Centre d'expertise en analyse environnementale du Québec

Sampling Guide for Environmental Analysis

BOOKLET 6

FORAGE SAMPLING FOR FLUORIDE ANALYSIS

English Version of
the 2nd French Edition

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Québec

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FOREWORD

The *Sampling Guide for Environmental Analyses* is a series of booklets providing detailed procedures for sampling in various locations. The booklets outline good practices for planning and carrying out sampling work. The purpose is to ensure that samples are of good quality and the resulting scientific data are valid.

The project was initiated by the *ministère du Développement durable, de l'Environnement et des Parcs* and especially by the *Centre d'expertise en analyse environnementale du Québec* because the samplers did not have the necessary instruments to quickly gain a working knowledge of sampling practices in Quebec.

This sixth booklet, entitled *Forage Sampling for Fluoride Analysis*, was prepared by the *Direction des politiques de l'air* of the *ministère du Développement durable, de l'Environnement et des Parcs* and the *Association de l'industrie de l'aluminium du Québec* (AIAQ). It mainly covers the sampling materials and methods used to analyse fluorides.

The content reflects the need to standardize feed sampling techniques and is intended to eliminate the difficulties related to the interpretation of different sampling methods. This standardization guarantees that results will be representative and will also make it easier to compare data collected from different geographical regions at different times.

Users of this booklet must take into account the information in Booklet 1, *Généralités* (in French only). Note that the first booklet covers the general aspects of a sampling campaign and the technical procedures related to quality, health, security and integrity of the sample.

The *Centre d'expertise en analyse environnementale du Québec* sincerely wish to thank the people who helped in any way with this document.

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INTRODUCTION

Certain industrial processes release compounds containing fluorides into the environment. In low doses, fluorides have a beneficial effect, such as improving the teeth health. In high doses, they cause an illness characterized by the disintegration of bone tissue, commonly called fluorosis of bone.

Herbivores are particularly susceptible to fluorides released into the atmosphere because they might graze on vegetation growing close to an emission source. To protect livestock from the ill effects of overconsumption of fluorides contained in forage they feed on, concentration level criteria were established and included in the regulation in force for air quality.

Aware of the fluorides problem, the ministère du Développement durable, de l'Environnement et des Parcs and its partners in the industrial sector began taking samples some time ago of the forage used in animal feed. Due to the need for rigour to reduce variations in fluoride analysis results, they decided to standardize the sampling method.

Forage sampling is aimed at proving that criteria are met in the surrounding sectors of the main emissions sources.

DEFINITIONS

Livestock: All domestic animals such as cattle, sheep and horses.

Fluorides: Fluoride ions solubilized during analysis.

Forage: Vegetation, except for grain intended for use in livestock feed.

Harvest: Period of the year during which forage is harvested by farmers. The period may vary depending on the sampling site and forage type, meteorological conditions and the farmer's planning.

Sampling plot: 10 x 10 meters reference area where the sample is collected. A sampling plot is selected in an agricultural area, a pasture or cultivated space where the harvest is to be used as animal feed. Its location may be changed to accommodate crop rotations, changes in emission source characteristics or any other factor likely to affect the sample's representativeness.

Benchmark sampling plot: Sampling area in the targeted area that is least affected by fluoride emissions.

1 CHARACTERISTICS OF THE SAMPLING SITE

Sampling is done exclusively in zones used to produce livestock feed. Depending on the importance of the surrounding agricultural environment, a varying number of sites (between four and ten), are determined for each emission source. In addition, a benchmark plot is sampled to determine the concentration of fluorides that is naturally present in a given area.

To ensure that forage samples are representative, the sampling plots must satisfy the following criteria:

- No obstacles, trees or buildings (maximum angle of 30° to obstacle);
- Located 30 meters from roads and at least 15 meters from fences bordering the lot;
- Outside industrial property or zones, unless the forage is for animal consumption;
- Normally located less than 10 kilometers from emission sources, preferably where prevailing winds converge, where maximum fluoride concentrations are predetermined (ideally by modelling);
- Be a square of 100 square meters.

Markers are used to delineate the sampling plot at each site. An identification card is completed for each plot and includes the following:

- Name and municipality code;
- Number of sampling site;
- Location of lot in relation to fluoride emission sources (in degrees and kilometers);
- Geographical datas (latitude and longitude);
- Farmer's coordinates;
- Types of forage sampled;
- Harvest date;
- Sampler’s coordinates.

The site identification card must be completed or updated each year. An example is given in Appendix I.

2 SAMPLING CALENDAR

As far as possible, samples should be taken at predetermined or fixed dates between June 1 and October 31. Samples must be taken on the dates appearing on the following calendar. Two days grace before or after the scheduled calendar date is allowed.

