

with low moisture content, usually have a higher content of water-soluble phosphorus.

Conclusions

In this study not enough samples represented any given set of chemical, mechanical, and physical conditions to prove any point. However, trends in results did suggest some factors or group of factors which influenced the water solubility of phosphorus in these fertilizers. Any addition to superphosphate (except sulfuric acid and borax) reduced the percentage of water-soluble phosphorus. High moisture in mixed goods usually reduced the content of water-soluble phosphorus, unless the superphosphate had been previously based down as ammoniated superphosphate. Rapid drying and cooling to decrease the moisture content generally maintained a high percentage of water-soluble phosphorus. Mechanical steps in plant

operation could be an important factor to watch in maintaining high water-soluble phosphorus.

The average water-soluble phosphorus value for about 250 samples was 48.4% well within the limits of 40 to 50% proposed by research agronomists. Less than 23% of the samples failed to reach the minimum value of 40%. These lower values were mostly from the southeastern part of the country, where the need for a high water-soluble phosphorus is less, as most soils have been fertilized for a long time and are higher in available phosphorus, and from the older and less modern plants. As the more modern plants manufacture fertilizer of consistently higher values, it seems that fertilizer of 60 to 65% water-soluble phosphorus content can be made in a regular fertilizer plant with the usual fertilizer ingredients, if continued agronomic study suggests that this is desirable.

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ATMOSPHERIC POLLUTION

Spanish Moss and Filter Paper Exposures for Detection of Air-Borne Fluorides

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Intensities of fluorine emissions to the atmosphere in certain eastern and central Tennessee locales were determined by month-long covered field-exposures of Spanish moss in cotton (cord), nylon, and dacron bags and of 12.5-cm. lined filter papers. Fixations in covered cord and nylon bags were similar to and greater than fixations in the less porous dacron bags, and were greater in the outer zones than in the cores of the moss. Drying the moss decreased its capacity to fix air-borne fluorides. Fixations by the moss in the protected cord and nylon bags and by protected lined filter papers were consistently concordant in spotting high and low occurrences of fluorine in the atmosphere.

THE WASHDOWN OF FLUORIDES and their fixation by Spanish moss have served to indicate atmospheric emissions deemed responsible for abnormal incidence of fluorine in nearby field crops (6) and a resultant economic problem in livestock farming (5). The quantities of fluorine carried by single rainfalls at six locations in 1948, 1949, and 1950 were reported in 1952 (8) and, in 1951, atmospheric occurrences were determined also through the quantities fixed in month-long exposures of Spanish moss at multiple locations in relation to industrial emissions in three Tennessee counties (7).

No fluorine contamination occurred in the vegetation grown in pot cultures

at Knoxville, but fluorine content increased during further growth outdoors at the Middle Tennessee Station, although not in the transported vegetation grown in the fluorine-free atmosphere of an adjacent chamber (7). Thus the transported plants acquired fluorine from both soil and air during their 21 days' growth at Columbia, whereas the plants in the chamber derived fluorine solely from the soil.

The atmosphere near Knoxville was examined frequently through exposures of sodium carbonate and hydrated lime, and hydrofluoric acid was identified as the chief fluorine contaminant at the university's Blount County Farm, some 6 miles from the manufacture of aluminum in a large operation (6). Hydrofluoric acid was identified also as the chief fluorine emission in the thermal con-

version in the defluorination of Tennessee brown rock phosphate into "fused tricalcium phosphate" (1), whereas hydrofluosilicic acid and silicon tetrafluoride are emitted in the nodulization of charges of rock phosphate for the electric reduction furnace and in acidulations of rock phosphate. At one time all three processes were in operation in Maury County.

The findings reported here were from further studies of the fixation of atmospheric fluorides by Spanish moss, variously bagged, and by exposures of lined filter papers at multiple locations in Blount and Maury Counties.

Source and Composition of Moss

Several 100-pound supplies of moss were obtained at intervals from the same

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Table I. Partial Analyses of Spanish Moss

(Before and after month-long exposures in Maury County in 1954, moisture-free basis)

Components ^a	Sample A	Sample E	Sample B	Sample C
	Parts per Million			
Fluorine	15	51	13	13
	Per Cent			
SiO ₂	1.05	1.40	1.43	0.93
Calcium	0.70	0.75	0.70	0.70
Magnesium	0.26	0.26	0.34	0.29
Potassium	0.76	0.95	0.97	0.63
Sodium	0.44	0.47	0.44	0.56
Fe ₂ O ₃	0.71	0.76	...	0.36
P ₂ O ₅	0.13	0.16	0.10	0.10
Al ₂ O ₃	0.50	0.39	...	0.30
Nitrogen	0.78	0.73	1.00	0.60
Sulfur	0.17	0.18	0.17	0.18
Ash	4.38	5.10	6.20	3.55

^a Determinations other than fluorine made by A. J. Sterges by AOAC methods. Determinations of fluorine made by junior author by 12 perchloric acid distillations of limed 5-gram charges calcined at 500° C. and calcines subjected to 3 KOH fusions (3).

Sample A. Not exposed; from bulk of moss received in February 1954, ground immediately.

