Fluoride Content of Commercial Dairy Concentrates and Alfalfa Forage

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The fluoride content of 168 samples of 16% dairy feed and 107 samples of alfalfa hay from different parts of the United States has been determined. The dairy feeds ranged from 3 to 296 p.p.m. of F with a mean of 21 p.p.m. of F and a median of 15 p.p.m. F. Only 7% of the samples exceeded the 90-p.p.m. limit set by the American Feed Control officials. Alfalfa hay from areas thought to be free of industrial fluoride pollution ranged from 0.8 to 36.5 p.p.m. of F, with a mean of 3.6 p.p.m. and a median of 2.0 p.p.m. There was no apparent relationship between alfalfa fluoride content and geographic location. The problem posed by dairy concentrates which are high in fluoride, but which are legally acceptable in areas where fluoride is also an industrial pollutant, is discussed.

The interest expressed in the past by dairy and beef cattle producers in fluorides as toxic agents has been directed toward the possible pollution of forages by industrial effluents containing fluorides, and the supplementation of grain rations by fluoride-bearing phosphate ingredients (Phillips *et al.*, 1960; Suttie, 1964). At the present time there is also interest in using forage fluoride analyses as the standard for protecting livestock, mainly cattle, from industrial pollution (Suttie, 1969). The standards proposed have assumed that the rest of the ration would contain relatively little fluoride. The Association of American Feed Control Officials (1966) sets a limit of 90 p.p.m. of F in feeds for cattle, and somewhat higher limits for other livestock species. It appears however that state feed control agencies seldom check feeds to determine if this standard is exceeded, and no recent analyses of a large number of feed samples are available to indicate if, in fact, the standard is routinely met.

A second question of current interest is the variation in forage fluoride levels in areas where there is no problem of industrial pollution; that is, what should be considered as "normal" forage fluoride concentrations. Most reviews on the fluoride problem in livestock production indicate that normal forages contain less than 10 p.p.m. F, but few extensive or systematic compilations of analyses are available. A series of publications by MacIntire *et al.* (1942, 1947, 1951, 1954), values cited in a review by McClure (1949), and surveys in the Tennessee area (Merriman and Hobbs, 1962; Merriman *et al.*, 1956) indicate that normal fluoride values are probably 5 to 10 p.p.m. for legumes, and about half of this for grasses. Since the time most of these values were obtained, there have been a number of advances in techniques for analyzing biological samples containing low levels of fluorides.

The purpose of this report is to present data indicating the range of fluoride content of dairy feed commercially available at the present time, and to present values for the fluoride content of alfalfa hay obtained from various parts of the country.

PROCEDURE

A total of 168 samples of dairy feed, most of them containing 16% but some 14 to 17% protein, were obtained from the feed control officials of seven states.

As alfalfa is probably the most widely grown of the important forage crops in the country, 107 samples of this forage which were obtained from agronomists in 13 different states were analyzed. Although information on the variety and stage of cutting was available for some samples, the only criteria required of all samples were that they were from a crop that would be accepted as a normal dairy feed and be more than 10 miles from a known industrial source of atmospheric fluoride.

All samples were analyzed on an air-dried basis. From 0.5 to 1.5 grams of alfalfa and from 0.5 to 1.0 gram of the dairy feed samples were weighed into 40-ml. Inconel crucibles and mixed with 100 mg. of calcium oxide and sufficient deionized water to form a loose slurry. The samples were dried on a hot plate and charred under infrared lamps for 1 hour. They were then ashed in a 600° C. muffle furnace for 2 hours and removed. Three grams of NaOH were added and the samples were reheated for 5 minutes. After the melt had cooled, it was suspended in 25 ml. of deionized water. Duplicate standards of from 2.5 to 12.5 μg. of fluoride (as NaF) in the case of the hay samples, or 12.5 to 62.5 μg. in the case of feed samples were added to calcium oxide and carried through the entire procedure. The standards and samples were placed in every other cup of a Technicon sample module II, alternate cups filled with deionized water, and analyses performed in the Technicon AutoAnalyzer essentially as in Mandl's modification (Mandl *et al.*, 1966) of the AutoAnalyzer method described by Weinstein *et al.* in 1965. Each dissolved melt was run through the analyzer two times and the standard curve was run at the start and finish of each series of samples. Duplicate samples of each hay and feed sample were analyzed.

RESULTS AND DISCUSSION

As a check on the accuracy of the method used, a series of forage samples which had previously been analyzed by the conventional Willard and Winter method (1933) were obtained. The comparison of these values with those obtained by the AutoAnalyzer method (Table I) demonstrates that there is excellent agreement between the two methods.

