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Influence of Stauffer Chemical Company on fluoride distribution in the Silverbow Montana area

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The University of Montana

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INFLUENCE OF STAUFFER CHEMICAL COMPANY ON FLUORIDE DISTRIBUTION IN THE SILVERBOW, MONTANA, AREA

By

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Approved by:

Chairman, Board of Examiners

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Dean, Graduate School

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Date

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INFLUENCE OF STAUFFER CHEMICAL COMPANY ON FLUORIDE DISTRIBUTION IN THE SILVERBOW, MONTANA, AREA

by

Charles van Hook
Missoula, Montana

SUMMARY: This study describes the concentration and distribution of fluoride contamination in a 16,000 acre area surrounding the Stauffer Chemical Company of Silverbow, Montana. The biological monitoring of the fluoride contamination was performed through field collection and laboratory analysis of indigenous vegetation of the area. The fluoroapatite ore reduction process in operation at the Stauffer Chemical Company emits fluoroapatite dust and hydrogen fluoride gas. These emissions were found to cause a flagrant violation of the Montana state standard for fluoride accumulation in forage grass throughout an area over 11,000 acres in size.

The biological monitoring method is presented as a model to be used by regulatory agencies for rapid determination of air pollution effects as they relate to violation of standards and the potential fluoride hazard to grazing livestock and wildlife.

Introduction

A fluoride emitting phosphorus extraction facility currently owned by the Stauffer Chemical Company has been operating in Silverbow, Montana, since 1951. Complaints concerning the effects of fluoride air pollution on local cattle (1) and request for governmental assistance in dealing with this problem (2) were first recorded in 1956 and 1957. The Montana State Board of Health initiated limited air pollution monitoring in the area in 1957 (3), the results of which indicate that fluoride concentrations in the ambient air exceed the present allowable concentration, which is one part per billion in a 24-hour average (4). In October, 1972, Carlson (5) conducted a brief survey of fluoride concentrations in vegetation in the area and found them to be as high as 74 ppm. To date there have been no in-depth studies of air pollution in the immediate Silverbow area.

The phosphorus extraction process at the Stauffer Company's Silverbow facility employs the electric furnace method. Raw phosphate rock containing fluoroapatite, $Ca_{10}F_2(PO_4)_6$, is agglomerated by nodulizing at high temperature in a rotating kiln. Dust and fluorides are emitted from this process. The nodulized material is cooled on conveyors and stored. Following storage, coke breeze and siliceous flux (sand) are added, and the mix is charged to the electric furnace. As the furnace is charged, gaseous and particulate materials again escape. The high temperature causes the phosphorus to be vaporized. Vaporized phosphorus is then cleaned of contaminating dust as it is passed through electrostatic precipitators and condensed into water. After a final filtration, the phosphorus is stored under water and shipped.

Accumulation of slag in the electric furnace in another point in the process where fluoride is lost, primarily as CaF_2 mixed with other impurities. The slag is periodically drained from the furnace and transported to the slag pile after it solidifies (6,7). A general chemical equation for the process is: $2Ca_{10}F_2(PO_4)6 + 18SiO_2 + 30C \rightarrow$

$(18 \cdot CaO \cdot SiO_2 \cdot 1/9CaF_2) + 30CO + 3P_4\uparrow$ (8). This equation, which describes the high temperature reaction occurring in the electric furnace, fails to indicate the gaseous and particulate fluoride loss which occurs as the furnace is charged. Also, the preparatory heating in the nodulizing kiln causes loss of gaseous and particulate forms of fluoride.

A 1968 emission inventory submitted by the Stauffer Chemical Company to the Montana State Board of Health listed fluoride emissions as: 1) 205 pounds of gaseous fluorides per day and 2) 200 pounds of fluoride tied into the fluoroapatite mineral, $Ca_3(PO_4)_2 \cdot \frac{1}{2}CaF_2$. The plant operates continuously. The above report also stated that 360,000 tons per year of phosphate rock were utilized containing 26 percent equivalent phosphate listed as P_2O_5 and 2.6 percent fluoride listed as F (9). Recent information from the company indicates that the phosphate rock consumption has increased from an annual use rate of 360,000 tons to 500,000 tons (10).

In view of the apparent problem and lack of data concerning the distribution of fluoride in the Silverbow area, this study was initiated in October, 1972. The objective was to determine through biological monitoring the distribution and concentration of fluoride in the area and its relation to the operation of the phosphorus extraction facility operated by the Stauffer Chemical Company. The concentration of fluoride was determined by the chemical analysis of indigenous vegetation and soils, with particular emphasis being placed on a forage grass species very common to the area.

Literature Review

Biological monitoring has become an accepted practice in determining the effects of many air pollutants resulting from mans' activities. Injury to vegetation has been increasingly recorded during the past hundred years near many industrial complexes and has more recently become of significant economic concern owing to the phytotoxicants produced in photochemical smog (11). Major efforts in biological monitoring have been put forth particularly in studies concerning the distribution and effects of sulfur dioxide (12). Detailed studies have often involved the evaluation of many physiological aspects other than visual foliar damage, such as general effects upon growth rate (13), metabolic changes (14), root growth (15), and many others.

With the development of modern aluminum smelting processes and increased demand for the production of phosphate fertilizer, the atmospheric emission of fluoride compounds (gaseous and particulate) has rapidly increased. Other major sources of atmospheric fluoride emissions include the manufacture of steel, brick and tile products, and the combustion of coal (16). The fluoride enrichment which occurs in the foliage of various plants exposed to atmospheric contamination in the field has been well demonstrated by Knabe (17). The phenomena of foliar uptake of atmospheric fluoride and problems associated with the separation of gaseous from particulate deposits has been described by Hill (18) as follows:

> Plant leaves are extremely effective in accumulating and concentrating fluoride in the atmosphere. Leaves exposed to HF can accumulate as much as 1,000,000 times as much fluoride as the atmosphere to which they are exposed. Leaves appear to be the best part of the plant to sample

> because they have a large surface area and structural features that facilitate gaseous exchange, and therefore, accumulate more fluoride than any other plant part.
>
> Since fluoride remaining on the outer leaf surface is harmless to the plant, the correlation between leaf injury and fluoride content is better for washed leaves than for unwashed leaves. If leaf analysis is used as a standard, the leaves should be washed by a standardized method. Washing is usually not just a simple matter of removing surface fluorides. Varying amounts of surface fluorides are left after washing and some fluoride is leached from the leaf interior.

Most residual particulate forms of fluoride found on the leaf surfaces are of an insoluble nature and pose no toxic influence on vegetation. Present evidence indicates that fluoride must exert its toxic effects after penetrating the cytoplasm (19). The manner in which atmospheric fluorides affect the metabolism of the plant is not well understood. This is due to a combination of incomplete knowledge of the normal metabolic processes of plants, the manner in which the processes are integrated and controlled, and the metabolic effects of fluoride itself (20).

Various laboratory and field studies have attempted to establish damage indices for plants which demonstrate various levels of fluoride tolerance--one of the most sensitive being the gladiolus (21). Aside from the relative sensitivity of plants, other environmental parameters seem to modify fluoride concentration and effects. Laboratory experiments demonstrate that the rate of fluoride accumulation by forage plants exposed to intermittent HF fumigation was greater than that of plants provided a continuous low exposure (22), and that the rate of air flow past the plant alters fluoride susceptibility in alfalfa (23). Furthermore, plants seem more susceptible to fluoride accumulation (from gaseous sources) during the growing season. However, this susceptibility varies with the stage of growth and relative age of foliage, and may be further modified by nutritional and moisture stresses (24).

Once gaseous fluoride begins to be absorbed and concentrated by the plant, continuous processes of translocation and dilution begin. Studies at the Boyce Thompson Institute indicate that fluoride loss results from the diluting effects of weathering, plant growth, and foliar abcission. These studies also have indicated that there is no translocation of absorbed HF into new growth (25). Detailed work done with the injection of NaF^{18} in tomato plants revealed that the F^{18} moves primarily to the leaf margins and tips, with none going to the roots (26). Field experiments done downwind from an aluminum smelter by Knabe (27) illustrated a large loss of accumulated fluoride in spruce when they were removed from the polluted atmosphere. The loss was not due to growth dilution, and washing due to rainfall was not allowed.

Another important area where biolobical monitoring has provided valuable information is in following the movement of fluoride through the food chain. Both the accumulation of gaseous fluoride compounds in plant tissue and the deposition of particulate fluoride compounds on foliar surfaces have led to toxic effects in grazing wildlife and domesticated animals. Most reviews have indicated that natural forage fluoride contents are about 5 to 10 ppm (mg/kg dry weight), but few extensive or systematic compilations of analysis are available. The major source of fluoride in the rations of livestock in areas with a fluoride pollution problem is the ingestion of high fluoride vegetation (28). Also, an increasing number of air quality standards specify acceptable concentrations of fluoride in forage, and the accumulation of fluoride by forage has been a basis for emission standards (29).

In an attempt to correlate fluoride concentrations in vegetation with concentrations in indigenous animal populations, some very diverse ecological surveys have been made. Studies by Gordon (30) and Carlson and Dewey (31) have analyzed the distribution and concentration of fluoride effluents from an aluminum smelter in plant and animal populations in a nearby national forest and national park. Gordon established sampling zones through which fluoride concentrations were illustrated. Chemical analyses to determine fluoride content in vegetation were employed, and histological examinations of conifer needles were performed. Bones from many species of birds and mammals were also analyzed for fluoride content and examined histologically.

Carlson and Dewey, working in the same area, utilized 10 radial sampling routes for the collection of vegetation and insects. Along with chemical analysis of vegetation and histological examination of conifer needles, a visual injury index was used for conifers. Fluoride content in herbivorous and carnivorous insects was determined, along with observations of species diversity relative to the degree of pollution. Carlson used his data to construct an isopol map which displayed acreages contaminated by various concentrations of fluoride. Both Carlson and Gordon separated conifer needles by age prior to chemical analysis in an effort to determine changes in fluoride uptake which occurred as emission controls were attempted at the aluminum smelter. The modifying effects upon fluoride dispersion of topography and meteorology were considered.