Sample Number	Sample Date
1	June 15
2	June 30
3	July 15
4	July 31
5	August 15
6	August 31
7	September 15
8	September 30
9	October 15
10	October 31

3 SAMPLING PROCEDURES

Quality of the results largely depends on the sampling method. Cahier 1 – *Généralités*, covers quality control in a general context, such as the use of blanks, duplicates and benchmark samples. The following section presents the forage sampling method.

3.1 Material required

- Scissors or knife;
- Kraft paper bags with an approximate 10 liters capacity;
- Perforated Kraft paper bags with an approximate 2 liters capacity;
- Sealed container to transfer samples to the analysis laboratory (e.g. Styrofoam cooler);
- Stapler;
- Ventilated oven or dessicator (optional).

3.2 Sampling protocol

It is strongly recommended that plants be collected after raindrops or dewdrops have evaporated to limit dissolution of the fluorides.

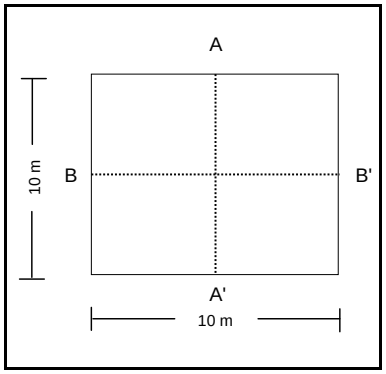

Figure 1.1 – First course

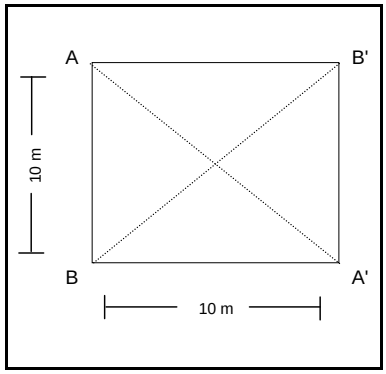

Figure 1.2 – Second course

Figures 1.1 and 1.2 represent a sampling plot. Samples are taken along the A-A′ and B-B′ axis. The courses of figures 1.1 and 1.2 are alternated on the scheduled sampling dates. For example, the course in Figure 1.1 is used for the June 15 sample and the course in Figure 1.2 are used for the June 30 sample.

A total of 10 sub-samples are taken during each sampling period, five along each axis. Each sub-sample consists of a handful of forage cut with scissors or a knife approximately 5 cm above the ground. With certain forage plants like alfalfa, the top 15 cm of the plant are usually collected.

During the sampling, the sub-samples are cut into 3 to 5 cm pieces and placed in a 10 liters paper bag. The total sample is then well mixed and a sufficient amount is collected to fill half a 2 liters bag. The bags must be perforated for air to circulate, then stapled or sealed. The minimum quantity required is 50 to 100 grams. To avoid contamination, a new 10 liters bag must be used for each sample.

If a dryer is available, the sample is placed directly into the oven or dessicator at a temperature of 60 ^{o}C for 24 or 48 hours, depending on how humid it is. Under no circumstances should the sample be washed.

If sampling is scheduled too soon after harvest and there is not enough vegetation to take a sample, more sub-samples must be taken to collect a sufficient quantity (50 to 100 grams), otherwise the sampling must be put off for two days or more. If it is impossible to collect a sufficient quantity of forage, the sampling is cancelled.

The harvest period may differ from one site to another depending on the local climate, crops under cultivation and the farmers' practices. As a result, in certain areas, there is a good chance that it will be impossible to collect samples scheduled at the beginning and end of the sampling period.

3.3 Identification and shipping of samples

A sample slip must accompany each sample shipped to a lab (example in Appendix II) and include the following information:

- Sampling date;
- Site identification number (e.g.: Bécancour, Site No.1);
- Sample number;
- Type of forage sampled (hay, clover, alfalfa, etc.);
- Sampling conditions (presence of dew, dust, recent harvest or any other information that will make it easier to interpret the results).

The first three items must be written on the bag containing the sample.

A sample that is not dry must be sent as quickly as possible to the lab to avoid deterioration. A maximum of 48 hours is allowed between sampling and shipping to the lab. Samples are placed in a Styrofoam container or padded envelope and shipped by express mail or messenger.

If the samples cannot be sent to the lab within 24 to 48 hours, it is better to dry them or freeze them (at about –18 ^{o}C). Dry samples keep for at least one year. Ship frozen samples to the lab in a Styrofoam container with a refrigerant.

