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University of Tennessee Agricultural Experiment Station

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Bulletin No. 279 *March, 1958*

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MAURY COUNTY, TENNESSEE

THE UNIVERSITY OF TENNESSEE
AGRICULTURAL EXPERIMENT STATION
JOHN A. EWING, *Director*
KNOXVILLE

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MAURY COUNTY, TENNESSEE

Its Occurrence and Relationships in Atmosphere, Soils, Vegetation and Waters

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Foreword

Investigations of the relationships of fluorine in agriculture were initiated by the Tennessee Agricultural Experiment Station as early as 1920. Fluoride insecticides were introduced about then in an attempt to control the invasion of the Mexican bean beetle and the entomological results were reported in 1924 (20). Information as to the effects of those insecticides on soils, plants, and animal life became an obvious necessity; therefore, the Chemistry Department, in 1929, inaugurated a 4-year lysimeter experiment to learn the effects of soil incorporations of a fluoric insecticide.

Subsequent chemical studies dealt with occurrences of fluorine in the atmosphere, in rain and surface waters, in phosphatic fertilizers, rock phosphate and slags. A succession of lysimeter experiments were devoted to investigations of the activity and fate of solid fluorides and hydrofluoric acid when they were incorporated with soils. Occurrences of fluorine in vegetation, and its uptake by plants from native and added fluorine materials in soils was determined in forage crops and pot cultures grown under various conditions.

A study of the purported effects of industrial fluoride effluents upon plant and animal life in two Tennessee counties was begun in 1947 as a Research and Marketing project in collaboration with the Animal Husbandry Department. The research work in Maury County reported here was made possible through State and Federal funds that were supplemented substantially by grants-in-aid from the Monsanto Chemical Company and the Victor Chemical Works. Considerable exploratory work was necessary for the development and adaptation of procedures both for sampling and analysis of soils, vegetation, air, rainwaters, lysimeter leachings, and animal products.

This bulletin gives results of studies and surveys conducted to determine the occurrence of fluorine in the atmosphere, soils, vegetation, and waters sampled at various points in Maury County and a few nearby areas. In general, these findings have not been published previously. I some cases, related findings that have been published are summarized with inclusion of appropriate literature citations.

J. A. EWING
Director

Acknowledgments

The authors acknowledge with appreciation the efforts of many workers in the laboratory and field who contributed to this project.

L. S. Jones, Earl Williams, Mary Ellen Tubb, Winnifred Hester, and L. B. Clements are due individual mention for their analytical service and help with development of procedures, attending pot culture, greenhouse, and field experiments.

The late Dr. Samuel H. Winterberg gave valuable assistance in organizing and setting up plot, greenhouse, pot culture, and lysimeter experiments throughout the project.

Particularly valuable assistance was rendered by Mrs. Lillian H. Murray and members of the office staff in keeping records, preparing charts, and compiling and tabulating data in connection with this bulletin.

Substantial assistance in laying out sampling areas and periodic collection of large numbers of samples was given by John A. Ewing, E. J. Chapman, James B. McLaren, and other staff members of the Middle Tennessee Experiment Station at Columbia. Members of the Animal Husbandry Department of the University also cooperated in that phase of the work.

Laboratory employees of the Monsanto Chemical Company and of the Victor Chemical Works gave valuable technical cooperation and assistance. The greenhouse at the Tennessee Experiment Station that was used in connection with the pot culture experiments was provided by the Tennessee Valley Authority.

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INTRODUCTION

Fluorine* in fertilizers, slags, crops, and soils has been investigated extensively and comprehensively by the Tennessee Agricultural Experiment Station in collaboration with the Tennessee Valley Authority. The results of those studies, along with reports of research on analytical procedures, have been published in the literature and were summarized with appropriate bibliography in three recent publications, "Resumé of Fluoride Research at The University of Tennessee Agricultural Experiment Station, 1920-1954," (10); "Air Versus Soil as Channels for Fluoric Contamination of Vegetation in Two Tennessee Locales," (9); and "Fate of Air-Borne Fluorides and Attendant Effects upon Soil Reaction and Fertility" (10-A).

Analytical findings on forage crops and animal tissues were correlated with the harmful effects that livestock suffers due to ingestion of fluoride-contaminated forage. Those data were presented in collaboration with the Animal Husbandry Department in Station Bulletin 235, "Fluorosis in Cattle and Sheep" (8).

Data obtained as a result of a survey of the fluorine content of vegetation in Blount County were incorporated with animal response data and published in a Station bulletin, "Survey of Possible Occurrence and Extent of Fluorosis in Cattle on Selected Farms in Blount County" (21).

It is the purpose of this bulletin to report the occurrence and related chemical aspects of fluorine in air, soils, crops, and waters in the Maury County area as shown by surveys and experiments conducted during 1947-55. The early impetus to the investigations was the result of observations of a sickness, later diagnosed as fluorosis, among livestock on the experimental farm of the Middle Tennessee Experiment Station (MTES), then located at Columbia.

Possible Sources of Fluorine in Atmosphere, Soils and Vegetation

Many soils, especially those of high apatite content, contain relatively large amounts of fluorine. Phosphatic fertilizers usually

*Fluorine does not occur naturally in the elemental form, therefore as used in this publication, the word signifies a fluoride combination. Analytical values are stated as fluorine, regardless of its combination.

contain appreciable amounts, as do certain slags and liming materials; their use would add to the natural fluorides in the soil. Application of fluoride-bearing insecticides, materials more in use formerly than currently, would impart fluorides to the surface of the crop, and to the soil. Analyses of rainwaters indicate that considerable quantities of fluorine are washed down from the atmosphere, especially in populated areas where combustion of coal is the source of heat and power, or where industries are located from which fluorine compounds are evolved in manufacturing processes (22).

Calculations were made from production data available for a 3-year period, as to the amount of fluorine released by one phosphate industry (23) that used a thermal process for production of tri-calcium phosphate. According to those calculations the fluorine released, and presumed to have entered the atmosphere, totaled 810,000 pounds for 1947 (6 months), 1,398,000 pounds for 1948 (11 months), and 1,029,000 pounds for 1948 (11 months). This amounted to an average daily emission during the operating periods of 4,426, 4,186, and 3,081 pounds for 1947, 1948, and 1949, respectively. A fluorine recovery system was installed at this plant, and during its operation thereafter it was reported that fluorine emission was largely controlled. The plant operation has now been discontinued.

It should be mentioned also that flourine recovery systems were installed at the other phosphorus processing plants. This was after the respective companies recognized that the effluent fumes could contribute to atmospheric-derived contamination of forage crops and to the related fluorosis in livestock.

In addition to the several industries that make elemental phosphorus or superphosphate by processing rock phosphate, two plants in the area were manufacturing—during the period under study—a rock wool insulation material from by-product slag by means of a fusion-steam expansion system. Specimens of the slag raw material contained 2.90 percent of fluorine compared with a content of 1.53 percent in the finished rock wool. Therefore, the indicated emission, presumably about 30 pounds of fluorine per ton of product, was emitted into the atmosphere, since production of a ton of the rock wool required use of a ton of slag.

Research by the Tennessee Station (19) (18), in an effort to evaluate the role of soil as a possible source of fluorine in vegetation, has resulted in the general conclusion that forage crops do not register a high content of fluorine as a result of uptake by roots from adequately limed soils. Soil particles splashed on vegetation by rain, or accumulated as dust, under certain conditions, however, have been found to be a contributing factor in areas of high-phosphate soils.

Occurrence of Fluorine in the Atmosphere

It is highly probable that the gaseous or solid fluoride materials emitted into the air from phosphate mining or processing operations ultimately will settle on the vegetation of the area. A surface deposit is likely to result, and such contamination would then be reflected in the total fluorine content of the exposed vegetation. The distribution of the emitted materials would depend on several factors, such as atmospheric conditions, winds, and topography. Investigations to determine probable sources of abnormal occurrences of fluorine in forage crops required information as to the presence and amount of fluorine in the air of the Maury County area.

In general, fluorides in the atmosphere have not been of sufficient concentration to cause visible damage to vegetation in the Maury County area. In some instances, however, chlorotic and necrotic conditions have been observed in corn plants in the vicinity of industrial operations that emit fluorides. This chlorotic condition resembles that induced experimentally by application of HF vapor (Figure 1).

In the earlier work on this problem, samples of filtered air were collected at several locations in Middle Tennessee as well as at other places. Any non-filterable fluorine compounds that were present in the air were determined after absorption in a suitable reagent. A mobile unit—consisting of a vacuum pump, metering device and absorption apparatus—was provided for the purpose.

Analyses of air samples collected with this apparatus usually showed a higher fluorine content in samples from the Middle Tennessee areas compared with samples from several control locations, such as at Crossville. The magnitude of the values was so low, however, as to be subject to challenge, and it was decided to discontinue collection and analysis of air samples.