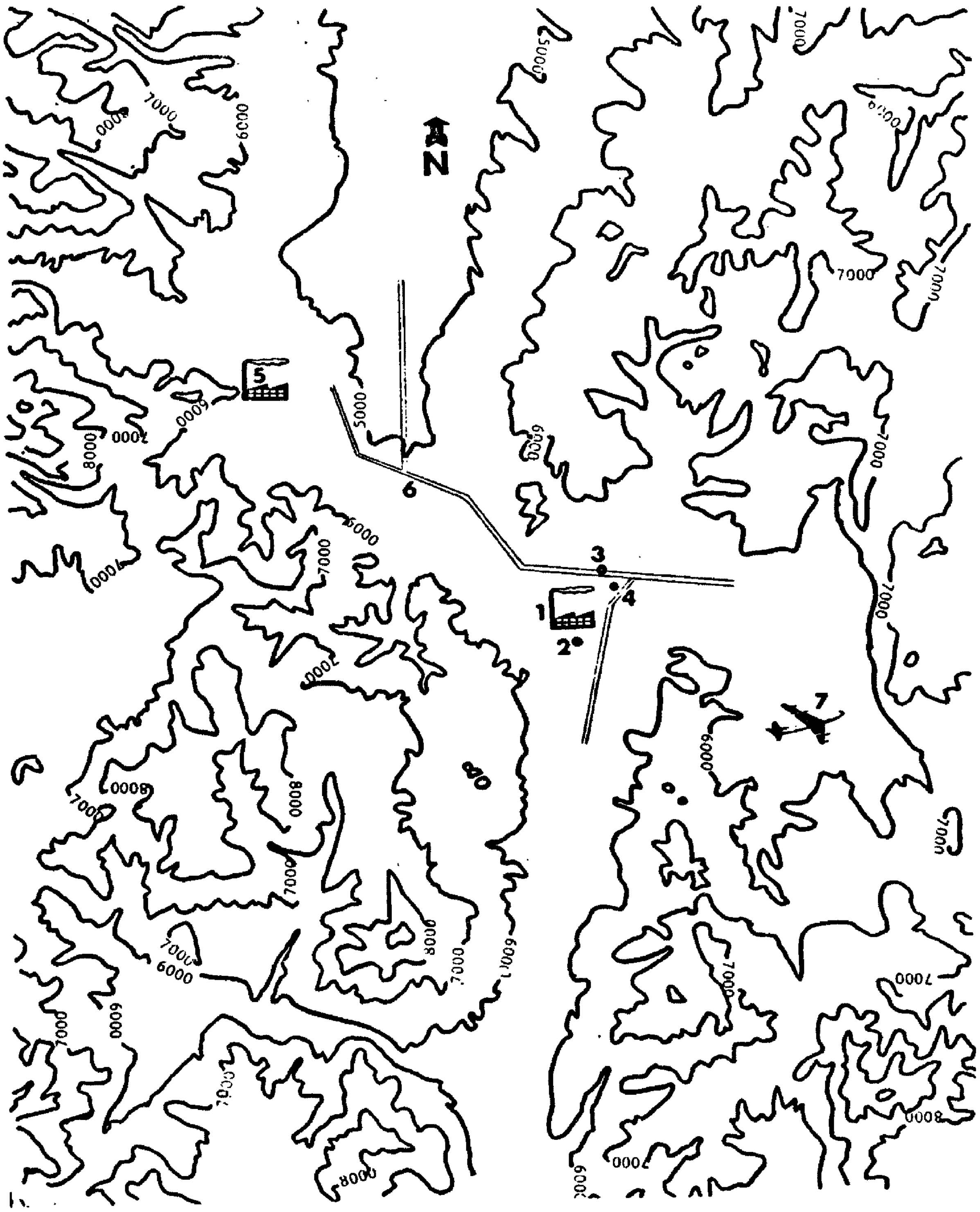
In another area of western Montana near a phosphate rock reduction facility, Gordon (32) and Kay (33) surveyed fluoride content in indigenous plant and animal populations. Both studies employed sampling zones based on property boundaries to express fluoride distribution in the area. Conifer needles were separated by age class to help evaluate fluoride emission controls installed at the phosphate rock processor. Extensive chemical analyses were performed on plant and animal samples. Gordon again performed histological examinations on conifer needles, and Kay utilized statistical analysis to determine relative fluoride uptake relationships between various plant and animal species of the area.

Diverse ecological surveys of air pollution effluent distribution involving many species of plants and animals over large areas of topography necessitate accurate and versatile methods of laboratory analysis. The studies mentioned here which were done by Gordon, Carlson, Kay, and many others have utilized the Specific Fluoride Ion Electrode as a method of chemical analysis. This electrode is a rapid, specific, efficient, and inexpensive method (34, 35, 36) for the determination of fluoride in environmental media as compared to other standard methods (37, 38, 39, 40).

Methods

Description of the Area

The Stauffer Chemical Company of Silverbow, Montana, is located in a prairie basin which is at the northern termination of a north-south valley (Map #1 page 9). The valley is enclosed by Fleecer Ridge to the west and south, the Highland Mountains to the east and south, and the



MAP #1

Topography Surrounding Silver Bow, Montana Study Area

1. Stauffer Chemical Company
2. Stauffer Plant Slag Pile
3. Bull Moose Fluorspar Deposit
4. Wrong Font Fluorspar Deposit
5. Anaconda Company Smelter
6. U.S. Highway 10 Road Fill
7. Butte Airport Weather Station

Contour Interval 1,000 ft.
From U.S.G.S. Map

Boulder River-Silverbow Divide to the north. These three mountainous barriers rise to elevations of 8,000 feet m.s.l. while the valley floor in the vicinity of the Stauffer plant is slightly above 5,300 feet m.s.l. This valley extends approximately eight miles due south where it is terminated by the Continental Divide. The northern end of the valley opens in two directions--to the northwest where highway Interstate 90 descends in the direction of Anaconda, Montana, seventeen miles away (west) and to the east where Interstate 90 ascends in the direction of Butte, Montana, seven miles away.

That section of Interstate 90 which connects Butte and Anaconda passes 1½ miles north of the Stauffer plant. The construction of this highway in 1957 utilized Stauffer slag material as a fill for the roadbed. Because the slag is believed to contain 3 percent CaF_2 (41), this project constitutes a man-made fluoride deposit.

The construction of Interstate 90 also covered some surface exposures of a naturally occurring fluorspar deposit (CaF_2). This deposit is located 1½ miles northeast of the Stauffer plant and is referred to as the Bull Moose deposit. Another poorly defined fluorspar deposit is believed to occur 1-3/4 miles northeast of the Stauffer plant and has been named the Wrong Front deposit (42). The presence of fluorspar in the area could cause higher background fluoride concentrations in the soils. Solubility of fluorspar is 0.0016 parts per gram in 100 cc. of cold water (43). This low solubility should tend to make fluoride from this source unavailable for plant uptake. Solubility of the Stauffer Chemical Company slag is unknown.

There is no weather station in Silverbow, Montana. The nearest weather station is approximately seven miles southeast in another valley. The climatological description of the area is obtained primarily from the U.S. Weather Bureau Narrative Climatological Summary for Butte, Montana. The only other source of information available concerning meteorological characteristics of the region is work compiled by the Environmental Protection Agency as part of a study conducted 33 miles north northwest in Garrison, Montana.

The yearly normal precipitation is 12.67 inches, two thirds of which is measured during the growing season--April through September. May and June are the wettest months. The summer maximum temperatures infrequently reach 90° F. and the hottest month is July followed by August. Zero minimums have been recorded as early as October and as late as April, and the average number of 0° F. readings is about 43 a year. Freezing temperatures can be expected any time of year but are least likely to occur from May through August. The average number of days between the last temperature of 28° F. in the spring and the first in the fall is about 120. The mean speed and direction of the wind are 7.9 mph and northwest, respectively (44).

Mountain valleys in this area are particularly subject to intense and long-lasting inversion conditions. These inversions are stated to be caused by: 1) the atmosphere being less dense at these higher elevations than air at lower altitudes and generally dry, 2) winter nights being relatively long, 3) surrounding mountains acting as a barrier to strong winds, and 4) snow cover during the colder months reflecting away solar energy and being an excellent radiator of heat at night. Furthermore; cool air in time drains to lower elevations because of its greater density and thereby causes deeper and more intense inversions in a valley than would occur on level ground.

The table below illustrates the inversion frequencies for this general region of the United States. Protected mountain valleys, similar to the one in which Silverbow is located have even higher percentages of inversions.

TABLE #1

INVERSION FREQUENCIES

Season	Percent of Total Hours
Winter	45-55
Spring	30
Summer	30-35
Fall	40-50
Annual 40	

Plume behavior is greatly affected by topography, inversions, and wind directions, and it follows that ground concentrations of air pollution are also affected. Air is channeled by a valley, especially during stable conditions, and a plume of air pollution is confined by a valley or will follow valley walls. Because of the "valley effect," high ground concentrations can occur at a greater distance downwind from the source than would occur in flat terrain (45).

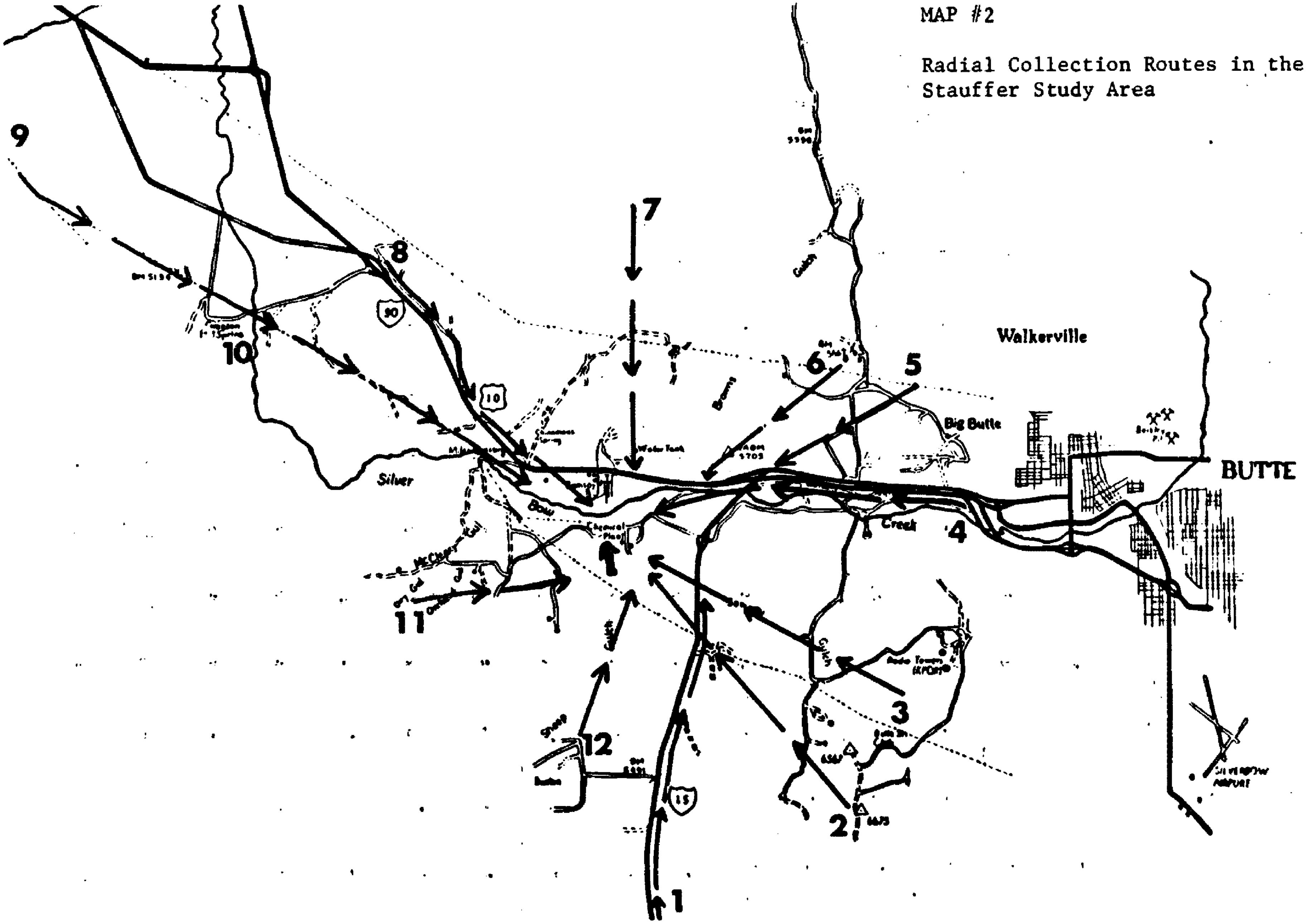
The relatively low annual precipitation, high altitude, and resultant short growing season are the main natural modifying factors governing the indigenous vegetation. Furthermore, the annual temperature distribution is such that the valley bottom grasslands usually become dormant in mid-July due to lack of soil moisture. Of the many species of range grasses present, the most frequently observed was bluebunch wheatgrass (*Agropyron spicatum*). Other grasses observed were crested wheatgrass (*Agropyron cristatum*), foxtail barley (*Hordeum jubatum*), and giant wild rye (*Elymus cinereus*). Scattered throughout the range grasses, the shrubs bitterbrush (*Purshia tridentata*) and rose (*Rosa spp*.) may also be found. The three species of trees found on the valley floor were widely scattered Rocky Mountain juniper (*Juniperus scopularum*), Douglas fir (*Pseudotsuga menziesii*) and lodgepole pine (*Pinus contorta*). Few trees observed exceeded a height of 15 feet. In many undisturbed areas, the vegetative cover was found to be 50 percent or less, leaving much exposed soil.

