Fluoride Concentrations in the Montreal Urban Community Wastewater: Seasonal Variations and Mass Balances

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ABSTRACT

Fluoride concentrations in the Montreal Urban Community's untreated wastewater were analyzed in an attempt to evaluate their levels and seasonal variations. Continual hourly monitoring of the raw sewage, between June 1992 and May 1993, yielded average monthly fluoride concentrations between 0.072 mg/L and 1.984 mg/L, with an annual mean of 0.45 mg/L. Daily varritions and frequency distributions showed a wider range of fluoride levels, with the maximum values possibly reaching as high as 4 fold the mean and well over 2 orders of magnitude higher than the minimum values. This suggests that significant massive point dischaiges occur in the sewer network. Daily monitoring of the precipitation showed that the mean fluoride concentration in liquid precipitation generally fluctuates between 0.030 mg/L and 0.741 mg/L, whereas the average fluoride specific mass in dry precipitation ranges between 0.096 kg/km^2 and 2.775 kg/km^2. Seasonal trends have been depicted for fluoride levels in both the raw wastewater and the precipitation. Groundwater sampling yielded an average fluoride concentration of 0.13 mg/L, and analysis of the melting salts used by the City revealed that these do not contain any fluoride. Data from the City's water treatment plants showed that the average fluoride concentration in their raw water is 0.20 mg/L. This is in contrast to the value of 0.13 mg/L used in the literature. Mass balance analyses have shown that the mass of fluoride resulting from infiltration and non-fluoridated waters, as well as that due to the domestic habits of the population constitute, among the identified sources, the major input of fluoride mass into the wastewater. Nevertheless, unidentified sources of fluoride, consisting essentially of industrial discharges, still account for the largest portion (≈ 50% of the total) and contribute, as an annual average, 375 kg/day

SOMMAIRE

Les analyses de fluorure dans les eaux usées de la Communauté Urbaine de Montréal ont été effectuées afin de déterminer leurs niveaux ainsi que leur variation saisonnière. Le monitorage horaire continu des eaux brutes, entre juin 1992 et mai 1993, a révélé que les concentrations moyennes mensuelles de fluorure variaient entre 0.072 mg/L et 1.984 mg/L, avec 0.45 mg/L pour moyenne annuelle. Les variations quotidiennes ainsi que les analyses de fréquences ont démontré une plus importante fluctuation des niveaux de fluorure, avec des valeurs maximales pouvant atteindre jusqu'à 4 fois la moyenne et plus que deux ordres de grandeur au-delà des valeurs minimales. Ceci suggère que d'importants déversements ponctuels se produisent dans le système d'égouts. Le monitorage quotidien des précipitations a montré que la concentration moyenne de fluorure dans les précipitations liquides se situait entre 0.030 mg/L et 0.741 mg/L, alors que les concentrations massiques dans les dépots secs variaient entre 0 096 kg/km^2 et 2 775 kg/km^2. Des variations saisonnières ont été mises en évidence aussi bien dans les eaux usées que dans les eaux de précipitation. L'échantillonage des eaux souterraines a donné une concentration moyenne de fluorure de l'ordre de 0.13 mg/L, alors que l'analyse des sels de déglaçage a démontré que ceux-ci ne renfermaient pas de fluorure. Certaines données obtenues des usines de traitement de l'eau ont révélé que la concentration de fluorure dans leur eau brute à la prise du fleuve est de 0.20 mg/L. Ceci est en contraste avec la valeur de 0.13 mg/L habituellement utilisée dans la bibliographie. Les analyses de bilans massiques ont démontré que la masse de fluorure provenant des eaux d'infiltration et des eaux potables non-fluorées, ainsi que celle résultant des habitudes domestiques de la population constituent, parmi les sources identifiées, l'apport majeur en fluorure. Cependant, les sources non-identifiées de fluorure, qui consistent principalement en déversements industriels, restent celles qui constituent la plus importante ($\approx$ 50% du total) proportion, et contribuent, en moyenne annuelle 375 kg/jour.

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1. INTRODUCTION

1.1. GENERAL

Since fluoridation was first introduced in water treatment systems as a means for the prevention of dental caries, fluoride levels and exposure have become an important issue. This is especially true now that man is being increasingly subjected to fluorides, either by water and beverages, food, dental products and air. The World Health Organization (1970) warns of possible cumulative effects resulting in long term intoxication, through repeated excessive absorption.

Air, soil and water can all serve as environments but also as modes of transport for fluoride entry into vegetation, and from there, into other living organisms. In addition to this natural food chain, the fluoride burden is being increased by human activity, through the processing of food and beverages, the use of fluoride-containing dental products, the use of fluoride-based fertilizers, the artificial fluoridation of potable water, and more importantly by industrial processes (Marier, 1972).

Researchers have found that, depending on the level of exposure and mechanism involved, fluoride can produce beneficial or adverse effects (U.S. Public Health Service, 1991).

Fluoride as a Health Benefit

With exposure to optimal levels of fluoride in the drinking water - 0.7 to 1.2 mg/L, depending on climatic conditions - (Health and Welfare Canada, 1989), there is a clearly demonstrated effect of a reduction in dental caries (WHO, 1984) Fluorides have also been used in the treatment of osteoporosis, but, though beneficial effects have been reported, the exact mechanisms are not yet fully understood (U S Public Health Service, 1991; WHO, 1984). In general, it is believed that fluoride's effect on bones and teeth is essentially an increased stability of the apatite crystal. This would result in a reduction in acid solubility in the teeth enamel (Whitford, 1983) and in a decreased rate of bone resorption (Navia and Aponte-Merced, 1988, Punyasingh and Navia, 1984, Prince and Navia, 1983).

However, although fluoride compounds occur naturally in most constituents of the body, there is no conclusive evidence that fluoride or any of its compounds are essential for human homeostasis or growth (McIvor *et al.*, 1985)

Fluoride as a Health Hazard

Although fluoride has beneficial effects on bones and teeth at appropriate doses, higher exposure levels produce correspondingly higher fluoride levels in bone and teeth and can result in chemical changes and structural defects known as dental and skeletal fluorosis, the long-term health significance of which is not known (Navia and Aponte-Merced, 1988; Rose and Marier, 1977; Groth, 1973;). Several different, and probably interrelated mechanisms may be involved in the development of dental and skeletal fluorosis. These may include fluoride interference with ameloblast activity, osteocyte activity, nucleation, crystalline growth, matrix formation, and calcium homeostasis (Punyasingh and Navia, 1984; Prince and Navia, 1983; Fejerkov *et al*, 1977; Hodge and Smith, 1970) In addition, high plasma levels of fluoride have been reported to complex biologically active calcium, resulting in life-threatening hypocalcemia (Greco and Hartford, 1988, Burke and Hoegg, 1973). Other studies have also shown that fluoride both inhibits and activates a wide variety of enzymes and enzymatic processes, probably due to the formation of fluoride-phosphate-metal complexes (Greco and Hartford, 1988; Sternweis and Gilman, 1982; Holland, 1979; Waldbott, 1962).

Fluoride as a Pollutant

Fluoride toxicity is such that, in 1947, it was considered by the American Association for the Advancement of Science as the most dangerous atmospheric pollutant after sulfur dioxide and ozone Accordingly, it was ranked third among the most urgent environmental problems to be assessed (Rose and Marier, 1977).

Although research is still far from being thorough and complete, current knowledge support the tentative conclusion that fluoride has great potential for ecological harm (WHO, 1984, Groth, 1975), especially when present with other atmospheric pollutants such as sulfur dioxide or aluminum (Driscoll *et al.*, 1980; Marier, 1972), or in an environment with decreased hardness (Pimental and Bulkley, 1983). Fluoride is a non-biodegradable, relatively persistent widespread pollutant, with a high biological activity enabling it to be transformed by some organisms into far more complex organic fluorides (Groth, 1975). One of the most notable characteristics of fluoride as a pollutant remains its tendency to accumulate in organisms, causing serious adverse effects possible even at very low levels of exposure, should exposure persist over time (Groth, 1975; National Academy of Sciences, 1971).

There are many unanswered questions in regard to long-term potential adverse effects of fluorides and fluoridation, and some indications of potential harm have not yet been shown to be unfounded (U.S. Public Health Service, 1991, WHO, 1984, Groth, 1973, National Academy of Science, 1971). Hence, little is still known about the *in vivo* effects of fluoride at the low levels occurring naturally and the various facets of its general metabolism in the living organism (WHO, 1970). In conclusion, it can only be stated that the available information is still insufficient in depth and scope to allow unequivocal statements to be made regarding the effects of fluoride at low atmospheric concentrations.

Fluoride: the Situation in Montréal

Several studies, including those conducted by MENVIQ (1986), Gauquelin (1979), Ouellet and Jones (1983), Bundock *et al.* (1982), Goyer (1980), and MENVIQ (1979) have strived to depict the situation in Quebec. However, several questions were still unanswered as to the present fluoride concentrations in the wastewater and the probable increase in fluoride levels should Montréal proceed with drinking water fluoridation

A study by Gehr *et al.* (1989) attempted to elucidate the problems related to the intention of the Executive Committee of the City of Montréal of proceeding with fluoridation of the city's drinking water in the near future. They aimed at addressing the questions of fluoride dilution in the sewer system due to leakage of groundwater, the possible removal of fluoride during the physico-chemical treatment at the wastewater treatment plant, the speciation of fluoride in the discharge to the St-Lawrence River, as well as the assessment of background concentrations and variations of fluoride levels in the raw wastewater. They concluded that fluoride below 1 mg/L were unlikely to be toxic to the aquatic system of the St-Lawrence River, especially that biotransformation was not found to be of concern because of the low likelihood of fluoride absorption by the aquatic microorganisms. However, based on the wide fluctuations in fluoride concentrations, especially during winter, and the relatively high percentage (40%) of unidentified sources, they recommended that further monitoring be undertaken for a longer period, preferably during a whole year. This would give the actual picture of the seasonal variations of fluoride levels in the raw wastewater and confirm the fluoride background concentration of 0.34 mg/L (Gehr *et al.*, 1989).

1.2. OBJECTIVES OF THE STUDY

Based on the recommendations by Gehr *et al.* (1989), the present study aims at evaluating the variations of the levels of fluoride concentrations in the Montréal Urban Community raw wastewater. Accordingly, continuous monitoring of the fluoride concentrations in the influent to the MUC wastewater treatment plant was conducted between June 1st, 1992 and May 31st, 1993. The variation in these fluoride levels will be presented herein by graphical illustrations of daily as well as monthly data. Descriptive statistics will also be used to estimate the levels of fluoride in the raw wastewater and confirm the seasonal variability.

In parallel, sampling of the precipitation was also undertaken, in order to estimate the levels and variations of fluoride concentrations in both the liquid precipitation as well as the dry fallout. The groundwater was also sampled in an attempt to estimate its fluoride content.

The fluoride levels in the precipitation and the groundwater will be linked to those in the raw wastewater through a mass balance analysis, in order to estimate the contribution of the various sources of fluoride to the total fluoride input into the raw wastewater. These fluoride sources are precipitation, infiltration of groundwater, non-fluoridated potable water, artificially fluoridated potable water, domestic habits of the population and unidentified sources. The latter generally consist of the dry fallout absorbed in runoff, and more substantially, the industrial fluoride discharges

While the general target of this study leans toward the evaluation of the fluoride concentration levels in the Montréal Urban Community wastewater, the more specific objectives may be subdivided into (1) the main objectives that are aimed at fulfilling the general target, and (2) the secondary objectives that assist in clarifying the main objectives

The main objectives are:

1. To evaluate the average monthly fluoride concentration in MUC wastewater
2. To confirm the baseline fluoride concentration in the MUC wastewater, as obtained by Gehr *et al.* (1989).
3. To depict any seasonal variation of fluoride concentrations in MUC wastewater
4. To evaluate the concentration of fluoride precipitation, in its components, dry and liquid.
5. To estimate the fluoride concentration in groundwater
6. To confirm (or deny) the assumption taken by Gehr *et al.* (1989) related to the presence of fluoride in the melting salts used by the City of Montréal.
7. To assess the importance of non-identified sources of fluoride in the MUC wastewater.

