THE EFFECTS OF FLUORIDE POLLUTANTS

ON AGRICULTURE IN WEST CENTRAL FLORIDA

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For the past few decades, environmentalists have concentrated their air pollution studies on the formation and dispersal of sulfur dioxide, nitrous oxides and ozone. Since the mid 1950's, environmentalists have become increasingly aware of the present and potential dangers of air-borne fluorides in west central Florida, due to the mining and processing of phosphate. The damage to various agricultural pursuits was first observed in cattle in the form of fluorosis which resulted from the foraging on pasture grasses. Damage to citrus and certain flowering plants was also found. Since 1960, many studies have been published which indicated specific effects of fluorides upon the plants and animals of the area. In addition, these studies established that this regions was one of the prime areas of fluoride pollution in the United States.

Nature of the Problem

The primary source of air-borne fluoride in this region is from the intensive mining and processing of phosphates (Fig. 1). Since the discovery of phosphate bearing rocks in central Florida in 1881 near Fort Meade, the industry expanded to become a major world supplier of phosphate by the mid-twentieth century. Secondary sources of fluorides in the region are attributed to aluminum, cement and coal-combustion industries.

Although phosphate mines and plants are scattered throughout west central Florida, the largest concentration of chemical plants (approximately twelve) are located in southwestern Polk and southern Hillsborough counties (Fig. 2). Except under abnormal weather conditions, the area of possible fluoride pollution is limited to approximately five miles diameter around each installation (Fig. 3).

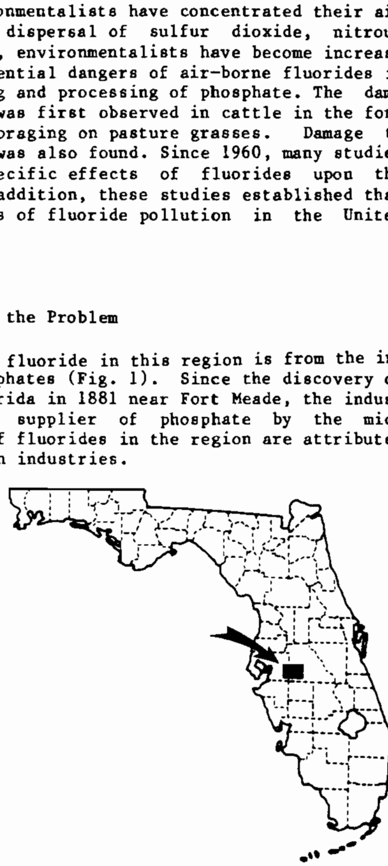

Fig. 1. Location of Florida Phosphate Industry

The principal phosphate concentration mined in this region for the production of fertilizer is fluor-apatite ($CA_5(PO_4)_3F$) which can contain up to 4 percent fluoride (Urone, 1983, p. 1). Fluor-apatite occurs in subsoils high in silicon content. This ore was originally deposited by sea water in beds near the surface. It is mined today by the strip mining process which incorporates the use of giant earth moving machines.