On the slopes of the surrounding mountains there is an abrupt transition to forest composed almost entirely of Douglas fir. In the few wet areas near creek beds are found isolated stands of willow (*Salix spp*.) and black cottonwood (*Populus trichocarpa*) as well as quaking aspen (*Populus tremuloides*) in some of the mountain side ravines.

Field Collection

On October 6, 1972, a study group began two days of field collection of vegetation and surface soil samples. Twelve collection routes were established which extended radially from the Stauffer Chemical property (Map #2 page 14). Collectors were transported as near as possible to the far end of their route, from which they began their sampling, MAP #2

Radial Collection Routes in the Stauffer Study Area



proceeding on foot toward the plant. Each collector utilized a compass when line-of-sight travel was prevented by the topography. Sampling along Route #1 was done from an automobile, since this route coincided with the location of Highway 15 which extends south from Silverbow Junction.

Among the forage grasses, bluebunch wheatgrass was most commonly collected. This was done by cutting through the base of the plant one inch above ground level, thus obtaining the current year's growth and the previous year's growth, which is found matted down near the base of the bunch or crown area of the plant. Other non-bunch grasses were simply cut one inch above ground level, thus yielding only one year's growth.

Coniferous trees were sampled whenever they occurred on a collection route. Coniferous tree samples were obtained by clipping terminal segments of at least three branches from each tree. Attempts were made to obtain foliage representing the last five years of growth. Juniper collections were made without consideration of foliage age, since separation of this foliage by year of growth is very difficult. Deciduous trees offered foliage representing only the current year's growth. The shrub species found in the area were generally deciduous and were collected as such. In addition to those shrubs noted previously, a few samples of currant (Ribes spp.) and mountain mahogany (Cercocarpus spp.) were taken. These two latter species were rare to the collection area.

Soil samples were collected less frequently than vegetation samples. The collector chose an area which was devoid of vegetation or organic debris and removed the upper half inch of soil. Immediately upon collection, all samples were placed in paper bags which were labeled as to sample type and location. Bags were rolled and sealed with rubber bands. Notations were also concurrently made in collection journals containing the same information with which the samples were labeled. Map locations of sample sites were made and sample sites were marked in the field.

Laboratory Analysis

Analysis for fluoride content in vegetation was performed after Gordon (46) and in soils after Ficklin (47). Fourteen species of vegetation were analyzed. Analysis was performed on 387 samples, including 25 reanalyses which were done to check the accuracy of laboratory work. Soil analyses were also performed, including reanalysis. All vegetation and soil results and all control values for fluoride in vegetation are found in Appendix I, page 43 through 52.

Graphic Display Method for Fluoride Distribution

Notations made by each field collector allowed the map location of each collection site to be plotted along the 12 radial collection routes. This location, in conjunction with the results of chemical analysis, allows each sample site to be labeled with a parts per million fluoride concentration. By drawing lines connecting sample sites of equal fluoride concentrations, the distribution of fluoride was mapped. The lines drawn on the map represent boundaries of equal concentrations and are referred to as "isopols." Two isopol maps were constructed to illustrate fluoride concentrations found in the two age classes of bluebunch wheatgrass. Two forage age classes of bunchgrass samples are recent growth which occurred during the summer of 1972 and material representing past growth (possibly five years) labeled "1971 and older" (Maps #3 and #4 pages 18 and 19).

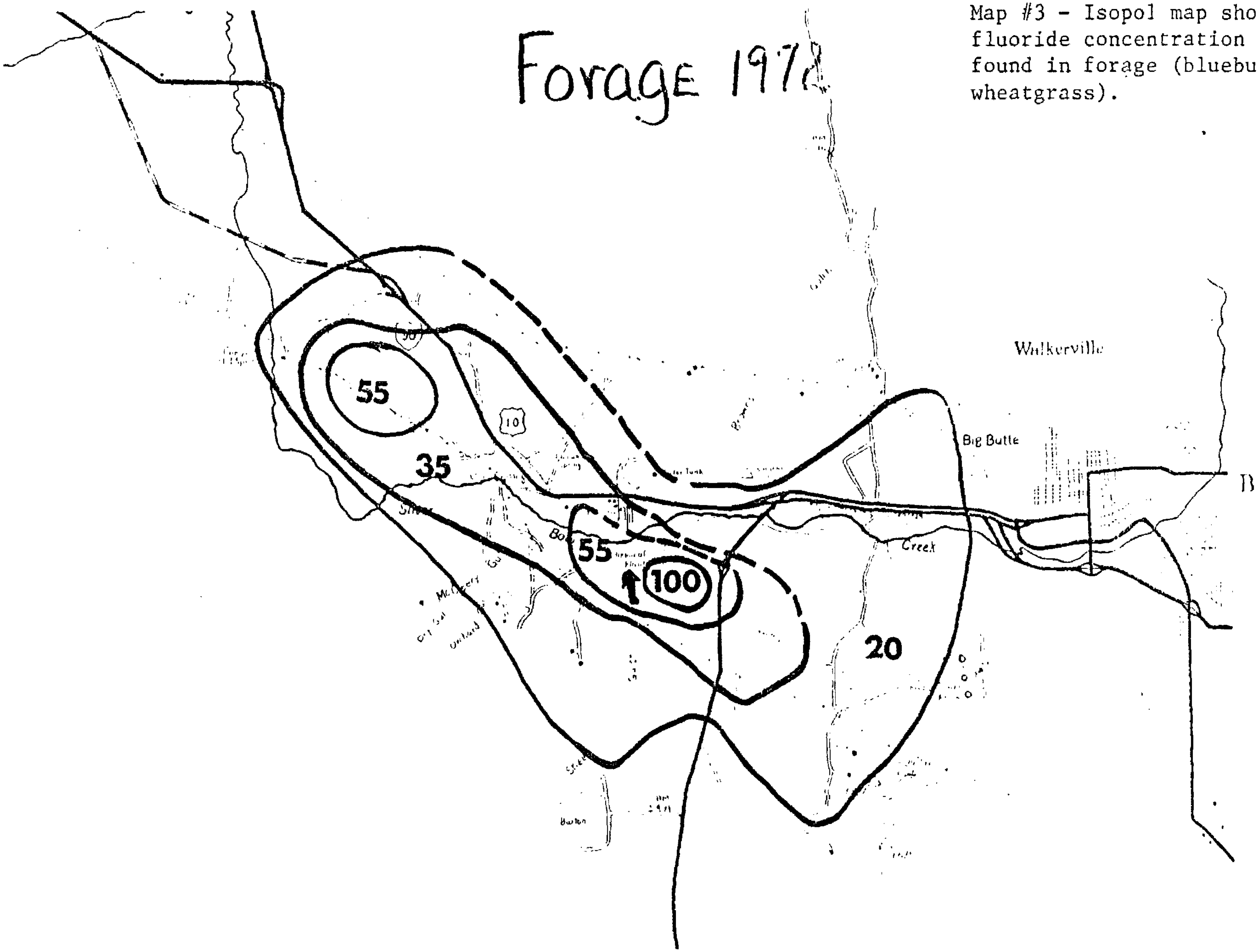
To further display the distribution of fluoride, the chemical concentrations found in the forage grass were graphed along each collection route as they relate to the topography. The profile of the elevation changes along each radius was plotted by the field collectors during the sampling trip. Each collection site is plotted on the topographic profile, and the value of fluoride concentration is above (or below) the sample site location.