E. Sample A after month-long exposure in Maury County.

B. Not exposed; received in August 1954.

C. Received in June 1954 and left in bulk indoors at Knoxville until ground for analysis, February 1955.

Table III. Fluorine Contents of Samples of Spanish Moss

(Through analyses of moist and dried charges and computations to dry basis subsequent to 2-weeks umbrellaed exposures in Middle Tennessee^a)

Placement	Bag	Moisture, %	Fluorine Content of Analytical Charge, P.P.M.		
			Undried charge ^b	Dried charge ^c	Computed to dry basis ^d
Original ^e	7.34	..	23.1
Old MTES	Cord	33.2	26	35	39
		35.6	32	43	50
		29.7	30	42	43
		30.9	36	51	61
	Mean	...	31	43	48
	Nylon	30.6	37	53	53
		31.4	40	55	58
		39.5	38	57	63
		31.7	43	56	63
	Mean	...	40	55	59
Baker farm	Cord	42.0	40	60	69
		28.6	32	44	45
		41.2	46	76	78
		29.1	40	58	56
	Mean	...	40	60	62
	Nylon	46.9	43	85	81
		51.3	33	64	68
		51.6	26	49	54
		56.9	30	58	70
	Mean	...	33	64	68
Crossville	Cord	36.2	22	25	34
		43.0	13	21	23
		38.0	14	22	23
		36.3	19	27	30
	Mean	...	17	24	28
	Nylon	41.9	16	26	28
		46.7	15	26	28
		50.1	15	25	30
		55.4	12	21	27
	Mean	...	15	25	28

^a Duration, April 17, 1954, to May 1, 1954.

^b Charge of undried moss was limed, dried, ashed, and fluorine distilled from ash by means of HClO₄.

^c Moss dried 5 days at 50° C.

^d Calculated from fluorine determination on undried charge in relation to per cent moisture by following equation:

$$\frac{\text{p.p.m. F, undried basis}}{1.00 - \text{fraction wt. H}_2\text{O}} = \text{fluorine, dry basis}$$

^e Findings are for actual contents; data for original sample are given in Table I.

Table II. Fluorine Occurrence in Spanish Moss

(HClO₄ distillations of 5-gram charges limed and calcined at 500° C. Calcines alone and after fusions with NaOH or KOH)

Moss	Nonfused, P.P.M.	NaOH	KOH
		Fusions, P.P.M.	Fusions, P.P.M.
1 ^a	19	20	20
	19	20	20
	18	20	21
Mean	19	20	20
2 ^b	29	30	27
	29	29	29
	29	30	..
Mean	29	30	28
3 ^b	..	76	83
	77	78	79
	78	77	79
Mean	78	77	80
4 ^b	81	80	..
	78	78	..
	76	74	..
Mean	78	77	..

^a Composite, not exposed.

^b Same composite, subsequent to exposure in field.

location near Tallahassee, Fla., through collaboration of R. C. Crooks, assistant state chemist. The analyses of Table I, other than determinations of fluorine, were made by AOAC methods (7). Although the moss is an epiphyte, it acquired appreciable mineral composition, nitrogen, and considerable ash during its life in Florida. Samples A and E were identical before the month-long exposure of sample E had caused significant increases in fluorine and silica content and some gains in calcium, potassium, phosphorus pentoxide and ash. The substantial intake of fluorine indicates that the moss had taken up atmospheric fluorides and the other increases suggest contamination from phosphatic dusts.

The compositions of the moss samples of Table I afforded an opportunity to ascertain whether the incidence of silica could be charged with the low value from the perchloric acid distillations from unfused calcines of limed charges of moss. The analyses of Table II show uniformity in the fluorine determinations on the unfused and the sodium and potassium hydroxide fusions of calcines of limed 5-gram charges of four samples of moss. The distillations were by means of the Willard and Winter procedure (12) with modifications (2).

Although silica is essential to the perchloric and sulfuric acid-induced expulsion of silicon tetrafluoride, the presence of hydrated silica in an analytical charge will cause incomplete recovery of fluorine, especially when silica accumulates on the walls of the Claisen flask.

The concordance in the distillates from

the unfused calcines and the parallel sodium hydroxide and potassium hydroxide fusions indicates that the silica contents of the moss did not necessitate the prefatory fusions that have been found imperative in the determination of fluorine in certain types of low-growth vegetation, such as Bermuda grass (17). The analyses also register identical values from the two hydroxides as fusion reagents (3). The alumina contents of samples A, E, and C were determined because experience demonstrated that although fluorine was recovered fully from greenhouse cultures on soils fortified with fluorides (9), fusion of the calcines of limed charges of Bermuda grass and similar field vegetation usually had a concomitant incidence of alumina with high contents of silica. Many samples of vegetation had higher silica and alumina contents in portions closer to the ground, and it appeared probable that the low values for unfused calcines of the lower growth field vegetation were attributable to splatterings of clayey material, rather than to silica itself.

Preliminary Determinations

Because of natural variance in the structure of the Spanish moss, exposures were made in quadruplicate. Grinding of the moss of multiple collections to provide analytical samples by means of the Wiley mill would have required many hours of labor. Although the moss seemed relatively dry, it had a moisture content of 60% and could not be ground without previous drying. A

Table V. Fluorine Acquired by Outer Layers and Cores of Umbrellaed (Figure 2) Charges of Spanish Moss

(After month-long exposures at two locations in Blount County in 1955)

Location ^a	Fluorine, P.P.M., Dry Wt. Basis		
	Entire exposure	Outer layer	Core
Alcoa 19 ^b	39, 24, 23, 44	29, 36, 32, 42	17, 37, 28, 47
Mean	33	37	32
Alcoa 20 ^b	47, 31, 33, 41	56, 38, 44, 32	42, 27, 38, 28
Mean	38	43	34
Alcoa 19 ^c		93, 113, 40, 62, 104, 141, 79, 97	54, 65, 29, 59, 56, 76, 27, 43
Mean	75 ^d	91	51
Alcoa 20 ^c		80, 76, 88, 62 100, 54, 78, 74	54, 30, 40, 37, 76, 24, 38, 48
Mean	63 ^d	77	42
Blank, applied	19		

^a Designations for locations given on grid of Figure 1.

