Fluorescence as a Means of Identifying Smog Markings on Plants

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Smog attacks are generally characterized by reduced visibility, eye irritation, and the marking of leaves of various plants. According to an article published in 1950 by Middleton *et al.* (*1*), it was recognized as early as 1944 that certain leaf markings observed in and around Los Angeles were the result of pollutants in the atmosphere. This article included the first description of the markings and stated that they were found throughout the Los Angeles Basin. More recently, Middleton *et al.* (*2*) indicated that the economic loss in leafy crops exceeded $500,000 yearly and that the area of damage was expanding. Similar markings have been found in the San Francisco Bay area (*2, 3*).

For about 2 yr, beginning in June 1951, a plant pathologist of the Stanford Research Institute staff continuously observed commercial vegetable fields and ornamental plants in the Los Angeles area and compared markings that appeared on them with those that developed on similar plants grown in greenhouses receiving cleansed and uncleansed air. It became apparent that, in addition to the commonly recognized smog markings, there were others that were commonly observed that could not be distinguished readily from markings caused by other factors: insects, poor cultural practices such as under- and overfertilization, flooding, and so forth. This ambiguity, as well as increases in economic loss and in the extent of the area affected, emphasized the desirability of an objective means of distinguishing between markings resulting from smog and those caused by other factors.

Following a smog attack in Menlo Park in 1953, it was discovered that the so-called "typical" smog markings that occurred on the leaves of *Chenopodium murale* and *Malva porviflora* fluoresced pale blue when irradiated with near ultraviolet light from a mercury vapor lamp. The unmarked portions of the leaves did not show this fluorescence.

In a review of the literature on fluorescence of vegetation (*4*), no mention was found of pale blue fluorescence of leaves under ultraviolet light. It seemed, therefore, that this property might provide, at least in part, an objective method of differentiation. To test this, leaves of a wide variety of plants, both unmarked and marked by several factors, were examined under ultraviolet radiation.

The source of the radiation was a spherical Bausch & Lomb microscope illuminator in which the socket was replaced by one that would take a GE BH4 100-w ultraviolet bulb, connected with the special transformer needed for its operation. The radiation was directed at the leaves from an angle, so that they could be observed under a microscope if desired. Five minutes in a dark room was allowed for the source to warm up and the eyes to become adjusted.

Smog-marked leaves of many weeds and leafy vegetables, gathered in Los Angeles, were wrapped in aluminum foil and shipped to Menlo Park, where they were examined the next day. These leaves, showing the visible smog markings, also showed the fluorescence. The marked areas appeared as sharply defined bright pale blue. Under visible light, their color showed little relationship to the fluorescent color; that is, silver, brown, and tan areas all fluoresced pale blue. As the leaves dried out for a day or so in air, the intensity of the fluorescence increased markedly. Leaves were therefore examined as soon as possible after collection and again a day or so later.

To determine whether unmarked leaves or leaves marked owing to nutrient deficiencies, insects, or insecticides also showed the fluorescence, a wide variety of economic, ornamental, and weedy plants were examined. None of these showed typical smog-induced fluorescence. Pubescence caused leaves to exhibit a dim background fluorescence quite different from that of smog-marked leaves. Specialized cells along the midrib of certain grasses also glow in ultraviolet radiation.

Fungus hyphae and insect deposits were found to fluoresce blue. It is therefore important to examine leaves microscopically with visible light.

As a further test, plants of spinach, romaine, endive, and sugar beets, and some weeds such as *Poa annua* and *C. murale,* were fumigated with mixtures of ozone and hexene, ozone and gasoline vapors, and ozone and auto-exhaust gases for sufficient time to produce leaf markings, using procedures similar to those of Haagen-Smit *et al.* (*5*). Previous work had shown that such fumigations would produce leaf markings similar to those produced by smog. The markings produced in these experiments fluoresced similarly to those produced by smog. However, the results were not very consistent, and further study is indicated.

To examine the effect of other possible air contaminants, markings were produced on vegetation by fumigation with HF, SO_2, H_2S, Cl_2, oxides of nitrogen, SO_3 and O_3. The methods used were generally taken from Thomas' review article (*6*). None of these markings fluoresced. However, care had to be taken not to confuse smog markings with pure white markings, produced at times with SO_2 and Cl_2, which readily reflect light and almost appear to fluoresce under ultraviolet. This is also true of the spotty, white, granular injury produced by SO_3.