Results

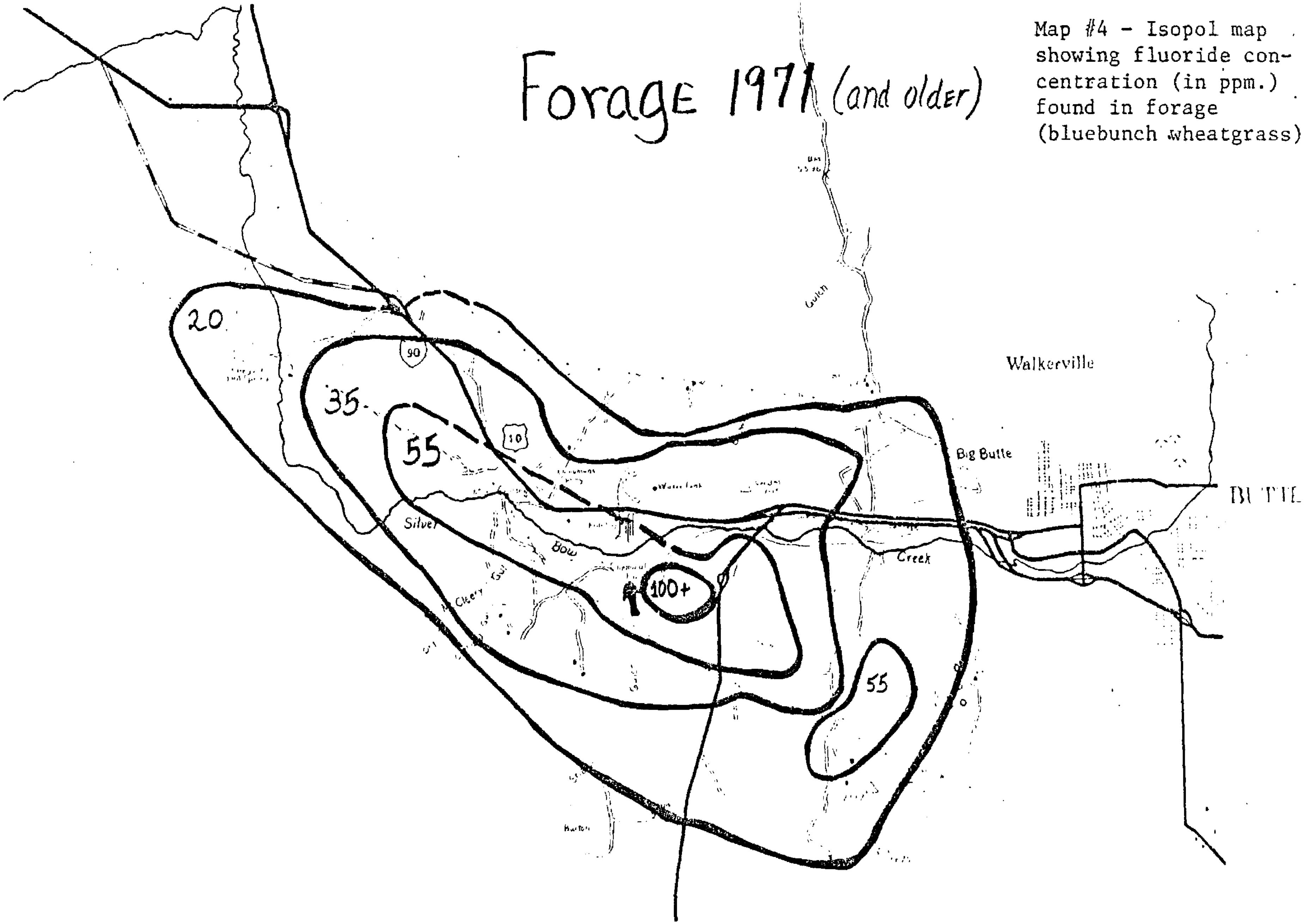
Fluoride Concentrations in Forage

The chemical analysis of vegetation surrounding the Stauffer Chemical plant revealed fluoride concentrations as high as 100 times greater than normal levels. The chemical analysis and sample site locations for the forage grass, bluebunch wheatgrass, were used exclusively in the construction if isopol maps. Fluoride concentrations were greater in older bunchgrass samples than they were in samples of new grass which had been exposed to the ambient atmosphere for only five months (Maps #3 and #4, pages 18 and 19). Even though fluoride levels were greater for old grass than they were for new grass, the patterns of fluoride accumulation were similar for both age classes.

The radial collection route method reveals a general increase in fluoride content as the chemical plant is approached from all directions.



Map #3 - Isopol map showing fluoride concentration (in ppm.) found in forage (bluebunch wheatgrass).



Map #4 - Isopol map showing fluoride concentration (in ppm.) found in forage (bluebunch wheatgrass).

The broken isopols indicate that sample density in the area was not such that clear concentration gradients could be established. Increase in fluoride concentration in the direction of the plant was evident throughout. Overlaying the isopols on a U.S. Forest Service map of the area reveals acreages at various levels of contamination. Table #2 depicts the acreages contaminated by fluoride at selected concentration levels.

TABLE #2

ACREAGE CONTAMINATED BY FLUORIDE

Age of Forage	ppm F^- Concentration ≧20 and <35	≧35 and <55	≧55 and <100	=100
1971 (and older)	16,704	11,520	4,736	448
1972	16,448	5,184	1,536	384

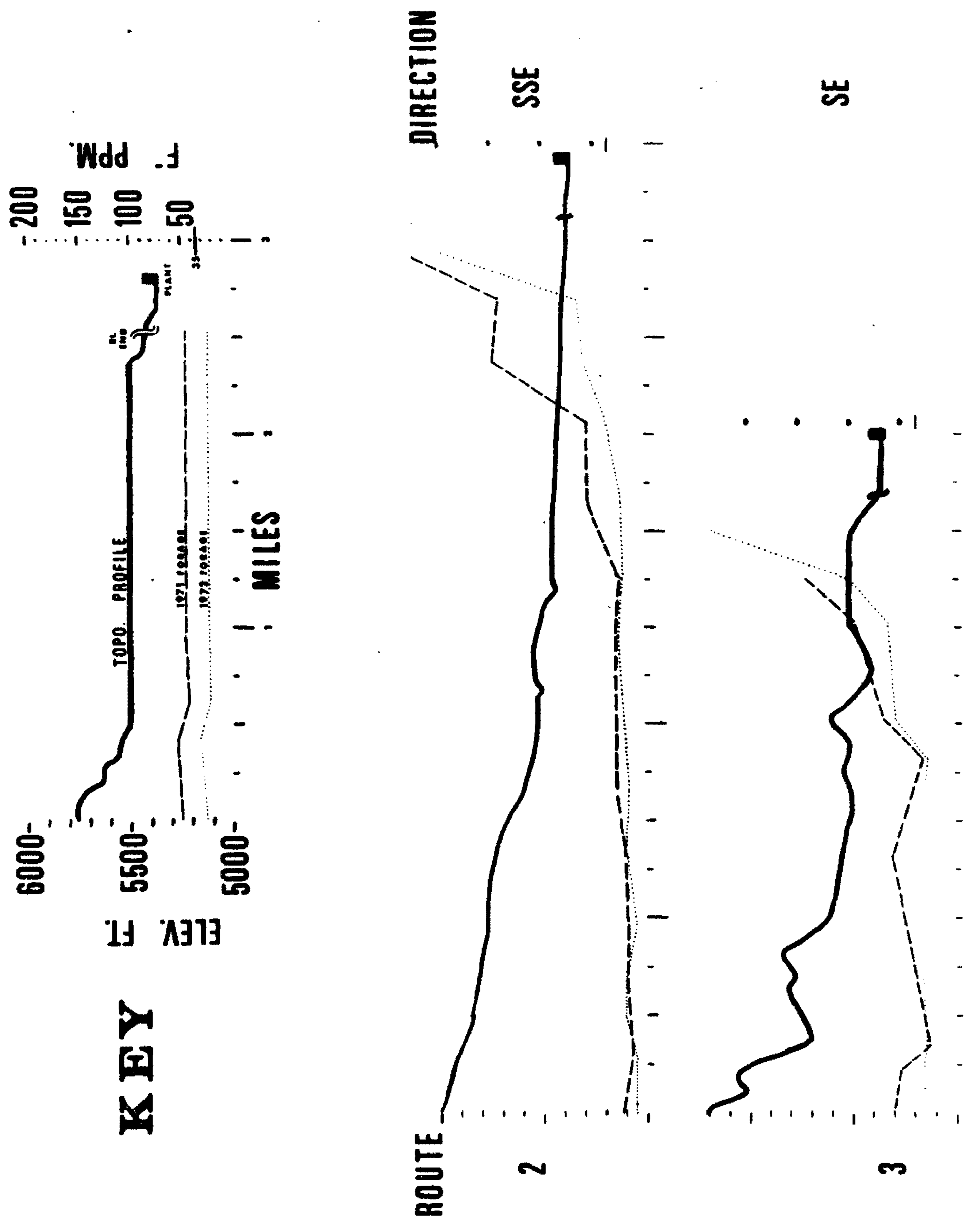
Compiling fluoride concentrations found in all forage samples collected within each isopol area allowed averages to be determined (Table #3).