^b Exposed April 22 to May 20.

^c Exposed May 20 to June 17.

^d Value computed.

partial drying of a month-long exposure of moss would have necessitated two moisture determinations on every "exposure." It was feared, however, that heating the bulk of the moss at the temperature of boiling water might cause an appreciable loss in fluorine content before analysis. The alternative was to heat the multiple tared exposures of normal moss moderately, immediately, and simultaneously upon receipt by the laboratory, the temperature and duration being such as to assure minimal losses of fluorine in the moisture-free samples for bottling and analysis. Consequently, multiple samples of unground normal

moss were subjected to 50° C. for successive weighings after intervals of 2, 3, 4, and 5 days and an uninterrupted interval of 5 days. In comparisons to register removal of moisture contents up to 59%, the moisture-free values obtained after the 2-day heatings at 50° C. were virtually the same as those obtained from the longer heatings.

However, because of the possibility that heating, even at 50° C. might cause the moss to lose fluorine, quadruplicates of unheated moss and of heated charges of the same moss were analyzed. The findings given in Table III are without deduction of the natural content of

Table IV. Fluorine Content of Spanish Moss

(After exposure inside and outside^a at 6 points in Blount County and at University of Tennessee lysimeters)

Exposure ^a	First Collection		Second Collection		Third Collection		Fourth Collection	
	Rainfall, inches	Fluorine, ^b p.p.m.	Rainfall, inches	Fluorine, ^b p.p.m.	Rainfall, inches	Fluorine, ^b p.p.m.	Rainfall, inches	Fluorine, ^b p.p.m.
	6-15-51		7-12-51		8-24-51		9-18-51	
Hitch farm (5-21-51)								
Inside	8.91	25	3.50	32	2.89	54
Outside	5.41 ^c	50	3.50	75	3.50	76	2.89	92
Magill farm (5-4-51)								
Inside	4.97	38	3.50	34	3.50	70	2.89	130
Outside	4.97	53	3.50	107	3.50	101	2.89	146
Kidd farm (5-4-51)								
Inside	4.97	91	3.50	80	3.50	168	2.89	192
Outside	4.97	64	3.50	105	3.50	63
Pumping station (5-14-51)								
In shed	4.19	52	3.50	91	3.50	268	2.89	534
In tree	4.19	99	3.50	107	3.50	210	2.89	67
Near pot room (5-26-51)		7-5-51		7-30-51				
Outside	7.78	1240	1.86	1300	1.42	2418	2.89	1760
Operation A (5-26-51)								
Outside	7.78	50	1.86	127	1.42	126	2.89	133
U.T. farm (Blount) (5-26-51)								
Inside	7.78	38	1.86	99	1.42	79	2.89	103
Outside	7.78	29	1.86	44	1.42	58	2.89	48
U.T. lysimeters (5-26-51)								
Inside	2.12	31	1.57	29	4.83	27
Outside	6.31 ^d	61	2.12	51	1.57	60	4.83	70

^a Inside, protected from rain, but subject to atmospheric circulation; outside, generally in tree.

^b Air-dry basis.

^c Rainfall at locations other than six U.T. lysimeters measured at U. S. Weather Bureau, Knoxville airport.

^d Rainfall measured at U.T. lysimeters. Fluorine content of Florida moss, 27 p.p.m. on air-dry basis.

fluorine, which is reported as "original." The moss exposures had been in cord and nylon bags at the abandoned Middle Tennessee Experiment Station, on location 15 (Baker farm) in Maury County, and near Crossville on the Cumberland Plateau.

The means of the quadruplicates of the dried charges were less than the corresponding means obtained through com-

putation of the analytical findings from the normal moss to dry basis. The six means for the 24 findings for fluorine contents of the dried charges registered 45 p.p.m. against a corresponding overall mean of 49 p.p.m. for the values calculated from the analyses of the original samples. The determinations by the two procedures indicate that the normal, or original, charges suffered

small losses of fluorine during the 2-day heating at 50° C. However, the analysis of variance showed no significant difference and possible losses of fluorine during the immediate conversion of the collections of the "exposures" to a moisture-free basis are not rated as enough to vitiate appreciably the analytical findings as to intake of atmospheric fluorides by the dried moss. Consequently, the subsequent periodic collections of moss were heated immediately at 50° C. for 2 days to obtain analytical charges of moisture-free vegetation.

Table VI. Fluoride Contents of Samples of Spanish Moss

(Unbleached, water-leached, and ethyl alcohol-leached before and after 2-week exposure at Blount County Farm, March 27, 1954 to April 10, 1954)

Sample	Bag	Moisture, ^c %	Fluorine Content, P.P.M.					
			In Unleached Charge		In H ₂ O-leached ^a Charge		In Ethyl Alcohol-Leached ^b Charge	
			Wet basis ^d	Calcd. to dry basis ^e	Wet basis ^d	Calcd. to dry basis ^e	Wet basis ^d	Calcd. to dry basis ^e
Original	...	57.9	9.0	21	8.0	19	7.8	19
	...	57.9	10	24	7.3	17	9.1	22
	...	56.2	9	21	5.4	12	7.7	18
Mean	9.0	22	7.0	16	8.2	20
Exposed	Nylon	57.9	13	31	10	24	14	33
		60.9	12	31	10	26	16	41
Mean	13	31	10	25	15	37
	Cord	58.0	12	29	9.0	21	11	26
		56.3	11	25	9.0	21	12	27
Mean	12	27	9.0	21	12	27

^a Charge of undried moss leached with 250 ml. of boiling distilled water, limed, dried ashed; fluorine determined through HClO₄ distillation.

