocarbons in both oxygen and air carriers. Concentrations of the reactants were in the range of parts per million. On irradiation from polychromatic sources, such as the sun or blue fluorescent lamps, oxidant was pro-

duced that was manifested by its ability to crack stressed rubber and to oxidize alkaline phenolphthalin reagent.

A verification of Haagen-Smit's findings was carried out in the course of our study of the photochemical reactions of trace constituents in the atmosphere (3). The purpose of this communication is to report the nature of the verifications obtained.

A series of experiments was run by one of us (A. M.) at California Institute of Technology laboratory of Haagen-Smit (4). A number of 5-lit flasks containing heptene-2 at 3 ppm and nitrogen dioxide at 0.1, 0.4, 1.0, and 3.0 ppm in humidified air were irradiated for 10 hours with a bank of Westinghouse 40-w fluorescent lamps. The flasks contained suspended strips of stressed rubber as oxidant traps (5). The degree of rubber cracking rose from zero to high values as a function of NO₂ concentration.

To determine the reproducibility of the quenching effect reported (2) at elevated hydrocarbon concentration, several runs were made in the same system using NO₂ at 1 ppm and 3-methyl heptane at 1 and 700 ppm. After 10 hours of irradiation, cracking of rubber was confirmed at the 1-ppm hydrocarbon level, with no cracking found at the 700-ppm concentration level.

Investigation of the photochemistry of the NO₂-3-methyl heptane system continued in our laboratory. A 2-lit Vycor photolysis flask was wrapped in aluminum foil except for an opening to admit the collimated radiation from a Hanovia Type A mercury arc that was filtered with a Pyrex filter to cut out radiations at wavelengths below 3000 Å. The use of the reflective lining on the flask to form a multiple reflection system was necessary to achieve sufficient light intensity with this system. A relatively uniform radiation flux was thereby obtained. The radiation intensity, as determined with a photoelectric probe, was approximately the same as that of noon sunlight in the ultraviolet region but considerably less in the visible region.

At the conclusion of photolysis, the reaction mixture was passed through liquid-oxygen-cooled traps packed with glass beads and then through a train of three bubblers containing alkaline phenolphthalin reagent. Oxidant values were obtained by spectrophotometric measurement of the partially oxidized reagent mixture. Controlled experiments revealed that NO₂ was efficiently trapped in the freeze-out traps and did not contribute to oxidation of the reagent. Presumably, oxidants less volatile than NO₂ (peroxides, and so on) would also be trapped. The physical evidence therefore points strongly to ozone as the principal oxidant product of the photochemical reaction.

Typical results of irradiation of NO₂ and 3-methyl heptane in oxygen are given in Table 1. No ozone was obtained when either the NO₂ or the hydrocarbon was omitted. Recovery of NO₂ from the freeze-out traps was checked by analysis with the Saltzman reagent (6). A tendency toward high recovery by this method has not been completely resolved, but the results consistently show low recovery (or none) in photolyses in which an appreciable quantity of ozone was found.

These experiments support the finding of Haagen-Smit that traces of NO₂ and hydrocarbon in air undergo a photochemical reaction to produce ozone. Furthermore, NO₂ is consumed in the course of the reaction, indicating that NO₂ is more than a radiation absorber. Work is in progress to determine the stoichiometric relation between ozone formed and NO₂ consumed. A paper presented late last year by Hanst and coworkers (7) confirms the oxidant as ozone by infrared spectroscopy and also shows disappearance of NO₂ as the reaction proceeds.

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Temperature Control in the Measurement of Particle Volumes by the Isopiestic Method

Crozier has recently reported (1) some observations on the relative volumes of small droplets (diameter about 10⁻³ cm) of sodium chloride solutions equilibrated in atmospheres of varying water vapor pressure. Rather large discrepancies were noted between observed volumes and those calculated from ICT values for the vapor pressures of NaCl solutions at the temperature employed (25°C), which the author was unable to explain. The particle sizes were in the range where the Thompson-Gibbs effect is slight, and this effect was, in any case, allowed for. We have been performing

Table 1. Photolysis results with full mercury arc (Hanovia Type A).

Time (hr)	Concentrations (ppm)			
	3-methyl heptane	NO ₂ initial	Ozone	NO ₂ recovered
3	13.2	1.36	0.89	0.08
1	14.7	1.47	0.33	1.44
1	8.9	0.76	0.38	1.07
3	20.4	0.93	0.86	0.24
17	10.0	0.48	0.53	0.18
3	3.5	0.65	0.97	0.05
3	0.97	0.50	0.59	0.20
5	0.00	1.11	0.0	1.47
3	3.9	0.72	0.2*	0.51
3	2.3	0.72	0.44	
3	1.35	0.48	0.39	0.51
3	0.04	0.50	0.0	0.76
3	3.3	0.00	0.00	0.00

* Corning -7380 glass filter 2 mm thick cut out 3130 Å radiation but passed 60 percent of 3660 Å.