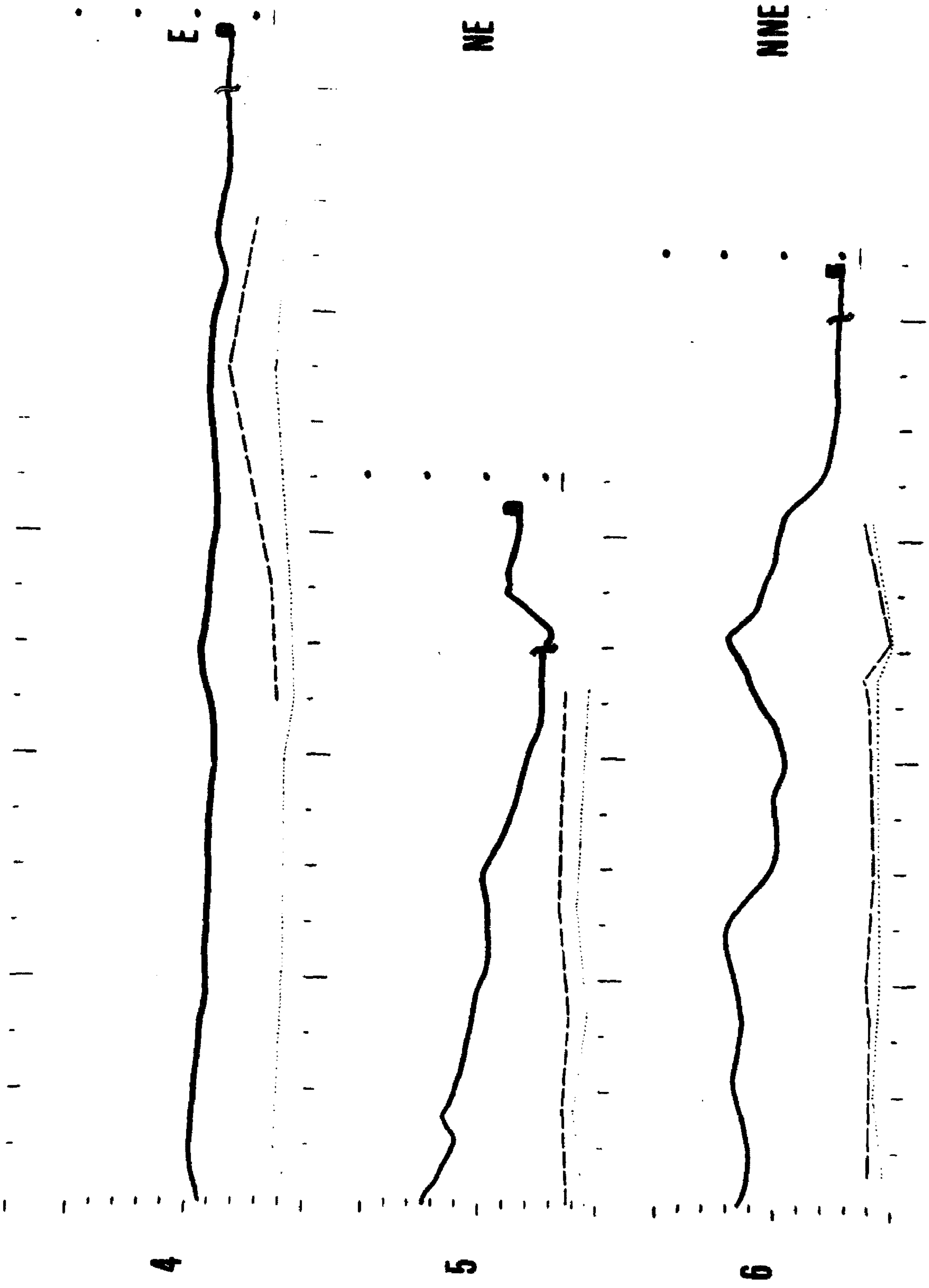
TABLE #3

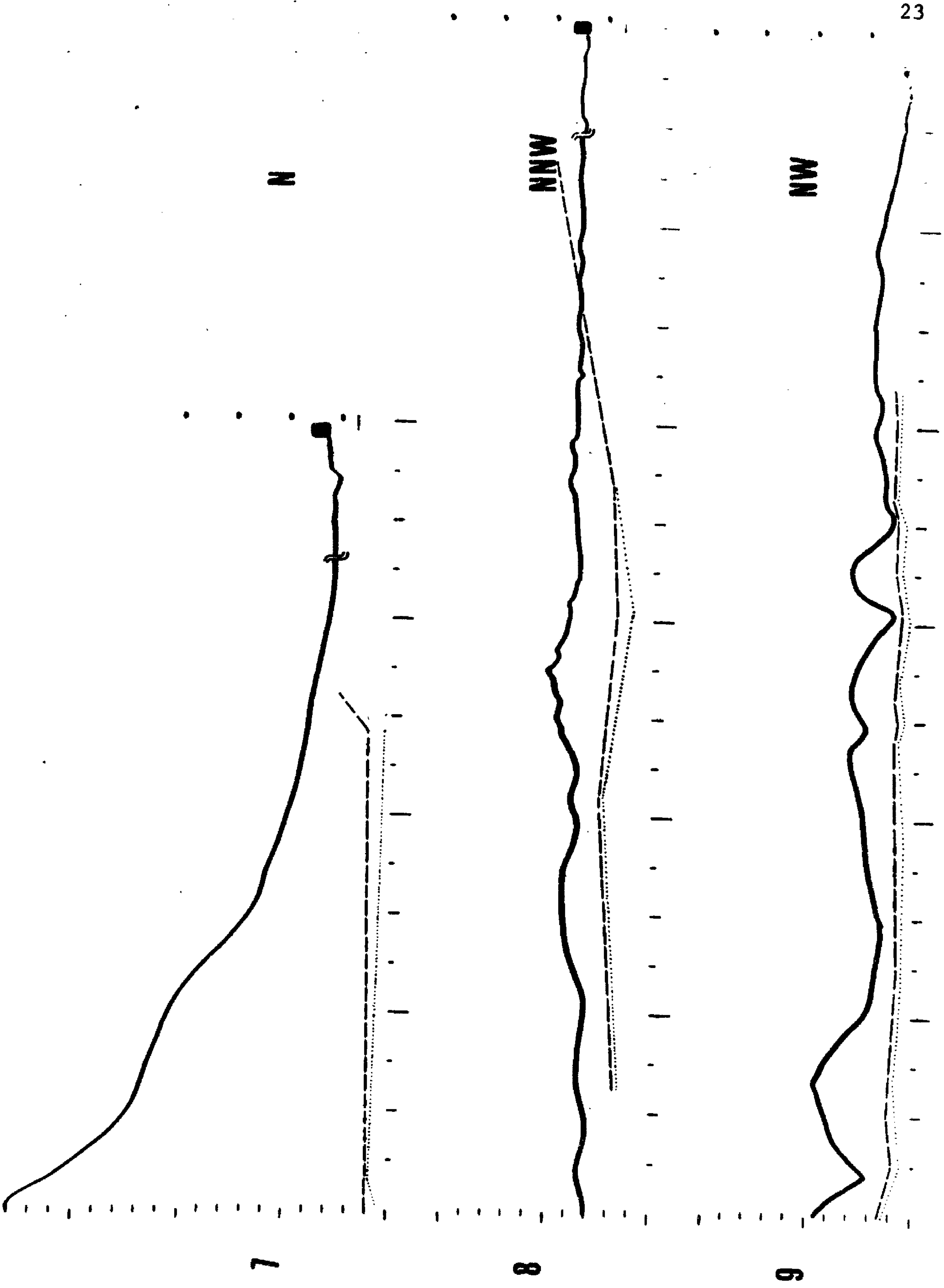
MEAN CONCENTRATION OF FLUORIDE IN EACH ISOPOL AREA

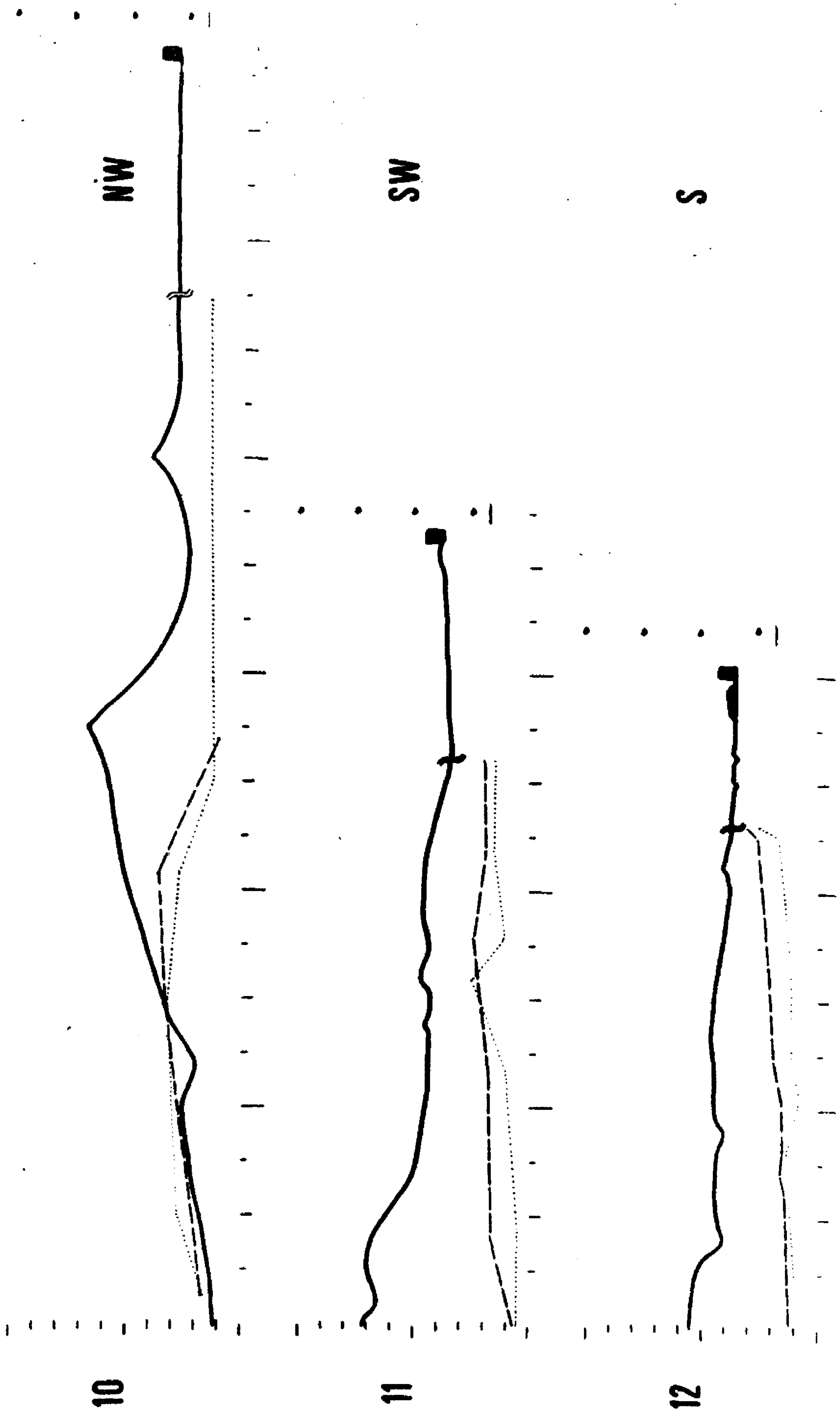
Isopol Area	1972 Forage	1971 (and older)
20 ppm F^-	N = 30 samples $\bar{x}$ = 22 ppm F^-	N = 35 samples $\bar{x}$ = 23 ppm F^-
35 ppm F^-	N = 18 samples $\bar{x}$ = 36 ppm F^-	N = 23 samples $\bar{x}$ = 39 ppm F^-
55 ppm F^-	N = 11 samples $\bar{x}$ = 59 ppm F^-	N = 15 samples $\bar{x}$ = 55 ppm F^-
100^+ ppm F^-	N = 5 samples $\bar{x}$ = 201 ppm F^-	N = 9 samples $\bar{x}$ = 342 ppm F^-

Graph #1 Topographic Profiles




E
NE
NNE
4
5
6


N
NNW
NW
7
8
9


NW
SW
S
10
11
12

The series of topographic profiles (Graph #1) illustrate the concentrations of fluoride (in ppm.) in forage grass, and the sample site distance and elevation relative to the fluoride source. Again, a trend of increasing concentrations as the source is approached from many directions is evident. The Key may be used as a guide in reading the topographic profiles. The right hand verticle scale (ppm F^-) is not large enough to accommodate the higher concentrations found in the forage grass samples. A more detailed listing of samples and F^- values may be found in the appendix.

Collection Route #1 was omitted because it entailed samplings from alternate sides of a highway, thereby contrasting the straight line-of-sight travel of the other routes. Collection Routes #9 and #10 are joined to form a single line of travel extending approximately 10½ miles in the direction of the Anaconda Smelter in Anaconda, Montana. The prominent ridge seen approximately 3½ miles northwest of Stauffer on Route #10 yielded forage with high fluoride content in an area facing away from Stauffer. The remainder of Routes #9 and #10 indicate a reduction of fluoride content from this point to a point within a few miles of the distant smelter. Along these two collection routes, fluoride content in forage drops to near control levels between the area of Silverbow and Anaconda.