The data shown in Figure 1 indicate that the mean fluoride content of the 107 samples of alfalfa hay was 3.6 p.p.m. and that 50% of the samples contain less than 2.0 p.p.m. fluoride. There does not appear (Table II) to be any difference in the fluoride content of alfalfa from different geographic areas of the country. The small differences in the averages are the result of a small number of high values influencing the mean. Although samples near known industrial sources of fluoride were excluded from the survey, it is of interest that five of the seven samples with over 10 p.p.m. of F were indicated to be from plots that were within 5 miles of a major urban industrial

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Table I. Comparison of Method of Forage Analyses[a]

Sample No.	Distillation and Titration, p.p.m. F, dry wt. Average	Range	AutoAnalyzer Duplicate Analyses, p.p.m. F, dry wt.	
1	104	98–112	112	118
2	55	50–60	58	62
3	25	23–27	27	26
4	35	32–38	33	32
5	26	21–32	25	23
6	50	48–52	59	57
7	18	15–20	18	19
8	19	15–31	19	17

[a] Each sample of mixed pasture or alfalfa forage was analyzed nine times by the conventional Willard and Winter method in the U.S. Steel Laboratory at Provo, Utah. Duplicate analyses of these samples by the AutoAnalyzer were carried out on different days following the procedure outlined in the procedure section.

Table II. Fluoride Content of Alfalfa Hay

Location	No.	P.P.M. F, Dry Wt. Mean	Median	Range
California	51	4.3	2.2	0.8–32.7
Washington, Oregon	9	5.6	1.7	0.8–36.5
Utah, Montana	8	2.5	2.5	1.5– 3.9
Ala., Ark., Miss.	5	1.3	1.3	0.9– 2.2
Wis., Iowa, Ill.	24	2.5	1.6	0.8– 8.4
New Jersey	3	4.0	4.0	3.5– 4.4
Arizona	7	3.4	3.0	1.3– 7.1
Total	107	3.6	2.0	0.8–36.5

Table III. Fluoride Content of Commercial Dairy Feed

State	No.	P.P.M. F, Dry Wt. Mean	Median	Range
Wisconsin	35	18	12	4– 92
Michigan	15	29	21	3– 95
New York	21	28	13	6–160
California	16	6	7	2– 10
Florida	18	50	20	3–296
Kentucky	57	16	15	4– 43
Arizona	6	7	4	3– 24
Total	168	21	15	3–296

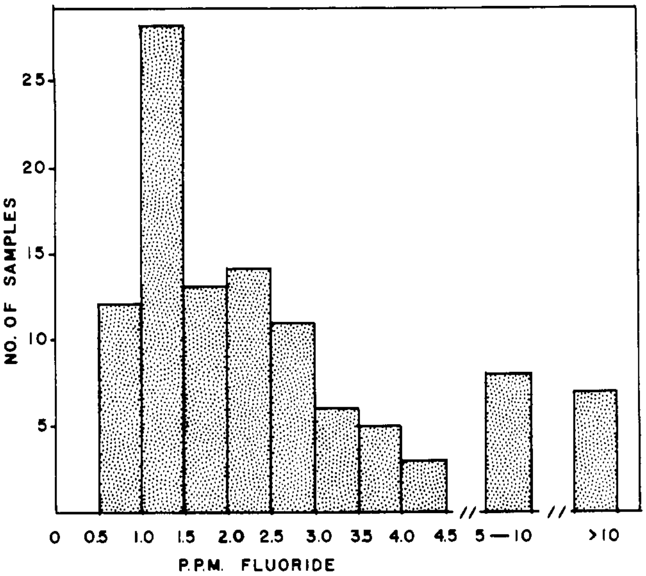

Figure 1. Fluoride content of alfalfa hay

Distribution by fluoride content of 107 samples of alfalfa hay

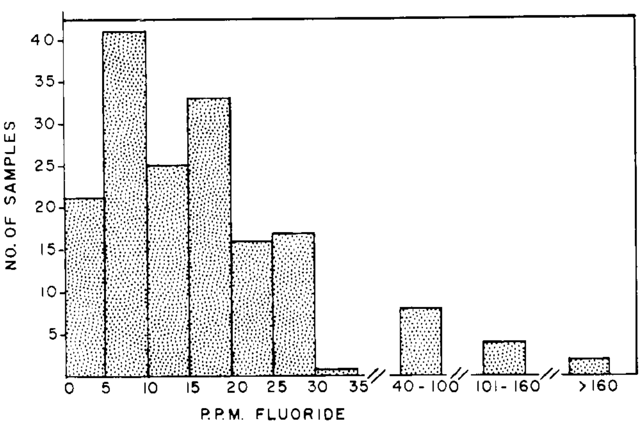

Figure 2. Fluoride content of dairy feed

Distribution by fluoride content of 168 samples of dairy feed containing 16% protein

center. The nine samples that were obtained which were known to be within 5 miles of such urban areas ranged from 2.2 to 32.7 p.p.m. and averaged 10.7 p.p.m. F.