The secondary objectives are:

1 To estimate the contribution of precipitation to the total fluoride input.

2 To estimate the contribution of groundwater infiltration to the total fluoride input.

3 To estimate the contribution of fluoridated and non-fluoridated potable water to the total fluoride input.

4 To estimate the contribution of the domestic habits of the population to the total fluoride input.

These secondary objectives would allow the estimation of the importance of the unidentified fluoride sources discharged into the MUC wastewater.

1.3. THESIS ORGANIZATION

Chapter 1: Introduction

This chapter introduces the problem and states the objectives of the present study.

Chapter 2: Literature Review

This chapter reviews the physical and chemical characteristics of fluoride, the presence and incidence of fluoride in the environment as well as the sources of human exposure to fluoride from the four major routes, namely water and beverages, food, dental products and air.

Chapter 3. Materials and Methods

This chapter presents the sampling procedure and the analytical techniques, and points out the main sources of errors involved therein.

Chapter 4: Results and Discussion

This chapter addresses the results and discussion in five different sections. *Section 1* presents a general evaluation of the fluoride levels in the MUC raw wastewater, along with their seasonal variations; *Section 2* presents an estimation of the fluoride concentration in both liquid and dry precipitation; *Section 3* seeks to estimate the fluoride concentration in the groundwater, whereas *Section 4* attempts to confirm (or deny) the presence of fluoride in the melting salts used by the City of Montréal; finally, *Section 5* is an overview of the contribution of the various sources of fluoride to the total fluoride content in the wastewater, with special attention given to the importance of unidentified sources of fluoride discharged into the sewer network.

Chapter 5: Conclusions and Recommendations

This chapter draws the general conclusions and suggests recommendations for further research

2. LITERATURE REVIEW

2.1. PHYSICAL AND CHEMICAL PROPERTIES OF FLUORIDE

Fluoride, the thirteenth most abundant element, is widely distributed throughout the earth (Ouellet and Jones, 1983; Finger, 1961). At standard conditions of temperature and pressure, fluorine is a pale, yellow gas, with an atomic number of 9 and an atomic weight of 18.9984 (WHO, 1984). Fluoride is classified as a halogen, one of the elements that make up Group VII of the Periodic Table of Elements. These are all electronegative and electromotive elements that can normally exist in the free state as diatomic molecules, or can react with less electromotive elements or chemical groups to form a wide variety of inorganic and organic halogenated compounds. Like all inorganic halogens, inorganic fluorides dissociate in aqueous solution to release the monovalent ion F^-, along with its associated cation. However, despite these common aspects, fluoride distinguishes itself by many unique chemical characteristics that impart special biochemical physiological properties to fluoride compounds, and thus affect its metabolism and mechanisms of action in the body (U.S. Public Health Service, 1991).

Because of its very compact atom (0.64 Å) and its special configuration, fluoride is indeed the most electronegative, reactive, aggressive and inaccessible of all elements

(Ouellet and Jones, 1983). Fluoride does not occur in a free state in nature (U S Public Health Service, 1991; Ouellet and Jones, 1983). It combines with other chemical elements to form fluoride compounds Several of these fluoride compounds (e g , F_2O, ClF_3 and B_2F_5) are known to be very strong oxidants and may replace hydrogen as the fuel source in space vehicles. Also, water and other non-combustibles (e g , brick and asbestos) can be burnt in a fluorine-rich environment (Ouellet and Jones, 1983)

In addition to its chemical properties, the isotopic nature of fluorine is quite characteristic, in the sense that the only naturally occurring isotope is 19-F, which has an extremely short half-life (Sharpe, 1957; Leech, 1956). The longest lived isotope (18 F), with a half-life of 1.87 hours, is prepared by nuclear reaction (U.S Public Health Service, 1991).

2.2. SOURCES OF FLUORIDE

Fluoride may arise from natural or man-made sources While natural sources of fluoride, such as volcanic gases and soluble fluorides in the earth's crust, are not to be neglected, modern man-made sources are of greater importance and impact; these can, individually or in combination, induce harmful levels of fluoride compounds in air, water, food or forage.

2.2.1. Natural Sources

Fluoride in the environment arises from chemical, physical and biological decomposition of surface rocks in the geosphere (Ouellet and Jones, 1983). Indeed, fluorine is a constant constituent produced by the slow weathering of eruptive rocks both on the soil as well as in sea and surface waters. However, the marked insolubility of most natural fluorides limit their diffusion in water. Studies carried out in North Africa and Colorado reported that fluoride is bio-accumulable and can thus move up the food chain (Rose and Marier, 1977).

Fluoride has geological concentrations varying normally from 650 mg/kg to 800 mg/kg, depending on the type of rock formation (Ouellet and Jones, 1983). Semrau (1957) reported that fluoride concentrations, in the United States, may vary between 20 and 1640 mg/kg, with an average value of 200 mg/kg. In Canada, Lalonde (1976) found an average fluoride concentration of 395 mg/kg in Abitibi, whereas Ouellet (1979) recorded extreme values of less than 50 mg/kg in the anorthosites and higher than 2800 mg/kg in the igneous lithologies in the Saguenay-Lac Saint-Jean region (Ouellet and Jones, 1983; Ouellet, 1979).

The principal fluoride-containing minerals are fluorspar (CaF_2) and cryolite or sodium fluoaluminate (Na_3AlF_6). The world's largest deposits of cryolite are found at Ivitgut, in Southern Greenland (MENVIQ, 1979). Fluoride may also be present as a secondary constituent or as an impurity in some mineral species, namely in the apatites having the general formula $3Ca_3(PO_4)_2,CaX_2$ where X may symbolize F, Cl or OH. It is important to note that fluoride emissions into the atmosphere which result in severe intoxication may be traced to this product; when the apatite is attacked by concentrated sulfuric acid, calcium fluoride (CaF_2) liberates hydrofluoric acid which yields silicofluoride (SiF_4) in the presence of silica (SiO_2), according to Equation 2.1:

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O \qquad (2.1)$$

When in contact with water, either in the atmosphere or in tower scrubbers, silicofluoride

(SiF_4) is then transformed into hydrofluoric acid (HF) and hydrofluosilicic acid (SiF_6H_2) as seen in equations 2.2 and 2.3 respectively; it is generally this acid or its salts that are found in polluted air.

$$SiF_4 + 4H_2O \rightarrow Si(OH)_4 + 4HF \qquad (2.2)$$

$$2SiF_4 + 4HF \rightarrow 2SiF_6H_2 \qquad (2.3)$$

It is to be noted that sodium and aluminum silicofluorides are soluble in water and are found in the superphosphate industry effluent (MENVIQ, 1979)

The recuperation of fluorides occurs through the decomposition of silicofluorides by heated alkalis, according to equation 2.4.

$$Na_2SiF_6 + 4NaOH \rightarrow 6NaF + SiO_2 + 2H_2O \qquad (2.4)$$

Fluoride in the Water

Fluoride, a universal mineralizing element, is present in both surface water and groundwater.

While surface waters may contain, under exceptional circumstances, up to 10 or 12 mg/L of alkaline fluorides (WHO, 1984), the fluoride concentration is generally low, ranging between 0.01 mg/L and 0.03 mg/L (WHO, 1984; Livingstone, 1963) In the former Soviet Union, average fluoride concentrations varied from 0.01 to 12 mg/L, with a most common value of 0.5 mg/L (Gabovich, 1952) The highest natural fluoride concentrations, which are found in the surface waters of East Africa, can reach values as high as 1,627 mg/L (Kilham and Hecky, 1973) and 2,800 mg/L (Geever et al., 1971).

These high concentrations were caused by the degradation of nearby volcanic rocks rich in fluoride (Ouellet and Jones, 1983).

In addition to the natural presence of fluoride in fresh water, the contribution of water fluoridation, which is becoming increasingly popular especially in North America, should not be neglected. In the United States, more than 1500 municipalities are supplied with raw water containing more than 1.2 mg/L fluoride concentration (Rose and Marier, 1977).

In marine waters, the fluoride concentrations range from 1 to 1.4 mg/L (Carpenter, 1969), 50 % of which is in the form of MgF (Mahadevan *et al.*, 1986; Rose et Marier, 1977)

In groundwater, the natural concentration of fluoride depends on factors such as the geological, chemical and physical characteristics of the water-supplying area (Worl *et al.*, 1973). Fluoride concentrations varies within wide limits, from less than 0.1 mg/L to more than 25 mg/L (WHO, 1984). In Québec, the average fluoride concentration was found to fluctuate between 9 and 2,016 µg/L, with an average of 0.13 mg/L (Simard and Desrosiers, 1979). These results are in accordance with those obtained by Goulet and Frigon (1980), and Lalonde (1976) for the Province of Québec, as well as the world average concentration of 100 µg/L, as reported by Carpenter (1969).

As for the fluoride concentrations in fresh snow, they were found by Carpenter (1969) to range between 1 and 42 µg/L, with an average of 5 µg/L. Similar results were reported by Sidhu (1982) on fresh snow in a Laurentian park, and by Barnard and Nordstrom (1982b) who found precipitation concentrations between 2 and 20 µg/L, with an average of 8 1 µg/L.

Fluoride in the Air

Although results obtained by Carpenter (1969) suggest that even air which has not been contaminated by human activity contains some fluoride, the fluoride levels of ambient air are usually below the detection level, defined roughly as less than 0.05 $\mu g/m^3$ air (Thompson *et al.* 1971). Soluble fluoride amounts in the atmosphere may be largely contributed by volcanic activity, and, to a lesser extent, by dust storms and forest fires (Rose and Marier, 1977). However, whereas fluoride concentrations caused by these natural phenomena can range between 0.05 and 1.2 $\mu g/L$, they can increase dramatically by industrial activity, reaching values as high as 80 $\mu g/L$. This industry induced fluoride air pollution may arise from several sources and may be either in the gaseous (such as hydrofluoric acid) or solid form (such as solid substances reduced to very fine dust particles) which may or may not be soluble in water (MENVIQ, 1979, Rose and Marier, 1977). Atmospheric pollution by industry-induced fluoride emissions are reviewed in the following section.

2.2.2. Man-Made Sources

Fluoride emissions data from industrial sources are most often surrounded by industrial secrecy and by industries' ability to have environmentally sound data classified as proprietary to the industry, in addition to government's reluctance to release information that may give rise to public clamour and emotionalism. However, despite this secrecy that has been detrimental to Canadian efforts to develop criteria relating the concentration of pollutants to their effects, some information has become available in recent years

Fluoride Emissions into the Atmosphere

For decades, the aluminum industry has been known to be at the origin of most of the fluoride emissions into the environment The fertilizers and steel industries, as well as the combustion of fossil fuels constitute another, however less important, source of fluoride pollution (MENVIQ, 1979; Rose and Marier, 1977). Data published by Environment Canada (1976) on fluoride emissions into the atmosphere during 1972 show that, with the exception of the aluminum industry, fluoride emissions are mostly in gaseous form.

The primary aluminum reduction industry is the largest single-industry source of atmospheric fluoride pollution in Canada and the third largest in the United States.

It is in the Bayer process for alum (Al_2O_3) electrolysis, that cryolite (Na_3AlF_6) is used to lower the melting temperature of the metal from 2,000^{0}C to 1,000^{0}C. These extremely high temperatures would induce the volatilization of an appreciable amount of fluorides (HF, SiF_4, Na_3AlF_6) and the production of hydrofluoric acid in the form of vapour Part of the fluorides is directly released and hence dispersed in the environment, which gives rise to much concern due to their toxic effects on living organisms (Ouellet and Jones, 1983; MENVIQ, 1979).