As a final test of the fluorescence method, one of us collected about 40 samples of leaves in Los Angeles. These were classified as definitely marked by smog, questionably marked by smog, marked by some other factor, and unmarked. They were numbered, wrapped in aluminum foil, and sent to Menlo Park for examination. Without knowing what the markings had been ascribed to, another one of us examined the leaves under ultraviolet radiation. Of 11 samples classified in the field as definitely showing smog markings, all exhibited the fluorescence after drying for a day. These markings included silvering on spinach and nettleleaf goosefoot, bronzing on romaine, lower-surface injury on beets, and white markings on *P. annua*. Of nine samples classed as having light smog damage, six fluoresced after drying for a day. Those that did not fluoresce may not have been damaged enough to cause extensive cell collapse (an apparent requisite for fluorescence). Nine samples were classified as having questionable smog markings. Six of these showed some fluorescence. The remaining samples were either not marked or were marked by some factor other than smog. Most of them showed no fluorescence at all, and the others showed either mild background fluorescence or the types produced by mildew and insects.

The reason for the development of the fluorescence of these leaf markings is not known, but it may be related to the "browning reaction" (*7*). In this reaction, a bright blue fluorescence in ultraviolet light develops in foods before the formation of the characteristic dark brown color.

In summary, the leaf markings that result from smog, and are the cause of extensive economic loss, appear to fluoresce distinctively under ultraviolet radiation. This observation has been checked by comparing the response to ultraviolet radiation of sensitive plants exposed to actual smog, to synthetic atmospheres, and to a variety of cultural conditions.

If further work confirms the results of these studies, the bright pale blue fluorescence of smog-marked leaves will provide the first objective means of assessing the responsibility of smog for vegetation damage.

References and Notes

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Desert Varnish

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Desert varnish is a blackish or brownish stain of iron and manganese oxides on rock surfaces. As the name implies, desert varnish is best developed, or at least most conspicuous, in arid or semiarid regions; but similar staining also occurs in humid regions—in northeastern United States, in tropical rain forests, at high altitudes in the Alps (*1*), and on tunnel walls in the southeastern United States. Glacial and periglacial boulders at alpine levels in the Rocky Mountains commonly are stained.

The stain occurs on nearly all kinds of rocks—glassy, volcanic, and granular plutonic rocks ranging in composition from granitic to basaltic, sandstone, dense chert, and, more rarely, bull quartz. It is less common on limestone than on the less calcareous rocks.

The varnish may coat isolated bodies or the exposed and now dry surfaces of pebbles or cobbles forming a desert pavement. It may coat vertical or overhanging cliffs, or rock surfaces that are splashed by rivers or wetted by springs or seeps. It may develop on surfaces that are dark or poorly lighted, such as tunnel walls or joint planes. The coatings on joint surfaces or other slightly opened planes of parting in the rocks grade into vein deposits.

Although the stain appears to be composed largely of iron and manganese oxides, the proportions of these must vary greatly from place to place. Certainly the color and luster vary, although they are controlled in part by the fineness of the grain of the rock that is coated and in part by wind polish.

Such widespread deposits in such heterogeneous environments assuredly have heterogeneous origins. At some places, the stain appears to have been transported a considerable distance to the surface that is coated; at other places the coating seems to have been derived from weathering of minerals in the rock beneath it. Some stain assuredly was deposited by physical-chemical processes, but other staining appears to have been deposited biochemically. Either process, however, requires active moisture. In southwestern United States, the desert varnish seems to be in large part the product of past pluvial climates.

The conspicuous deposits of desert varnish on the Colorado Plateaus today are being eroded. On the cliffs, the varnish is preserved on smooth flat cliff faces or beneath overhanging ledges, but it has been largely removed from the rounded edges of joint blocks and from the more exposed upward-facing parts of the sandstone cliffs or buttes. Recent rock falls from the cliffs leave bright scars on surfaces otherwise darkened with varnish. Varnish still coats protected parts of isolated boulders, but it has been removed from their weathered rounded edges. Moreover, the conspicuous and extensive deposits are associated with a topographic unconformity that reflects a past climatic change. It seems clear that the conspicuous deposits of varnish in the Colorado Plateaus have a respectable antiquity and are the product of a past epoch.

The deposits of varnish that are forming today are restricted to places that are wetted frequently. Boulders lying between the high- and low-water stages of the Colorado River, for example, are stained; so are the sandstone cliffs where they are moistened by seeps. Such deposits suggest that the moisture requirements for deposition of desert varnish are considerable.

Archeological evidence indicates that the principal deposits of varnish on the Colorado Plateaus were formed prior to introduction of pottery. The masonry dwellings of the pottery-making Anasazai and related