

## USE OF POLLUTION BIOINDICATORS FOR FLUORIDE IN THE VICINITY OF COAL THERMOELECTRIC POWER PLANTS

Érico M. M. Flores and Ayrton F. Martins\*

Departamento de Química  
Universidade Federal de Santa Maria  
Santa Maria, RS, BRASIL 97119-900

## ABSTRACT

*Determination of fluoride in environmental samples of pasture and honey lead to the conclusion that these materials may be used as pollution bioindicators in areas of industrial activity. Concentrations of fluoride determined in recent times are above reference values. This observation is reinforced by the occurrence of various cases of bone deformation (fluorosis) and dental problems of ruminants in the area. A synergetic effect of fluoride on the abrasion of coal ash deposited on graze lands is also observed.*

KEYWORDS: Fluoride, Pollution Bioindicators, Pasture, Honey.

## RESUMO

*A determinação de fluoreto em amostras de pastagem e mel permite concluir que estas matrizes podem ser utilizadas como bioindicadores de poluição em zonas de atividade industrial. Valores determinados em épocas mais recentes encontram-se acima de valores de referência. Esta constatação é reforçada pela ocorrência de diversos casos de deformação óssea (fluorose) e acentuado desgaste dentário em ruminantes nas imediações. Verificou-se, também, um efeito sinérgico da abrasão da cinza de carvão depositada com a ação do fluoreto sorvido na pastagem.*

## INTRODUCTION

Among the common air contaminants, fluoride is generally considered the most dangerous phytotoxic agent, even when polluting in trace amounts<sup>1</sup>. Plants grown in areas contaminated by fluoride show a series of physiologic injuries caused by the absorption of fluoride<sup>2,3,4</sup>.

The intensive use of coal in the generation of thermoelectricity is along with the processing of phosphate minerals a very important source of fluorine dispersion in the environment<sup>5,6,7</sup>. Fluoride concentrations above 100 ppm are common in mineral coal<sup>8,9</sup>. During combustion, this air pollutant is volatilized and expelled through the chimney along with fly ash and gases<sup>10</sup>.

\* Author to whom correspondence should be addressed.

Under the influence of climactic factors, the emitted fluorine returns to the soil in the form of fluoride, it is deposited and interacts with the components of the biosphere (water, soil, vegetation, fauna, etc.)<sup>11</sup>.

The concentration of fluoride in environmental materials can be an indicator of the degree of environmental contamination. It is a function of regional climactic factors and the distance from the source of the emission<sup>12,13</sup>.

This paper deals with the determination of fluoride concentration in samples of pasture and honey collected for a period of three years (1987-90) using ion-selective electrode techniques. Samples were collected in the vicinity of two thermoelectric power plants located in Southern Brazil. One is Usina Termoelétrica Presidente Medici (UTPM/446 MW), located at Candiota, Bagé, Rio Grande do Sul. The other is Usina Termoelétrica de Charqueadas (UTC/72 MW), situated at Charqueadas, Rio Grande do Sul. In both areas, besides the generation of thermoelectricity, coal mining is also practiced - in open pits in Candiota and 300 m deep mines in Charqueadas.

The experimental results obtained by the analysis of the environmental samples were submitted to statistical treatment in order to verify the behavior of concentration (dependent variable) as a function of three factors: distance from the plant, time of collection of samples and direction of collection of samples.