In Canada, the aluminum industry alone contributes 56% of fluoride emissions into the atmosphere (Environment Canada, 1976). Between 1901 and 1972, this industry has released into the Canadian atmospheric environment more than 222,500 metric tons of fluorides. This quantity would be sufficient to fluoridate the supply waters for a population of 100 million inhabitants, for 11 years! In Québec, in 1972, the vast majority (92%) of the 7,000 metric tons of total fluorides emitted into the atmosphere originated from the primary aluminum reduction industry in Arvida, Ile Maligne, Shawinigan, Beauharnois, and Baie-Comeau. The fluoride emissions (both in the gaseous and particulate forms) from these plants were respectively 3519, 600, 700, 380 and 1300 metric tons, during that year (Ouellet and Jones, 1983). These high fluoride atmospheric discharges are mainly due to the fact that the production of one ton of aluminum requires one ton of cryolite, 20 kg of which are lost by vaporization into the atmosphere (about a third of this in the gaseous state, and two thirds in the form of particulates) (Rose and Marier, 1977). Recent data (Duguay, 1993) indicate that fluoride emissions resulting from the ALCAN plant at Beauharnois has been maintained at around 9.0 kg/d (3.3 metric tons per annum) since 1991. These emissions were almost twice as high in 1990 (17 kg/day or 6.2 metric tons per annum). Table 2.1 shows fluoride emission rates from the aluminum industry.

Table 2.1. Fluoride Emission Rates (kg/metric ton) from the Aluminum Industry (Rose and Marier, 1977).

Industry	Reported emission rate (kg/metric ton)
Sweden, newest installations	1.0 total F
U.S. new control technology	0.25 gaseous F 0.64 solid F
OECD countries, actual emissions	6.1 total F
OECD, obtainable emissions	2.3 total F
U.S.	4.1 soluble F
U.S. best primary system	1.2 - 4.7 total F
Best primary & secondary system	0.8 - 2.0 total F
U.S. weighted average	5.1 total F 2.1 gaseous F
U.S. new construction	1.0 total F

It is essential to note that "total" or "gaseous" data cannot be directly related to environmental criteria; the solubility of particulate matter is an important factor to take into consideration, as it varies widely and consequently affects the toxicity of particulate emissions to the fauna and flora. "Total soluble" would generally be more indicative of the environmental impact

The low emission rates noticed in recent smelters are indicative of the progressive efforts made by this industry in controlling atmospheric pollutant emissions. An interesting comparison between the emissions from U.S. primary smelters and those of Canadian smelters in 1972 has shown that effluent fluorides (prior to passage through emission control units) per unit of aluminum produced were similar. However, the average amount of fluoride released into the atmosphere, per ton of aluminum produced, was markedly higher for Canadian smelters than for U.S. smelters (Rose and Marier, 1977).

When fluoride emissions are investigated, the steel industry has not been the focus of as much attention as the aluminum industry, although it is considered to be the greatest source of fluoride emissions in the United States and the third one in Canada. This is partly due to the fact that steel mills emissions contain other pollutants of greater concern such as sulfur dioxide and particulate matter (Rose and Marier, 1977). Nevertheless, it is known that the production of each kg of steel requires 5 to 40 kg of fluorspar, which is used to remove the impurities during metal fusion and to facilitate the separation of the liquid metal from the slag, namely by increasing the fluidity of slags (MENVIQ, 1979).

The phosphate industry is another major source of fluoride emissions. These emissions result from the manufacture of apatite-based superphosphates, in the process of which tricalcium fluorophosphate is soaked for 30 to 60 days in concentrated sulfuric acid (Goyer, 1980), thus causing an atmosphere containing up to 86 mg of HF/m^3 (MENVIQ, 1979; Rose and Marier, 1977). Table 2.2 shows fluoride emissions at various steps of the process.

Table 2.2. Fluoride Emissions from Phosphate Fertilizer Plants (Rose and Marier, 1977).

Fluoride source	kg F/metric ton of P_2O_5 input	
	Industry-wide	Best-controlled
Wet process phosphoric acid	0.01 - 0.30	0.001 - 0.010
Superphosphoric acid	0.06	N/A
Diammonium phosphate	0.03 - 0.25	0.012 - 0.030
Triple superphosphate	0.10 - 0.30	0.015 - 0.155
Granular Triple Superphosphate	0.10 - 0.30	0.020 - 0.135

Other important sources of fluoride emissions are the clay products industry, the manufactures of glass, ceramics and bricks, as well as the petroleum and the coal burning industries (Goyer, 1980; MENVIQ, 1979; Rose and Marier, 1977).

As reported by Environment Canada (1976), estimates for possible fluoride emissions by the clay products industry vary from 249 to 2,239 metric tons per annum. On the other hand, fluoride emissions by the glass manufacturing industry are thought to be very low, in the order of 4.5 metric tons per annum, due to the fact that this industry has almost totally phased out by 1972 its use of fluorspar.

As for fluoride emissions by the petroleum industry (hydrofluoric acid alkylation process), Environment Canada (1976) reports a hydrofluoric consumption of only 0.14 to 0.36 kg HF/barrel of alkylate. Although no indication was given on the emission rates, or the relation between consumption and emission, the estimated total emissions of less than 0.5 kg in 1972 (Environment Canada, 1976) were probably based on a production of less than 37 barrels per day, assuming that emissions occur at the same rate as in the U.S. However, data published by Energy, Mines and Resources of Canada, and quoted in Rose and Marier (1977), indicate that Canadian HF alkylation

capacity was 13,470 barrels per day in 1972 and increased to 24,620 in 1975. Recent data indicate that the average annual production for the Shell Canada petroleum industry has reached 110,000 barrels/day; fluoride emissions from this industry were reported to be 40 kg/day in 1992 (Duguay, 1993; Paquet, 1993)
Hydrofluoric acid is also used in the oil industry to catalyze the alkylation reaction which results in high octane gasoline A refinery may lose 500 to 700 metric tons of hydrofluoric acid annually (MENVIQ, 1986; MENVIQ, 1979; Rose and Marier, 1977).

Regarding fluoride emissions from the burning of coal, Garber (1970) reported that these may contain 550 mg of fluoride per kg, part of which is volatilized with the ashes. In England and Wales, it was estimated that, during the year 1961, 25,000 tons of fluoride were dispersed in the atmosphere from the burning of coal (MENVIQ, 1979). However, in the absence of more recent data, these emissions are assumed to have decreased, due to the extensive use of other fuels for domestic heating in Canada (MENVIQ, 1986; Rose and Marier, 1977).

It is essential to note that, most often, the usual water sprays, electrostatic precipitators and chemical absorbers are not sufficient to prevent the escape of fluorides. Proper hermetic sealing of the plants to prevent fluoride from escaping through doors, windows and air shafts may be necessary (Rose and Marier, 1977). Table 2.3 gives a general idea of fluoride emissions from the above-mentioned sources.

Fluoride Discharges Into the Aqueous Environment

Although little information is available on the volumes and concentrations of fluoride discharged into surface waters, some data on the volumes and fluoride contents of industrial wastewaters (Table 2.4) make it obvious that large quantities of fluoride are being rejected into the aquatic environment. It was estimated (Rose and Marier, 1977) that if all North American plants discharge fluoride at a rate of 14 kg/metric ton, then the total industrial discharge would exceed 63,000 metric tons, which is about 4-fold the amount discharged into the atmosphere.

Table 2.3. Industrial Sources of Fluoride Emissions into the Atmosphere (Rose and Marier, 1977).

Industry	Fluoride emission rates in the U.S	% of total emissions in Canada	% gaseous fluoride
Aluminum	3.7 kg/t Al	56.6	55
Steel	0.45 kg/t mineral	15.5	80 - 85
Phosphates	1.4 - 1.9 kg/t P_2O_5	17.1	>96
Ceramics	0.37 kg/t product	3.4	70 - 75
Glass	7.7 kg/t glass		
Petroleum	0.07 kg/barrel of alkylate		
Cement	0.004 kg/t cement		
Carbon	0.07 kg/t carbon	7.4	>90
Incineration of wastes		<0.1	>90

Table 2.4. Volumes and Fluoride Contents of Some Industrial Wastewaters (Rose and Marier, 1977).

Industry (location)	Wastewater	
	Volume	F content (ppm)
Aluminum (Germany)	200,000 L/metric ton Al	70
Phosphate fertilizer (U.S.)	90,800 L/hr	35
Phosphate fertilizer (India)	13,240 L/hr	14 - 29
Stainless steel (U.K.)	N/A	8
Steel (U.S.)	N/A	0.17 kg/metric ton of product

The production of uranium tetra- and hexa-fluorides contributes to the discharge of significant quantities (625 to 1,134 tons per year in the U.S.) of hydrofluoric acid. The production of other inorganic fluoride compounds would result in the discharge of 5.7 and 55 kg/metric ton of product for aluminum fluoride and cryolite respectively (Rose and Marier, 1977).

Effluent and overflows from limed settling ponds also contribute to fluoride discharges into the environment (Cheremisinoff and Habib, 1973). Wet-scrubbing systems for control of atmospheric fluoride emissions are also suspected to contribute some fluoride to aqueous discharges, although recovery of fluoride from these scrubbers as precipitated calcium fluoride, and the re-use of the water are becoming increasingly popular (Rose and Marier, 1977)

Fluoride Solid Wastes

Despite the lack of information related to the disposal of fluoride solid wastes, large quantities are buried or disposed of in landfills (Williams, 1975). Several cases of surface and groundwater contamination with fluoride from solid wastes have been reported (Stepanek *et al.*, 1972).

With regard to the solid wastes from the aluminum industry, individual smelters were reported to produce from 15 to 30 kg of calcium fluoride sludge per metric ton of aluminum produced (Williams, 1975).

Another major source of high-fluoride solid wastes is the reprocessing of nuclear fuels (Fitzgerald *et al.*, 1969; Emma *et al.*, 1968). In this case, chemical treatments to reduce volatility followed by sintering and canning are prerequisites for safe long-term disposal (Rose and Marier, 1977).

Polluted soils are also considered to be another form of solid wastes and hence all the above-mentioned air-borne emissions can be regarded as potential soil pollutants, except for the portion that is carried to rivers and lakes by run-off This amount cannot be neglected, especially as it is reported to be about 18,000 tons per year in North America (Rose and Marier, 1977) Soil pollution can also arise from the use of fluoride containing fertilizers This is however highly variable, since the fluoride content of fertilizers varies widely depending on the method of processing and on the fluoride content of the phosphate raw material (Foster, 1969) Examples include dicalcium phosphate (0.14% fluoride), triple superphosphate (1 87%) and diammonium phosphate (2.00%) (Ammerman, 1974).

2.3. HUMAN FLUORIDE EXPOSURE

Water, food, dental products and air are the major "routes" for fluoride intake, the contribution of each of which varies on an individual basis, depending upon several factors, including lifestyle, dietary practices, age, gender, and health status Weather and climatic conditions are also of great importance The U S Public Health Service (1962) correlates the recommended fluoride concentration standards with temperature conditions, as presented in Table 2.5.

In Southern Québec, although the average annual maximum temperature ranges between 7.5°C and 11.5°C, the abrupt variations in temperatures should be taken into account, for these certainly contribute to variations in daily water consumption, and hence fluoride intake (MENVIQ, 1979)

Table 2.5. Fluoride Concentration Recommended for Drinking Water (U.S. Public Health Service, 1962; Health and Welfare Canada, 1989).

Average annual maximum temperature (°C)	Fluoride concentration (ppm)		
	Minimum	Optimum	Maximum
10.0 to 12.0	0.9	1.2	1.7
12.0 to 14.5	0.8	1.1	1.5
14.5 to 17.5	0.8	1.0	1.3
17.5 to 21.5	0.7	0.9	1.2
21.5 to 26.0	0.7	0.8	1.0

2.3.1. Fluoride Intake from Water and Beverages

The quantity of fluoride ingested from water supplies depends on the fluoride levels in the water and on the quantity of water consumed (Goyer, 1980). Whereas the fluoride concentration can easily be determined, the water consumption, being a function of the individual, regional and climatic conditions, is rather difficult to assess (MENVIQ, 1979; Rose and Marier, 1977)

Several studies by Groth (1973), Marier and Rose (1966), Bonham *et al.* (1964) and McClure (1943) have attempted to evaluate the amount of fluoride consumed with water.

More recently, it was estimated by the U.S. Environmental Protection Agency (U.S. EPA, 1985), that about 195.6 million people were served by public water supplies in the United States More than 86% of these are exposed to fluoride levels of 1.0 mg/L or less, while 0.4% of them are exposed to drinking water with natural fluoride exceeding 2.0 mg/L, predominantly from groundwater sources.