^b Charge of undried moss leached with 100 ml. of boiling ethyl alcohol, limed, dried, ashed, and fluorine determined as in ^d.

^c Mean of five moisture determinations on charges of each of 9 samples after 5-day drying at 50° C. was 58%.

^d Charge of undried moss was limed, dried, ashed, and fluorine determined by means of HClO₄ distillation (8).

^e Calculated from wet moss fluoride determination and per cent moisture, using equation:

$$\text{P.p.m. F, dry basis} = \frac{\text{p.p.m. F}^-, \text{ wet basis}}{1.00 - \text{fraction wt. H}_2\text{O}}$$

Intake of Air-Borne Fluorides by Field Exposures of Spanish Moss

In Blount County Table IV reports occurrences of fluorine in moss after month-long exposures in 1951 at the six locations in Blount County, where aluminum is manufactured in absence of phosphate operations, and at the lysimeters at Knoxville. The exposures were made in outdoor shelters and in the open. In general, the "outside" exposures showed larger fixations of fluorine, in spite of rainfall or because of it; but the relationships varied. The nearer the location to the "pot room" of the aluminum operation, the higher was the fluorine fixation by the moss, to a maximum of 2418 p.p.m. All the collections at the lysimeters in Knoxville showed gains in fluorine content, presumably because of emissions from the stacks of manufacturing operations.

Surface vs. Cores of Moss Exposures. A question arose as to whether the fixation of fluorine was effected throughout

Table VII. Fluorine Acquired from Atmosphere

[By identical charges of Spanish moss placed 7 feet above ground at 12 locations in Middle Tennessee, 1954, as indicated by analyses of charges after month-long exposures in coarse-mesh cotton and nylon bags, under individual umbrellas of aluminum foil (Figure 2)]

No.	Farm	May		June		July		August		September		October		November		Mean	
		C ^a	N	C	N	C	N	C	N	C	N	C	N	C	N	C	N
Parts per million																	
1	Old Station	77	81	35	26	43	29	60	45	23	24	43	34	44	41	46	40
18	New Station	67 ^b	46 ^b														
		41	45	31	30	38	32	43	64	19	19	27	29	21	26	32	35
15	Franklin Baker	38	30	13	15	20	19	32	45	22	12	27	25	19	23	24	24
		97	117	145	144	63	53	99	106	38	30	40	41	38	41	74	76
78	Goodwin (Dungye)	57 ^b	56 ^b														
		92	103	37	37	102	65	41	24	51	49	63	53	130	123	74	65
90	Southern	78	69	29	37	36	42	28	17	38	18	35	31	50	53	41	37
66	Webster	34	41	28	28	40	45	25	36	22	17	67	59	56	53	39	38
58	Pitts (Allen)	81	91	42	34	68	43	33	40	37	27	132	162	88	97	69	72
37	John Gray (Garrett)	41	36	21	27	39	34	35	23	25	15	41	35	43	27	35	28
23	Holcomb	34	37	...	27	38	34	31	24	15	17	16	10	25	16	27	24
5	Watson	52	62	34	32	41	25	43	33	17	21	36	39	31	33	36	35
109	Murrey	126	135	60	46	55	76	23	23	33	30	50	40	58	58
Mean			62		48		43		44		25		46		49		44
	Crossville	11	10	1	6	11	10	13	18	1	0	3	3	9	4	7	7
		8 ^b	6 ^b														
Blank	12																

^a C. Coarse-mesh cotton bag. N. Nylon bag, comparable to C in size.

^b After 15-day exposures, quadruplicate bags were removed to ascertain whether 2-week duration was ample for exposure; not included in means of month-long exposures.

^c On parallel charges sterilized before exposure.

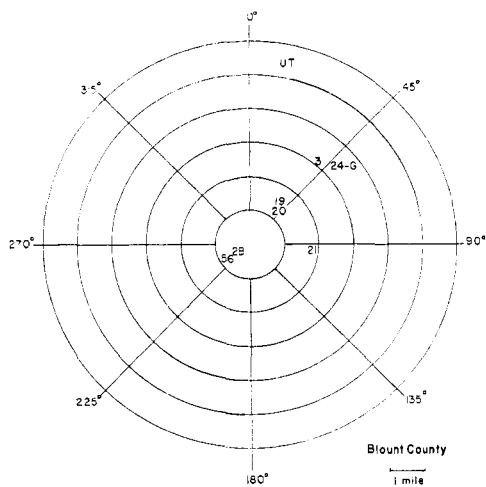


Figure 1. Grid showing numerically locations of exposures of Spanish moss and limed filter papers in Blount County

Numbers correspond to those used in general fluorine survey, center being Alcoa pot rooms

the bulk of a moss exposure, or entirely on its outside layers. Consequently, the normal exposures were made in parallel with exposures in which the cores were demarcated and made available for comparative analyses. The data of Table V show that the outer layers of the "umbrella"-protected exposures acquired somewhat higher fluorine contents; but the cores also effected considerable stoppages of the air-borne fluorides (Figure 2).

Nature of Fluorine Fixations. The findings in Table VI are for fluoride residua after separate aqueous and alcoholic extractions from moss charges that had been exposed in cord and nylon bags under the protection afforded by the aluminum foil umbrellas on the Blount County farm, March 27 to April 10, 1954. The nine charges of the original moss had a common moisture content of 58%, and 9 p.p.m. of fluorine, which was computed to 23 p.p.m. on a dry basis.