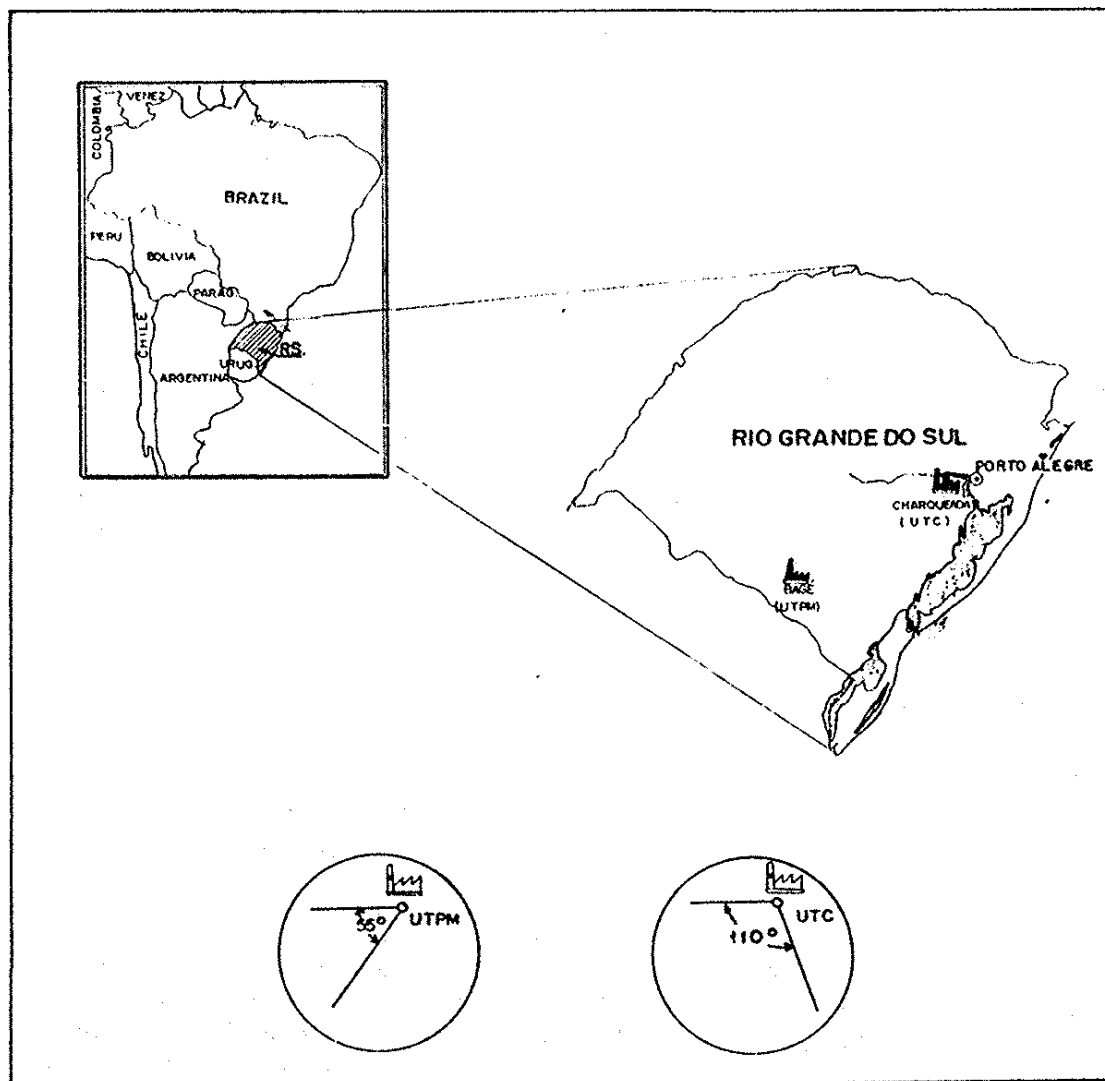
## MATERIALS AND METHODS

The aerial parts of predominant forage grasses (*Panicum gramineae*, *Piptochaetium montevidense*, *Paspalum notatum*, *Aristida* sp. e *Eupatorium buniifolium*) were collected within a 1.3 - 11.8 km range of UTPM (63 samples) and 0.5 - 5.6 km of UTC (29 samples) in the direction of prevailing winds (SW in Candiota and SE in Charqueadas). The sampling was restricted to previously determined areas, with the plants at the center and angles of 55° and 110°. (See Figure 1).

The samples of honey were collected in the places of production within a range of 0.5 - 22.0 km (17 samples) from UTPM and 3.5 - 32.0 km (13 samples) from UTC in the areas of sampling previously determined.

Reference forage grass samples were collected at about 50 km from UTPM and 20 km from UTC in a direction contrary to prevailing winds. Reference samples of honey were obtained from different localities, in areas not affected by anthropogenic processes.