Table 2.6 shows the estimated fluoride intake from drinking water with distinction between infants, children and adults.

Table 2.6. Estimated Fluoride Intake from Drinking Water (U.S. EPA, 1985)

Fluoride Concentration (mg/L)	Estimated Percent U.S. Population[1] Served	Estimated Fluoride Intake Per Individual (mg/kg/day)		
		Infants[2]	Children[3]	Adults[1]
>0.1 to 2.0	99.6	0.24	0.042	0.029
>2.0 to 4.0	0.3	0.73	0.13	0.086
>4.0 to 6.0	<0.1	1.2	0.21	0.15
>6.0 to 8.0	<0.001	1.7	0.30	0.20
>8.0	<0.01	2.4	0.42	0.29

[1] Estimated percentage of U.S. population served by public water systems exposed to fluoride in drinking water at indicated concentration ranges

[2] Calculation based on infants weighing 3.5 kg and consuming 0.8 litres of infant formula per day

[3] Calculation based on a 10 year old child weighing 33 kg and consuming 1.4 litres of water per day

[4] Calculation based on a man weighing 70 kg and consuming 2.0 litres of fluid per day

It is important, when estimating the fluoride intake of an infant during the first 6 months of life, to consider whether the infant is breast-fed or formula-fed. While the concentrations of fluoride in human breast milk are very low, ranging from 5 to 25 μg/L (Krishnamachari, 1987; Spak and Hardell, 1983), they can be substantially higher in milk formulas, depending on the mode of preparation. Commercially available infant formulas processed from cow's milk contain about 0.1 to 0.4 mg/L when prepared with deionized water (McKnight-Hanes *et al.*, 1988, Johnson and Bawden, 1987, Taves, 1983). When these dry or powdered formulas are mixed with fluoridated water (0.7 to 1.2 mg/L), the fluoride levels reach as high as 1.45 mg/L (McKnight-Hanes *et al.*, 1988; Johnson and Bawden, 1987), which is within the current recommended daily intake for maximum dental benefit (National Academy of Science, 1989).

In the United States, the average intake of formula-fed infants is estimated to range from 0.09 to 0.13 mg/kg body weight in fluoridated areas, and from 0.01 to 0.02 mg/kg in non-fluoridated areas (Singer and Ophaug, 1979b). These estimates are considerably lower than the EPA estimates of 0.24 mg/kg/day reported in Table 2.6. Breast-fed infants, on the other hand, may receive from 0.003 to 0.004 mg/kg of fluoride by body weight, assuming that the fluoride level in human breast milk is 25 μg/L (Ericsson, 1969)

Where tea drinking is common, tea can contribute substantially to total fluoride intake. Results from the United Kingdom Total Diet Study showed that tea was the major source of dietary fluoride for adults in that country, resulting in 1.3 mg of the total 1.8 mg fluoride intake (Walters and Sherlock, 1983). Similar findings were obtained by Groth (1973) who noted that heavy tea drinkers and beer drinkers would ingest between 2 and 3 mg/day, and 6 mg/day respectively, from these sources alone.

2.3.2. Fluoride Intake from Food

Fluoride, a natural constituent of all foods, is generally found in most of them, at varying levels and concentrations. Table 2.7 shows the fluoride content of the most common foods.

It should be noted that natural fluoride concentrations increase in the event of using fluoride-containing pesticides and fertilizers, fluoridated water for irrigation, washing and even food and beverage processing, as well as the exposure of crops to air-borne fluoride. The effects of these environmental factors can be clearly seen in Table 2.7.

Table 2.7. Fluoride Contents in Selected Foods and Beverages (Taves, 1983; Goyer, 1980; Rose and Marier, 1977; Farkas, 1975a).

Food kind	Fluoride content (mg/Kg or mg/l, or ppm)
Roast beef	0.22 - 0.96
Cow beef	3.10 - 3.50
	30.4 - 41.7[3]
Beef bouillon	1.04 - 1.48
Pork	1.70 - 3.20[2]
	8.80 - 13.5[3]
Chicken breast	0.29 - 0.76
Chicken legs	0.16 - 0.48
Chicken bouillon	0.55 - 1.04
Gouda cheese	0.27 (mean)
	up to 2.16[4]
Bread (low calcium concentration)	0.75 - 1.38
Potatoes	0.32 - 0.95
Rice	0.90 - 1.67
Spaghetti	1.22 - 1.62
Peas[1]	0.24 - 1.07
Carrots[1]	0.34 - 2.02
Green beans[1]	0.32 - 0.72
Tomatoes[1]	0.14 - 0.63
Cabbage	2.80 - 3.24[5]
Lettuce	12.0 - 19.6[5]
Pears[1]	0.48 - 1.11
Peaches[1]	0.49 - 1.14
Apricots[1]	0.32 - 1.28
Apple compost[1]	0.61 - 1.28
Apple juice[1]	0.44 - 1.15
Orange juice[1]	0.21 - 0.76
Grape-fruit juice[1]	0.20 - 0.84
Coffee	0.80 - 1.19
Decaffeinated coffee	0.88 - 1.16
Tea	1.90 - 2.78
Dry tea leaves	14.0 - 88.75
Milk	1.0 (mean)
Baby formula	0.10 - 1.45
Beers	up to 1.00[4]
Wines	up to 0.70[4]
Sugar and adjuncts	0.02 - 0.78
Oils and fats	0.02 - 0.44
Non classifiable foods	0.29 - 0.87[6]

[1] canned food
[2] manually deboned
[3] mechanically deboned
[4] fluoridated processing water
[5] exposed to airborne fluoride pollution and washed with fluoridated water
[6] These include certain soups and puddings, among other items

The effect of fluoridated water used for food processing is apparent from the data on Gouda cheese, beers and wines, and most probably on baby formula. Moreover, the effect of airborne fluoride is obvious in the high values for leafy vegetables; these may have also resulted from the use of fluoride-containing fertilizers. On the other hand, the high fluoride content of mechanically deboned meats results from the inclusion of bone chips, and is hence related to the fluoride uptake of animals.

At this stage, it is also important to consider the contribution of processed foods. When fluoridation was first introduced, it was accepted that this will add only little to fluoride intake. However, since the consumption of processed foods has outstripped that of fresh foods, and knowing that most of the North American food-processing industries are supplied with fluoridated water, facts were felt to have changed.

It was shown by Martin (1951) that the fluoride content of foods cooked with water containing 1 ppm of fluoride would increase three to five times, thus demonstrating the multiplier effect of water fluoridation. In a similar context, a study conducted by Marier and Rose (1966) showed that commercial foods and beverages prepared with fluoridated water contain on average three and a half times more fluorides than the amount established by Hodge and Smith (1965) for non-fluoridated regions.

Also, it is suspected that cooking foods in Teflon-lined cookware increases their fluoride concentration (Goyer, 1980; Full and Parkins, 1975).

Such an increase in the fluoride content of food, due to the reasons outlined above, is thought to be one of the major factors contributing to the increase in human exposure to fluoride (Rose and Marier, 1977; Farkas and Farkas, 1974; Farkas and Parsons, 1974).

In conclusion, Tables 2.8 and 2.9 summarize the daily fluoride intake by adults in communities with low and high fluoride levels in drinking water respectively.

Table 2.8. Daily Fluoride Intake of Adults in Communities with Low Fluoride Levels in Drinking Water (less than 0.4 mg/L)

Adult fluoride intake (mg/day)			References
Dietary sources[1]	Beverages and water	Total fluoride intake	
0.27 to 0.32	N/A	N/A	Armstrong & Knowlton (1942)
0.30 to 0.50	N/A	N/A	McClure (1943)
0.40 to 0.80	0.00 to 0.30	0.40 to 0.88	Ham and Smith (1954)
0.30 to 0.80	N/A	N/A	Cholak (1959)
0.80 to 1.00[2]	N/A	N/A	Kramer *et al.* (1974)
0.70 to 0.90[2]	N/A	N/A	Osis *et al.* (1974)
0.30 to 0.40	0.20 to 0.76	0.91	Singer *et al* (1980)
0.41	0.20	0.61	Becker and Bruce (1981)

[1] Excluding beverages and water
[2] Includes tea and coffee

Table 2.9. Daily Fluoride Intake of Adults in Communities with Fluoridated Drinking Water (approximately 1 mg/L).

Adult fluoride intake (mg/day)			References
Dietary sources[1]	Beverages and water	Total fluoride intake	
0.80 to 0.90	1.30 to 1.50	2.10 to 2.40	San Filippo and Battistone (1971)
1.00 to 2.10	1.00 to 3.20	2.00 to 5.30	Marier and Rose (1966)
1.20 to 2.70	1.60 to 3.20	2 80 to 5.90	Spencer and Lewin (1970)
1.70 to 3.40[2]	N/A	N/A	Kramer *et al* (1974)
1.60 to 1.80[2]	N/A	N/A	Osis *et al* (1974)
0.30 to 0.60	0.60 to 1.10	1.00 to 1.70	Singer *et al* (1980)
0.40	1.60 to 1.90	2.00 to 2 30	Becker and Bruce (1981)

[1] Excluding beverages and water
[2] Includes tea and coffee

2.3.3. Fluoride Intake from Dental Products

Several studies conducted by Whitford (1989, 1987), Ophaug and Singer (1988) and Beltran and Szpunar (1988) have identified fluoride-containing dental products as sources of systematically available fluoride. Such fluoride-containing dental products include dentifrices or toothpastes, mouthrinses, fluoride supplements or professionally applied topical fluoride (U.S. Public Health Service, 1991).

Toothpastes, followed by treatment gels and mouthrinses, are the most commonly used dental treatment products. The vast majority (more than 90%) of the toothpaste available in the United States contains fluoride, in concentrations ranging between 1000 to 1500 ppm (Beltran and Szpunar, 1988), depending on the fluoride compounds used (e.g. sodium fluoride, sodium monofluorophosphate, or calcium pyrophosphate). Fluoride concentration ranges between 230 and 900 ppm in fluoride mouthrinses and 970 to 19,400 ppm in treatment gels (Whitford, 1989).

Depending on the amount of toothpaste used, the amount of fluoride introduced into the mouth with each brushing ranges from 0.1 mg to more than 2.0 mg, with an average of 1.0 mg (Brunn and Thylstrup, 1988; Dowell, 1981). Similar range and average are reported for fluoride mouthrinses (Bell and Whitford, 1985; Wei and Kanellis, 1983). Based on these reports and on the fact that part of the dental product introduced into the mouth is swallowed rather than expectorated, Whitford (1989, 1987) estimated that 25% of the fluoride in toothpastes and mouthrinses is swallowed and absorbed.

As a conclusion, the U.S. Public Health Service (1991) noted that the use of fluoride dental products and fluoride supplements in communities that do not have fluoridated drinking water can result in levels of total fluoride equal to that in communities with optimally fluoridated water supplies. In addition, based on a mean retention and absorption estimate of 25% and on the assumption that teeth are brushed twice daily, the amount of fluoride ingested through dental products would approximately equal the amount ingested from the diet.

2.3.4. Fluoride Intake from Air

In a study conducted by Martin and Jones (1971) and based on an average consumption of 12 to 15 m^3 of air/day for an inactive individual and 20 m^3/day for a working person, it was estimated that the quantity of fluorides absorbed by a worker on a clear day in the heart of London would be 0.003 mg/day as opposed to 0.03 mg/day during a very foggy and exceptionally polluted day. It was hence concluded that, even under intense and severe pollution rates which are usually localised and occasional, a very hard working person would absorb fluoride quantities far below the maximum safe doses

On the other hand, Goyer (1980) reported that individuals who spend all their working hours in a fluoride-rich atmosphere would inhale 25 mg of fluoride in 10 hours. According to Hodge and Smith (1970), such an employee may retain 5 to 6 mg/day of fluoride, the rest being excreted or eliminated through transpiration (Rose and Marier, 1977).