Three additional approaches were devised to show the occurrence of fluorine in the atmosphere: 1) analysis of rainwater to ascertain the fluorine washdown; 2) exposure and subsequent analysis of Spanish moss and lime-impregnated filter paper; and 3) analysis of pot culture plants grown in a sealed chamber into which all of the air admitted was water-washed to remove any

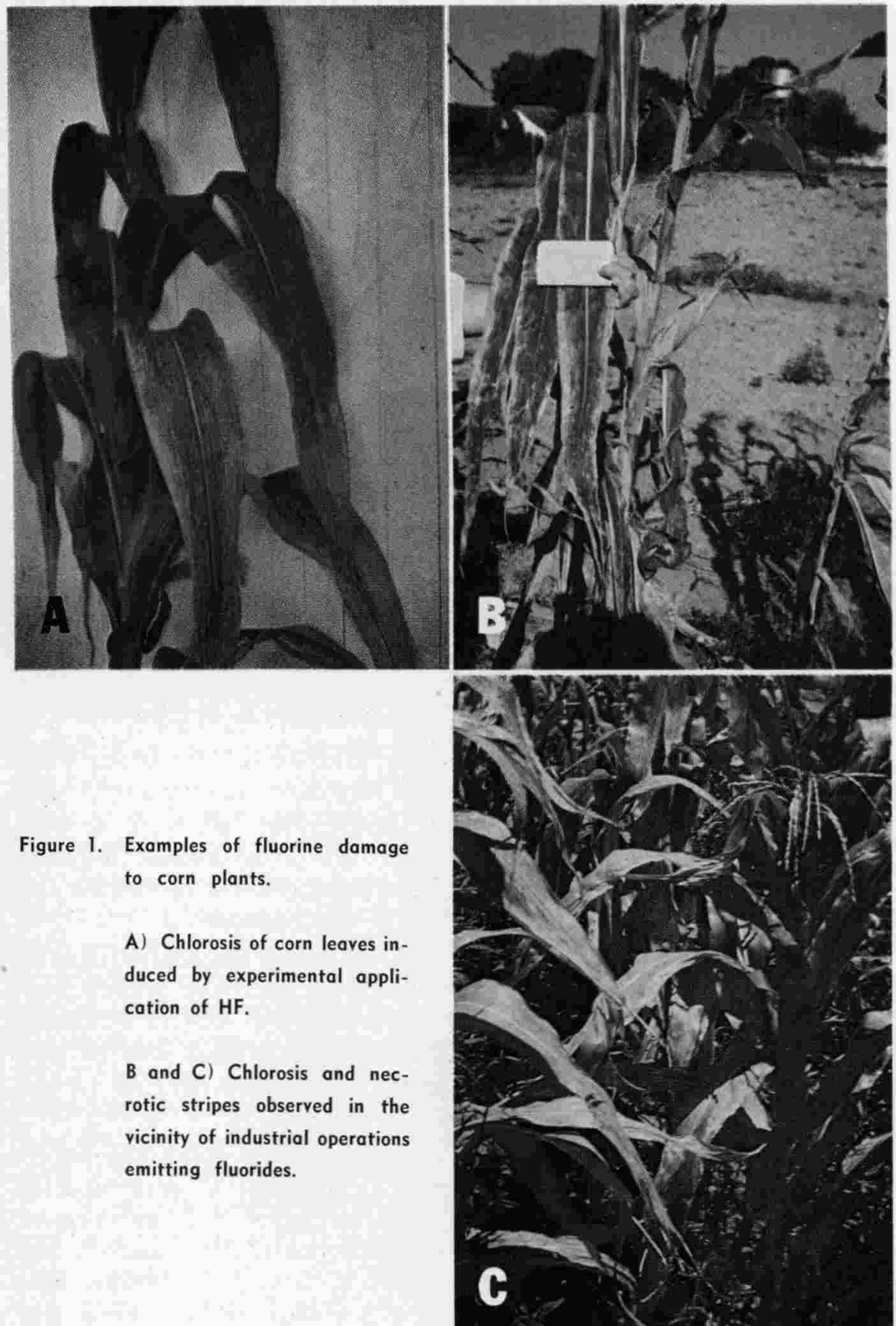

Figure 1. Examples of fluorine damage to corn plants.

A) Chlorosis of corn leaves induced by experimental application of HF.

B and C) Chlorosis and necrotic stripes observed in the vicinity of industrial operations emitting fluorides.

fluorine contamination. Control plants were grown simultaneously in the normal atmosphere just outside the chamber, and at Knoxville and Crossville.

Fluorine in Rainwaters. It has been pointed out by Hignett (7) and by Farr (2) that fluorine, principally in the form of HF or SiF_4, is released into the atmosphere as the result of phosphate processing. Combustion of coal and other industrial operations also release fluorine compounds. The washing down by rainwater of such contamination would be a logical expectation and serve to explain the occurrence of at least some of the fluorides in rainwater. Likewise, the presence of fluorides in rainwaters at certair locales serves as a strong indication that there must be a source or, sources of fluoride emission in or near those locales.

As a means of ascertaining the amount of atmospheric con tamination in the area, rainwater samples were collected at two points on the old Middle Tennessee Experiment Station in Maury County, during the period 1948-1952. The samples were collected by means of a sheet metal, asphalt-coated funnel with an area of 1/10,000 acre. That apparatus was supported above, and connected to, a large Pyrex glass bottle. The water caught was analyzed for fluorine content after each rain, or series of rains, and the amount of rainfall for the corresponding sample was obtained from the nearest rain gauge.

The amount of fluorine washed down at those locations was calculated from the analyses as pounds per acre, and is shown in Table 1. Also shown, for comparison, are similar values (1948-53) from other locales. The amount of washdown is decidedly higher at two points on the Middle Tennessee Experiment Station farm near Columbia, and on the University farms in Blount County and near Knoxville, all potentially contaminated areas, than at the Experiment Station farms near Crossville and Springfield, where contamination from industrial effluents is considered unlikely.

Fluorine Acquired by Plants Grown in Washed Air. It was thought that analysis of plants grown in a chamber into which only water-washed air was admitted would reflect only the fluorine from sources other than the atmosphere. To demonstrate this point, a system of pot cultures was set up whereby only washed air was admitted into an airtight chamber during growth and the fluorine content of plants grown under that condition was determined. Control pot cultures grown in the normal air just outside the chamber and at other locations were used to obtain comparative results. Soil of low fluorine content was used for all pot cultures.

Table 1 — *Annual Fluorine Washdown*[a] *by Rainfall*[b] *at Five Locations in Tennessee.*

Year	Knoxville lysimeters		Blount County Farm		Crossville Station		MTES, Columbia			Springfield Station	
								Fluorine			
	Rainfall	Fluorine	Rainfall	Fluorine	Rainfall	Fluorine	Rainfall	1[c]	2[d]	Rainfall	Fluorine
	inches	lb./A.	inches	lb./A.	inches	lb./A.	inches	lb./A.	lb./A.	inches	lb./A.
1948	55.72	1.99	51.15	2.13	53.13	0.62	46.23[e]	2.68[e]	2.50[e]	48.57	0.16
1949	52.62	1.74	48.64	2.53	62.69	0.31	50.70	2.28	1.95	40.25	0.09
1950	56.20	1.48	50.33	1.30	67.68	0.23	62.88	1.01	0.62	—	—
1951	59.37	2.63	52.73	1.97	66.68	0.58	63.63	3.39	2.77	—	—
1952	40.37	1.19	36.00	1.55	39.97	0.25	33.96	1.19	1.19	—	—
1953	41.81	1.33	39.55	2.55	50.43	0.42	—	—	—	—	—
Mean	51.02	1.73	46.40	2.01	56.76	0.40	51.48	2.11	1.81	44.41	0.13

[a]Computed upon basis of 1 inch of rainfall being equivalent to 226,512 lb. of water per acre:

$$\frac{\text{Rainfall (inches)} \times 226{,}512 \times \text{Fluorine (ppm)}}{1{,}000{,}000} = \text{lb. Fluorine/acre}$$

[b]Total measurement from records of nearest U.S. Weather Bureau reporting station, in some cases supplemented by local measurements.

[c]At MTES Office.

[d]On MTES Plots.

[e]Rainfall reported for 11 months; fluorine analyses on samples collected during 10 months.

The fluorine content of Sudangrass grown in the washed-air chamber at Columbia was appreciably less than that of the plants grown just outside the chamber, thus reflecting the contamination of the air at that point. The fluorine content of the plants grown at Knoxville was comparable to that in the plants grown in the chamber at Columbia (Table 2). The lowest occurrence of fluorine

Table 2 — *Fluorine Content of Sudangrass Grown Simultaneously in Washed-Air and in Outside Air at Columbia and in Outside Air at Knoxville.*[a]

	Fluorine content of air-dry sudangrass					
	After 21 days growth at Columbia				After 42 days growth at Knoxville	
	June 1953		Sept. 1953		June 1953	Sept. 1953
Pot no.	Outside	In filtered air chamber	Outside	In filtered air chamber	Outside	Outside
	ppm	ppm	ppm	ppm	ppm	ppm
1	34	11	40	10	4	10
2	37	12	51	10	7	13
3	37	9	45	8	2	15
4	39	9	47	10	—	14
5	36	7	51	12	—	14
Mean	37	10	47	10	4[b]	13
Increase[c]	27	—	37	—	—	—

[a]The cultures were seeded and grown 21 days at Knoxville before transfer to the Middle Tennessee Experiment Station.