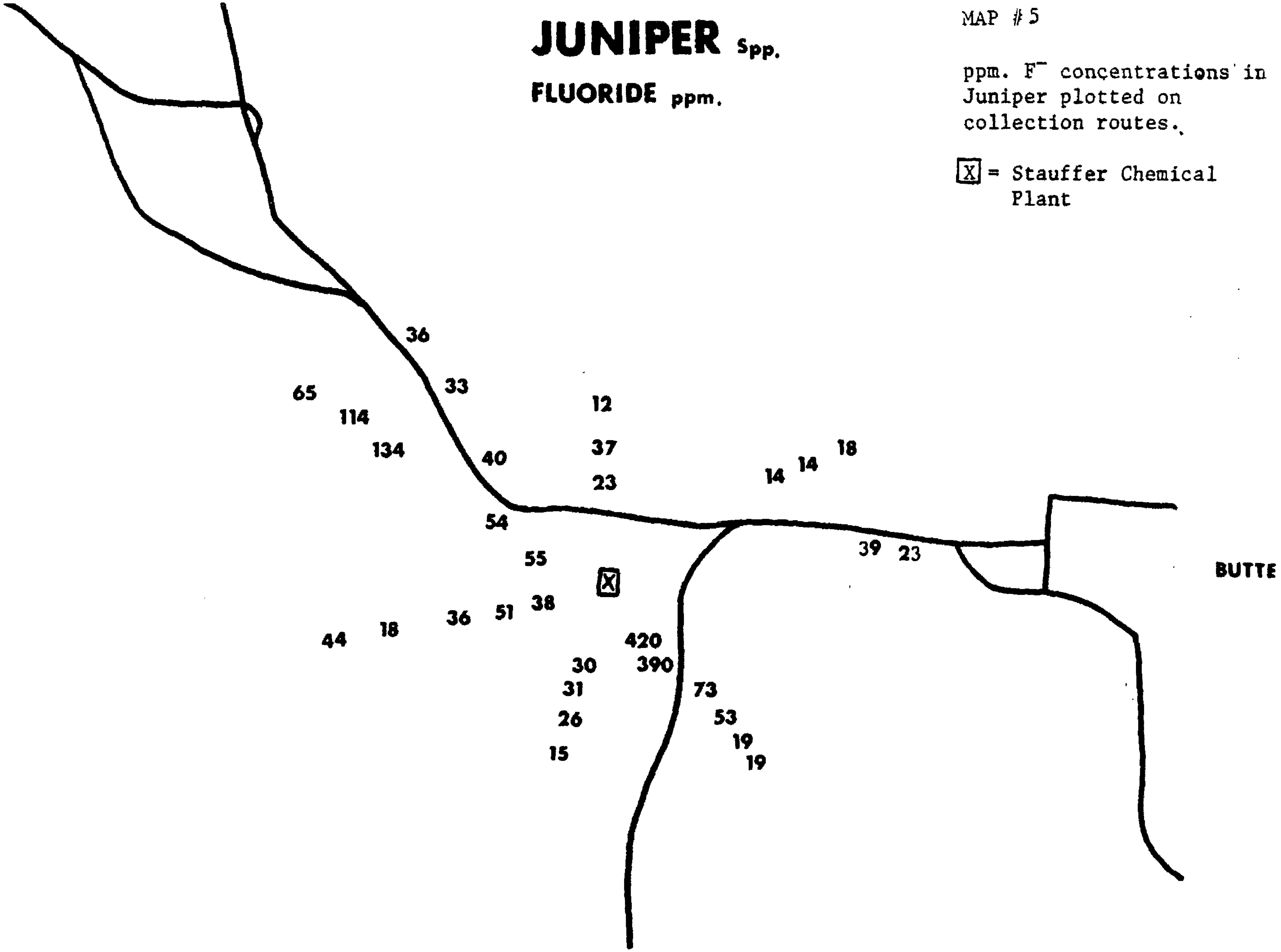
Detailed air flow patterns for this valley system are unknown. However, the general deposition of airborne fluoride compounds is indicated by some of the graphs. Those collections taken nearest the Stauffer plant indicate a high concentration increase within 1½ miles in several directions: S, SSE, SE, NNE, N, and NNW. Several prominent hillsides facing the Stauffer plant appear to be plume impingement zones--for example, Route #3 (1½ miles, 2¼ miles, and 3¼ miles southeast of the plant) and Route #11 (2 miles southwest of the plant). Other patterns of fluoride deposition are seem on Routes #6 and #10, where higher concentrations are found on hillsides facing away from the Stauffer plant, implying turbulent effects of various topographic features upon local air movements.

Fluoride Concentration in Juniper

Rocky Mountain juniper was the most commonly sampled tree in the study area. No samples of this species were found to contain control levels of fluoride. Juniper control collections made in other areas are listed in the appendix. The composite foliage of this tree yielded fluoride concentrations as high as 420 ppm, about 40 times greater than control values. Thirty-one of the 41 juniper samples collected are displayed in terms of fluoride concentrations on Map #5. Those samples omitted from this map had concentrations similar to or less than adjacent samples. The pattern of fluoride distribution found in juniper was similar to the pattern seen in forage grasses, though the range of concentration was not as great. Juniper collections were not made on collection Routes #1, #3, #6, and #9 due to low population density of this species in these locations.

Fluoride Concentration in Soils

Analysis results from 46 surface soil samples collected in the study area are shown on Map #6. The fluoride content is expressed by



JUNIPER Spp.

FLUORIDE ppm.

MAP #5

ppm. F^- concentrations in Juniper plotted on collection routes.

X = Stauffer Chemical Plant

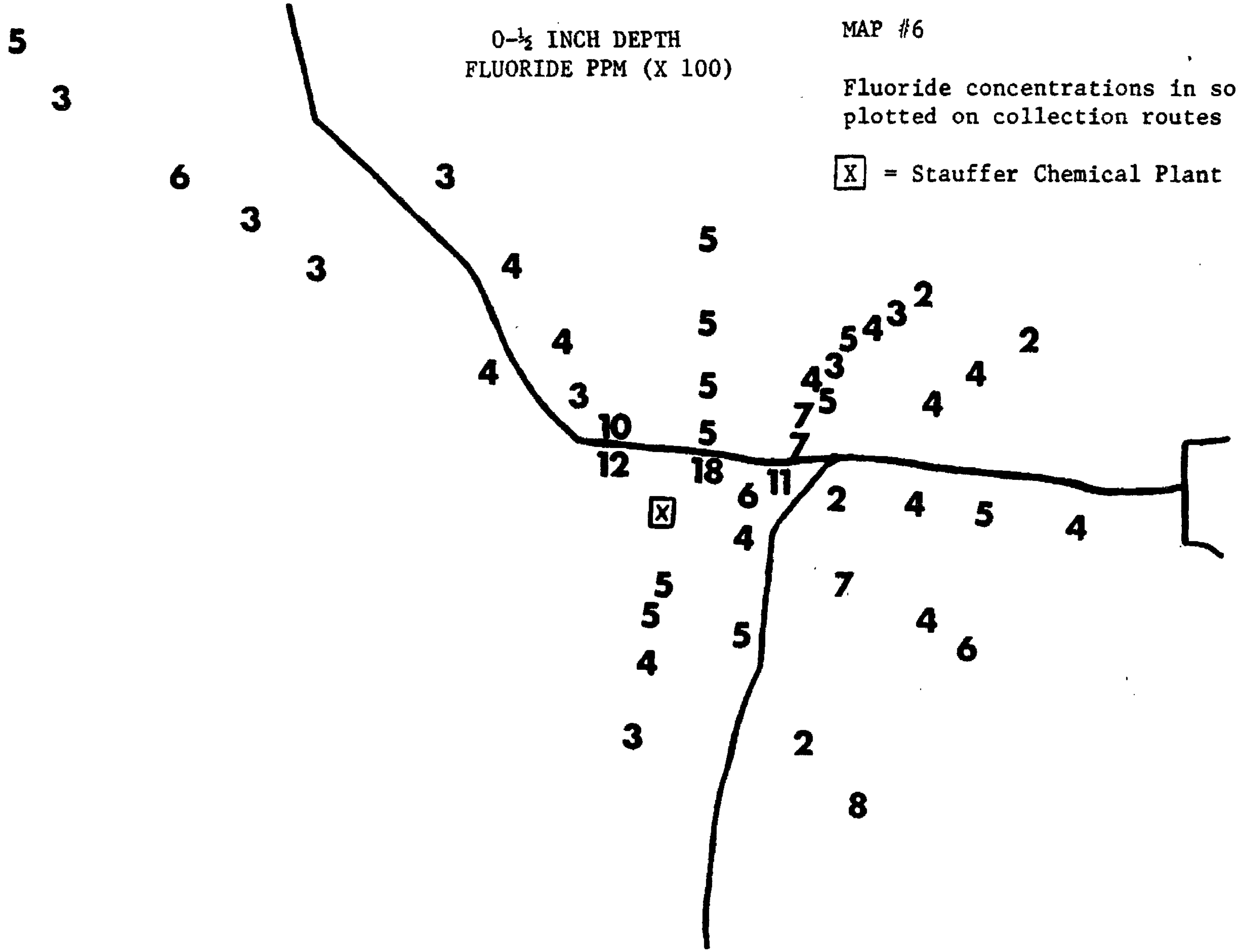
SURFACE SOIL

0-½ INCH DEPTH
FLUORIDE PPM (X 100)

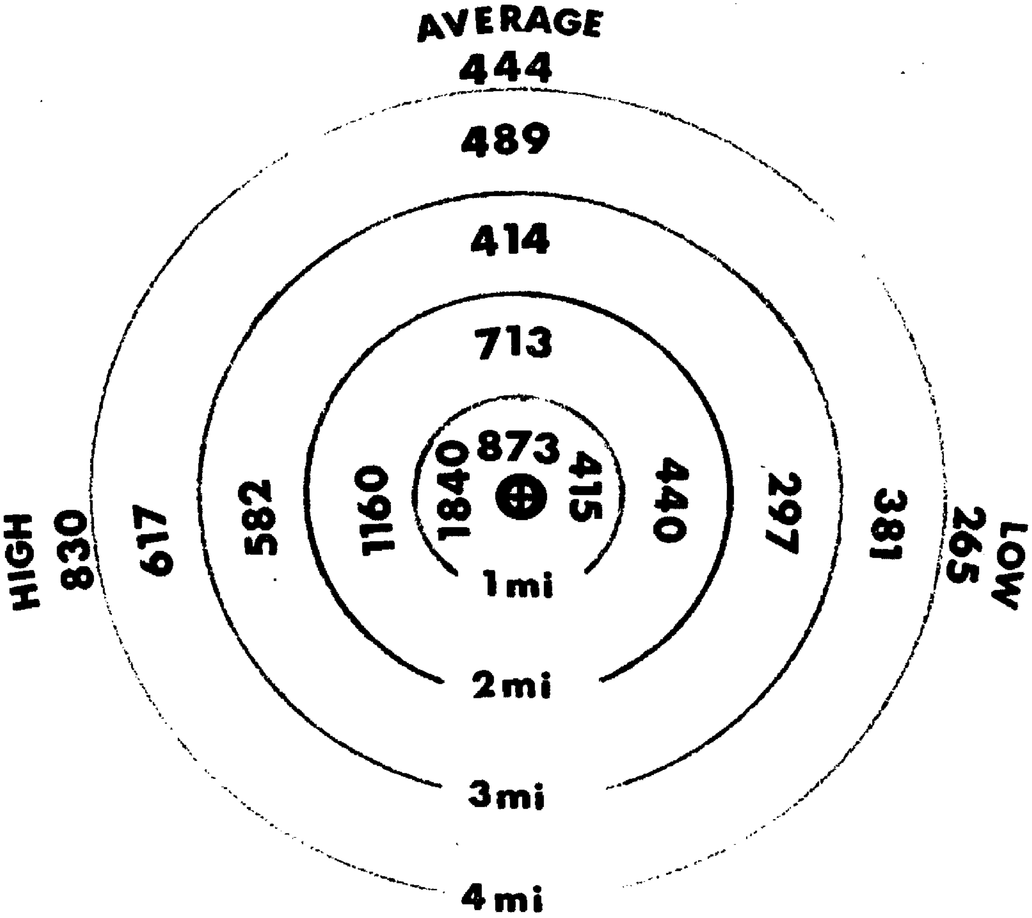
MAP #6

Fluoride concentrations in soils plotted on collection routes

☒ = Stauffer Chemical Plant



GRAPH #3



Fluoride concentration in soils
as a function of distance
from the Stauffer Chemical Plant

rounding off parts per million to the nearest 100 to simplify the map. The fluoride distribution pattern seen here indicates more localized high concentrations in the area of the Stauffer plant. By following the concentrations on each collection route it appears that the plant has had less measurable widespread effect on the surface soils of the area, than on the vegetation. The actual values of the soil samples are found listed in the appendix. Graph #2 illustrates the average concentrations of fluoride in soils as a function of distance from the Stauffer plant.