A copy of the sampling slip is stapled to each bag. The sampler keeps one copy and the third copy is sent to the person in charge of the sampling program.

At the end of the sampling campaign, a final sampling report must be written and archived. It must at least contain the following information:

- The business' name and address if applicable;
- Location of the sampling points;
- Contaminants measured;
- Results with appropriate units of measure and applicable standards;
- Report date;
- Signature and function of the person responsible for the report's content;
- In the appendix: identification cards for the sampling sites, sampling slips for forage samples to be analyzed for fluorides, the results of analyses obtained from accredited laboratories and spreadsheets of the results.

4 REQUIREMENT FOR THE ANALYSIS

To ensure a quality analysis, samples must be submitted to a lab that is accredited by the ministère du Développement durable, de l'Environnement et des Parcs for the measurement of fluorides in vegetation.

5 CALCULATING THE AVERAGE CONCENTRATION OF FLUORIDES AT A GIVEN SITE

To establish an average level of exposure to fluorides in animals, the monthly and yearly averages must be determined based on the results for each sample. The following explains an aggregation method that takes irregularities in the sampling frequency into account.

5.1 Monthly average

The monthly concentration is evaluated by calculating the average of the two results for each month. When, in a given month, one of the two required samples cannot be collected, the second result is used as the monthly average.

$$Monthly\ average = \frac{C_1 + C_2}{2} \quad (1)$$

where C_1 *is the representative concentration for the first part of the month;*
C_2 *is the representative concentration for the second part of the month.*

If a sample was taken on a different date (two days more or less) than the one scheduled, it is included in the calculation of the monthly average as if it was taken on the scheduled date.

Example: For samples taken on June 16, July 2 and 14, August 1, 16 and 29, September 16 and October 1, 15 and 30 at Site 1, the representative average concentration for June is calculated based on the concentrations for June 16 and July 2; the one for July based on the concentrations for July 14 and August 1, the one for August is based on the concentrations for August 16 and 29; September's based on the concentrations for September 16 and October 1; and finally October's would be based on the concentrations for October 15 and 30.

5.2 Annual average

The calculation method for the annual average takes summer harvests into account because they are used to feed the livestock over the winter. Fluoride concentrations measured immediately before the harvests are considered to be representative of exposure over the winter and are used as the basis for the calculation for the seven months during which the forage is consumed. The following are descriptions of the various calculation scenarios.

5.2.1 No forage harvest

If there is no harvest at a given site (pasture or fallow land):

$$Annual\ average = \frac{C_{june} + C_{july} + C_{aug} + C_{sept} + C_{oct}}{5} \quad (2)$$

where C_{june} *to* C_{oct} *are the average monthly concentrations.*

The annual exposure here is equivalent to the exposure calculated based on the average monthly concentrations during the five sampling months.

5.2.2 One forage harvest

If there has only been one harvest at a site, the result obtained prior to the harvest is used as the weighting value for the seven months of the year during which the livestock is fed forage from this harvest.

$$Annual\ average = \frac{(C_r \times 7) + (C_{june} + C_{july} + C_{aug} + C_{sept} + C_{oct})}{12} \quad (3)$$

where C_r *is the concentration of the sample taken before the harvest;*
C_{june} *to* C_{oct} *are the average monthly concentrations.*

5.2.3 Two forage harvests

If there are two harvests at a site, the result obtained prior to each of the two harvests are used as the weighting value for the months of the year during which the livestock is fed forage from this harvest.

$$Annual\ average = \frac{(\frac{C_r 1 + C_r 2}{2} \times 7) + (C_{june} + C_{july} + C_{aug} + C_{sept} + C_{oct})}{12} \quad (4)$$

where C_r1 *is the concentration of the sample taken before the first harvest;*
C_r2 *is the concentration of the sample taken before the second harvest;*
C_{june} *to* C_{oct} *are the average monthly concentrations.*

5.2.4 Three forage harvests

If there were three forage harvests at a site, the result obtained prior to each of the three harvests are used as the weighting value for the months of the year during which the livestock is fed forage from this harvest.

$$Annual\ \ average = \frac{\left(\frac{C_r 1 + C_r 2 + C_r 3}{3} \times 7\right) + (C_{june} + C_{july} + C_{aug} + C_{sept} + C_{oct})}{12} \quad (5)$$

where C_r1 *is the concentration of the sample taken before the first harvest;*
C_r2 *is the concentration of the sample taken before the second harvest;*
C_r3 *is the concentration of the sample taken before the third harvest;*
C_{june} *to* C_{oct} *are the average monthly concentrations.*

5.3 Calculation examples for the averages

Examples of how the monthly and annual averages are calculated (following various hypotheses) are given below. The data used for the calculations appear in tables 1, 2 and 3.