The pasture material collected was reduced to maximum lengths of 2 mm using a micromill and dried in an oven at 50° C for 5 hours. Two-gram samples of the dried material was subsequently washed for 2 hours with 70 ml of 0.46% HNO<sub>3</sub>. The solution was filtered using filter paper and the volume was



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FIGURE 1. SAMPLING AREAS: CANDIOTA ( UTPM - USINA TERMOEL TRICA PRESIDENTE MEDICI ) AND CHARQUEADAS ( UTC - USINA TERMOEL TRICA DE CHARQUEADAS ), RIO GRANDE DO SUL, BRAZIL.

completed to 100 ml with 0.46%  $\text{HNO}_3$  (Solution 1;  $\text{F}^-$  extracted). The residue was dried at 50° C for 8 hours and transferred to a 250 ml PTFE container and subjected to acid digestion under pressure. After adding 10 ml of conc.  $\text{HNO}_3$  and 2 ml of 30%  $\text{H}_2\text{O}_2$ , the system was hermetically sealed and heated at 150° C for 6 hours. After cooling and relieving the pressure, 5 ml of conc.  $\text{NH}_4\text{OH}$  were added. The solution was filtered and diluted to 100 ml with 0.46%  $\text{HNO}_3$  (Solution 2;  $\text{F}^-$  absorbed).

The treatment of the samples of honey was also done using high pressure and PTFE containers. To a 2 g sample of honey 7 ml of conc.  $\text{HNO}_3$  and 1 ml of 30%  $\text{H}_2\text{O}_2$  were added and the system was heated at 130° C for 4 hr. Subsequently the solution was cooled, the system opened, 3 ml of concentrated  $\text{NH}_4\text{OH}$  were added, followed by dilution to 50 ml with 0.46%  $\text{HNO}_3$  (Solution 3,  $\text{F}^-$ , honey).

Solutions 1, 2 and 3 were analyzed by direct potentiometry using a fluoride ion-selective electrode (ISE- $\text{F}^-$  Analion F656) and a calomel reference electrode (Jena Glass B281) coupled with a Philips PW 9409 digital potentiometer. Buffer solution for total ionic strength adjustment (TAFIT) was added to the samples at 1:1 (v/v) ratio<sup>14</sup> and the measurements were made under constant agitation. Blank samples were also analyzed using the technique of standard addition.

## RESULTS AND DISCUSSION

Fluorine, like other elements such as Hg, As and Se passes with relative ease through electrostatic filters and for this reason thermoelectric power plants exhibit a high concentration of emission of this atmospheric pollutant (up to 75%)<sup>10</sup>. (See Table I).

Deposition of fluoride from the atmosphere is an important factor in the contamination of biosphere reservoirs. Plants are particularly affected, since they absorb fluoride easily from the air<sup>15,16,17</sup>. They show cellular membrane damage and leaf necrosis<sup>18,19,20</sup>. The absorption of fluoride from the soil is relatively low, due to its reduced mobility in this environment. Fluoride is concentrated in the aerial parts of plants, where its physiologic effects are more pronounced<sup>21,22</sup>. For this reason, bioindication of pollution can be done using only the superior parts of the plants and analysis of the roots is not necessary.

Tables II and III show the concentration of fluoride ( $\text{F}^-$  extracted,  $\text{F}^-$  absorbed and  $\text{F}^-$  total) from pastures in the regions studied as a function of distance, time of collection and direction. Individual values of total fluoride concentration surpass 30 to 40 ppm, usually referred to as a limiting value, above which there is clear indication of physiologic damages<sup>23,24,25,26</sup>.

TABLE I. MATERIAL BALANCE FOR UTPM POWER PLANT.<sup>10</sup>

Element	Coal (ppm)	Bottom Ash (ppm)	Light Ash (ppm)	Emission (kg/d)	Losses (%)
F	169	48.5	83.5	1,115	75
Hg	0.76	0.18	0.43	4.8	73
As	2.56	0,05	0.15	21.7	97
Se	1.46	0.34	0.83	9.3	73

Coal consumption: 10,300 t/d; Effectiveness of electrostatic filters: ~92.5%

TABLE II. CONCENTRATION (PPM) OF FLUORIDE IN SAMPLES OF PASTURE FROM CANDIOTA REGION (INDIVIDUAL VALUES). AVERAGE VALUES AND STANDARD DEVIATIONS OF TWO OR MORE DETERMINATIONS FOR EACH SAMPLE.