The boiling water extractions effected 23% removal of the original fluorine content, but the leachings with hot ethyl alcohol did not remove fluorine. The alcohol-leached charges showed a mean of 27 p.p.m. of fluorine against 26 p.p.m. for the unleached moss. Although initial and acquired contents of fluorine were retained tenaciously against the alcoholic extractions of the moss, the question remains as to whether the retentions are attributable to engendered organic forms or to surface tension.

In Maury County Fluoric pollution of the atmosphere from multiple phosphate operations in Middle Tennessee locales was decidedly more complicated than in Blount County where the emissions were from a single operation. The intensities of atmospheric occurrences of fluorine at 12 loca-

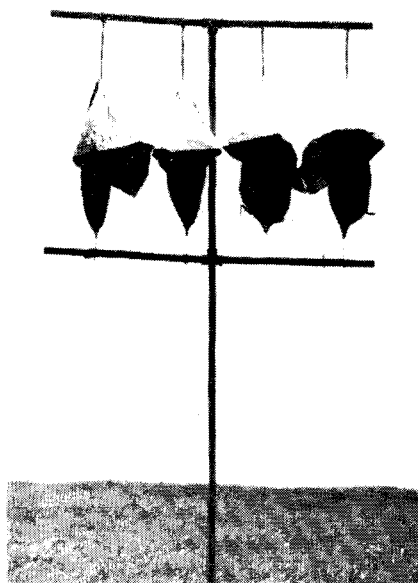


Figure 2. Spanish moss exposures 7 feet above ground

In cord and nylon bags with aluminum foil umbrellas and bottoms tied to lower horizontal pipe to keep bags upright

tions in Maury County were indicated by means of month-long umbrella-protected exposures of Spanish moss (Figure 2) in cord and nylon bags, side by side, from May through November 1954. The exposures at each location in Maury County were in quadruplicate at 7-foot elevation (Figure 2); but because of the meager occurrences of fluorine in the atmosphere at Crossville, eight bags of each type—cotton cord and nylon—were exposed there as controls. The bags were protected from rain by umbrella cones of aluminum foil, shown in Figure 2. The 100-gram charges of moss of established content of fluorine were bagged at Knoxville and transported to the Maury County locations designated on the grid of Figure 3, and to Crossville on the Cumberland Plateau. Because Spanish moss would not be expected to survive through the winters of East and Middle Tennessee, the moss exposures were made in the interim between the frosts of spring and fall.

The fixations by moss in the side-by-side exposures in the cord and nylon bags represent parts per million of acquired fluorine. The fluorine fixations by exposures in cord (C) bags and by the nylon (N) bags may show some variance for a given month in 1954; but the pairings in Table VII indicate no decided differences between maximal or between minimal fixations by the moss at the several locations. In May, June, and August, location 15 (Baker) showed the largest gains in fluorine content but the intakes at that location were less in September, October, and November. This was true also for 10 of the other 11 locations.

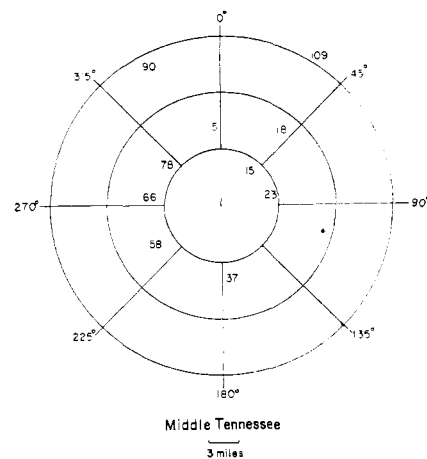


Figure 3. Grid showing numerically locations of exposures of Spanish moss and limed filter papers in Middle Tennessee, chiefly in Maury County

Numbers correspond to those used in general fluorine survey, center being the old Middle Tennessee Experiment Station

The largest over-all means for fluorine gains in the 7-month interval were at locations 15, 78, and 58. The largest mean of the gains per month was 62 p.p.m. for the 22 fixation values by exposures in May, and the smallest mean was that of 25 p.p.m. in September. The other means for monthly gains were in the range of 43 to 49 p.p.m.

The over-all comparisons of fluorine gains (last two columns in Table VII) register close to identical values for the moss in the two types of containers.

The greater occurrence of fluorine in the atmosphere of Maury County is reflected in contrast with indicated occurrence at Crossville in Cumberland County, the grand mean for the fixations at the 12 points in Maury County being 6.4 times the fixations at Crossville.

The fixations of fluorine by the moss in cord bags at the same 13 points were determined in May, June, July, and August 1955 (Table VIII). In general, the fixations were less than those in the corresponding months of 1954, especially in locations 15 (Baker), 78 (Goodwin), and 58 (Pitts).