During the production of fertilizer, fluor-apatite is combined

FLORIDA PHOSPHATE MINE SITES

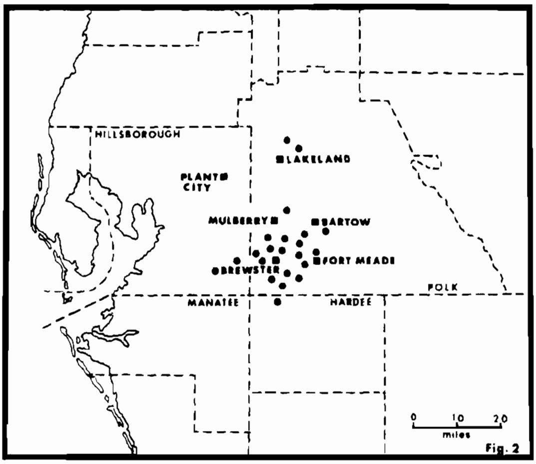

Fig. 2

FLORIDA PHOSPHATE PLANT SITES

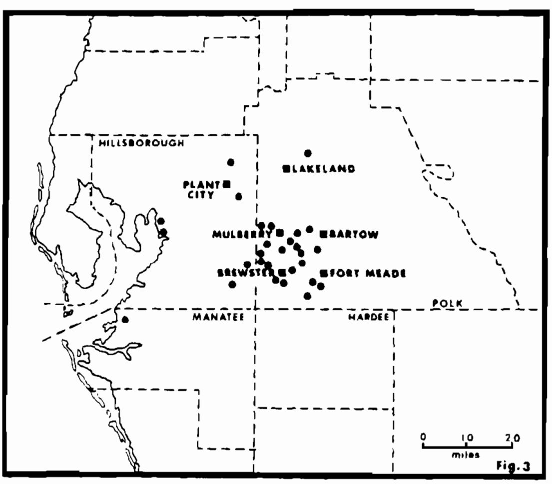

Fig. 3

with sulfuric acid which results in the formation of phosphoric acid, hydrofluoric acid (HF) and gypsum. The HF then reacts with the silicon in the ore to produce tetrafluoride gas (SiF_4) (Urone, 1983, p. 1). This gas in turn is removed from the stack emissions by scrubbers, which are anti-pollution devices commonly attached to or located adjacent to smokestacks. Originally, the resultant aqueous solution was then released into waste ponds, where it decomposed into HF, subsequently escaping into the atmosphere. The incorporation of a new generation of scrubbers now removes a large percentage of the fluorides and converts it into a marketable by-product, thus reducing the amount released into the ponds.

There are three fertilizer products produced, given the abbreviations of MAP, DAP, and GTSP (Fig. 4). The basic difference between MAP and DAP processes is the relationship of the amount of ammonia (NH_3) added in the reactor process. The GTSP process involves recycling the phosphoric acid with ore to provide a more concentrated result.

Table 1

Fertilizer Production, January 1984

Fertilizer	Production (Short Tons)
DAP	946,034
GTSP	192,922
MAP	100,000*

*Figure approximate

Source: Chemical Marketing Reporter, 1984, p. 4

For many years GTSP was the leading fertilizer produced. The processing of GTSP produced large quantities of HF. However, approximately ten years ago, the production of GTSP was significantly reduced in favor of DAP, which produces significantly less HF. This is shown clearly in the production figures of January 1984 (Table 1). This shift to an emphasis upon the primary

THE PRINCIPAL PHOSPHATE PRODUCTS

MONO AMMONIUM PHOSPHATE (MAP)

$(NH_4)H_2PO_4$

DI AMMONIUM PHOSPHATE (DAP)

$(NH_4)_2HPO_4$

GRANULAR TRIPLE SUPERPHOSPHATE (GTSP)

$Ca(H_2PO_4)_2$

Fig. 4

production of DAP has reduced significantly the presence of both gaseous and particulate HF emissions over the area. Also, new manufacturing techniques, such as enclosing the reactor and adding more efficient stack scrubbers, have reduced HF from escaping during processing.

Attempts at Solutions

Establishing of Standards

It is important to recognize that fluoride pollution is not basically a national problem. Relatively few areas of the country are affected. Thus, any action to establish standards is consummated on a state and/or local level.

This problem was addressed by the Florida Department of Environmental Regulation (FDER) in conjunction with local county pollution commissions in 1961. Although a dry weight pasture grass standard of 45 ppm fluoride was adopted, it was later eliminated in 1972 because of dramatic reduction in fluoride emissions and improvements in production processes made by the phosphate industry (Sanderson, 1983, p. 1). During this period the fluoride level in the grass actually averaged below the recommended 45 ppm (Fig. 5).