As a conclusion, it can be argued that, although it is generally agreed that air borne fluoride would not contribute significantly to the total human fluoride uptake, even at points of very high fluoride concentration caused by industrial pollution (U.S. EPA, 1985), the situation may be different for individuals who spend all their working hours in an atmosphere in which the fluoride concentration exceeds the maximum allowable limit of 2.5 mg/m^3 (Goyer, 1980). Under all circumstances, it is necessary to point out that these air-borne fluoride sources are to be added to the daily human diet (MENVIQ, 1979; Rose and Marier, 1977).

2.3.5. Total Fluoride Intake

The fluoride intakes resulting from food sources, drinking water and beverages, as well as fluoride dental products (fluoride toothpaste and fluoride mouthrinse) are summarized in Tables 10 and 11, quoted from the U.S. Public Health Service (1991). It should be noted that the fluoride intake from air is not included since it is estimated to be negligible as compared to the other sources (U.S. Public Health Service, 1991; Mahadevan *et al.*, 1986; WHO, 1984; Barnard and Nordstrom, 1982b; Rose and Marier, 1977)

Table 2.10. Summary of the Total Daily Fluoride Intake of Adults(1) (U.S. Public Health Service, 1991).

Concentration of fluoride in drinking water (mg/L)	Intake estimate	Fluoride intake				
		Food sources	Water and beverages	Fluoride Toothpaste(2)	Fluoride Mouthrinse(2)	Estimated total
<0.3 mg/L	mg/day mg/kg/day	0.2 to 0.8 0.004 to 0.016	0.1 to 0.7 0.002 to 0.014	0.018 to 0.145 0.0004 to 0.003	0.56 0.01	0.88 to 2.2 0.016 to 0.04
0.7 to 1.2 mg/L	mg/day mg/kg/day	0.4 to 2.7 0.008 to 0.54	0.6 to 3.2 0.012 to 0.064	0.018 to 0.145 0.0004 to 0.003	0.56 0.01	0.58 to 6.6 0.03 to 0.13
>2.0 mg/L	mg/day mg/kg/day	1.2 to 3.4 0.02 to 0.07	0.9 to >3.5 0.018 to >0.07	0.018 to 0.145 0.0004 to 0.003	Not Recommended	2.1 to >7.05 0.04 to >0.14

(1) Calculation based upon adult weighing 50 kg
(2) Assumed that fluoride toothpaste and mouthrinse used twice per day

Table 2.11. Summary of the Total Daily Fluoride Intake of Children(1) (U.S. Public Health Service, 1991).

Concentration of fluoride in drinking water (mg/L)	Intake estimate	Fluoride intake				
		Food sources	Water and beverages	Fluoride Toothpaste	Fluoride Supplement(3)	Estimated total
<0.3 mg/L	mg/day mg/kg/day	0.15 to 0.3 0.007 to 0.015	0.1 to 0.3 0.005 to 0.015	0.2 to 1.2 0.01 to 0.06	0.50 0.025	0.95 to 2.3 0.047 to 0.115
0.7 to 1.2 mg/L	mg/day mg/kg/day	0.4 to 0.6 0.02 to 0.03	0.3 to 1.8 0.015 to 0.09	0.2 to 1.2 0.01 to 0.06	Not Recommended	0.9 to 3.6 0.045 to 0.15
>2.0 mg/L	mg/day mg/kg/day	1.0 to 2.0 0.05 to 0.10	0.6 to >3.0 0.03 to >0.15	0.2 to 1.2 0.01 to 0.06	Not Recommended	1.8 to >6.2 0.09 to 0.31

(1) Calculation based on child weighing 20 kg
(2) Assumed that fluoride toothpaste used twice per day
(3) Assumed that dental fluoride supplement taken daily

3. MATERIALS AND METHODS

3.1. GENERAL

Fluoride concentrations in the wastewater flowing to the Montréal Urban Community (MUC) wastewater plant may be the result of:

i. The natural concentrations in the waters from the MUC water treatment plants, i.e., Atwater, Des Baillets, Lachine, Ste-Anne de Bellevue and Pierrefonds

ii. The artificial fluoridation of the water from those treatment plants fluoridating their waters, i.e., Dorval and Pointe-Claire.

iii. The domestic habits of the population, such as food and fluoride-containing dental products.

iv. The infiltration of groundwater.

These four types, showing slight variation with time, constitute the "base concentration" or background fluoride concentration. This baseline concentration will be determined based on statistical analysis of the daily data. In a previous study conducted by Gehr *et al.* (1989), it was estimated to be 0.34 mg/L.

In addition, non-baseline contributions include:

v. the direct industrial discharges
vi. the liquid precipitation, i.e., rainfall and natural snowmelt
vii. the solid precipitation, i.e., dust and dry deposits carried out by runoff, and melting salts from winter street-cleaning operations.

These last three types can be classified into two different categories, namely industrial discharges and precipitation.

3.2. MONITORING

3.2.1. Wastewater Sampling

Sampling of the MUC wastewaters was carried out over a 12-month period, from June 1, 1992 to May 31, 1993.

Continuous sampling over the 24-hour period was accomplished by using an automatic sampler placed at the inlet canal to the MUC wastewater treatment plant, after the grit removal facilities. Wastewater composite samples were collected in 1L polyethylene bottles. Twenty-four bottles corresponding to the 24 hours of sampling per day were brought back daily to the laboratory for analysis.

It should however be noted that continuous sampling and measurement were discontinued for a few periods of time. In the early stages of the sampling campaign, sampling was interrupted due to clogging problems arising with the automatic sampler. At later stages, the continuous measurement in the laboratory was interrupted for a few days in September and November 1992, and for longer periods in October and December 1992, as well as in January 1993 The main reason for these regrettable gaps is the difficulties that arose with the operation of a continuous automatic electrode that was designed to replace continuous manual measurement in the lab. In fact, it was first intended that the automatic electrode would operate continuously during the 24 hours of each day and measure automatically the fluoride concentration in the wastewater. Only those specific bottles corresponding to the peaks registered by the automatic electrode would have to be measured in the laboratory. However, several problems prevented adequate operation of the continuous electrode to take place, the most important of these being the constant clogging of the pipes where the measurement occurred and the excessive cleaning and maintenance required to cope with this. At any rate, even under good operating conditions, the automatic electrode did not prove to be a reliable means for continuous fluoride measurement. Indeed, a comparison between the two measurement modes, i.e. that in the laboratory and that by the automatic electrode, carried out at times when both were in operation, showed that the results obtained by the continuous electrode did not give a good picture of the actual fluoride variation as measured in the lab; consequently, all the results obtained by the automatic electrode were completely disregarded. In addition to these interruptions, continuous sampling and measurement were entirely suspended during February and March 1993, as well as during the first half of April 1993.

3.2.2. Precipitation Sampling

In order to estimate the quality of the precipitation, both the liquid precipitation (rainfall or snowfall) and the dry precipitation (dry fallout and dust particles) were collected daily, from a station on the roof of the MUC wastewater treatment plant. The dry precipitation was collected by rinsing the collector with a fixed volume (100 mL, in the present case) of fresh deionized water. One sampling station was found to be sufficient based on the fact that the rainfall quality is relatively homogeneous and shows no statistically significant differences over the island. These precipitation samples were analyzed for the same parameters as for the wastewater. It is to be noted that this station was equipped for snow collection in winter.

Melting salts, which were suspected by Gehr *et al.* (1989) to contribute to increased fluoride levels, were also analyzed at vaious concentrations (50 to 1000 mg/L).

3.2.3. Groundwater Sampling

The location of the wells to be sampled was chosen, in conjunction with the City of Montréal (Barbeau, 1993), to be representative of the groundwater quality on the Island of Montréal. Information regarding the wells specifications is presented in Appendix E.

Groundwater samples were collected by means of a bailer, or a pump when piezometers were too small to fit a bailer. Samples were taken before and after purging the wells. Though the maximum discharge rate should, usually, be based upon the hydraulic conductivity of the aquifer and various properties of the well screen (Mayer et al., 1993), the common practice of purging the well to three times the well casing volume was undertaken in this case, due to the unavailability of more specific information.

Special attention was directed towards the well at Faubourg Québec in Montreal, essentially because the nearby-site had been known, for a few decades, to be a deposition site for ferrous railway equipment. Groundwater contamination with iron was thus suspected and the addition of a decomplexing agent (CDTA) was deemed necessary in order to release the free fluoride ion from the complexes that are readily formed in the presence of iron. Consequently, and in order to estimate the importance of using the CDTA in the case of the well at Faubourg Québec as well as for all other wells, the fluoride analyses of all groundwater samples were performed with and without the CDTA. Also, in addition to those samples taken before and after purging and measured with and without the CDTA, an initial sample of the stagnant water in the well was taken, and another sample was drawn after a very heavy storm shower. Concerning the stagnant water sample, the water was so turbid that it was allowed to settle, and the supernatant was also analyzed. As for the sample taken after the storm shower, the analysis was undertaken mainly to establish any direct effect of precipitation on the groundwater quality.

3.3. ANALYTICAL METHODS

Wastewater and precipitation samples were collected and stored in 1L polyethylene bottles. These were cleaned with a powerful detergent (Decon, 12%), followed by acetone and hydrochloric acid (HCl, 5%), and washed alternately with distilled and deionized water (nanopure), in order to ensure that no contamination could take place.

It should also be noted that all reagents and high concentration standards (1,000 mg/L) were prepared using fresh deionized water and stored in clean polyethylene bottles leached with deionized water. Lower concentration standards used for daily calibration were freshly prepared, on a daily basis, and checked at various stages during sample measurements.

Wastewater and precipitation samples were analyzed daily for fluoride, chloride, pH and conductivity, according to *Standard Methods* (APHA-AWWA-WPCF, 1989)

Fluoride measurements, which were performed to answer the main objectives of the present study, were accompanied by chloride, pH and conductivity measurements. These were important in conjunction with the operation of the continuous automatic electrode. Indeed, it was felt necessary to differentiate between real fluoride peaks registered in the influent wastewater and those peaks corresponding to high fluoride concentrations in the recycle line. Fluoride is expected to be present in the recycle line because, as concluded by Gehr *et al.* (1989), no fluoride removal occurs during the physico-chemical treatment at the MUC wastewater treatment plant. Chloride, which is also found in the coagulant (ferric chloride $FeCl_3$) that is recycled back in the recycle line, serves the purpose well, especially since its measurement does not warrant special measures in the laboratory. Conductivity and pH were also measured for the same purpose, since they give an indication about the activity of ions in solution.

3.3.1. Fluoride Measurement

Fluoride was measured, according to method 413B in *Standard methods* (APHA AWWA WPCF, 1989) approved by ASTM D1179-72B, with a combined ion-selective electrode (Orion# 96-09) connected to an Acumet 925 digital pH/ion meter. The filling solution (Orion Cat. No. 900001) was used to minimize junction potentials and fluoride contamination of the sample.

Rather than measuring the concentration of fluoride directly, the fluoride electrode measures the ion activity of fluoride in solution, and transmits a voltage signal proportional to the fluoride concentration. However, because the fluoride ion activity depends essentially on the pH, the total ionic strength of the solution and the fluoride complexing species, it is necessary to provide for a buffer solution; hence, the addition of the Total Ionic Strength Adjustor (Low level TISAB) to provide a uniform ionic strength, to adjust pH, and to ensure the complexation of interfering cations such as Al^{3+} and Fe^{3+} and the release of free fluoride ions. In addition, the TISAB maintains a pH around 5.5 at which no hydroxide interference or proton association occur, and increases the rate of electrode response due to the increased conductivity (Barnard and Nordstrom, 1982a). Low-level TISAB is generally used when measuring samples containing less than 0.4 ppm ($2x10^{-5}$M) fluoride and no fluoride complexing agents such as iron or aluminum are present (Orion catalogue). This was considered to be the case based on results obtained by Gehr *et al.* (1989). Where the samples were felt to contain higher levels of iron, specifically in the case of some groundwater samples, the low-level TISAB was combined with the decomplexing agent CDTA (cycloexylen-ediamine-tetraacetic acid), according to *Standard Methods* (APHA-AWWA-WPCF, 1989).