After the analyses of Table VII had registered only small difference between fixations by the moss in the cord and nylon bags, a similar comparison was made for the moss in cord and dacron bags at three locations in May, June, July, and August 1955, with inclusions of nylon bags in exposures in July and August (Table IX). Nylon and dacron cloths were compared. Intake of fluorides was less in dacron bags of finer mesh. Every comparison shows a substantial difference between the fixations of fluorine by the moss charges in cord and dacron bags, as indicated by the ratios of 43:11; 46:16; 48:13, and 28:16 for month-long exposures. The

Table VIII. Fluorine Acquired by Month-Long Umbrellaed Exposures of Live Spanish Moss

[In cord bags at 13 points in Middle Tennessee, May-August 1955 (Figure 2)]

No.	Location	Fluorine, P.P.M., Dry Wt. Basis ^a			
		May	June	July	August
1	Old MTES ^b	33	21	34	26
18	New MTES ^b	20	..	29	22
	Franklin	22	..	16	20
15	Baker	44	54	60	31
78	Goodwin	31	63	61	36
90	Southern	35	27	28	14
66	Webster	33	31	48	14
58	Pitts	51	62	50	26
37	Gray	20	23	25	11
23	Holcomb	24	22	25	18
5	Watson	39	34	26	23
109	Murrey	29	..	24	18
	Crossville	5	8	4	8
	Blank, applied	19	19	18	18

^a Means of quadruplicate determinations of fluorine contents of monthly samples.

^b Middle Tennessee experiment stations.

Table IX. Fluorine Acquired by Month-Long Exposures of Live Moss

(In umbrellaed cord, nylon, and dacron bags at three locations in Middle Tennessee, May-August 1955)

No.	Location	Fluorine, P.P.M., Dry Weight Basis									
		May		June		July			August		
		Cord	Dacron	Cord	Dacron	Cord	Nylon	Dacron	Cord	Nylon	Dacron
1	Old MTES	33	8	21	9	34	38	13	26	34	12
15	Baker	44	12	54	15	60	29	13	31	39	12
58	Pitts	51	13	62	24	50	44	14	26	33	23
	Mean	43	11	46	16	48	37	13	28	35	16
	Blank applied	19		19		18			18		

differences reflect the restricted movement of air into and through the moss in the dacron bags. The fixations in the nylon bags were intermediate between the fixations in the cord and dacron bags in July, but in August were somewhat greater than in the cord bags. However, the over-all means for the cord and nylon bags were 38 and 36 p.p.m., respectively.

Effect of Heating Moss upon Its Capacity to Fix Fluorine

To obtain an indication as to whether fluorine gains by the live moss might be due in part to stomatal action, charges were heated 5 days at 50° C. and then exposed in juxtaposition to like unheated charges for 4 weeks at the Baker farm, location 15 on the grid of Figure 3, where the atmospheric occurrences of fluorine are always high.

The comparisons for the May, June, July, and August exposures show that the heating of the moss caused a decided decrease in its capacity to fix fluorine from the atmosphere. The means for the fluorine fixations by the live moss and heated moss in May, June, July, and August 1955 were 43:32; 46:33; 48:31, and 28:29, respectively (Table X).

It is uncertain whether a substantial fraction of the fluoride fixation by the live moss was through stomatal action, because the heating effected dehydration

and permanent contraction in the physical structure of the moss, with resultant decrease in surface capable of mechanical stoppage of air-borne fluorides.

Field Exposures of Limed Filter Papers in Buckets

The fluorine fixations by the bagged moss in month-long exposures were paralleled through quadruplicate fixations by lime-saturated 12.5-cm. filter papers that were clipped to four wires strung perpendicularly inside inverted half-gallon new lard cans or buckets (Figure 4). The cover of each can was soldered to the outside of what had been its bottom for protection against rainfall and to allow ready passage of air through the containers. An advantage in the use of the protected papers in the field is that month-long exposures can be obtained throughout the year, regardless of weather, whereas the moss exposures are restricted to certain seasons. The fluorine content of every filter paper was determined, but the values given are means. Lime-soaked filter paper exposures were used by Miller and others (10) for chemical measurement of extent of fluorine damage to tips of field grown gladiolus and nearby pasture grass.

In Blount County The micrograms of fluorine fixed by the limed papers exposed in the buckets at seven locations in Blount County in the

Table X. Fluorine Acquired by Month-Long Exposures of Live and Dried Moss

(In umbrellaed cord bags at three locations in Middle Tennessee, May-August 1955^a)

No.	Location	Fluorine, P.P.M., Dry Weight Basis																
		May			June			July			August							
		Live	Mean	Dried	Live	Mean	Dried	Live	Mean	Dried	Live	Mean	Dried					
1	Old MTES	36, 44, 29, 23	33	25, 13, 26, 17	20	13, 23, 23, 25	21	7, 18, 22, 22	17	36, 40, 27, 32	34	29, 58, 34, 33	29	32, 23, 23, 27	26	29, 19, 29, 28	26	
15	Baker	36, 41, 50, 47	44	36, 43, 37, 26	36	49, 49, 65, 52	54	24, 32, 34, 38	32	47, 55, 74, 63	60	28, 32, 35, 44	35	29, 34, 28, 34	31	23, 23, 28, 32	27	
58	Pitts	50, 63, 47, 45	51	47, 39, 41, 38	41	66, 71, 60, 52	62	63, 52, 34, 46	49	46, 49, 54, 52	50	31, 31, 19, 32	28	23, 22, 30, 30	26	33, 32, 39, 28	33	
	Crossville	6, 4, 6, 5	5	5, 3, 2, 6	4	5, 6, 10, 11	8	6, 10, 3, 5	6	2, 3, 2, 7	4	3, 3, 2, 12	5	11, 8, 6, 7	8	8, 7, 15, 7	9	
	Blank, applied		19															18

^a In comparison with Crossville parallels as controls.