Formula 1: Calculation of the monthly average for June for Site 1

$$Average_{june} = \frac{(86\ ppm + 37\ ppm)}{2} = 62\ ppm \quad (a)$$

To calculate the monthly average, the sample taken on June 16 is associated with the value for June 15; the one for July 2 with the one for June 30.

Formula 2: Calculation of the annual average for Site 1 (no harvest)

$$Annual\ average = \frac{(62\ ppm + 76\ ppm + 35\ ppm + 36\ ppm + 35\ ppm)}{5} = 49\ ppm \quad (b)$$

The monthly averages (from June to October) are added and the total divided by 5. The average is attributed to the whole year.

Formula 3: Calculation of the annual average for Site 1 (one harvest, on July 13)

$$Annual\ average = \frac{(37\ ppm\ x\ 7) + (62\ ppm + 76\ ppm + 35\ ppm + 36\ ppm + 35\ ppm)}{12} = 42\ ppm \quad \text{(c)}$$

The July 2 result, that is, the date of the sample taken before the harvest, is used to calculate the months from November to May. This result is therefore multiplied by 7, and the result is added to the average monthly concentrations for the months of June to October. That total is then divided by 12.

Formula 4: Calculation of the annual average for Site 1 (two harvests: June 24 and July 13)

$$Annual\ average = \frac{\left(\frac{(86\ ppm + 37\ ppm)}{2}\ x\ 7\right) + (62\ ppm + 76\ ppm + 35\ ppm + 36\ ppm + 35\ ppm)}{12} = 56\ ppm \quad \text{(d)}$$

The results from June 16 to July 2, that is, the dates of the samples taken before the harvests, are used to calculate the months of November to May. These results are added together and divided by 2. The average for the concentrations associated with the harvests is then multiplied by 7, and the result is added to the average monthly concentrations for the months of June to October. That total is then divided by 12.

Formula 5: Calculation of the annual average for Site 1 (three harvests: June 24, July 13 and August 25)

$$Annual\ average = \frac{\left(\frac{(86\ ppm + 37\ ppm + 34\ ppm)}{3}\ x\ 7\right) + (62\ ppm + 76\ ppm + 35\ ppm + 36\ ppm + 35\ ppm)}{12} = 51\ ppm \quad \text{(e)}$$

The results for June 16, July 2 and August 16, that is, the dates of the samples taken before the harvests, are used to calculate the months of November to May. These results are added together and divided by 3. The average for the concentrations associated with the harvests is then multiplied by 7, and the result is added to the average monthly concentrations for the months of June to October. That total is then divided by 12.

Table 1 – Concentrations in fluorides (ppm) measured at two sites during one season

Scheduled Sampling Dates	Sample Collection Dates	Fluoride Concentrations (ppm) Site No. 1	Fluoride Concentrations (ppm) Site No. 2
June 15	June 16	86	3
June 30	July 2	37	5
July 15	July 14	125	25
July 31	August 1	26	6
August 15	August 16	34	5
August 31	August 29	36	22
September 15	September 16	52	8
September 30	October 1	20	8
October 15	October 15	16	11
October 30	October 30	54	34

Table 2 – Average monthly concentration of fluorides in forage (ppm)

Month	Site No. 1	Site No. 2
June	62	4
July	76	16
August	35	14
September	36	8
October	35	23

Table 3 – Average annual concentration of fluorides in forage (ppm)

Hypotheses for Harvest Rates	Site No. 1	Site No. 2
No harvest	49	13
1 harvest (July 13)	42	8
2 harvests (June 24 and July 13)	56	8
3 harvests (June 24, July 13 and August 25)	51	8

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Appendix I - Identification Card for Sampling Site

SAMPLING SITE IDENTIFICATION

MUNICIPALITY Name: _____

Code: _____

Sampling site no.: _____

Lot location in relation to emission sources: _____ degrees _____ kilometers

Geographical datas: _____ degrees _____ minutes _____ seconds

FARMER Name: _____

Address: _____

City: _____

Telephone: _____

Type of forage sampled: _____

Harvest dates:

1st harvest: _____
2nd harvest: _____
3rd harvest: _____

SAMPLER Name: _____

Address: _____

City: _____

Telephone: _____

Appendix II - Example of sampling slip
for samples of forage to be analyzed for fluorides

Receipt date:	
Laboratory:	

Project name: _____

Person in charge: _____

Address: _____

Sampling date: _____

Sampling location:

Municipality: _____

Site no.: _____

Forage type: _____

Sampler: _____

Sample no.: _____

Particular observations: _____

_____

_____

_____

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