[b]Composite of three pots.

[c]Over the content of fluorine in the plants grown in the chamber.

was in the similar control cultures grown at Crossville. These comparisons—with a complete description of apparatus, discussion of results, and references—were published, (12) and later were summarized in another publication (10).

Fluorine Acquired by Spanish Moss and by Lime-Impregnated Filter Paper when Exposed in the Atmosphere. Exposure and subsequent analysis of sodium carbonate placed at elevated positions in Maury County during 1948 indicated that this alkaline material acquired fluorine during the exposure period. The results were not conclusive, and certain mechanical difficulties were encountered; therefore this procedure was discontinued. Later, it was learned that Spanish moss seemed to have a particular affinity for absorption of fluorides from the atmosphere, as had been demonstrated by exposing the moss near phosphate manufacturing operations in Florida.

Table 3 — *Fluorine Content of Spanish Moss after Exposures on Farms in Maury County.*

Map location[a]	Location no.[a]	Initial exposure[b c]	First collection		Second collection		Third collection		Fourth collection	
			Rainfall	Fluorine[d]	Rainfall	Fluorine[d]	Rainfall	Fluorine[d]	Rainfall	Fluorine[d]
			inches	ppm	inches	ppm	inches	ppm	inches	ppm
			6/1/51		7/1/51		8/1/51		9/1/51	
315-6	59	5/1/51								
		Inside	1.01	154	7.69	243	2.68	244	1.16	256
		Outside	1.01	55	7.69	271	2.68	340	1.16	290
315-4	58	5/1/51								
		Inside	1.01	53	7.69	157	2.68	141	1.16	184
		Outside	1.01	52	7.69	196	2.68	264	1.16	200
225-12	41	5/1/51								
		Inside	1.01	31	7.69	56	2.68	51	1.16	56
		Outside	1.01	46	7.69	112	2.68	131	1.16	192
225-6	39	5/1/51								
		Inside	1.01	34	7.69	51	2.68	38		
		Outside	1.01	41	7.69	111	2.68	146	1.16	164
90-8	21	5/2/51								
		Inside	1.01	28	7.69	63	2.68	31	1.16	40
		Outside	1.01	53	7.69	86	2.68	109	1.16	112
180-8	31	5/2/51								
		Inside	1.01	37	7.69	42	2.68	46	1.16	48
		Outside	1.01	38	7.69	86	2.68	169	1.16	137
			6/7/51		7/7/51		8/7/51		9/7/51	
0-0	1	5/7/51								
		Inside	1.74	43	8.36	63	1.25	62	1.72	113
		Outside	1.74	48	8.36	92	1.25	204	1.72	213
45-4	13	5/8/51								
		Inside	1.74	51	8.36	158	1.25	226	1.72	246
		Outside	1.74	103	8.36	233			1.72	624
45-10	16	5/8/51								
		Inside	1.74	20	8.36	30	1.25	32	1.72	21
		Outside	1.74	34	8.36	47	1.25	64	1.72	67

[a]Map locations given in degrees and miles from the old Middle Tennessee Experiment Station near Columbia. Samples were collected on a farm corresponding as nearly as possible to the indicated map location shown by the number on the map, Figure 3.
[b]Initial fluorine content of North Carolina moss, 22 ppm on air-dry basis.
[c]Inside exposure provided protection from rain but subject to atmospheric circulation; outside exposure was generally in a tree.
[d]Air-dry basis.

Accordingly, in 1950-51 a series of Spanish moss samples were placed well above ground level at several locations in Maury County. Initial exposures of the moss were intended to find out the possible relationship of the location of potential sources of fluorine emissions to the prevalence of fluorosis in cattle at the old Middle Tennessee Experiment Station. The exposed moss near sources of fluorine emission acquired a significantly higher content of fluorine in comparison with controls placed at other locations. The increases were cumulative and they indicated that fluorides had been acquired from the air of the area near supposed fluoric emissions. Table 3 shows the fluorine content of the moss periodically during exposure. Complete results and discussion of this early work have been published (13).

Later, in 1954-55, additional studies using Spanish moss were begun on a larger scale and with parallel exposures of lime-impregnated filter papers. One important feature of these exposures was that they were contained in an apparatus intended to eliminate direct contamination by fall-out dust that might have high contents of fluorine material originating from mining operations, road dust, or splash.

The analytical findings after exposures showed enhancements in the fluorine content of both the moss and the lime-impregnated filter papers. In general, the values at the various locations correlated with the fluorine occurrence in the rainwater and vegetation collected from the respective areas. Control exposures at the Tennessee Plateau Experiment Station, a location remote from probable fluorine emissions, showed relatively little enhancement. The results of these experiments, description and illustrations of apparatus, procedures, and pertinent literature citations have been published (15).

The foregoing experiments showed that occurrence of fluorine in rainwater, in exposed Spanish moss, on lime-impregnated filter papers, and in pot cultures was relatively higher in the vicinity of supposed fluorine effluents compared with occurrences under parallel conditions at other locations considered free of such contamination. These findings led to the conclusion that the enhanced fluorine contents observed at certain locations were caused largely by fluorine arising from industrial operations and contaminating the air in those areas.

Relation of Fluorine in Soils to the Fluorine Content of Plants Grown on Them

Many soils of Middle Tennessee have a high content of fluorine. Therefore, in any investigations to determine the sources of fluorine (6) in plants the possibility of its uptake from the soil as well as contamination due to soil splash or dust must be considered.

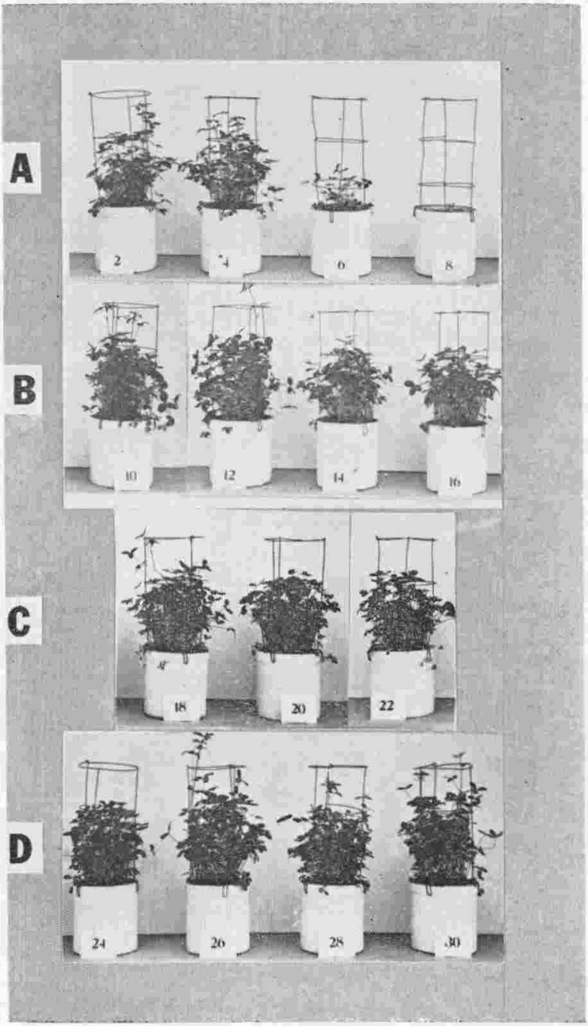

Figure 2. Typical pot culture growth as used in greenhouse experiments to show the effects of added hydro-fluoric acid on crops grown on limed and unlimed soil.

A) Unlimed
B) Limestoned
C) Limestoned
D) Limestoned

The Tennessee Experiment Station has carried on extensive greenhouse and lysimeter studies mostly at Knoxville to determine the relation of soil fluorides to the fluorine content of the plants grown on that soil. These experiments have included both soils of naturally high fluorine content and those to which fluorine from many sources and in various combinations have been added. The results from these Tennessee experiments have been reported in the literature (9) (19) (18) (17) and summarized in a more recent publication (10). In general, the findings demonstrated that plants do not acquire abnormal contents of fluorine nor show deleterious effects through uptake of fluorine from soils adequately supplied with calcium (Figure 2).

Occurrence of Fluorine in Plants Grown on Transported Soils. As a further practical demonstration of the possible effect of soil fluorides on the fluorine in vegetation, several soils of various fluorine contents were transported to different locations, placed in rims of 1/10,000 acre area and planted to crops. Table 4 shows the source, type and fluorine content of the soils, and the fluorine contents of different crops grown on them at different locations. In every case, plants grown at the Middle Tennessee Experiment Station had a decidedly higher fluorine content, regardless of the soil, than the plants grown in the same soil and under similar conditions at other locations. This is brought out particularly in the case of the Maury silt loam (1,300 ppm F) from Lexington, Kentucky on which the crops grown at Lexington and at Knoxville contained 7 and 10 ppm F respectively. A similar Maury silt loam (with only 500 ppm F) from Middle Tennessee Experiment Station produced crops that had 26 ppm F when grown simultaneously at the Middle Tennessee Experiment Station, although crops grown simultaneously on that soil at Knoxville and at Crossville contained 9 and 8 ppm respectively.