Table XI. Fluorine^a Acquired by Bucket-Contained Lined Filter Papers^b (Figure 4)
(In 9-month-long exposures in atmosphere at seven farms in Blount County)

No.	Exposure on Farm ^c	Intake of Fluorine in Quadruplicated Pairs of Inside and Outside Papers, γ												Over-all Mean										
		October 1954		November 1954		December 1954		January 1955		February 1955		March 1955		April 1955		May 1955		June 1955		July 1955		August 1955		
		Ins.	Out	Ins.	Out	Ins.	Out	Ins.	Out	Ins.	Out	Ins.	Out	Ins.	Out	Ins.	Out	Ins.	Out	Ins.	Out	Ins.	Out	
56	Alcoa	43	51	68	81	63	65	114 ^d	123 ^d	29	55	67	140	161	66	72	34	40	52	48	55	59	65	72
19 ^d	Alcoa	45	40	45	55	65 ^d	63 ^d	91 ^d	94 ^d	33	35 ^d	41 ^d	45 ^d	52 ^d	60	64	38	41	55	63	46	54	52	55
20 ^d	Alcoa	33	54	69	69	124	154	84	109	315	398	50	52	96	107	232	225	32	43	76	103	111
21	Manning	69	61	108	131	223	236	159	195	553	576	42	44	79	86	165	214	31	43	79	111	
24 ^e	Alcoa	13	20	58	67	74 ^d	70 ^d	91	107	33	48	45	79	43	53	50	53	37	35	21	20	40	41	
3	Alcoa	16	17	21	27	56	62	24 ^d	25 ^d	25 ^d	23 ^d	30	31	35	34	5	5	21	24	
	Alcoa	12	23	32	31	26	32	33	36	118	136	47 ^d	65 ^d	56	77	65	64	18	20	47	63	
	Blank, applied	11	9	9	9	9	9	3	3	11	11	2	2	5	5	5	4	4	20	20	8	8	8	
	Rainfall, inches	0.76	2.97	7.08	7.08	6.19	6.19	2.05	2.05	7.64	7.64	3.62	3.62	3.82	3.82	4.15	4.15	4.15	4.15	20	20	8	8	

^a Means for fluorine acquired by filter papers placed in each pair of ventilated buckets. Two innermost papers were "ins"; two papers nearest wall of bucket were "out".
^b Whatman No. 2 filter paper, 12.5-cm., saturated with 0.5M aqueous suspension of Ca(OH)₂ and dried in air before placement.
^c Locations for exposures designated by numbers in relationship to pot rooms on grid of Figure 1.
^d Mean of determinations on papers contained in one bucket.
^e For intakes of fluorine at 5 locations other than Alcoa 19 and Alcoa 20.

Table XII. Fluorine^a Acquired by Bucket-Contained Lined 12.5-Cm. Filter Papers^b
(In month-long exposures in the atmosphere at 12 farms in Middle Tennessee, 4th quarter 1954 and 6 months in 1955)

On Grid	Taking point	Microgram Intakes of Fluorine in Quadruplicated Pairs of "Outside" and "Inside" Papers												Over-all Mean										
		October 1954		November 1954		December 1954		January 1955		February 1955		March 1955		April 1955		May 1955		June 1955		July 1955		August 1955		
		Ins.	Out	Ins.	Out	Ins.	Out	Ins.	Out	Ins.	Out	Ins.	Out	Ins.	Out	Ins.	Out	Ins.	Out	Ins.	Out	Ins.	Out	
1	Old MTES	29	35	33	40	38	39	58	70	73	79	94	111	76	80	60	69	44	52	61	70	52	55	64
18	New MTES	6	21	16	19	16	21	56	52	23	27	47	60	35	33	32	29	27	34	20	29	37	40	29
15	Franklin ^d	9	12	21 ^e	17	14	11	30	38	18	16	31	43	22	29	29	32	19	24	18	18	11	12	20
78	Baker ^e	17	24	35	40	38	38	78	100	45	52	51	61	56	64	53	41	62	74	55	76	55	59	57
90	Goodwin ^f (Dungyc)	201	244	318	336	191	199	219	287	78	103	130	146	407	510	154	174	229	228	164	197	84	104	198
66	Southern	16	30	55	70	45	40	61	75	45	53	56	68	74	78	41	56	39	42	21	18	10	13	42
58	Webster	29	45	55	58	77	72	141	148	77	82	62	82	49	57	48	54	52	64	39	39	24	27	59
37	Pitts (Allen)	139	204	192	228	170	207	303	365	127	154	191	204	122	146	95	91	144	146	94	95	48	59	148
23	Gray (Garrett)	24 ^e	27 ^e	64	77	72	73	67	78	52	55	42	42	40	44	39	49	33	38	16	20	45
5	Holcomb	5	11	15	22	21	25	47	44	18	22	38	41	26	34	36	38	29	31	20	21	22	27	25
3	Watson	26	42	28	29	38	37	74	66	60	65	150	182	53	65	64	70	49	56	33	35	30	29	61
109	Murray ^d	8	10	26	25	13	10	31	29	8	16	54	44	24	30	33	32	22	23	13	12	15	17	22
	Crossville ^g	4	5	0	1	11	15	8 ^h	9 ^h	15 ⁱ	9 ⁱ	7	7	9	6	0	1	7
	Blank, applied	11	9	9	9	9	9	3	3	11	11	2	2	5	5	5	4	4	4	8	8	8	8	12
	Rainfall, inches	0.76	2.97	7.08	7.08	6.19	6.19	2.05	2.05	7.64	7.64	3.62	3.62	3.82	3.82	4.15	4.15	4.15	4.15	20	20	8	8	

^a Means for fluorine acquired by filter papers placed in each pair of ventilated buckets.
^b Whatman No. 2, 12.5-cm. filter paper, saturated with 0.5M aqueous suspension of Ca(OH)₂ and dried in air before placement.
^c Designations for locations given numerically on grid of Figure 3.
^d Near Franklin, Tenn.
^e Mean of determinations of papers contained in six buckets.
^f Mean of determinations of papers contained in single buckets.
^g Intended as control.
^h January blank applied to samples left in field from December 15, 1954, to March 14, 1955.
ⁱ 2-month exposure, as mean for papers in two buckets.
^j Grand mean for intakes of fluorine at ten locations other than Goodwin and Pitts.