Time of Collection	(km)*	F <sup>-</sup> abs.	F <sup>-</sup> ext.	F <sup>-</sup> total
November/1987	1.5	9.00±0.15	44.39±0.30	53.30
November/1987	3.5	11.13±1.52	20.65±3.42	31.78
November/1987	5.0	39.73±0.15	5.61±0.21	45.34
November/1987	5.0	47.87±4.58	11.91±1.57	59.78
November/1987	5.0	8.38±1.90	2.42±1.06	10.70
April/1988	1.5	27.82±0.84	18.63±2.54	46.45
April/1988	3.5	16.09±1.83	9.21±1.13	25.30
April/1988	4.0	20.23±2.75	10.45±1.13	30.68
April/1988	5.0	15.84±1.97	9.35±1.55	25.19
April/1988	5.0	41.23±3.96	17.02±3.11	58.25
April/1988	6.0	18.20±0.85	11.01±1.41	29.21
April/1988	6.5	28.42±0.48	11.20±0.22	39.62
April/1988	7.0	29.82±0.36	10.45±1.42	40.27
April/1988	9.0	24.63±0.18	8.82±0.48	33.45
April/1988	10.0	18.03±2.45	5.84±0.84	23.87
August/1988	1.3	8.46±0.82	3.01±0.42	11.47
August/1988	1.5	20.95±2.19	4.60±0.35	25.55
August/1988	1.5	6.67±0.60	2.51±0.57	9.18
August/1988	2.8	28.15±1.20	3.04±0.15	31.19
August/1988	3.0	27.70±2.40	3.98±0.68	31.68

TABLE II. (CONTINUATION)

August/1988	3.0	7.75 $\pm$ 1.06	2.74 $\pm$ 0.05	10.49
August/1988	4.7	9.67 $\pm$ 0.24	3.00 $\pm$ 0.70	12.67
August/1988	5.0	6.65 $\pm$ 0.71	2.45 $\pm$ 0.14	9.10
August/1988	5.0	23.42 $\pm$ 0.59	5.05 $\pm$ 0.21	28.47
August/1988	6.7	10.87 $\pm$ 0.17	2.40 $\pm$ 0.14	13.27
August/1988	7.0	9.32 $\pm$ 0.45	3.12 $\pm$ 0.03	12.44
August/1988	7.0	7.05 $\pm$ 0.21	1.97 $\pm$ 0.17	9.02
August/1988	8.6	4.95 $\pm$ 0.63	1.93 $\pm$ 0.11	6.88
August/1988	9.0	12.12 $\pm$ 0.53	1.55 $\pm$ 0.14	13.67
August/1988	11.0	5.50 $\pm$ 0.71	1.67 $\pm$ 0.24	7.17
August/1988	11.5	3.95 $\pm$ 0.35	1.49 $\pm$ 0.21	5.44
August/1988	11.8	6.16 $\pm$ 0.59	3.26 $\pm$ 0.13	9.42
January/1989	1.3	8.17 $\pm$ 0.24	6.27 $\pm$ 0.03	14.44
January/1989	1.6	8.22 $\pm$ 1.73	2.74 $\pm$ 0.70	10.96
January/1989	1.6	6.77 $\pm$ 0.10	2.52 $\pm$ 0.03	9.29
January/1989	2.8	12.50 $\pm$ 2.96	2.07 $\pm$ 0.11	14.57
January/1989	3.1	15.37 $\pm$ 0.17	4.03 $\pm$ 0.18	19.40
January/1989	3.1	4.26 $\pm$ 0.68	2.10 $\pm$ 0.14	6.36
January/1989	4.6	6.00 $\pm$ 0.28	4.65 $\pm$ 0.21	10.65
January/1989	5.0	4.50 $\pm$ 0.28	2.25 $\pm$ 0.21	6.75
January/1989	5.0	4.25 $\pm$ 0.35	2.43 $\pm$ 0.11	6.68
January/1989	7.0	7.67 $\pm$ 0.25	3.78 $\pm$ 0.60	11.45
January/1989	7.1	5.05 $\pm$ 0.28	3.60 $\pm$ 0.28	8.65
January/1989	7.0	5.43 $\pm$ 0.11	3.33 $\pm$ 0.18	8.76
January/1989	8.2	14.65 $\pm$ 0.21	3.13 $\pm$ 0.32	17.78
January/1989	8.5	16.30 $\pm$ 1.55	3.17 $\pm$ 0.10	19.47
January/1989	11.0	3.87 $\pm$ 0.53	3.58 $\pm$ 0.24	7.45
January/1989	11.3	4.67 $\pm$ 0.95	1.96 $\pm$ 0.24	6.63
January/1989	11.8	4.05 $\pm$ 0.14	2.40 $\pm$ 0.13	6.45
August/1989	1.3	4.60 $\pm$ 2.69	2.03 $\pm$ 0.31	6.63
August/1989	1.6	9.20 $\pm$ 0.08	2.89 $\pm$ 0.49	12.09
August/1989	1.6	3.80 $\pm$ 0.28	2.45 $\pm$ 0.97	6.25
August/1989	2.8	6.00 $\pm$ 0.00	2.69 $\pm$ 1.10	8.69
August/1989	3.1	3.15 $\pm$ 0.35	1.80 $\pm$ 0.14	4.95
August/1989	3.1	2.75 $\pm$ 0.35	1.70 $\pm$ 0.14	4.45
August/1989	4.6	2.55 $\pm$ 0.92	1.80 $\pm$ 0.08	4.35
August/1989	5.0	3.60 $\pm$ 1.65	1.87 $\pm$ 0.04	5.47
August/1989	5.0	4.45 $\pm$ 0.21	2.45 $\pm$ 0.07	6.90
August/1989	7.1	2.48 $\pm$ 0.11	1.68 $\pm$ 0.74	4.16
August/1989	7.0	3.20 $\pm$ 0.14	2.50 $\pm$ 0.00	5.70
August/1989	8.5	2.15 $\pm$ 0.07	1.35 $\pm$ 0.21	3.50
August/1989	11.3	2.00 $\pm$ 0.28	1.05 $\pm$ 0.07	3.05
August/1989	11.8	4.05 $\pm$ 0.21	1.95 $\pm$ 0.07	6.00