Also, based on the results obtained by Gehr, et al. (1989), it was assumed that all the fluoride would be in the soluble ionic form F^-.

It should be noted that an important modification was brought to the analytical procedure in order to decrease the error in readings for samples with very low fluoride concentrations. The known addition of a high concentration standard was especially important to ensure that readings would fall in the linear portion of the calibration curve, knowing that non-linearity starts below 0.01 mg/L (Barnard and Nordstrom, 1982a). Hence, 5 mL of 5 mg/L fluoride standard were added to each sample (or standard), thus increasing its concentration and allowing more accurate readings, within the linear portion. Equal volumes of buffer and total sample (or standard) were combined, in the following manner: 1 mL of the actual sample (or standard), 5 mL of the 5 mg/L standard, and 6 mL of the low-level TISAB. Both Samples and standards were stirred with a Teflon-coated stir bar close to the electrode membrane. The use of Teflon-coated stir bars was not felt to contribute significantly or differentially to the fluoride content of the sample or standard. Potential readings were recorded to the nearest 0 1 mV, after a 5-minute stabilization period. Appropriate conversions accounted for in the calibration procedure were performed to obtain actual sample concentrations

The calibration equation, based on standard fluoride concentrations ranging from 0 01 to 1.00 mg/L was determined to be:

$$y = 104.51 - 53.56 \log(x)$$

where, y is the fluoride concentration (mg/L), and x is the voltage reading (mV).

It is worthwhile noting that the calibration curve determined in the initial steps of the analysis was designed to accommodate for changes in the value of the standards. Since the standards were expected to vary slightly from day to day, this corresponding variation was accounted for by shifting the calibration curve upwards or downwards, based on the intercept value given by the 1 mg/L standard, and assuming that the slope remains essentially constant. This assumption is strengthened by the fact that the calibration curve determined by Gehr *et al.* (1989) was very similar to that obtained in the present study and shown previously. Most importantly, both have the same slope

$$y = 108.46 - 53.49 \log (x)$$

Sources of errors induced by such a practice will be discussed in Section 3 5

3.3.2. Chloride Measurement

Chloride was measured, based on the same principle as for fluoride, using a combined ion-selective electrode (Orion #96-17B), connected to an Accumet 925 digital pH/ion meter. The filling solution (Orion Cat. No. 900017) is used to minimize junction potentials and chloride ion contamination of the sample. An Ionic Strength Adjustor (ISA), 5M $NaNO_3$, is also used to adjust ionic strength of samples and standards. Preparation of the samples (or standards) was done in the following proportion: 10 mL of the sample (or standard) and 0.2 mL of the ISA.

Because of a linear calibration equation, the pH/mV meter was programmed to measure chloride concentrations directly, based on standard chloride concentrations of 10 mg/L and 1,000 mg/L.

3.3.3. Conductivity Measurement

Conductivity was measured with a Radiometer Copenhagen CDM83 Conductivity meter. In its memory, the CDM83 has an algorithm for the calculation of the conductivity of 0.05% NaCl at different temperatures; hence, the CDM83 and the conductivity cell were calibrated automatically with 0.05% NaCl.

3.3.4. pH Measurement

The pH of the wastewaters was expected to be about neutral, whereas that of precipitation was expected to be slightly acidic. Calibration of the electrode was therefore done with the 4.00 and 7.00 buffer solutions. pH was measured directly with a HANNA 8417 digital pH-meter.

3.4. METHODOLOGY

Since chloride, pH and conductivity could no longer be used as intended, in conjunction with the wastewater measurement by the continuous automatic electrode (as discussed in Section 3.2.1), the results of their monitoring will not be discussed hereafter. Only fluoride concentrations will be addressed in terms of levels and variations, as well as mass balance analyses. It should be noted however that the possible correlation between chloride and fluoride will be investigated when analysing melting salts and precipitation. The results will be shown in the corresponding sections.

3.4.1. Descriptive Statistics and Frequency Distributions

Descriptive statistics (obtained with STATISTICA by Statsoft, 1991) and frequency distributions will be used to estimate the fluoride levels in the raw wastewater as well as in the liquid and dry precipitation. Also, they will be used to assess any seasonal variations. For the duration of the present study, five seasons have essentially been identified: spring 1992 (only June 1992), summer 92 (July and August 1992), fall 1992 (September, October and November 1992), winter 1992-93 (December 1992 and January 1993), and spring 1993 (April and May 1993).

The results and discussion of these analyses will be addressed in Sections 4.1 and 4.2 for wastewater and precipitation respectively

3.4.2. Mass Balance Analysis

Mass balance calculations will be used to estimate the fluoride input from the various sources identified as follows: precipitation, infiltration of groundwater, non-fluoridated water, artificially fluoridated water, and unidentified sources. Since the latter consist mostly of industrial discharges the frequency of which is practically impossible to predict, the relative importance of these unidentified sources will be assessed over the one-year period.

The results and discussion of these analyses will be addressed in Section 4.5.

3.5. SOURCES OF ERRORS

Errors may have been introduced at various stages and steps during the measurement process, and may have arisen from human as well as mechanical sources.

3.5.1. Human Errors

Although human interferences were reduced to a minimum by the use of digital apparatuses, automatic pipettes (0.1 mL to 10 mL), and ready-prepared reagents (which include the electrode filling solutions and the 1,000 mg/L standards for both fluoride and chloride, the Ionic Strength Adjustor for chloride measurement, as well as the buffer solutions for pH calibrations), slight variability may have been introduced when standards were diluted daily to be freshly used in the preparation of the low-level TISAB as well as in the preparation of samples for measurement. This factor is more pronounced in the case of fluoride measurements, because (1) the 5 mg/L standard was added to each sample before analysis, based on the principle discussed in Section 3.3.1, and (2) standards were measured daily to re-adjust the calibration curve. At this stage, it becomes important to discuss the errors that may be introduced, in the case of fluoride, while using the calibration curve to convert the voltage readings to a concentration scale. As discussed previously in Section 3.3.1, since standards were expected to vary, though slightly, from day to day, the calibration curve was designed to account for that variation, by shifting it upwards or downwards, based on the value of the 1.0 mg/L standard. This is considered to be a correct practice, only if the slope of the calibration curve remains constant. Repeated verification of the calibration showed that results could be altered by 5%. This was deemed acceptable for the course of this research.

3.5.2. Mechanical Errors

Mechanical errors, on the other hand, have proved to be more serious, especially in the case of the fluoride electrode which has exhibited a "fatigue" behaviour. Indeed, plotting the data on a continuous scale showed that, in some cases, drastic changes have been witnessed from one day to another; more specifically, a gradual increase of fluoride concentration would happen during a certain day, followed by an abrupt drop in the fluoride measurement at the beginning of the next day. This phenomenon is illustrated in Figures 3.1, 3.2 and 3.3.

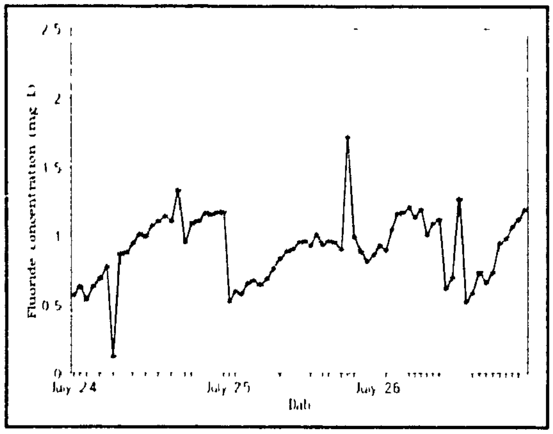

Figure 3.1. Variation in Fluoride Concentrations Illustrating Electrode "Fatigue" (July 24 - 26, 1992).

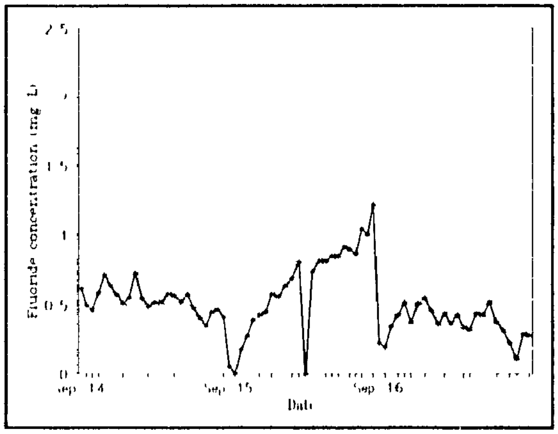

Figure 3.2. Variation in Fluoride Concentrations Illustrating Electrode "Fatigue" (September 14 - 16, 1992).

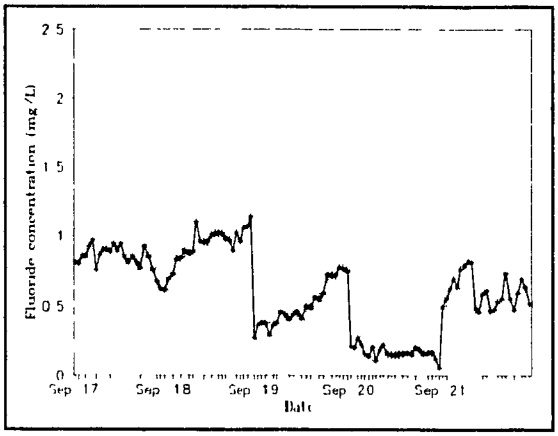

Figure 3.3. Variation in Fluoride Concentrations Illustrating Electrode "Fatigue" (September 17 - 21, 1992).

It can be seen in Figure 3.1 that the fluoride concentration increases uniformly during July 24 and drops abruptly on July 25. This phenomenon is also witnessed in Figure 3.1 for September 15, and in Figure 3.3 for September 19 & 20. Such abrupt changes in fluoride concentrations cannot usually be expected in the case of continuous measurement, and it can fairly be suspected that these were due to a problem with the fluoride electrode.

However, since this phenomenon has only occurred for very specific days, and no other means exist for checking the results[1], there can be no absolute certainty in suspecting and consequently neglecting the corresponding values. For instance, in Figure 3.3, there can be no logical reason to question the high values recorded at the end of September 18 rather than the low values at the beginning of September 19, or those high values at the end of September 19, rather than the lower ones at the beginning of September 20.

Accordingly, it can be concluded, that, although this electrode fatigue phenomenon can be suspected, it cannot be fully ascertained, hence, the corresponding results will generally not be disregarded in the analyses.

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[1] Fluoride standards were usually checked at various points during measurements, except for a few days during which standards were checked only at the beginning of the day, prior to sample measurement. In such cases, there can be no way of checking the results. During those days where standards were checked repeatedly, there was no significant change in the electrode response.

4. RESULTS AND DISCUSSION

4.1. WASTEWATER ANALYSIS

4.1.1 General

As mentioned in Chapter 3 (Materials and Methods), wastewater samples were collected daily from the inlet canal of the MUC wastewater treatment plant. Twenty four composite hourly samples were analyzed daily for fluoride, according to *Standard Methods* (APHA-AWWA-WPCF, 1989). Hourly fluoride concentrations are shown in Appendix B from June 1992 to May 1993, except for the two months of February and March during which continuous analysis was interrupted (as explained in Section 3.2.1).

The daily average fluoride concentrations in the MUC wastewater are plotted (prior to any screening of outliers) on a monthly basis, for each season. These are shown in Figures 4.1 through 4.5.

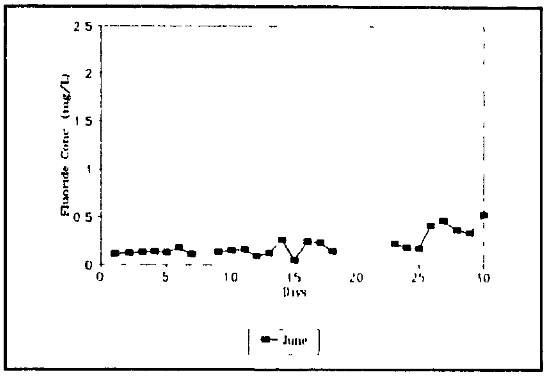

Figure 4.1. Variation of Average Daily Fluoride Concentrations (Spring 1992).