Discussion

The fluoride emission problem occurring in Silverbow, Montana is common in many industrial operations which utilize phosphate rock. Throughout this country and many other countries similar air emissions have arisen resulting from the extraction of phosphate for use as a fertilizer or livestock feed supplement. The high temperature necessary to purify the fluoroapatite content of the raw ore invariably results in defluorination. The production of phosphorus examined here simply adds one final step to the process--the electric furnace catalytic reaction of phosphate to phosphorus. Fluoride compounds, P_2O_5, combustion products, and numerous unidentified compounds common to the crude ore are either emitted into the atmosphere, collected as slag, or filtered and washed into the settling pong. The air effluents are primarily vented through several 85-foot stacks, though other emission points exist in the plant. The possibility of gaseous and particulate emissions from the settling pond near the plant has not been examined, though some emissions have been documented in other industrial operations engaged in similar processes.

The most detailed and comprehensive emission inventory submitted by the Stauffer Company to date (1968) is based on a raw ore utilization rate of 360,000 tons per year. The increase in ore use to 500,000 tons per year is difficult to correlate with expected increase in fluoride emissions due to insufficient information concerning plant operation. However, it is expected that fluoride emissions are increasing.

During July, 1972, 150 union workers at the Stauffer plant went on strike. The strike reportedly lasted for 90 days and resulted in a 50 percent reduction in plant operations. To what extent this affected the fluoride emission rate is also unknown.

The fluoride compounds released into the atmosphere from this source are of both a gaseous and particulate nature, and will behave in a somewhat different manner. The gaseous effluent is primarily hydrogen fluoride (HF), and the particulate is primarily fluoroapatite dust. The atmospheric transport of these fluoride effluents will be modified by certain characteristics of the source such as height of the point of release, velocity of air movement in the stack, and termperature of the stack effluent, among others. It is generally accepted that hydrogen fluoride gas has the potential to be more widely dispersed by atmospheric transport than the particulate. The particulates emitted, depending on their size and density, will either settle out rapidly on the surrounding terrain or may be carried further downwind. Since the air movements in this valley have never been studied, climatological information has been used from the Butte weather station which is situated on the other side of the Highland Mountains. Though the elevations at the Stauffer plant site and the weather station are very similar, these mountains create a barrier which isolates the Silverbow area from the weather station sufficiently enough that the wind directional data should not be relied upon.

The general direction of gaseous and particulate transport from the source will be governed by generalized air flow in the valley. These directions can change seasonally, as the whole region is affected by continental air masses. Daily changes in air movements are caused by thermal effects resulting from heating and cooling of the mountainous terrain subject to solar radiation. This area is also subject to intense atmospheric inversions which will result in high rates of gaseous fumigation and localized particulate fallout. While air movements are greatly confined by the valley structure, those confining topographic surfaces are subject to greater exposure to fluoride pollutants. Small scale topographic features within the valley may channel air movements causing very high concentrations of fluoride in some areas distant from the source, while other areas close to the source may suffer little contamination. Vegetative cover on the valley floor and slopes can modify surface wind speeds and cause a filtering effect of the pollutants.

Due to the higher dispersion potential of the gaseous effluents, it should be possible to define the range of particulate fallout within the contaminated zone by washing the vegetation samples at different locations from the source. This procedure was not utilized in this study. The literature indicates problems in the separation of particulate and gas-induced fluoride compounds due to inefficient removal of surface particulates while internal fluoride is inadvertantly leached. This process occurs naturally in the field subject to frequency, intensity and duration of rainfall.

Experiments performed with other forage plants at the Boyce Thompson Institute and by Knabe with spruce trees demonstrate a natural loss of fluoride concentrations which were induced by fumigations of hydrogen fluoride. This loss appears to be independent of washing, leaching, and growth dilution. These experiments imply that fluoride uptake and fluoride loss occur concurrently in living vegetation. Such findings do not apply to the accumulation of fluoride as a particulate surface deposit. Particulates respond to washing only to a limited entent and are considered to be far more cumulative. While gaseous uptake in plants appears to occur primarily during the growing season, particulate deposition occurs at all times of the year on active, dormant, or dead vegetative surfaces. The data presented in this study reflects total fluoride accumulation and retention on vegetation subject to all natural biological and climatological influences. To describe those influences as they function in Silverbow, Montana helps to evaluate the vegetative accumulation of fluoride in that area.

During the months of November through February, precipitation averages one half inch or less and is primarily in the form of sleet or snow. Monthly precipitation gradually increases to nearly two inches of rainfall during May. At this time the soils become warmer and the new growth begins to emerge from the dormant bluebunch wheatgrass. Also during this period, the uptake of HF gas will reach a high level and particulate accumulation will begin on the new growth. The heavy rainfall and the diluting effect of vegetative growth will actively reduce fluoride accumulation. The month of June is the highest rainfall month, averaging 2½ inches. Though the growing season in the area lasts until October, the growing conditions necessary for bluebunch wheatgrass often cause the onset of dormancy during July. The July rainfall averages over one inch, but the increase in temperature and rapid loss of soil moisture create an unusual stress on this plant. As dormancy occurs the absorption of HF gas will dissipate, but particulate deposition will continue through September until October when the rainfall average drops below one inch per month. On October 6, field collections were made. These collections occurred at the end of the greatest foliar washing period--May through September. These collections also occurred at the end of a month of dormancy, which allowed gaseous induced accumulations to be in a state of decline. In addition, this collection period followed the 90-day labor strike which probably reduced the amount of fluoride emissions during that period. The fluoride concentration and distribution displayed by the isopol map (Map #3, page 18) is believed to be a very conservative evaluation of contamination of the Silverbow area during the summer of 1972.

The forage collections representing vegetative remains of previous years' growth (1971 and older) have been subject to year-round contamination for possibly five years. To estimate the cumulative effects of HF induced contamination at this time is difficult. However, the accumulation of the highly insoluble fluoroapatite particulate is certain to comprise the majority of the fluoride found in these samples. If the increased production capacity of the Stauffer plant in any way leads to increased emissions of fluoride effluents, then these vegetation samples do not accurately depict future trends. Since the increase in production has occurred since 1968, it should take a few more years before an equilibrium is established between vegetative accumulation and contaminate loss.

Juniper samples were not separated by age class. These composite samples have simply served to support the pattern of fluoride distribution found in the bluebunch wheatgrass.

Soil samples collected in the area do not display fluoride distribution patterns as clearly as vegetation samples. The reason for this is probably due to higher background levels of fluoride naturally occurring in the soils. The fluorspar deposits found in the area may account for part of this background level. To determine control levels for soils under these circumstances would not help clearly establish the range of contamination originating at the air pollution source. The rapid rate of fluoride increase in the surface soils within a radius of two miles from the source does indicate a heavy particulate fallout zone. As particulate concentrations increase on the surface of exposed, uncultivated soils another problem arises. During dry periods, surface air movements may transport these particulates and deposit them on foliar surfaces (49). These particulate deposits on the soil surface can then become a long-lasting insidious source of future fluoride contamination for forage crops in the area.

Under normal range conditions, the consumption of juniper by wild and domestic herbivores is minimal. However, cattle, horses, sheep, deer, and elk have shown a preference for bluebunch wheatgrass in many areas (50, 51, 52). This species of forage grass in this study is abundant, regularly consumed by herbivores, and highly contaminated.

Conclusions

The phosphorus extraction process employed at the Stauffer Chemical Company in Silverbow, Montana, has resulted in the atmospheric emission of gaseous and particulate fluoride compounds. These contaminants have been demonstrated to occur at excessive concentrations throughout a 16,000 acre area surrounding the company property. Over 11,000 acres within this area contain fluoride concentrations in forage grasses which exceed the maximum allowable limits (35 parts per million) imposed by the State of Montana.

Determination of gaseous vs. particulate fluoride accumulations has not been done, but should be done in future studies to determine the exact character of the contamination and to predict its persistence in the area. The fluoroapatite particulate found in the area is considered to be a highly insoluble compound. This form of effluent is known to be cumulative in nature and will continue to increase in concentration until the source emissions cease.

The accumulation of fluoride compounds in and on indigenous forage grasses of this area is a most significant problem due to the regular utilization of this resource by cattle and wildlife.

Field collection and chemical analysis of composite juniper samples revealed a fluoride distribution pattern identical to that found in forage grass.

Collection and analysis of surface soils in areas distant from the source yielded less distinct distribution patterns, due to greater particulate fallout near the source and/or due to higher natural levels of soil fluoride in the area. Substantial increases in soil fluoride concentration were found at locations within two miles of the source.

Biological monitoring for fluoride accumulation in the Silverbow area, through chemical analysis of indigenous vegetation and soil is demonstrated and recommended as one of the best means of evaluating the ecological impact of fluoride air pollution.

Continuing Studies Needed

Further monitoring of this area should be undertaken in order to evaluate the potential fluoride-induced damage to livestock and the grazing resources. It is suggested that the State Regulatory Agency establish permanent vegetation sampling plots at locations where livestock and wildlife use of forage is deemed most probable. It is further recommended that HF effects on timber growth rates in areas of higher elevation should be investigated.

The local patterms of daily and seasonal air movements need to be monitored in this valley system. For purposes of evaluating human exposure to these contaminants, air sampling needs to be done for determination of fluoride, phosphorus, and radio isotope concentrations (53) in the nearby communities of Ramsay and Nissler, Montana.

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APPENDIX I

All fluoride concentrations listed in Appendix I are in parts per million (dry weight).

Numbers in parenthesis are re-analysis of same sample.

ANALYSIS RESULTS IN PPM F^-
FOR AGROPYRON SPICATUM
1971 (and older) Growth

Isopol Area Grouped by ppm. F^-	Collection Route #												
	1	2	3	4	5	6	7	8	9	10	11	12	
Below 20 ppm.	16					18 18					14		
≥20 and <35	26(30) 19	24 14 17 19 17 27		26 32	24 27 25	22 20 16 10 23 27 6 28	20 23		30 22 18 28 20	32		20 28 33 31 32 33	N = 35 X = 23ppm.
≥35 and <55	41 48 52	32(35) 23(21)			35 28		52	37 51 35 41 50			34 36 48 38 28 40	43 26 32 53	N = 23 X = 39ppm.
≥55 and <100		55 55	61 54 31 60 30 66(70)	70 47						54 20	86 67	60	N = 15 X = 55ppm.
≥ 100		97 91 450 1090 19(18)	96 142 590 500										N = 9 X = 342ppm.

Re-analysis + original analysis are averaged as one value.
N = Number of samples analyzed
X = Mean F^- concentration of all samples within the specific isopol areas.