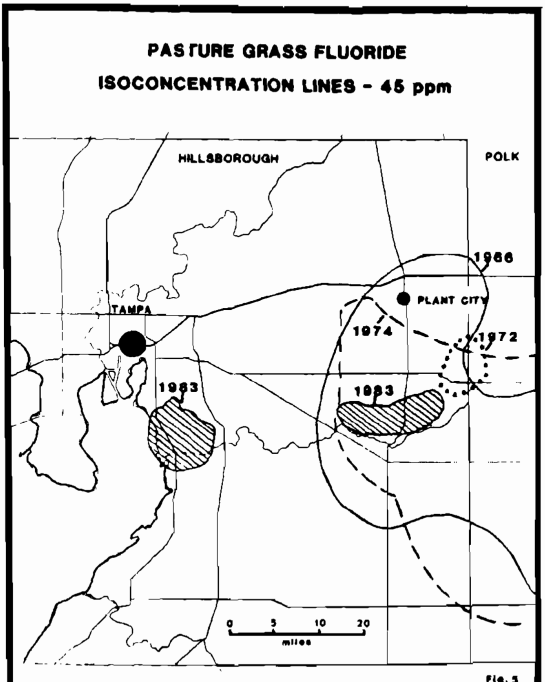

Fig. 5

By 1976, the ambient fluoride levels elevated significantly as phosphate production increased. Consequently, the FDER proposed a fluoride rule for pasture grass and ambient air (Sanderson, 1983, p. 1): (1) for ambient air, 0.9 ppb for twelve months, 1.8 ppb for 30 days, and 5.6 ppb for 24 hours; and (2) for pasture grass, 45 ppm for a twelve month average. Unfortunately, however, due to the lack of supportive research, and because of intense lobbying by the Florida Phosphate Council, no rule was adopted for fluoride standards by Florida. Notwithstanding, local EPC commissions generally did follow the proposed standards. It is interesting to note that today, of the two counties most affected, only Hillsborough County has its own EPC. In Polk County the monitoring is done by the FDER. There are at present ten fluoride monitoring sites in Hillsborough County and three in Polk County.

Monitoring Systems

In 1981, the Hillsborough County EPC received a $33,800 grant from the United States Environmental Protection Agency (EPA) (Sanderson, 1983, p. 3). This grant was used to purchase monitoring and laboratory equipment to pursue the study. The equipment was operating by the spring of 1982.

Two methods are employed to measure gaseous ambient fluorides: (1) fluoride static plate, and (2) continuous ambient fluoride analyzer. Both methods are currently in use by the Hillsborough County EPC and FDER in this region.

The fluoride plate method of passive static sampling that is in use was developed by the Alcoa Aluminum Company. These plates consist of a pad made from cellulose which is filled with a fluoride absorber which is placed inside a disposable plastic petri dish (Sanderson, 1983, p. 6). This unit is placed on an eight foot pole over the grass or in a grove. The plates are inexpensive and easy to locate, and the results are easy to evaluate chemically.

The most widely used gaseous fluoride analyzer is the Model 745 produced by Tess-Com, Inc. While this analyzer is EPA approved, its use has revealed several recurrent problems inherent in wet systems. After being scrubbed in de-ionized water mist, the metered sample is delivered to a mixing chamber where a constant amount of buffering reagent is added to fix the pH of the sample and to eliminate hydroxide ion interference. The sample is then introduced into a cooled temperature block (18^{0} C) and passed on a surface of a fluoride measuring electrode creating a potential difference (Sanderson, 1983, p. 7). This difference between sample and electrode is fed by voltage to an electronic package for amplification to a chart recording system.

Use of this analyzer has revealed a high maintenance problem, particularly in reference to the vacuum pump. It is likely that if gaseous fluoride pollution continues to be a major problem in identified sites, a dry system such as utilized in SO_2 analyzers will be developed. In addition to the maintenance problems encountered with this wet system there are problems of expense and difficulty in installation and calibration.

The results of these measurements, analyzed in conjunction with applicable standards in current use, provide accurate means to measure fluoride pollution levels and possible damage to adjacent plant and animal life.

Cause and Effect of Fluoride Toxicity

Fluoride toxicity in vegetation is caused primarily by the gaseous compounds hydrogen fluoride (HF) and silicon tetrafluoride (SiF_4). The particulate materials are deposited on leaf surfaces where it appears to have little effect upon the plant, unless dissolved by moisture and absorbed by plant tissues.