The fluorine contents of the four samples of vegetation collected at the Kentucky Experiment Station near Lexington in late September and late October averaged 14 ppm, compared with the average of only 6 ppm for the samples collected in May thru early September. That increase may have been due to possible fluorine contamination from increased coal smoke from nearby Lexington as a result of colder weather at that season, or to splash from the exposed soil as a result of diminished growth of the alfalfa and bluegrass at that late season, or to both conditions.

The factors of both soil splash and uptake have been considered as possible explanations for the increases shown on the

Table 4 — *Fluorine Contents of Vegetation Grown on Soils at Points of Origin and at Points to Which the Soils were Transported.*

Soil[a]			Crops[b]			
Type	Source	Fluorine	No. of samples	Grown at[c]	Fluorine Av.	Fluorine Range
		ppm			ppm	ppm
Maury Silt Loam	MTES, Columbia	500	6	Columbia	26	16-42
			6	Crossville	8	2-15
			12	Knoxville	9	3-16
			6	Springfield	8	5-11
Maury Silt Loam	Kentucky Expt. Sta.	1300	22	Lexington	7	2-17
			6	Knoxville	10	7-14
Clarksville Silt Loam	Anderson County	200	6	Columbia	27	21-32
			2	Crossville	3	2-4
			2	Knoxville	8	7-9
Hartsells Sandy Loam	Plateau Expt. Station, Crossville	260	12	Columbia	22	12-41
Hermitage Silt Loam	Dairy Expt. Station, Lewisburg	[d]	6	Columbia	24	13-33
			2	Lewisburg	5	4-6
Talbot Silty Clay Loam	Dairy Expt. Station, Lewisburg	[d]	6	Columbia	20	15-25
			2	Lewisburg	5	3-7

[a]Soils were transported from the respective original locations to the points where the crops were planted and grown.

[b]Samples were collected periodically during the 1950 growing season from crops of alfalfa, millet, bluegrass, and ryegrass. The samples from Lexington were collected simultaneously from alfalfa and bluegrass growing in adjacent field plots.

[c]With the exception of Lewisburg, Tennessee, and Lexington, Kentucky, where the samples were field-grown at the same locations from which the transported soil came, the crops were grown on transported soils placed at 12-inch depths over undisturbed subsoil in metal rims with areas of 1/10,000 acre. All placements were on the respective Experiment Stations near the town indicated.

[d]Tests on samples of the soils used showed them to be low in phosphorus, an indication of low fluorine content. Analyses of other samples of these soil types from about the same location gave values of 200-270 ppm F.

Columbia growth, but as the growth conditions on the respective soils were essentially the same at all locations, those factors would be equalized. Furthermore, the combined fluorine content from all sources in the vegetation grown at locations other than at Columbia was below the level considered detrimental to livestock. It was clearly indicated, therefore, that the relative increases shown at Columbia were caused by fluorine contamination from the air.

In another comparison, 10 different surface soils were placed in pots and planted to red clover at Knoxville. One Maury silt loam had a fluorine content of 3,344 ppm whereas all the others were in the low range of 200 to 300 ppm of fluorine. The data for the 10 soils, and crops, treatments, yields, pH, fluorine and P_2O_5 contents are shown in Table 5. The mean uptake of fluorine from the soils that had been treated with 200 pounds per acre of F as HF was significantly higher than the uptake from the other treatments. The pH values of all the original soils except the Dickson indicated inadequate liming for red clover. This is true for several soils even after the 2-ton per acre additions of limestone and of slag. The mean fluorine uptake from the other treatments was not significantly different and the actual fluorine contents in all cases were below the levels considered detrimental to livestock. These findings, even though the fluorine content of the clover grown on the high-fluorine Maury No. 1 soil was somewhat higher than that grown on the low-fluorine soils, do not alter the conclusion from other findings: that plants do not take up significant amounts of fluorine from adequately limed soil.

Effect of Soil Splash on the Fluorine Analysis of Vegetation

The possibility of vegetation being contaminated by rain-splashed, fluorine-bearing soil was recognized in the early stages of these studies. A preliminary test was made in which 8 x 8-foot plots of alfalfa, growing on soil of relatively high fluorine content, were laid off and the entire soil surface covered to a depth of 1 inch with clean quartz sand. Samples of alfalfa were collected periodically from these plots and from adjacent plots that were not covered with sand. The analyses of samples from the sand-covered and exposed-soil plots showed practically identical fluorine content. These findings indicated that soil splash was of slight importance at that location in imparting fluorine to growing crops. However, in this case both the vegetative growth and the stand were good, conditions that minimize soil splash. The location of

Table 5 — *Fluorine Content of Red Clover Grown on Ten Soils with Different Treatments.*

				Treatment[a]															
Original Soil				No F added				200 lbs. F as HF				Limestone — 2 tons[b]				W.D. Slag — 2 tons[b]			
		Content of		Dry	Content of		pH of	Dry	Content of		pH of	Dry	Content of		pH of	Dry	Content of		pH of
Nomenclature[c]	pH	F	P_2O_5	weight	F	P_2O_5	soil	weight	F	P_2O_5	soil	weight	F	P_2O_5	soil	weight	F	P_2O_5	soil
		ppm	%	grams	ppm	%		grams	ppm	%		grams	ppm	%		grams	ppm	%	
Maury No. 1	5.3	3344	5.08	14.0	13	0.92	5.2	9.4	16	0.99	5.2	20.1	14	0.78	5.7	16.6	12	0.83	5.6
Mountview	5.3	104	0.10	14.2	10	0.46	5.2	11.7	21	0.52	5.2	17.6	9	0.37	5.9	20.0	10	0.48	5.7
Maury No. 2	5.3	260	0.55	17.1	9	0.62	5.3	16.4	12	0.63	5.2	23.3	9	0.62	6.0	20.5	10	0.62	6.0
Delrose No. 1	5.3	246	0.28	18.8	9	0.66	5.2	16.1	14	0.73	5.2	18.6	9	0.71	5.9	20.6	10	0.72	5.6
Delrose No. 2	5.1	284	0.48	21.3	9	0.76	5.0	17.6	13	0.76	4.9	22.8	8	0.74	5.7	23.7	9	0.76	5.5
Baxter No. 1	5.1	168	0.21	17.4	10	0.54	5.0	15.7	19	0.55	5.0	13.1	8	0.46	5.9	14.8	7	0.54	5.9
Baxter No. 2	5.5	140	0.29	15.2	9	0.61	5.3	12.6	13	0.59	5.3	17.8	8	0.58	5.9	15.9	9	0.60	5.7
Dickson	7.0	136	0.06	20.9	9	0.47	6.6	23.6	10	0.47	6.5	22.3	10	0.46	7.0	22.7	9	0.54	7.3
Maury No. 3	5.2	232	0.24	6.3	6	0.50	5.1	7.0	16	0.54	5.1	11.1	8	0.55	5.9	11.7	7	0.62	5.8
Baxter No. 3	5.8	128	0.11	15.2	8	0.40	5.7	16.3	10	0.41	5.7	15.0	9	0.38	6.4	19.4	8	0.44	6.2
Mean					9				14				9				9		

L.S.D. for dry weight — 1.2 grams at 5% level and 1.6 grams at 1%.
L.S.D. for fluorine content — 2 ppm at 5% level and 3 ppm at 1% level.

[a]All cultures received 50 pounds of K_2O as K_2SO_4 added to the surface. All cultures except the Maury No. 1 received 80 pounds of P_2O_5 as F-Free Monocalcium Phosphate. Phosphate, HF, Limestone, and Slag were incorporated full depth. All cultures were grown in the greenhouse at Knoxville and the fluorine values of the crops are the average of duplicate analyses of the four cultures.

[b]Actual tons per acre surface.

[c]All soil-textures were classified as silt loams.

this comparison was not in a region of probable fluorine effluents; therefore atmospheric contamination did not influence the results.

Effect of Fluorine Content of Soil, Ground Coverage and Washing of Samples on the Fluorine Analysis of Crops. To obtain more conclusive information on this point, a series of frames, 1/2,000 acre each, were filled to a depth of 12 inches with Maury County soils of low, medium, and high fluorine contents. The same five crops were planted at the new Middle Tennessee Experiment Station (Spring Hill, Tennessee) near where the soils were collected and at Knoxville to where the soils were transported. Each crop was planted both in 4- and 8-inch rows and all treatments were replicated three times. Extreme to moderate drought prevailed at the Middle Tennessee Experiment Station during both 1952 and 1953, a condition that adversely affected both growth and ground coverage at that location. As a result, the crops were replanted in the fall of 1952 for sampling in 1953.

The analyses of washed and unwashed samples of the five crops were averaged for 1952-53 and are summarized in Table 6. All crops acquired a higher fluorine content at the new Middle Tennessee Experiment Station than at Knoxville; in general, the fluorine content of the crop was in proportion to that of the respective soil; crops grown in 8-inch rows, with some exceptions, had higher fluorine than those in 4-inch rows; washing of the samples removed a considerable amount of the fluoride and the amount of fluorine in all the washed samples from Knoxville was below the level considered damaging to livestock, whereas several samples grown at the Middle Tennessee Experiment Station were excessively high by that criterion, even after washing.