F<sup>-</sup> concentration in reference samples: F<sup>-</sup> abs.=2.26 $\pm$ 0.02;

F<sup>-</sup> ext.=1.15 $\pm$ 0.00; F<sup>-</sup> total=3.35 ppm

\* Distance from UTPM

TABLE III. CONCENTRATION (PPM) OF FLUORIDE IN SAMPLES OF PASTURE FROM CHARQUEADAS REGION (INDIVIDUAL VALUES). AVERAGE VALUES AND STANDARD DEVIATIONS OF TWO OR MORE DETERMINATIONS FOR EACH SAMPLE.

Time of Collection	(km)*	F <sup>-</sup> absorbed	F <sup>-</sup> extracted	F <sup>-</sup> total
July/1988	1.0	13.00±1.03	4.43±0.11	17.43
July/1988	2.0	6.87±0.04	4.05±1.20	10.92
July/1988	3.0	4.58±0.11	2.60±0.95	7.18
July/1988	4.0	6.20±0.39	2.51±0.49	8.71
July/1988	5.5	5.57±0.26	2.78±0.38	8.35
December/1988	0.5	10.28±1.19	4.53±0.78	14.81
December/1988	1.3	6.75±1.06	5.50±0.00	12.25
December/1988	1.6	5.63±0.32	2.23±0.03	7.86
December/1988	2.0	5.28±0.26	2.90±0.92	8.18
December/1988	2.6	4.52±1.02	2.93±0.25	7.45
December/1988	2.8	5.18±0.11	4.60±0.42	9.78
December/1988	3.5	32.25±2.47	4.75±0.90	37.00
December/1988	3.8	5.15±0.85	2.76±0.17	7.91
December/1988	5.0	16.70±1.84	2.03±0.32	18.73
December/1988	5.5	5.85±0.85	1.75±0.14	7.60
June/1989	0.5	26.90±0.56	27.85±0.21	54.75
June/1989	1.3	45.55±0.35	5.00±0.28	50.55
June/1989	1.3	47.15±0.21	13.55±0.07	60.70
June/1989	1.6	13.65±0.21	8.10±0.14	21.25
June/1989	2.0	24.35±0.64	8.50±0.00	32.85
June/1989	2.3	33.10±0.28	8.05±0.07	41.15
June/1989	2.6	36.30±0.00	7.13±0.18	43.43
June/1989	2.8	21.05±0.35	5.15±0.21	26.20
June/1989	3.5	3.10±0.28	3.00±0.14	6.10
June/1989	3.8	5.25±0.07	7.40±0.14	12.65
June/1989	3.9	4.75±0.07	6.70±0.42	11.45
June/1989	5.0	4.55±0.35	4.45±0.07	9.00
June/1989	5.5	3.25±0.07	6.40±0.14	9.65
June/1989	5.6	3.65±0.22	4.93±0.11	8.58

F<sup>-</sup> concentration in reference samples: F<sup>-</sup> abs.=2.26±0.02;

F<sup>-</sup> ext.=1.15±0.00; F<sup>-</sup> total=3.35 ppm

\* Distance from UTPM

The data in Tables II and III was submitted to two types of statistical treatment. The first one involved Analysis of Variance (ANOVA) and had as an objective to test if the factors such as distance, time of the year and/or direction of collection of samples interfere with the total concentration of fluoride in pasture. The level of significance adopted for ANOVA was 5%.