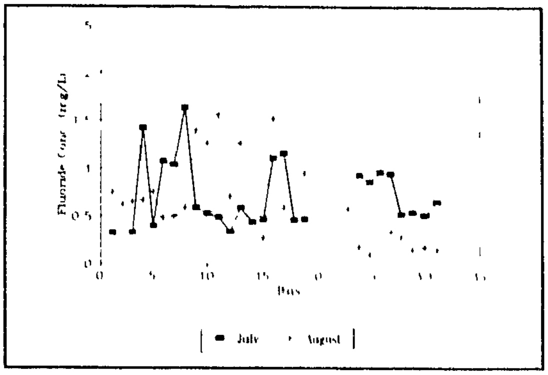

Figure 4.2. Variation of Average Daily Fluoride Concentrations (Summer 1992).

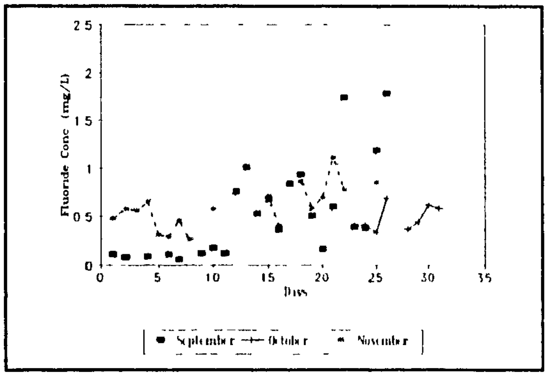

Figure 4.3. Variation of Daily Average Fluoride Concentrations (Fall 1992).

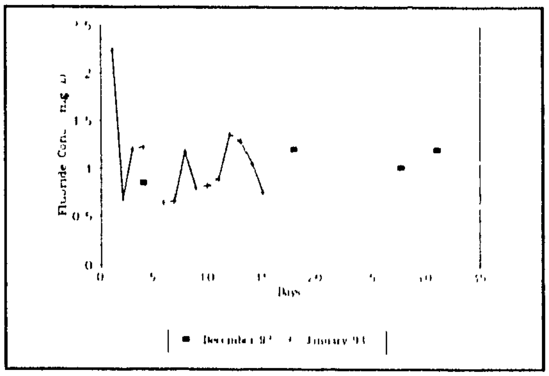

Figure 4.4. Variation of Daily Average Fluoride Concentrations (Winter 92-93).

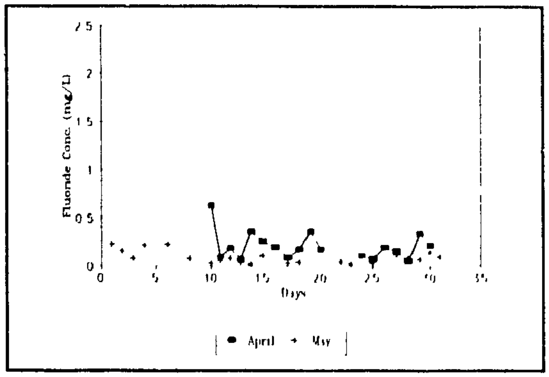

Figure 4.5. Variation of Average Daily Fluoride Concentrations (Spring 1993).

Based on the statistical results presented hereafter in Table 4.1, the monthly variation of the mean, minimum and maximum fluoride concentrations, prior to any screening, is illustrated in Figure 4.6.

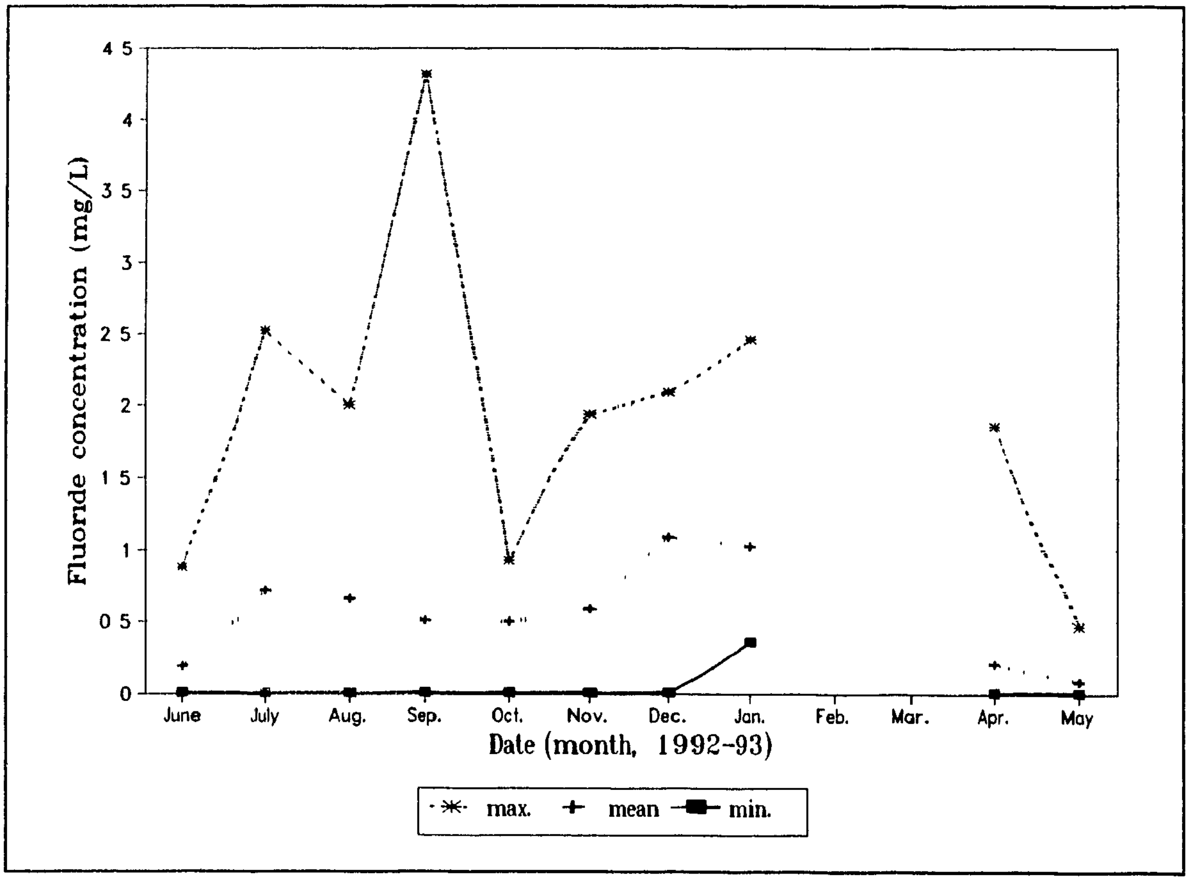

Figure 4.6. Monthly Variation (June 1992 to May 1993) of the Minimum, Mean and Maximum Fluoride Concentrations in the MUC Raw Wastewater (Prior to Data Screening).

4.1.2. Screening of Questionable Data

Prior to any data manipulation, questionable extreme data will be investigated and outliers removed. In the absence of better estimates, the general procedure for eliminating questionable extremes and hence "screening" the data will be based upon the combination of descriptive statistics, and more importantly the standard deviation, the standard error, the maximum value, the skewness and the kurtosis. The combination of these parameters can eventually give an idea about the distribution of the data around the mean, the tendency to "shift" towards higher or lower values, and the "flatness or peakedness" of the distribution. Generally, those values falling beyond ± 3 standard deviations will be considered as outliers (as opposed to ± 2 standard deviations generally considered acceptable in most research) and consequently will be disregarded from the analysis.

Descriptive statistical results, showing the total number of available data (i.e. including those samples that yielded a fluoride concentration below the detection limit of 0.01 mg/L), the minimum, maximum and mean values, the standard deviation and the standard error of the mean, as well as the skewness and the kurtosis, are presented in Table 4.1, for all monthly fluoride concentrations in the raw wastewater, prior to the removal of outliers.

Based on the criteria defined above for removing outliers, computations performed with the descriptive statistics presented in Table 4.1 show that all minimum values are within -3σ from the mean. However, the maximum values in each of June, July, September, November, January, April and May lie outside their respective $+3\sigma$ range.

Hence, setting the maximum acceptable concentration, for each of these months, to be equal to its corresponding $+3\sigma$, all extreme values exceeding this limit were removed

Table 4.1. Descriptive Statistical Results for Monthly Fluoride Concentrations in Raw Wastewater (prior to screening).

Months	Valid cases	Min (mg/L)	Max. (mg/L)	Mean (mg/L)	St. Error	St. dev. (mg/L)	Skewness	Kurtosis
June 92	579	0.005	0.877	0.190	0.007	0.161	1.029	0.963
July 92	608	0.005	2.519	0.717	0.018	0.440	1.264	1.593
Aug 92	600	0.005	1.999	0.660	0.019	0.476	0.779	- 0.170
Sep. 92	567	0.060	4.313	0.512	0.024	0.570	1.966	6.070
Oct 92	151	0.005	0.926	0.500	0.015	0.184	0.049	- 0.496
Nov. 92	399	0.005	1.935	0.592	0.016	0.324	1.071	1.799
Dec 92	76	0.005	2.091	1.084	0.042	0.362	- 0.183	1.131
Jan. 93	265	0.360	2.456	1.023	0.029	0.469	1.462	1.780
Apr 93	371	0.005	1.860	0.208	0.010	0.199	2.534	13.153
May 93	572	0.005	0.469	0.082	0.004	0.090	1.476	1.724

(1) The valid cases represent all available data, including those at or below the detection limit (0.01 mg/L). These data points were considered to be equal to 0.005 mg/L, i.e., half the detection limit

(2) Results for February and March were not obtained due to the interruption of the wastewater sampling

Several iterations (five in all) were required to account for the decrease in standard deviation after each series of removal of extreme values. In total, 3% of the data were screened out. The final descriptive statistics for the screened data are presented in Table 4.2.

Comparing Tables 4.1 and 4.2, one can see that, as expected, screening the data resulted in a net decrease in the values of all descriptive statistics. The standard error decreased significantly in most cases. The final skewness and kurtosis values that have also decreased significantly indicate that the distribution tends towards normality, after the removal of the abnormally high maximum values. The percent decrease in the values of the mean and standard deviation is shown in Table 4.3.

Table 4.2. Final Descriptive Statistical Results for Monthly Fluoride Concentration in Raw Wastewater.

Months	Valid cases	Min. (mg/L)	Max. (mg/L)	Mean (mg/L)	St. Error	St.dev. (mg/L)	Skewness	Kurtosis
June 92	566	0.005	0.601	0.179	0.006	0.143	0.692	- 0.255
July 92	595	0.005	1.848	0.686	0.016	0.389	0.956	0.388
Aug. 92	600	0.005	1.999	0.660	0.019	0.476	0.779	- 0.170
Sep. 92	534	0.005	1.580	0.412	0.017	0.390	0.747	- 0.465
Oct. 92	151	0.005	0.926	0.500	0.015	0.184	0.049	0.496
Nov. 92	389	0.005	1.388	0.564	0.014	0.277	0.471	0.174
Dec. 92	76	0.005	2.091	1.084	0.042	0.362	- 0.183	1.131
Jan. 93	241	0.360	1.705	0.902	0.018	0.279	0.420	0.557
Apr. 93	361	0.005	0.601	0.180	0.007	0.140	0.788	0.035
May 93	554	0.005	0.291	0.072	0.003	0.076	1.210	0.483

(1) The valid cases represent all available data, including those at or below the detection limit (0.01 mg/L). These data points were considered to be equal to 0.005 mg/L, i.e., half the detection limit.

(2) Results for February and March were not obtained due to the interruption of the wastewater sampling

It can clearly be seen, from Table 4.3 following, that the effect of data screening was greatest for September, January and April. Indeed, the aberrant maximum values associated with these months had a great effect on the distribution, in September and April, the maximums, 4.31 mg/L and 1.86 mg/L respectively, were 9-times their corresponding mean values. In January, however, the maximum of 2.5 mg/L was only

2.5-times its mean In this particular case, the significant decrease in the statistical mean and standard deviation is due to the removal of several values clustered around the maximum.