Previous analyses of crops have indicated that fluorine contamination from the atmosphere was relatively slight at the location of the new Middle Tennessee Experiment Station. The higher fluorine values shown in the present comparisons may have been due to the poor growth as a result of the drought that prevailed and to the greater opportunity for soil splash due to the resultant poor ground coverage.

Effect of Height of Cutting on the Fluorine Content of Vegetation. Close grazing by animals, under circumstances where the stand of forage is sparse or the growth is short, is considered conducive to ingestion of excessive soil-derived fluorine. Soil splash likely would contaminate the lower parts of the plants to a greater extent under those conditions. Also, the same possibility would exist when the forage is cut close to the ground for hay.

Table 6 — *Fluorine Content of Forage of Five Species Grown in Frames on the Three Maury Silt Loams, Simultaneously at Knoxville and at the New MTES,* 1952-1953.

Soil[a]	Mean content of fluorine, parts per million, dry weight							
	From growth at Knoxville				From growth at New MTES			
	4 in. rows[b]		8 in. rows[b]		4 in. rows[b]		8 in. rows[b]	
	Unwashed	Washed[c]	Unwashed	Washed[c]	Unwashed	Washed[c]	Unwashed	Washed[c]
ppm								
				Rye				
A 1400	6	4	5	4	9	7	26	8
B 3200	5	5	6	4	16	9	44	11
C 6500	7	5	8	5	23	14	83	13
				Millet				
A 1400	3	2	3	2	14	9	18	14
B 3200	4	2	3	2	24	12	37	17
C 6500	5	2	4	2	63	13	58	17
				Clover				
A 1400	9	6	10	6	25	18	23	18
B 3200	13	7	15	8	52	18	54	29
C 6500	24	8	35	10	110	35	66	31
				Alfalfa				
A 1400	11	8	14	8	23	15	31	29
B 3200	13	9	18	10	26	17	90	77
C 6500	14	10	26	12	28	15	154	108
				Orchardgrass				
A 1400	10	6	10	5	36		39	
B 3200	11	6	17	7	62		78	
C 6500	12	8	16	7	135		110	

[a]Based on averages of the analyses of separate samples from the individual rims. Previously reported values, based on analyses of exploratory field samples, showed the fluorine content as 700, 3500 and 9000 ppm respectively, or they were referred to as "low, medium or high fluorine soils." Actually, a soil of 1400 ppm F would not be considered as low in fluorine.

[b]Row plantings, or "spaced stands," of the grains and grasses were 8 inches apart and the legumes were 12 inches apart; the "full stand" plantings were made in drills about 4 inches apart. All plantings were randomized triplicates. No fertilizer was added at time of planting, but during the second year the crops were fertilized with KH_2PO_4 and NH_4NO_3.

[c]One-half of each of the green forage samples was washed in tap water of negligible fluorine content and rinsed three times, then dried and ground for analysis The other half was analyzed without washing.

To find the effect of height of cutting, or grazing, on the fluorine acquired by vegetation, the frames and the Maury soils previously used in the splash comparisons were planted to new crops in 1954. Sudangrass was planted for harvest at 1½ and 3 inches above ground at the new Middle Tennessee Experiment Station and at Knoxville. Alfalfa and orchardgrass were grown at Knoxville and were harvested at 1, 2, 3, and 4 inch levels. All

Table 7 — *Fluorine Content of Sudangrass Grown on Three Maury Silt Loam Soils Simultaneously at Knoxville and at the New MTES and Harvested at Two Heights of Stubble.*

	Mean content of fluorine, parts per million, dry weight			
	From growth at Knoxville[b]		From growth at New MTES[b]	
Soil[a]	Stubble Height 1½ in.	Stubble Height 3½ in.	Stubble Height 1½ in.	Stubble Height 3½ in.
ppm				
	4 inch rows			
A 1400	7	9	16	13
B 3200	21	11	24	21
C 6500	21	13	24	22
	8 inch rows			
A 1400	7	11	11	13
B 3200	20	15	20	17
C 6500	21	13	19	17

[a]See footnote[a], table 6.
[b]All plantings were in triplicate.

Table 8 — *Fluorine Content of Alfalfa and of Orchardgrass Grown Simultaneously at Knoxville on Three Maury Silt Loams and Harvested at Four Heights of Stubble.*

	Mean content of fluorine, parts per million, dry weight							
	Alfalfa,[b] Stubble height, inches				Orchardgrass,[b] Stubble height, inches			
Soil[a]	1	2	3	4	1	2	3	4
ppm								
	4 inch rows							
A 1400	11	8	9	10	10	6	5	6
B 3200	20	13	8	10	9	6	8	8
C 6500	23	14	13	11	9	10	7	7
	8 inch rows							
A 1400	19	14	12	9	7	9	8	7
B 3200	38	20	18	13	10	6	8	7
C 6500	40	29	29	16	8	7	6	7

[a]See footnote[a], table 6.
[b]All plantings were in triplicate.

crops were grown in both 4-inch and 8-inch spaced rows. At the time of harvest, the crop on each frame was divided and an equal portion cut at the various heights above ground for analysis. The summaries of the means of the fluorine contents of Sudangrass

Table 9 — *Fluorine Content of Vegetation Sampled in Maury County, Tennessee During a Seven Year Survey 1949-1955.*

		Average fluorine content and range											
		1949			1950			1951			1952		
Map location[a]	Location No.[a]	No. samples	Flourine	Range	No. samples	Fluorine	Range	No. samples	Flourine	Range	No. samples	Flourine	Range
			ppm	ppm		ppm	ppm		ppm	ppm		ppm	ppm
0-0	1[b]	105	36	7-186	169	39	7-149	169	33	5-121	43	28	7-105
0-2	2	18	41	13-93	18	28	7-71	25	33	9-125	12	34	11-83
0-4	3	16	16	6-45	18	18	5-62	25	17	5-50	12	22	4-51
0-6	4	17	67	8-255	19	174	15-678	25	446	16-3350	12	264	17-1160
0-8	5	17	40	8-126	18	36	2-90	25	18	4-71	12	33	4-103
0-10	6	18	16	3-81	17	47	9-189	25	14	3-39	12	9	3-21
0-12	7	17	27	4-180	18	38	3-314	25	10	3-25	12	14	3-34
0-17	8	0			0			0			0		
23-4	9	0			0			0			0		
22-5	10	0			39	102	14-360	50	77	10-435	24	93	9-547
30-4	11	0			0			0			0		
45-2	12	17	48	5-122	18	47	10-119	25	42	13-87	12	48	10-123
45-4	13	16	65	14-121	18	138	15-540	25	200	32-546	12	185	58-540
45-6	14	17	24	9-54	18	29	8-58	25	23	5-42	11	39	11-88
45-8	15	17	17	5-72	16	18	5-43	25	13	3-50	12	13	7-24
45-10	16	17	11	2-31	23	13	6-27	25	22	4-184	12	14	5-31
45-12	17	16	23	7-47	18	20	10-40	25	15	6-47	12	18	7-36
45-14	18	10	21	3-70	17	27	5-122	25	18	2-117	12	11	3-26
90-4	19	15	13	5-24	16	18	6-60	24	14	2-44	13	18	2-42
90-6	20	16	12	4-24	18	22	3-76	24	17	5-46	13	22	7-57
90-8	21	16	40[c]	4-206	17	17	6-71	24	15	1-45	13	26	1-149
90-10	22	14	13	1-78	17	14	1-31	24	9	2-24	13	16	2-40
135-4	23	16	20	8-49	17	16	6-35	24	11	4-26	13	25	6-59
135-6	24	17	19	4-80	18	14	5-32	24	10	3-23	13	16	3-50
135-8	25	17	20	6-91	18	15	2-37	24	13	4-33	13	38	2-164
135-12	26	12	23	1-89	18	10	4-31	24	11	3-34	13	19	3-50
135-21	27	0			0			0			0		
180-2	28	17	42	11-135	17	23	10-56	24	27	8-61	13	39	7-141