A comparison with the fluoride values calculated using ANOVA (*F-test*) showed that for Candiota there was a real difference between the average values of fluoride as a function of time and for Charqueadas as a function of distance. The differences in each group were identified using Tuckey's Test with a significance level of 5%. (Table IV).

This means that for Charqueadas the average values of fluoride are statistically equal when grouped as a function of time and site of sampling and different when the concentrations are grouped as a function of distance.

On the other hand, in Candiota the average values of fluoride concentrations are statistically equal when grouped as function of site of collection and distance and are different and decrease when grouped as a function of the time of sampling (Figure 2). This fact can be explained by the use of new, more efficient electrostatic filters in UTPM starting with April 1988. These new filters have a higher capacity to capture the finer fraction of ash, possibly richer in fluoride.

Interestingly, the ANOVA test also showed, as expected, that the average concentrations were equal as a function of site of collection in both Candiota and Charqueadas. In Candiota this was explained by the major dispersion of the emitted fluorine due to the tall chimney (140 m). In Charqueadas, on the other hand, where the chimney is shorter (60 m) the possible explanation is the change in direction of the winds in the region.

The second statistical treatment involved identifying the average concentrations that are statistically equal as a function of time (in Candiota) and distance (in Charqueadas). Tuckey's Test, with significance levels of 5% was employed and the results are shown in Table IV.

It was shown that there are no real differences for the average values as a function of distance and direction in Candiota and time and direction in Charqueadas.

In Charqueadas, the concentration of fluoride decreases with the increase of distance from UTC. Statistically, this does not happen in Candiota, where the apparent decrease of concentration with distance from UTPM is casual and not real (Figure 2). This is in agreement with the ANOVA test and also with Tuckey's Test.

The tendency of increasing values as a function of time obtained in Charqueadas is apparent and is not confirmed by the ANOVA test. The decreasing variation of concentration in Candiota as a function of time of sampling is confirmed by the ANOVA test and may be explained by the use of new electrostatic filters, as previously mentioned.



TABLE IV. CONCENTRATION (PPM) OF FLUORIDE IN SAMPLES OF PASTURE FROM CANDIOTA AND CHARQUEADAS REGIONS (STATISTICAL VALUES).

	Lower limit ( $\alpha/2=5\%$ )	Average	Upper limit	Number of samples	F-test (calculated)	Tukey's test ( $\alpha=5\%$ )*
CANDIOTA REGION						
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Distance (km)						
1→3	14.35	18.58	22.80	14	1.79	•
3→5	17.05	21.28	25.51	14		•
5→7	10.22	15.23	20.23	10		•
7→9	7.77	12.34	16.91	12		•
9→11	14.53	23.66	32.80	3		•
11→13	0.86	6.45	12.05	8		•
Time of Collection						
November 1987	33.12	40.20	47.28	5	23.97*	•
April 1988	27.51	33.10	38.70	8		•
August 1988	10.70	14.54	18.37	17		•
January 1989	7.09	10.93	14.76	17		• •
August 1989	1.64	5.87	11.00	14		•
CHARQUEADAS REGION						
-----						
Distance (km)						
0→3	19.12	26.25	33.39	16	3.82*	•
3→5	2.21	13.00	23.79	7		•
5→7	0.00	10.32	21.97	6		•
Time of Collection						
July 1988	0.00	10.51	23.28	5	2.76	•
Dezember 1988	4.13	13.16	22.18	10		•
June 1989	20.15	27.77	35.40	14		•

\* Significant value at level of 5% ( $\alpha=5\%$ )