Injury to any plant occurs from a gradual accumulation of fluorides within the plant leaf tissues and is manifested in several ways. Some species exhibit observable damage at ambient air concentrations as low as 1 ppb (Urone, 1983, p. 2). Damage from fluoride exposure at low concentrations includes modified growth and lowered resistence to insect and disease, as well as chlorosis. Chlorosis is an abnormally yellow color of plant tissues, resulting from partial failure to develop chlorophyll, caused by nutrient deficiency or activities of a pathogen. Emphasis has been placed upon gladiola plants because they are very sensitive to air-borne fluorides and they are an important commercial flower crop. Gladiolas exhibit leaf injury of the tipburn type known as "leaf scorch," and red flowers exhibit a bluing effect.

High leaf fluoride has been associated with leaf scorch which has been observed at Ruskin and Sun City and throughout the southwestern part of Hillsborough County (Woltz, Magie, and Geraldson, 1954, p. 308; Woltz and Waters, 1980). Studies with gladiolas have established this plant as an indicator species for fluorides and standards have been tentatively set at 40 ppm for gladiolas (Woltz and Waters, 1980, p. 2). Broad-leaf plants exhibit injury along the margin and in other plants injury appears as spots or chlorosis.

In 1955, a new type of chlorosis was found on the leaves of citrus trees near Bartow in Polk County, which was attributed to air-borne gaseous fluoride compounds from a nearby phosphate plant (Wander and McBride, 1955, 23-24). Polk County is not only the center of the phosphate industry but is the leading producer in Florida's citrus industry, To evaluate the situation, citrus groves were monitored and experiments conducted during the 1960's and 70's to determine the extent and effect of fluoride on citrus (Leonard and Graves, 1969, pp. 717-22; Leonard and Graves, 1972, pp. 13-18; Woltz, Waters, and Leonard, 1971, pp. 30-36; Leonard and Graves, 1970, pp. 34-41). Experiments and field studies have shown that chlorophyll and leaf development are inhibited severely in young leaves by relatively low levels of F^-, 20-50 ppm. Injury during the time of flower bloom and early fruit set may cause blossom or fruit drop, severely reducing yields. Mature leaves may accumulate large amounts of F^- without much apparent damage, although the long-term effects are not known. The various species of citrus differ considerably in their tolerance of F^-. The lemon, tangerine, and tangelo are very sensitive; the Valencia orange is moderately sensitive, whereas the Hamlin and Pineapple orange and grapefruit are most tolerant.

Fluoride poisoning in livestock, especially beef cattle and dairy cows, is usually encountered as chronic fluorosis which involves the hard tissues of the body. Approximately 96 percent of all fluorine retained in the body is found in bones and teeth. The most common source of the fluoride is pasture grass subject to air-borne contamination. The current pasture grass standard is 45 ppm, reflecting an accepted belief that cattle can be successfully raised on grass containing 45 ppm F^- or less on an average annual basis (Crum, 1980). However, fluorosis is a chronic disease caused by an excess of fluoride over prolonged periods and there is cause for concern when levels exceed 45 ppm. Dental lesions may develop as well as mottled enamel and brown teeth which are susceptible to abnormal and uneven wear. The bone lesions result in enlargement and roughening of the bone which may lead to spurring at joints and subsequent stiffness and lameness. The major economic losses are due to the general unthriftiness of the animals rather than to death. Most of the fluorosis reported in central Florida occurred during the 1960's and is not as prevalent today. There are currently large numbers of beef cattle pastured on phosphate industry land. Most of these herds are privately owned and are commercially profitable.

During the past two decades significant gaseous and particulate fluoride pollution have been observed in west central Florida, with damage primarily to cattle and various plants such as citrus and ornamentals. In the past ten years the introduction of new types of stack scrubbers, modern processing techniques, the change to primary production of DAP, and the decrease in phosphate production resulting form a depressed market have reduced the effect of gaseous and particulate fluoride damage. More research on this topic is needed, and meaningful state standards should be established. A complete and fair evaluation of the Florida fluoride pollution problem only then can be ascertained.

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