180-4	29	6	23	4-51	7	39	2-106	24	47	8-279	13	65	18-140
180-6	30	16	23	2-75	19	30	9-135	24	14	3-28	13	13	5-30
180-8	31	17	35	9-110	18	29	9-70	24	19	6-48	13	22	6-40
180-10	32	14	58[d]	6-183	18	98	3-530	24	60	3-460	13	27	18-52
180-12	33	17	6	2-18	17	15	1-100	24	12	5-40	13	14	3-33
180-14	34	17	25	5-80	17	38	8-78	24	18	1-47	13	17	4-42
215-10	35	0			24	106	19-364	24	62	13-145	13	86	18-196
225-1	36	16	23	6-62	19	66	8-217	24	23	8-39	13	42	12-162
225-2	37	17	21	3-47	24	49	7-303	24	22	8-41	13	20	11-30
225-4	38	16	27	7-62	19	35	9-91	24	19	5-44	13	21	6-39
225-6	39	16	68	10-174	4	193	65-325	24	46	7-265	13	186	13-1405
225-10	40	16	49	10-107	18	69	11-432	24	38	13-93	13	52	9-128
225-12	41	15	63[e]	12-161	19	72	9-238	24	24	10-72	13	21	11-48
225-14	42	16	21	5-60	19	27	2-113	24	14	5-32	13	19	9-45
225-16	43	8	13	6-27	16	15	3-42	24	9	2-32	15	12	3-25
235-8	44	0			22	102	30-395	24	67	12-243	13	72	19-208
240-10	45	0			22	138	8-682	24	90	7-890	13	118	8-401
240-12	46	0			19	76	16-287	24	27	7-125	13	31	10-73
247-8	47	0			0			0			0		
270-2	48	18	31	12-59	19	31	5-66	24	39	9-71	13	37	13-64
270-4	49	16	37	7-77	19	35	5-63	24	41	8-156	13	244	12-1320
270-6	50	17	35	7-183	19	26	9-65	24	25	6-44	13	25	12-44
270-8	51	17	26	6-67	19	45	12-142	24	28	2-120	13	18	5-32
270-10	52	12	27	9-72	9	21	9-53	24	22	3-112	13	17	6-52
270-12	53	16	21	6-60	17	18	3-54	24	18	5-79	13	17	7-28
270-14	54	11	35	6-126	19	42	6-317	24	25	4-190	13	51	3-225
292-8	55	0			0			0			0		
295-6	56	0			23	200	51-497	25	153	39-538	16	63	17-155
315-2	57	16	45	14-106	18	37	13-597	25	65	8-270	12	94	11-390
315-4	58	16	82[f]	13-327	18	111	28-300	25	89	25-321	12	39	7-85
315-6	59	17	57	18-120	18	39	13-62	25	43	10-112	12	31	7-82
315-8	60	17	50	11-160	18	45	13-96	25	34	6-122	12	22	6-41
315-10	61	17	20	8-54	18	35	10-105	25	21	2-107	12	43	9-151
315-12	62	17	29	5-95	16	20	4-68	25	25	5-68	12	19	8-38
315-14	63	17	32	8-94	16	37	8-132	25	23	2-109	12	102	4-588
315-16	64	11	43	7-176	16	27	6-127	25	11	3-43	12	10	3-23
320-4	65	0			23	132	49-290	24	96	12-263	12	187	48-414
320-5	66	0			24	133	40-281	25	89	21-506	12	106	12-266
338-15	67	0			0			0			0		

See footnotes for Table 9 on page 22.

Table 9 — (Continued)

Map location[a]	Location no.[a]	1953 No. samples	1953 Flourine	1953 Range	1954 No. samples	1954 Fluorine	1954 Range	1955 No. samples	1955 Fluorine	1955 Range	1949-1955 Total samples	1949-1955 Av. fluorine
		Average fluorine content and range										
			ppm	ppm		ppm	ppm		ppm	ppm		ppm
0-0	1[b]	6	29	24-39	7	30	13-50	16	46	13-147	515	35
0-2	2	0			0			0			73	34
0-4	3	0			0			0			71	18
0-6	4	0			0			0			73	257
0-8	5	5	29	8-78	7	27	16-48	11	36	10-166	95	31
0-10	6	0			0			0			72	21
0-12	7	0			0			0			72	22
0-17	8	5	11	7-15	10	17	7-28	20	14	5-29	35	14
23-4	9	2	644	145-1142	8	740	214-1661	10	614	224-1463	20	667
22-5	10	0			0			0			113	89
30-4	11	2	182	73-291	9	72	33-208	19	68	28-168	30	77
45-2	12	2	212	172-252	9	55	28-113	13	59	15-135	96	52
45-4	13	0			10	78	13-426	11	36	12-60	92	130
45-6	14	6	36	17-53	8	23	11-47	16	26	10-77	101	27
45-8	15	0			0			0			70	15
45-10	16	8	14	6-29	11	14	6-33	20	18	6-107	116	16
45-12	17	0			0			0			71	19
45-14	18	0			0			0			64	20
90-4	19	0			0			0			68	15
90-6	20	6	16	10-27	9	35	14-173	18	52	5-352	104	25
90-8	21	0			0			0			70	23
90-10	22	0			0			0			68	12
135-4	23	0			0			0			70	17
135-6	24	0			0			0			72	14
135-8	25	5	15	10-20	8	13	8-22	19	17	6-56	104	18
135-12	26	0			0			0			67	14
135-21	27	14	9	4-23	16	16	4-95	21	19	4-80	51	15
180-2	28	0			0			0			71	32

180-4	29	0			0			0			50	48
180-6	30	4	24	11-40	7	42	14-117	12	111	10-706	95	33
180-8	31	5	16	10-24	9	29	9-91	14	23	6-60	100	25
180-10	32	0			0			0			69	63
180-12	33	0			0			0			71	12
180-14	34	0			0			0			71	24
215-10	35	0			0			0			61	84
225-1	36	0			0			0			72	38
225-2	37	6	33	18-86	13	25	9-52	18	23	11-35	115	28
225-4	38	0			0			0			72	25
225-6	39	0			0			0			57	94
225-10	40	0			0			0			71	51
225-12	41	0			0			0			71	45
225-14	42	6	24	16-47	6	40	17-118	11	18	9-49	95	21
225-16	43	0			0			0			63	12
235-8	44	0			0			0			59	81
240-10	45	0			0			0			59	114
240-12	46	0			0			0			56	45
247-8	47	5	40	22-56	9	25	14-42	19	29	13-77	33	30
270-2	48	5	33	18-53	9	70	20-275	2	201	126-275	90	42
270-4	49	0			0			0			72	75
270-6	50	0			0			0			73	28
270-8	51	7	26	13-67	11	21	10-55	15	17	7-33	106	27
270-10	52	0			0			0			58	22
270-12	53	0			0			0			70	19
270-14	54	0			0			0			67	37
292-8	55	4	21	12-34	8	20	8-28	13	26	9-66	25	23
295-6	56	7	38	24-62	10	49	14-120	20	26	10-51	101	106
315-2	57	4	59	34-86	7	37	13-80	11	39	12-77	93	54
315-4	58	2	52	45-58	10	114	15-280	17	68	16-182	100	84
315-6	59	3	58	17-105	8	52	17-119	11	34	11-103	94	43
315-8	60	6	44	8-66	12	29	11-59	21	52	11-113	111	40
315-10	61	0			0			0			72	28
315-12	62	8	27	7-55	9	23	8-54	19	16	6-51	106	23
315-14	63	0			0			0			70	42
315-16	64	0			0			0			64	20
320-4	65	0			0			0			59	129
320-5	66	0			0			0			61	110
338-15	67	4	14	6-20	6	13	11-19	10	12	5-26	20	13

See footnotes for Table 9 on page 22.

FOOTNOTES FOR TABLE 9

[a]Map locations are given in degrees and miles from the old Middle Tennessee Experiment Station near Columbia. Samples were collected on a farm corresponding as nearly as possible to the indicated map location shown by the number on the map, Figure 3.
[b]The Middle Tennessee Experiment Station, designated as "Old MTES," map location 1, consisted of a 600-acre farm on which there were eight locations where samples were collected regularly. The maximum distance between the most extreme points was about 1 mile. The number of samples and fluorine contents shown at that location include all samples from the eight points on the farm. The "Old MTES" was discontinued as an experimental farm in 1952, although samples were collected at a few of the locations throug 1955.
[c]One high sample—840 ppm—May, 1949, not included in average.
[d]Two high samples—448 and 440 ppm—December, 1949, not included in average.
[e]One high sample—719 ppm—December, 1949, not included in average.
[f]One high sample—617 ppm—December, 1949, not included in average.

grown at the new Middle Tennessee Experiment Station and at Knoxville are shown in Table 7. Comparisons of the mean fluorine contents of cuttings at 1, 2, 3, and 4 inches for orchardgrass and alfalfa grown at Knoxville are shown in Table 8. The results show a higher average fluorine content in samples cut at the 1½ inch height than those cut at 3 inches on both the 4-inch and 8-inch rows; also, values ranged progressively higher from the 4-inch level to the 1-inch level on both the alfalfa and orchardgrass at Knoxville.

Fluorine Occurrence in Vegetation, Soils and Surface Waters of Maury County, Tennessee

Fluorosis in livestock was identified in Middle Tennessee about 1946 and was the primary reason for undertaking this phase of the fluorine studies. As ingestion of fluorine was the known cause of fluorosis, it was considered important to determine the amounts of fluorine in vegetation, soils, and waters at various points in the affected area; equally important was to correlate the amounts of fluorine found in the vegetation at a given location to the proximity of industrial operations capable of emitting fluorides.

During 1949-1955, samples of vegetation, soils, and surface waters were collected at selected locations in the Maury County area on a grid pattern laid out from the old Middle Tennessee Experiment Station. These sampling locations are designated on the map or Figure 3 by a number, and are shown in relation to the more important landmarks.