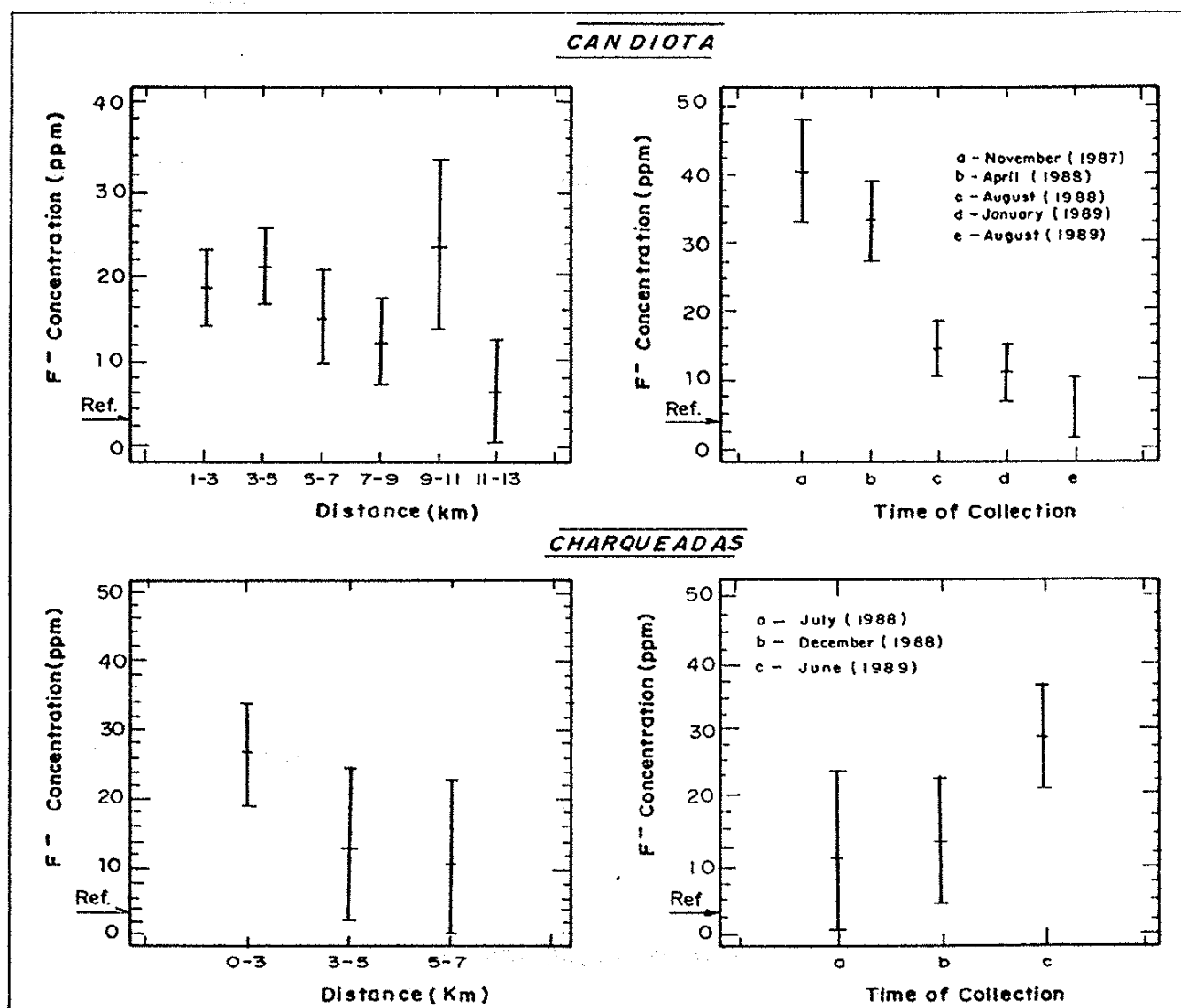


FIGURE 2. AVERAGE VALUES OF FLUORIDE CONCENTRATION (TOTAL) IN PASTURE FROM CANDIOTA AND CHARQUEADAS REGIONS AS A FUNCTION OF THE DISTANCE FROM UTPM AND UTC POWER PLANTS AND THE TIME OF COLLECTION.

TABLE V. CONCENTRATION (PPM) OF FLUORIDE IN SAMPLES OF HONEY FROM CANDIOTA AND CHARQUEADAS REGIONS.