Table XIII. Fluorine Fixations

[Exposures of eight bucket-contained limed filter papers, (Figure 4) and companion exposures of 100 grams of Spanish moss umbrella] (Figure 2) at 12 locations in Middle Tennessee]

Micrograms of Fluorine per 8 Limed Papers and 100 Grams of Moss, Moisture-Free Basis

No.	Farm ^a	October 1954		November 1954		May 1955		June 1955	
		By papers	By moss	By papers	By moss	By papers	By moss	By papers	By moss
1	Old MTES ^b	32	4,300	37	4,400	65	3300	48	2100
18	New MTES ^b	18	2,700	19	2,100	31	2000	31	...
	Franklin	11	2,700	19	1,900	31	2200	22	...
15	Baker	21	4,000	38	3,800	47	4400	68	5400
78	Goodwin	223	31,800	58	13,000	164	3100	229	6300
90	Southern	23	3,500	63	5,000	49	3500	41	2700
66	Webster	37	6,700	57	5,600	51	3300	58	3100
58	Pitts	172	13,200	210	8,800	93	5100	145	6200
37	Gray	...	4,100	26	4,300	42	2000	44	2300
23	Holcomb	8	1,600	19	2,500	37	2400	30	2200
5	Watson	34	3,600	29	3,100	67	3900	53	3400
109	Murrey	9	3,300	26	5,000	33	2900	23	...
	Crossville	5	300	1	900	12	500	7	800

^a As on grid of Figure 3.

^b Middle Tennessee experiment stations.

last quarter of 1954 and the first 6 months of 1955 are reported in Table XI. The amounts fixed at Alcoa 19 and Alcoa 20 were always substantially greater than at the other five locations, although four of these also registered considerable intakes of fluorides, an exception being Alcoa 24G.

The analyses of the "outside" and "inside" pairs of the perpendicularly placed papers were combined, as shown in Table XI. In most cases, the sweep of air through the buckets was registered by a larger fixation of fluorine by the outside papers, the over-all mean for which was 82 γ against 71 γ for the inside papers. The grand means for the 14 individual means of fixations, from 428 analyses, register 53 γ of fluorine against 47 γ for the 10 findings other than those for Alcoa 19 and Alcoa 20.

In Maury County The 30-day exposures of the bucket-contained limed filter papers at seven locations in Blount County (Figure 4) were duplicated in Maury County and increased by exposures at five additional locations, against control exposures at Crossville, 2000-foot elevation, on the Cumberland Plateau. The fluorine contents of the exposed papers in 107 of 121 comparisons register the larger fixations by the outside papers (Table XII). Again, as in the Blount County findings of Table XI, a freer passage of air around the outside filters was probably responsible for the larger fixations of air-borne fluorides.

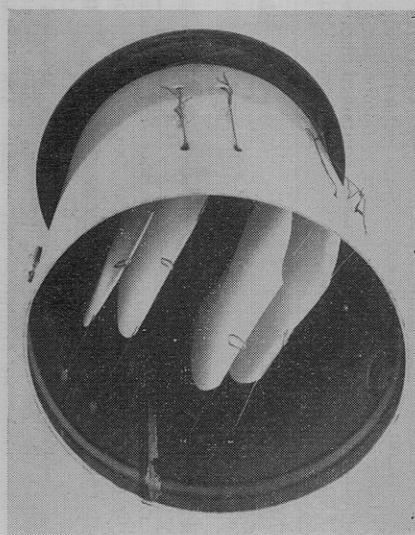
At two locations in each county the fixations exceeded greatly the fixations at the other locations in that county. The grand mean for the fixations in Maury County was less than the corresponding mean for Blount County. That relationship obtained also when the grand means were lessened through deletions of the respective pairs of the

high values for fixations. Hence the analyses indicate that, in the 9 months of the parallel exposures of the doubly quadruplicated limed papers, fluoride concentrations in the atmosphere at the Blount County locale were somewhat greater than the corresponding concentrations in Maury County.

Fluorine Fixations by Parallels of Limed Papers and Moss

The data of Table XIII register the gains of fluorine by companion exposures of bucket-protected limed filter papers and charges of moss at 12 locations in Maury County in October and November 1954 and May and June 1955. Obviously, a direct quantitative comparison of the fluorides taken from the air cannot be made. Because of the large difference between the surfaces of the two fixatives, one alkaline and the

Figure 4. Interior view of field-placed receptacle



other neutral, it is not feasible to establish direct quantitative comparisons of the fixations effected by the two media. However, maximal and minimal occurrences of atmospheric fluorides are registered alike by the two fixatives. That fact is shown by the mean of 168 γ of fluorine as the maximal fixation by the limed papers and the corresponding mean of 13,550 γ for the fixation by the moss exposures, against which were the 24- γ mean of the minimal fixations by the exposed papers and the 2175- γ mean of the minimal fixations by the moss exposures. The ratios for the maximal and minimal fixations of fluorine by the papers and moss on locations 78 and 23 were 1:81 and 1:91, respectively. The paper and moss register in similar manner also for the decidedly smaller fixations at Crossville. Both media can be relied upon to register abnormal occurrences of fluorides in the atmosphere at a particular locale.

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