ANALYSIS RESULTS IN PPM F^- FOR AGROPYRON SPICATUM 1972 Growth

Collection Route #

Isopol Area Grouped by ppm. F^-	1	2	3	4	5	6	7	8	9	10	11	12	
Below 20 ppm.	6 12(11) 7 18	12 11		14 11 16	11 16 11 18 12	8 15 12(11) 10 9 13 15 15 4	11 17 6				12 12 16	17	
≥20 and <35	26 31	20 20(20) 11 17(23) 33(34) 22(23) 24		30 22		22			27 8 16 10 16 13	22 30 27	22	26 20 27 17 28(25) 24(23) 24 18	$\underline{N} = 30$ $\bar{X} = 22$ppm.
≥35 and <55		37	35 35(33) 33 50 25					34 44 32 26 29			51 24 31 29 29	34 50	$\underline{N} = 18$ $\bar{X} = 36$ppm.
≥55 and <100		59 65	56(69) 65							55 65 72 26 30	68 78		$\underline{N} = 11$ $\bar{X} = 59$ppm.
≥100		196 450 16	100 244										$\underline{N} = 5$ $\bar{X} = 201$ppm.

JUNIPER (Juniperus spp.)

Composite Samples

Route#-Sample#	PPM Fluoride	Route#-Sample#	PPM Fluoride
2 - 7	19	10 - 16	42
2 - 9	19(25)*	10 - 18	54
2 - 14	53(59)	10 - 21	36
2 - 15	68	10 - 22	55
2 - 16	73	10 - 23	48
2 - 18	390	11 - 1	44
2 - 19	420(420)	11 - 2	18
4 - 6	23	11 - 3	33
4 - 7	39	11 - 4	23
5 - 4	18	11 - 5	36
5 - 5	14	11 - 6	27
5 - 7	14	11 - 8	36
7 - 4	12	11 - 9	51
7 - 14	37	11 - 10	32
7 - 17	23	11 - 11	38
8 - 5	36	12 - 4	15
8 - 6	33	12 - 6	26
8 - 11	40	12 - 9	25
10 - 10	65	12 - 12	31
10 - 12	114	12 - 15	30
10 - 14	134		

*Numbers in parenthesis are re-analysis of same sample

DOUGLAS FIR (*Pseudotsuga menziesii*)

PPM Fluoride

Route#-Sample#	1972	1971	1970	1969	1968
2 - 0	-	15	19	-	-
2 - 1	10(10)	15	24	-	-
2 - 2	15	15	15-18	-	-
2 - 8	13	10(14)	14(15)	-	-
2 - 14	25	38	34	-	-
2 - 16	42	87	68	-	-
3 - 1	36	44	50	-	62
3 - 3	19	25	19	24	27
4 - 6	18	19	17	14	-
5 - 3	13	5	13	-	-
5 - 7	6	10	11	14	-
7 - 3	19	14	17	24	13
7 - 10	11	12	14	15	18
8 - 7	35	32	-	34	37
10 - 8	-	50	46	70	-
10 - 11	62	73	83	118	116
10 - 20	28	35	-	-	-
11 - 1	13	18	21	-	-
11 - 2	16	17	20	-	-
11 - 3	17	24	28	-	-
11 - 5	30	27(28)	29	-	-
11 - 6	-	32	38	-	-
11 - 8	36	34	47	-	-

DOUGLAS FIR (*Pseudotsuga menziesii*)

PPM Fluoride

Route#-Sample#	1972	1971	1970	1969	1968
11 - 9	42	49	70	-	-
11 - 10	44	47	50	-	-
12 - 10	15	16	16	-	-
12 - 17	17	20	21	20	-

LODGEPOLE PINE (*Pinus contorta*)

Route#-Sample#	1972	1971	1970	1969	1968
2 - 17	51	126	70	-	-
2 - 18	48	220	290	-	-
4 - 1	11	19	-	-	-
5 - 2	4	13	11(6)	6	12
5 - 6	6	15	11	11	-
12 - 8	11	14	-	-	-
12 - 13	11	21	26	15	-

BLACK COTTONWOOD (*Populus trichocarpa*)

Route#-Sample#	PPM Fluoride
1 - 8	10
8 - 2	7

QUAKING ASPEN (*Populus tremuloides*)

Route#-Sample#	PPM Fluoride
4 - 8	53
7 - 11	15

BITTERBRUSH (*Purshia tridentata*)

Route#-Sample#	PPM Fluoride
7 - 7	12
8 - 7	29
8 - 8	27

CURRANT (*Ribes spp.*)

7 - 2	24

ROSE (*Rosa spp.*)

10 - 9	76

WILLOW (*Salix spp.*)

8 - 13	119
8 - 15	100

MOUNTAIN MAHOGANY (*Cercocarpus spp.*)

2 - 0	18(14)
6 - 11	13
7 - 8	71

GIANT WILD RYE (*Elymus cinereus*)

Route#-Sample#	1972	1971 and older
2 - 3	17	14
2 - 12	30	33
2 - 13	36	162
4 - 8	32	-
11 - 7	26	32

FOXTAIL BARLEY (*Hordeum jubatum*)

Route#-Sample#	1972	1971 and older
4 - 2	25	-
4 - 3	19	-

CRESTED WHEATGRASS (*Agropyron cristatum*)

Route#-Sample#	1972	1971 and older
4 - 4	20	-

SOIL ANALYSIS

Route #	Site	F^- Average ppm.	Analysis F^- ppm.
2	1	830	(792-869)
	6	296	
	10	516	
3	5	617	(599-635)
	8	440	
	10	700	
	13	415	(383-448)
4	2	482	(542-422)
	4	548	
	5	469	
	6	274	(314-274)
	7	1160	
	9	620	
5	1	265	
	4	423	(344-502)
6	1	292	
	2	334	
	3	424	
	4	516	
	5	381	
	8	582	
	9	440	
	10	772	(618-826)
	11	708	

SOIL ANALYSIS

Route #	Site	F^- Average ppm.	Analysis F^- ppm.
7	6	519	
	12	574	(440-708)
	21	536	(577-492)
	25	551	
8	3	366	(373-355)
	6	427	(413-440)
	9	428	
	11	391	
	12	1036	
	13	1265	
	14	1840	(1839-1840)
9	1	560	
	2	381	
	3	680	
	4	326	
10	28	395	(375-419)
	47	488	
11	5	324	
12	1	318	
	6	440	
	19	560	
	20	536	

APPENDIX II

Controls*

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*All fluoride concentrations for control vegetation are taken from the files of the Environmental Studies Laboratory, University of Montana, Missoula, Montana.

All fluoride concentrations listed in Appendix II are in parts per million (dry weight).

CONTROLS

BLUEBUNCH WHEATGRASS (Agropyron spicatum)

Composite Samples

Sample #	Collection Date	Location	PPM Fluoride
K-55	10/10/71	1 mi. below Nevada Cr. Reservoir (near Avon)	5.0
K-60A	10/10/71	East of Avon, Montana	3.6
K-87	10/11/71	Ray Murray's, Avon, Montana	6.4
K-88	10/11/71	West of Helena, Mont. on U.S. 12	3.8
K-159B	10/22/71	Quigglies Pond, Avon, Montana	3.5
K-162C	10/23/71	Kieleys' Ranch Nevada Cr., Montana	5.2

CRESTED WHEATGRASS (Agropyron cristatum)

Sample #	Collection Date	Location	1970	1971	Fall '71
K-56	10/10/71	Mont. 272, South of Kenny Price Ranch	8.0	7.2	7.8
K-57	10/10/71	Avon Valley Divide on Mont. 272	3.2	4.4	3.4

ROCKY MOUNTAIN JUNIPER (Juniperus scopularum)

Sample #	Date	Location	PPM Fluoride
K-89A	10/11/71	3 mi. east of MacDonald Pass	4.6
K-162B	10/23/71	Kieley's Nevada Creek	5.8
K-163	11/5/71	1 mi. east of Luke Mine	5.8
K-165	11/7/71	R.R. Bridge 5 mi. east of Garrison	7.0
K-166	11/7/71	1/2 mi. west of Deerlodge cut-off on U.S. 12	8.0
K-166A	11/7/71	1/2 mi. west of Deerlodge cut-off road on U.S. 12	7.4

DOUGLAS FIR (*Pseudotsuga menziesii*)

Sample #	Date	Location	68	69	70	71
STR.C-18	7/16/70	St. Regis, Mont.	1.95	1.85	1.52	
RP.C-2	7/17/70	Roger's Pass, Montana 200	2.9	3.2	1.8	
TWC-2 (1)	8/9/70	Twin Creek, Blackfoot	1.8	4.1	1.55	
TWC-2 (2)	8/9/70	Twin Creek, Blackfoot	1.7	1.5	1.55	
K-60D	10/10/71	East of Avon		4.6	4.2	4.4
K-90	10/11/71	Campground west of MacDonald Pass		3.0	3.6	3.2
K-159A	10/22/71	Quigglies Pond, Avon		5.8	4.6	3.8
K-160A	10/23/71	Ray Murray's Nevada Creek		3.7	3.9	2.8
K-162A	10/23/71	Kieley's Nevada Creek		3.2	2.4	3.1
Hall 34	Nov/71	Bass Creek	3.0	2.2	2.7	5.6
Hall 35	Nov/71	Bass Creek	2.7	2.8	2.5	5.3
Hall 110	Nov/71	Bass Creek	2.8	3.2	2.8	3.2
Hall 111	Nov/71	Bass Creek	3.8	3.2	4.6	4.8

LODGEPOLE PINE (Pinus contorta)

Sample #	Location	1968	1969	1970
C-2	Elk Creek, Mont.	2.2	2.1	2.0
C-3	Elk Creek, Mont.	2.0	1.9	3.2
STR-3	St. Regis, Mont.	2.4	2.3	1.7
STR-7	St. Regis, Mont.	1.0	1.0	1.2
STR-9	St. Regis, Mont.	1.2	1.2	1.1
STR-14	St. Regis, Mont.	1.2	1.5	1.4
STR-17	St. Regis, Mont.	1.4	5.2	1.2
STR-20	St. Regis, Mont.	1.3	3.9	1.0
RP-1	Roger's Pass, Mont	2.1	2.4	2.8
SWC-5	GNP Swiftcurrent, Mont.	2.9	2.3	1.6

BLACK COTTONWOOD LEAVES (*Populus trichocarpa*)

Sample #	Date	Location	PPM Fluoride
K-60B	10/11/71	East of Avon	5.4
K-61A	10/10/71	Red Bridge, south of Avon	9.2
K-62	10/10/71	Small rest area, west of Avon	4.4
K-63	10/10/71	State rest area west of Avon	5.6
K-63A	10/10/71	State rest area west of Avon	5.4
K-64	10/10/71	River Bridge Deerlodge Cut-off Rd.	8.4
K-88A	10/11/71	West of Helena on U.S. 12	6.1

BITTERBRUSH LEAVES (*Purshia tridentata*)

Sample #	Date	Location	PPM Fluoride
K-60	10/10/71	East of Avon, Mont.	8.8
K-89	10/11/71	3 mi. east of MacDonald Pass	8.4