CANDIOTA		
Distance from UTPM (km)	Time of Collection	Concentration of Fluoride (ppm)
4.5	November/1988	$4.92 \pm 0.14$
4.0	November/1988	$8.21 \pm 0.49$
6.0	April/1988	$4.22 \pm 0.74$
8.0	April/1988	$4.50 \pm 1.41$
12.0	April/1988	$4.20 \pm 1.27$
0.5	June/1988	$1.60 \pm 0.14$
6.0	June/1988	$1.45 \pm 0.14$
8.5	June/1988	$8.80 \pm 0.63$
12.0	June/1988	$1.98 \pm 0.17$
10.5	November/1988	$7.81 \pm 2.04$
12.0	November/1988	$1.42 \pm 0.30$
12.1	November/1988	$1.85 \pm 0.35$
22.0	November/1988	$1.50 \pm 0.08$
22.0	June/1989	$1.25 \pm 0.08$
11.5	January/1990	$1.52 \pm 10.09$
12.0	January/1990	$1.43 \pm 10.11$
22.0	January/1990	$1.01 \pm 10.07$
CHARQUEADAS		
Distance from UTC (km)	Time of Collection	Concentration of Fluoride (ppm)
3.5	May/1988	$6.83 \pm 0.41$
15.0	May/1988	$1.76 \pm 0.51$
20.0	May/1988	$5.18 \pm 0.21$
4.0	November/1988	$5.54 \pm 1.13$
4.0	November/1988	$1.57 \pm 0.17$
4.0	November/1988	$3.55 \pm 3.25$
4.0	November/1988	$1.26 \pm 0.03$
4.0	May/1989	$0.77 \pm 0.04$
6.0	May/1989	$1.15 \pm 0.03$
6.5	May/1989	$0.12 \pm 0.04$
18.0	May/1989	$0.15 \pm 0.06$
32.0	May/1989	$5.50 \pm 0.09$

Average values and standard deviations of two or more determinations for each sample

F<sup>-</sup> concentration in reference samples: <0,02 ppm

The variation of concentration as a function of direction is not statistically real and is not significant according to the ANOVA test for both power plants. In Candiota this may be attributed to a greater dispersion of the emitted fluorine, considering the high chimney (140 m). In Charqueadas, on the other hand, where the chimney is lower (60 m), the explanation given is as a function of possible variations in the direction of winds in the region.

In Candiota the average concentration of fluoride in pasture varied from 6.5 to 23.7 (as a function of distance); 5.9 to 40.2 (time of collection) and 8.3 to 15.3 ppm (direction). In Charqueadas the respective ranges were 10.3 to 26.3 ; 10.5 to 27.8 and 16.3 to 30.5 ppm (Table IV ).

The samples of honey analyzed exhibited higher concentration of fluoride when compared to samples from non-contaminated areas. Table V shows the concentration of fluoride as a function of distance from UTPM and UTC at the respective times of sampling.

In Candiota, the concentration of fluoride in honey ranged from 1.0 to 8.8 ppm and decreased as a function of time and distance from UTPM. In Charqueadas the values ranged from 0.12 to 6.8 ppm . The variation of concentration as a function of distance passes through a minimum at about 15 km from UTC and subsequently increases. This may be explained due to the presence of another power plant about 30 km from UTC ; in the direction of the collection of samples (Usina Termoeletrica de São Jerônimo , 17 MW).

In both cases, the concentration of fluoride in honey decreased as a function of time of sampling and exhibited values considerably higher than in reference samples (0.02 ppm). See Table V.

No correlation was found between the concentration of fluoride in the samples and the distance from the respective power plants. Eight different models were tested ( linear, exponential, multiplicative and their variations).

The experimental results obtained for the determination of fluoride in the environmental samples of pasture and honey studied, lead to the conclusion that these materials may be used as bioindicators of pollution in areas of industrial activity.

In spite of the decreasing tendency of the values observed as a function of time in Candiota, we may generally conclude that even more recent values of fluoride concentration are above those of reference samples. This conclusion is reinforced by the occurrence of various cases of bone deformation (fluorosis) and pronounced dental wear and waste in ruminants in the vicinity<sup>27</sup>. A synergetic effect of fluoride adsorbed on pasture on the abrasion of coal ash deposited on graze lands is observed. The use of samples of pasture and honey, coupled to a convenient statistical treatment, as bioindicators of pollution is recommended. They may be part of a procedure to evaluate possible contamination and consequent damages resulting from the anthropogenic dispersion of fluoride in the environment.

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