Fluorine Content of Vegetation. The occurrence of fluorine in the vegetation was found by analyzing large numbers of samples collected periodically as near as possible to the designated locations. Due to seasonal conditions, it was sometimes necessary to alter the location somewhat to find growing forage. The kind of crop available also was subject to variation. In general, it was the practice to obtain the sample intended for analysis from a field or pasture that was being grazed or was to be used for hay. A quantity of vegetation was cut, usually within a 50- to 100-foot

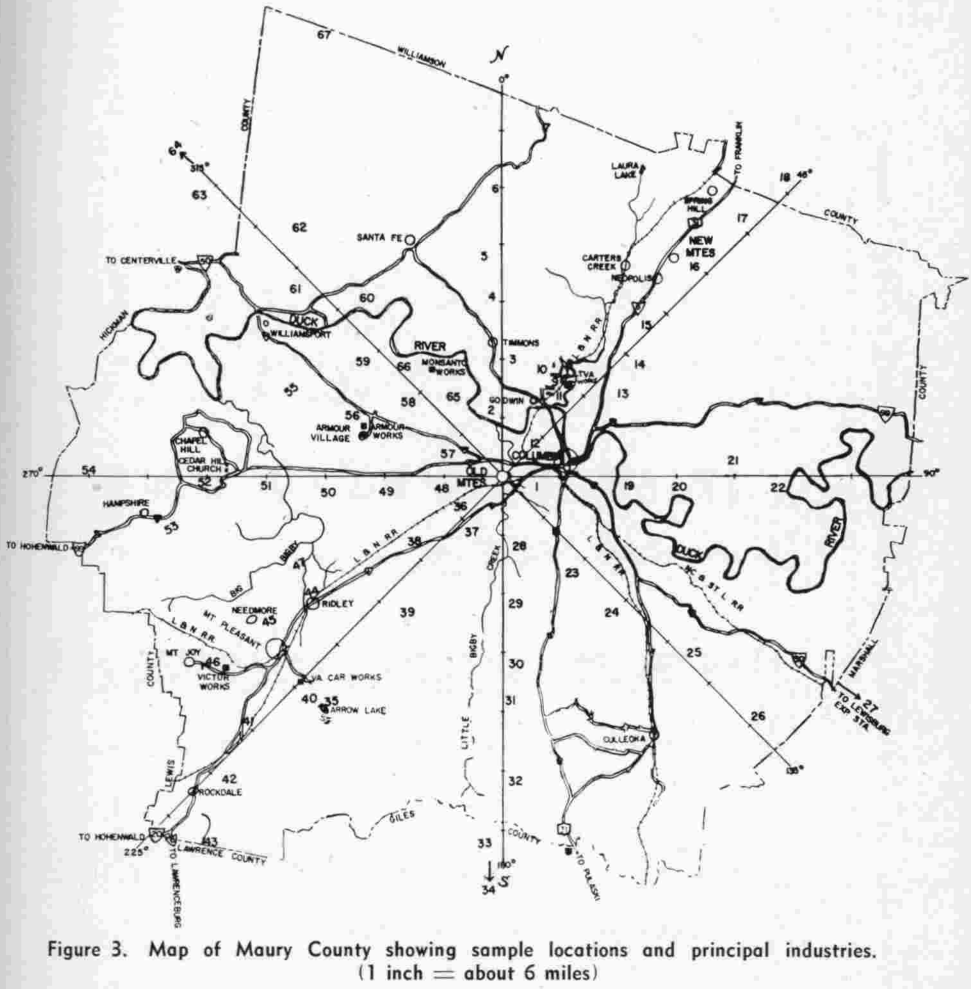

Figure 3. Map of Maury County showing sample locations and principal industries. (1 inch = about 6 miles)

radius from a point in the field, and well away from dusty roads. For the purpose of this survey, vegetation samples were cut some 3 to 4 inches above ground to minimize soil contamination, unless the growth was insufficient to permit this. The cut forage was placed in a 2-quart jar to which 5 grams of low-fluorine calcium oxide and a lump of ammonium carbonate had been added as fluorine fixatives. The closed jar was shaken to distribute the fixative materials throughout the sample, and after standing at

Table 10 — *Fluorine Content*[a] *of Soils Sampled in Maury County, Tennessee.*

Map location[b]	Location no.[b]	1949 No. of samples	1949 Fluorine	1952 No. of samples	1952 Fluorine	1953 No. of samples	1953 Fluorine	1954 No. of samples	1954 Fluorine	1955 No. of samples	1955 Fluorine	Total samples	Mean
			ppm		ppm		ppm		ppm		ppm		ppm
0-0	1	3	1170	3	561	5	353			1	1380	12	695
0-2	2	2	1470	1	1505							3	1482
0-4	3	2	2850	1	883							3	2194
0-6	4	1	210	1	5325							2	2768
0-8	5	2	1200	1	821	3	483	1	568			7	748
0-10	6	2	430	1	805							3	555
0-12	7	2	350	1	248							3	316
0-17	8	1	130			3	161	1	185			5	160
23-4	9					1	739	1	2961	1	1023	3	1574
22-5	10	1	1700	1	2250							2	1975
30-4	11					1	1433	1	443	3	603	5	864
30-5		2	520	1	909							3	650
45-2	12	2	350	1	1280	2	285	1	338			6	563
45-4	13	2	950	1	851			5	699			8	781
45-6	14	2	835	1	181	3	402			4	422	10	475
45-8	15	2	415	1	370							3	400
45-10	16	2	335	1	215	5	331	2	673	2	507	12	408
45-12	17	2	245	1	185							3	225
45-14	18	1	280	1	230							2	255
90-4	19	2	980	1	450							3	803
90-6	20	2	1100	1	721	3	426	2	1923	1	756	9	978
90-8	21	2	4600	1	336							3	3179
90-10	22	2	410	1	523							3	448
135-4	23	2	660	1	216							3	512
135-6	24	2	310	1	240							3	287
135-8	25	2	455	1	298	2	228	3	373			8	348
135-12	26	1	560	1	380							2	470
135-21	27					8	469	3	442	3	347	14	437
180-2	28	1	760									1	760
180-4	29	1	830	1	1935							2	1383
180-6	30	2	4780	1	456	2	499					5	2203

180-8	31	2	1055	1	216	2	888	2	660	1	250	8	709
180-10	32	2	1515	1	1560							3	1530
180-12	33	2	230	1	206							3	222
180-14	34	2	1450	1	275							3	1058
215-10	35	1	2500	1	1255							2	1878
225-1	36	2	375	1	392							3	381
225-2	37	2	485	1	270	5	344	3	404	8	476	19	420
225-4	38	2	1285	2	605							4	945
225-6	39	3	1535	1	397							4	1251
225-10	40	2	1800	1	628							3	1409
225-12	41	2	720	1	699							3	713
225-14	42	2	630	1	365	4	437			2	328	9	448
235-8	44	2	1030	1	533							3	864
247-8	47	1	390			3	506	2	459			6	471
270-2	48	2	2185	1	4815	3	1162	3	1788			9	2004
270-4	49	2	1980	1	383							3	1448
270-6	50	2	2450	1	315							3	1738
270-8	51	2	520	1	315	3	273	2	332	4	202	12	304
270-10	52	2	1165	1	510							3	947
270-12	53	3	643	1	863							4	698
270-14	54	2	1600	1	1370							3	1523
292-8	55					2	1221					2	1221
295-6	56	2	415			5	862	1	328			8	684
315-2	57	3	3675	1	1360	2	582	2	1631			8	2101
315-4	58	2	1675	1	968	2	287	3	392	4	311	12	609
315-6	59	2	275	1	200	1	193	3	206			7	223
315-8	60	1	5600	1	2150	5	1058	1	236	1	363	9	1515
315-10	61	1	2000	1	1940							2	1970
315-12	62	2	270	1	186	3	166	1	205	1	165	8	199
315-14	63	2	890	1	310							3	697
315-16	64	1	260	1	410							2	335
320-4	65	2	3040	1	361							3	2147
320-5	66	1	4500	1	1790							2	3145
338-15	67	1	200			2	147			1	153	4	162

[a]Average of the analyses of the number of samples shown.

[b]Map locations given in degrees and miles from the old Middle Tennessee Experiment Station near Columbia. Samples were collected on a farm corresponding as nearly as possible to the indicated map location shown by the number on the map, Figure 3.

least overnight, the entire sample was dried in an oven at about 60 degrees C., then ground in a Wiley mill preparatory to analysis.

In the laboratory, appropriate analytical charges (2 to 5 grams) of the sample were mixed with a slurry of low-fluorine lime, dried and incinerated at 550-600 degrees C. The F (in the ash) was then steam-distilled from perchloric acid at 135 degrees C. and the fluorine in the distillate was analyzed in accordance with the Willard and Winter procedure (24). Results were corrected for reagent blank and for the weight of lime added to the green sample as fixative, and reported as parts per million F.

The designation of the sample locations, number of samples analyzed, minimum and maximum fluorine content and the average fluorine content for the years 1949-1955 are given in Table 9.

Fluorine Content of Soils. Because of the possible relationship of the fluorine in the soil to the fluorine content of the crop grown on it (11) (9), a survey was made to determine the amount of fluorine in many soils of the area. The samples were taken from the upper 6-inch level of soil and at the same map locations designated for collection of vegetation samples (Figure 3). After reaching the laboratory, the soil samples were dried, crushed and thoroughly mixed. A representative subsample was ground to pass a 100-mesh sieve and 0.5 gram portions were analyzed by the A.O.A.C. method (1). By this method, the analytical charge is steam-distilled from sulfuric acid at 165 degrees C to collect 500 milliliters of distillate. The distillate is maintained at a slightly alkaline condition by addition of sodium hydroxide, evaporated to dryness, then transferred to the distillation flask and again steam-distilled from perchloric acid at 135 degrees C. The fluorine of this purified distillate is determined by titration with thorium nitrate (24).