The 168 samples of dairy feed which were collected from seven states were analyzed and the distribution of the results is shown in Figure 2. Only 7% of the samples exceeded the 90 p.p.m. F standard set by the American Feed Control officials and 90% of the samples contained less than 30 p.p.m. F. The state of origin of the different samples is indicated in Table III. All of the samples obtained from California, Kentucky, and Arizona met the 90 p.p.m. F standard, while the other states had at least one sample exceeding this value. The mean fluoride concentration found for samples from different states varied considerably, depending on the number of high samples included, but the median values were rather similar and were all under 25 p.p.m. F.

The analysis of samples by the AutoAnalyzer system represents a considerable saving in time and has been shown (Jacobson *et al.*, 1966) to be similar in precision to the modifications of the Willard and Winter (1933) method which have been used. When those dairy feed samples with a fluoride content of from 10 to 40 p.p.m. were considered, it was found that the deviation in fluoride content of duplicate analyses of the same sample was less than 5% of the mean of the duplicates in 65% of the samples analyzed, and over 10% in only 8% of the samples. This agreement between duplicate samples is better than what we have usually achieved for such analyses with the Willard and Winter method. For the feed samples with a lower fluoride content, or the majority of the hay samples, the deviation expressed as per cent of the mean would be somewhat higher, but would be of little practical importance because of the low concentrations of fluoride involved.

As these samples were obtained as a voluntary response to a request for such material, there has been no attempt to apply any statistical treatment to the data. However, there were sufficient numbers of samples involved to indicate that the values obtained might be rather representative of the fluoride content of the alfalfa hay and dairy feed currently available to the livestock industry.

The fluoride concentrations found for alfalfa hay, with about 75% of the samples containing 3 p.p.m. F or less, may be somewhat lower than that often quoted as a "normal" forage fluoride content. However, it should be noted that these samples were obtained mainly from University Experiment Station plots, and were presumably harvested at the correct stage of maturity. Many samples obtained from average farming areas might include some mature, overripe forage that would be higher in fluoride content. These data point out that some rather high fluoride forages can be found in areas with no known source of industrial fluoride, making it important to obtain a number of samples in any area where industrial fluoride pollution is suspected.

These data indicate that the vast majority of commercial dairy feed samples do meet the current 90 p.p.m. F standard, and that, in fact, most of them contain less than 30 p.p.m. F. The finding of any samples of commercial dairy feed with over 200 p.p.m. F would, however, suggest that regulatory agencies should be continuously concerned with the possibility of these high fluoride feeds reaching dairy herds. The physical nature of the two samples with over 200 p.p.m. F suggested that they may have contained soft phosphate-colloidal clay as a phosphate source. There are indications that fluoride in soft phosphate may be as available as that in rock phosphate (Ammerman *et al.*, 1964), and if so, inclusion of these high fluoride feeds in a normal ration would certainly exceed the recommended tolerance levels for livestock (Phillips *et al.*, 1960).

Dairy concentrates with a fluoride content of from 40 to 90 p.p.m. meet the current standard and under normal conditions will represent no hazard to the productive ability of dairy cattle. However, some consideration should perhaps be given to the amount of fluoride in commercial feeds in those extremely limited areas of the country where there is fluoride contamination of local forages by industrial sources. State regulatory agencies are now setting air quality standards which define a maximum allowable concentration of fluoride in forages. These standards are based on the assumption that the contribution of fluoride in the dairy concentrate to the total fluoride intake of animals in the area is likely to be small. In such an area, 80 p.p.m. F in a commercial dairy ration, even though it falls within the present legal standard, may be too much. It seems unrealistic to assume that air pollution standards should be written to protect animals against this rare combination of conditions. It may be equally unrealistic for the feed industry to impose a lower nation-wide standard to protect those few herds of cattle in areas where there is a fluoride pollution problem. It would seem more reasonable that the feed industry in cooperation with state air pollution agencies try to ensure that commercial feeds sold in these extremely limited areas contain less than 30 p.p.m. F. As this value was met by about 90% of the feed samples obtained in this study, it should impose no real burden on the manufacturers.

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