This method, as it now appears in the Book of Methods, was developed from work in the Tennessee Station laboratories as a part of the investigation of the fluorine problem. Before final acceptance as "Official," comparisons were made on samples of many soil types and collaborative results from several other laboratories were evaluated and published (16) (14) (3) (4) (5).

The results of the analyses of Maury County soils are shown in Table 10. The fluorine contents varied widely, ranging from high values comparable to the percentage found in phosphate rock of near-commercial quality, to low values similar to those characteristic of non-phosphatic soils.

As a more specific comparison between the fluorine content of the soil and that of the vegetation grown on it, samples of soils and vegetation were collected simultaneously at nine locations for 4 years. The results of this study are shown in Table 11.

Table 11 — *Fluorine in Crops and Soils Sampled Simultaneously at Nine Points in Maury County.*

Map location[a]	Location no.[a]	Fluorine content, dry basis[b]									
		1949		1952		1953		1954		Mean	
		Veg.	Soil	Veg.	Soil	Veg.	Soil	Veg.	Soil	Veg.	Soil
		ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
0-8	5	35	1000	18	821	43	483	24	568	30	718
45-2	12	46	310	31	1280	212	285	52	338	85	553
90-6	20	24	1700	24	721	19	426	99	1923	42	1193
135-8	25	14	510	20	298	14	215	14	373	16	349
180-8	31	20	650	20	216	22	888	65	660	32	604
225-2	37	21	483	17	270	34	344	39	404	28	375
270-2	48	33	470	38	4815	32	1162	125	1788	57	2059
315-2	57	73	1900	24	1360	73	582	37	1631	52	1368
315-12	62	43	380	9	186	25	166	8	205	21	234

[a]Map locations given in degrees and miles from the old Middle Tennessee Experiment Station near Columbia. Samples were collected on a farm corresponding as nearly as possible to the indicated map location shown by the number on the map, Figure 3.

[b]The values for 1949 are for single samplings per farm other than the mean for 2 samplings at location No. 37; the 1952 values are from single samplings; the 1953 values are respective means for 3 to 5 samplings on each farm; the 1954 values are for either single samplings or for the respective means of three samplings on each farm.

There seems to be no definite correlation between the fluorine content of the soil and that of the vegetation. In some cases it is observed that the fluorine content of the soil is very high, whereas that of the vegetation from the same farm is low. The opposite condition also is observed. A possible explanation may be that the high fluorine contents of crops grown on soils of low fluorine content are due to effluent fluorine materials; also, the opposite condition, in which the fluorine content of vegetation is low although that of the soil is high, may be due to the presence of good growth that serves to minimize soil contamination by splashing.

Fluorine Content of Surface Waters. As an additional means of establishing the fluorine distribution in the area, the survey was extended to include collection and analysis of water samples from various streams, rivers, farm ponds, and springs at, or in the vicinity of the regular sampling locations.

The fluorine contents of the Maury County water samples probably are due principally to suspended soil particles that are high in fluorine, as would be expected, as apatite the main fluoride-mineral is highly insoluble. Analyses of both unstirred and stirred, or muddy, waters are shown in Table 12. In general, the fluorine

Table 12 — *Fluorine Content of Surface Waters*[a] *Sampled Before and After Stirring in Maury County.*

Map location[b]	Location no.[b]	Fluorine content[c] Unstirred[d]	Fluorine content[c] Stirred[d]
		ppm	ppm
0-0	1	(2) 0.15	1.10
0-2	2	0.85	
0-4	3	0.10	
0-6	4	0.34	
0-8	5	(2) 0.27	8.44
0-10	6	0.25	
0-12	7	(2) 0.32	1.36
0-17	8	0.13	1.18
23-4	9	2.03	17.23
30-4	11	0.35	2.43
45-2	12	0.23	0.33
45-4	13	(3) 0.51	(2) 4.06
45-6	14	(3) 0.52	(2) 4.39
45-8	15	0.29	
45-10	16	(14) 0.47	(11) 3.66
45-12	17	0.21	
90-4	19	0.11	
90-6	20	(2) 0.43	7.50
90-8	21	(2) 0.65	5.99
90-10	22	0.40	
135-4	23	0.42	
135-6	24	0.29	
135-8	25	(2) 0.48	9.44
135-12	26	0.29	
135-21	27	(2) 0.57	(2) 1.92
180-2	28	0.98	
180-4	29	0.62	
180-6	30	(2) 0.26	0.78
180-8	31	(2) 0.40	3.63
180-10	32	(2) 0.26	
180-12	33	0.06	
180-14	34	0.10	
225-2	37	0.26	0.25
225-4	38	0.26	
225-6	39	0.33	
225-10	40	0.26	
225-12	41	0.41	
225-14	42	(2) 0.15	1.78
225-16	43	0.06	
247-8	47	(2) 0.14	0.19
270-2	48	(2) 0.52	0.38
270-4	49	0.88	
270-6	50	0.52	
270-8	51	0.45	

Table 12 — (Continued)

Map location[b]	Location no.[b]	Fluorine content[c]	
		Unstirred[d]	Stirred[d]
		ppm	ppm
270-9		1.63	1.65
270-10	52	0.45	
270-12	53	0.02	
270-14	54	0.43	
292-8	55	(2) 0.45	10.69
300-5		(3) 0.41	(2) 5.67
315-2	57	(2) 0.67	15.50
315-6	59	(4) 0.85	3.36
315-8	60	(4) 0.42	(2) 3.51
315-10	61	0.24	
315-12	62	(2) 0.11	0.48
315-14	63	(2) 0.14	
315-16	64	0.12	
330-5		0.17	1.68
338-15	67	0.09	0.31

[a]Ponds, streams, springs, etc. used as drinking water for livestock on the respective farms.

[b]Map locations given in degrees and miles from the old Middle Tennessee Experiment Station near Columbia. Samples were collected on a farm corresponding as nearly as possible to the indicated map location shown by the number on the map, Figure 3.

[c]Averages of analyses of samples collected in 1949, 1951, and 1954. Single samples unless otherwise indicated by a number in parenthesis beside the fluorine value.

[d]Ponds or streams were actually stirred up to simulate a muddy condition such as caused by livestock wading or by run-off from heavy rains. The unstirred samples represented relatively clear water sampled under normal conditions.

contents of the clear waters were below the level that would be damaging to livestock that drink those waters, but might be sufficient to supplement the fluorine intake from other sources so that the total amount would be detrimental. The data in many cases indicate amounts of fluorine in excess of tolerance levels in waters when muddied, either by animals wading in ponds or by soil wash due to heavy rainfall.

Summary and Conclusions

A condition in livestock diagnosed as fluorosis was observed in Maury County about 1946.

Possible sources of fluorine in vegetation were explored by analyses of air, waters, soils, and industrial materials. The uptake of fluorine by plants from soils, with and without fluorine additives, was studied in greenhouse and field cultures. The fate of fluorine in soils was studied by means of water leachings in lysimeters. The fluorine content of vegetation was determined when grown on soils of high and low fluorine contents at the native locations of the soils and at various locations to which they were transported.

The fluorine content of plants grown in washed air was determined in comparison with that of plants grown in normal air at several locations; Spanish moss and lime-impregnated filter papers were found to acquire fluorine during exposure at above-ground locations and registered differences that were attributed to variations in atmospheric fluorine at various locations.

Surveys, including analyses of a large number of samples collected at many locations in Maury County over a period of several years, established the occurrences and geographical distribution of fluorine in vegetation, soils, and waters.

From the results obtained in these studies and surveys it was concluded that:

1) Appreciable amounts of fluorine were present in the atmosphere in certain areas as shown by analyses of rainwater and by enhancement in the fluorine content of exposed Spanish moss and lime-impregnated filter paper.

2) The amount of fluorine washed down in rainwater and the enhancement in the fluorine content of moss and filter paper were in relation to the proximity of the samples to areas of fluorine emissions.

3) Fluorine present in the atmosphere is one source of abnormal fluorine content of vegetation as shown by the low fluorine content registered by plants grown in washed air in comparison with those grown in unwashed air in an area that was subjected to fluoride effluents.

4) Plants grown on soils of high natural or added fluorine content do not acquire abnormal fluorine contents provided that the soil contains adequate calcium, that the growth is made at a location remote from fluorine emissions, and that there is no contamination by splash or dust; the clear drainage waters from such soils do not contain appreciable amounts of fluorine.

5) Crops grown on soils of moderate to high fluorine content may acquire abnormal fluorine from soil dust or from soil splash by rains, especially under conditions of poor ground coverage due to sparse stand, poor growth, over-grazing, or drought.

6) Dust and soil splash caused by rain, as well as atmospheric contamination from industrial fluoride effluents, may contribute to the occurrence of fluorine in forage above levels considered critical for animals consuming that forage.

7) Clear waters from ponds, streams and springs usually did not contain sufficient fluorine to be of any consequence as a cause of fluorosis.

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