Table 4.3. Percent Decrease in the Values of the Mean and Standard Deviation.

Date	Percent decrease (%) in	
	Mean	Standard deviation
June 92	5.8	11.2
July 92	4.3	11.6
Aug 92	-	-
Sep 92	19.5	31.5
Oct. 92	-	-
Nov. 92	4.7	14.5
Dec. 92	-	-
Feb. 92	(1)	(1)
Mar. 92	(1)	(1)
Jan. 93	11.8	40.6
Apr. 93	13.5	29.6
May 93	12.2	15.6

(1) Not included in the present study

It is very important, at this stage, to point out the fact that, although the abnormally high maximum values were removed from analysis based on the 3 standard deviations range, it cannot be ruled out with absolute certainty that they may have represented actual peaks corresponding to very important "unauthorized" discharges However, in the absence of better evidence, they were regarded as outliers and consequently disregarded from analysis

The variation of fluoride concentrations in wastewater samples after the removal of all outliers is addressed in the following sections.

4.1.3. Variation of Fluoride Concentrations in Wastewater

Monthly Variations

Based on Table 4.2, the monthly variation of the mean, maximum and minimum fluoride concentration after screening, is illustrated in Figure 4.7.

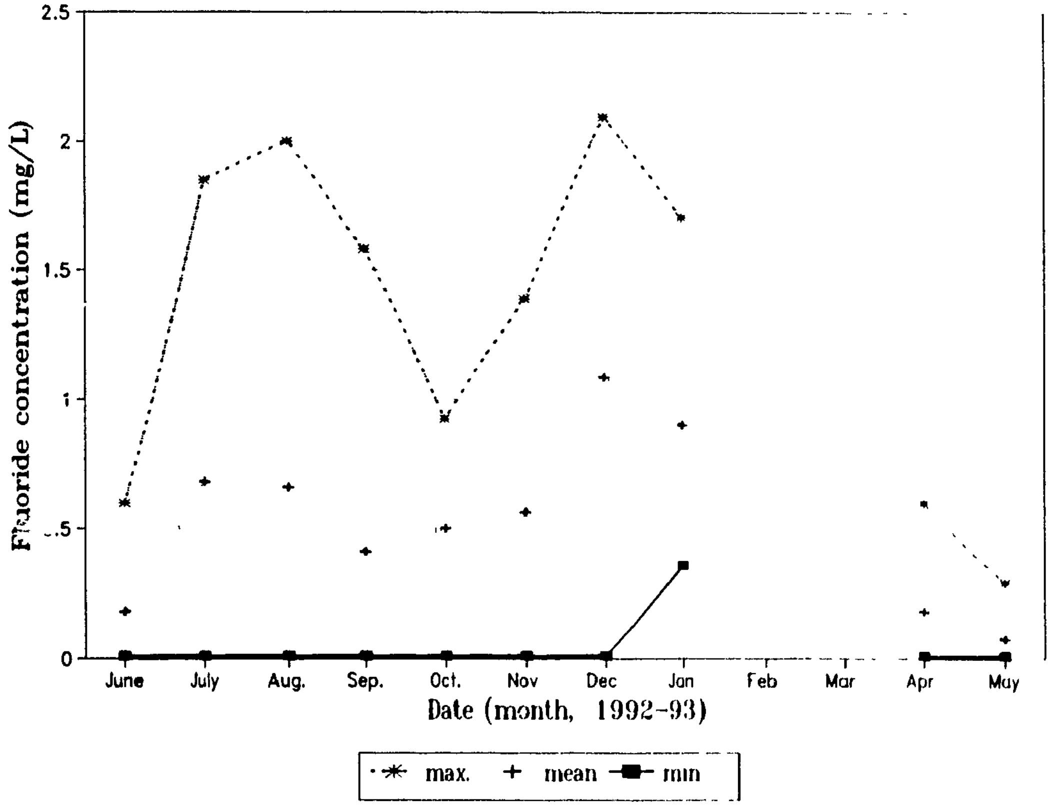

Figure 4.7. Monthly Variation (June 1992 to May 1993) of the Minimum, Mean and Maximum Fluoride Concentrations in the MUC Raw Wastewater (After Data Screening).

The monthly statistical results presented in Table 4.2 show that the mean fluoride concentrations range between 0.072 mg/L and 1.084 mg/L, with an average of 0.45 mg/L. In the study conducted from February to May 1989, Gehr *et al.* (1989) found that average fluoride concentrations varied between 0.22 mg/L and 0.58 mg/L, with a mean of 0.34 mg/L. The increase in the mean value here (from 0.34 mg/L to 0.45 mg/L) may be due to the fact that the present study involved a continuous hourly monitoring over a longer period, hence increasing the representativeness of the data and the chances of depicting fluoride peaks. On the other hand, this increase may also have been due to a true increase in the wastewater fluoride concentration. Assuming that the input by infiltration and by the domestic habits of the population did not change substantially between 1988 and 1992-93, this increase in fluoride concentration may only have resulted from an increase in the fluoride concentration in precipitation or an increase in the fluoride concentration of industrial discharges. These, however, are two factors that cannot be predicted either in quality or magnitude. It should be noted, at this stage, that the increased demand for water consumption between 1988 and 1992 (Table 4.25) is not expected to cause an increase in the wastewater fluoride concentration; this is because the possible increase in fluoride concentration that may result from the increased use of fluoridated water (having a fluoride concentration of approximately 1.0 mg/L, i.e., more than twice as high as the mean) is balanced by the increased use of non-fluoridated water (having a fluoride concentration of approximately 0.20 mg/L, i.e. less than half the mean). Actually, since the contribution of non-fluoridated water is much higher than that of fluoridated water (Table 4.26), the increase in water supply may finally result in a dilution of the raw wastewater and hence, a decrease, rather than an increase, in the wastewater fluoride concentration. At any rate, the combined effect of the increase of both fluoridated and non-fluoridated water is not expected to have a noticeable effect on the wastewater fluoride concentration. Accordingly, the increase in water supply should not be viewed as a factor causing the increase in the fluoride concentration of the raw wastewater. This holds true as long as water fluoridation is undertaken in the same proportion as in the present time. Should there be a more widespread use of water fluoridation, this conclusion will not remain valid.

Another interesting point emerges from Table 4.2 when considering the standard deviations. It can be noticed that fluoride concentrations are more widely scattered during the summer and the winter, whereas they are the least scattered during the spring. No specific trend could be determined for the fall

Finally, it can be noticed from Table 4.2 that the maximum values may reach as high as 4-fold the mean, and well over two orders higher than the minimum values. This suggests that non-regulated discharges of fluoride are taking place. These are expected to be quite high in magnitude or concentration, considering that the fluoride concentration at the inlet to the wastewater treatment plant is already very high, despite the dilution in the sewers by groundwater infiltration.

Seasonal Variation

A clear trend in seasonal variation can be discerned from Figure 4.7. The fluoride concentration is lowest during the spring, increases during the summer, decreases in the fall and reaches its maximum during the winter. It is also interesting to see that the seasonal trend is continuous and seems to repeat itself; this is illustrated by the continuity of the fluoride variation between the spring 1993 (April and May 1993) and the spring 1992 (June 1992). However, the results showing low fluoride concentrations during the spring do not confirm the results obtained by Gehr *et al* (1989), which showed an increasing trend during spring. Because of the continuous sampling and the consequently greater number of samples involved in the present study, the current results and trends are expected to give a better picture of the actual situation.

In the spring, the low fluoride concentrations can be due to (1) increased infiltration (Table 4.22), causing increased dilution of the raw wastewater with a corresponding decrease in fluoride concentrations, (2) snow melting, which also causes a dilution of the raw wastewater; this is true because the melting salts that were suspected to contain fluoride (Gehr *et al.*, 1989) and hence lead to increased fluoride concentration in the deposited snow, were found to include no fluoride (as will be shown in Section 4.4), and (3) negligible input of fluoride by precipitation; this is the case because fluoride concentrations in precipitation were found to be very low during the spring (Table 4.10, Figure 4.7).

In the summer, the increase in fluoride concentrations is mainly due to the increased input of fluoride by precipitation (higher fluoride concentrations were found in precipitation samples during the summer; Table 4.10) and to decreased infiltration (Table 4.22). As discussed in the previous subsection, the increased demand for water consumption during the summer is not expected to cause an increase in the fluoride concentration in the raw wastewater.

In the fall, the lower fluoride concentrations are mainly due to the combination of (1) lower fluoride concentrations in precipitation (Table 4.10 and Figure 4.7), and (2) slightly increased infiltration (Table 4.22). The slight steady increase in the mean fluoride concentration from September to November may have resulted from an extended dry period and a consequently lower dilution; indeed, Table 4.20 shows that the volume of precipitation was lowest during fall and more specifically during October.

During the Winter, fluoride concentrations are maximum. This can be explained primarily by the increased fluoride input from precipitation. Indeed, Table 4.10 shows that fluoride concentrations in precipitation are very high during the winter.

As a conclusion, it can generally be noted that a clear seasonal trend can be discerned, with fluoride concentrations being lowest during the spring, higher during the summer, lower in the fall and at their maximum during the winter. Increased fluoride concentrations can result from decreased infiltration and increased fluoride input from precipitation. Low fluoride concentrations, on the other hand, may be due to increased infiltration and decreased fluoride input by precipitation. The increase in water consumption is not expected to affect significantly the fluoride concentration in the wastewater. It is however anticipated that the variations in industrial inputs would have a notable effect on the fluoride levels in the raw wastewater. The contribution of the industrial sources of fluoride, which constitute a non-negligible part of the unidentified sources, are seen to vary from one month to another, in Table 4.34 (Section 4.5.4).

Frequency Analysis

The percentile distributions of hourly fluoride concentrations in the MUC wastewater are presented in Figures 4.8 through 4.12.

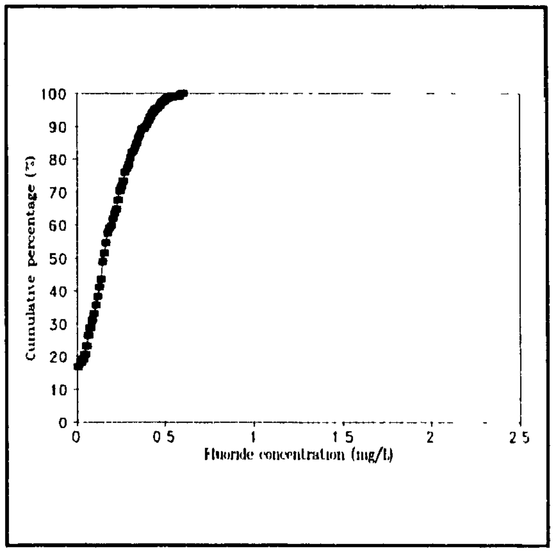

Figure 4.8. Fluoride Frequency Distribution in the MUC Wastewater (Spring 1992).

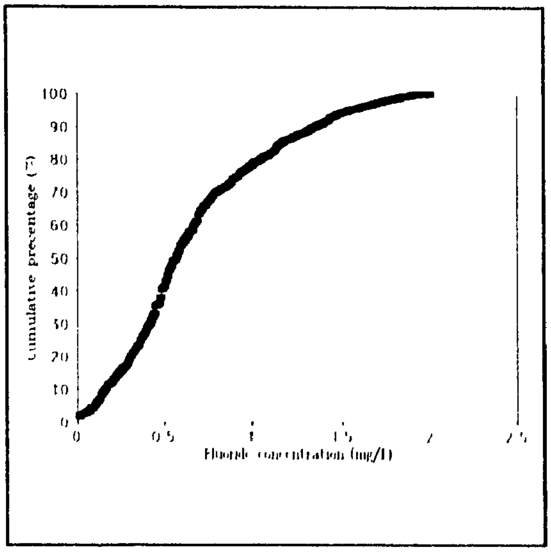

Figure 4.9. Fluoride Frequency Distribution in the MUC Wastewater (Summer 1992).

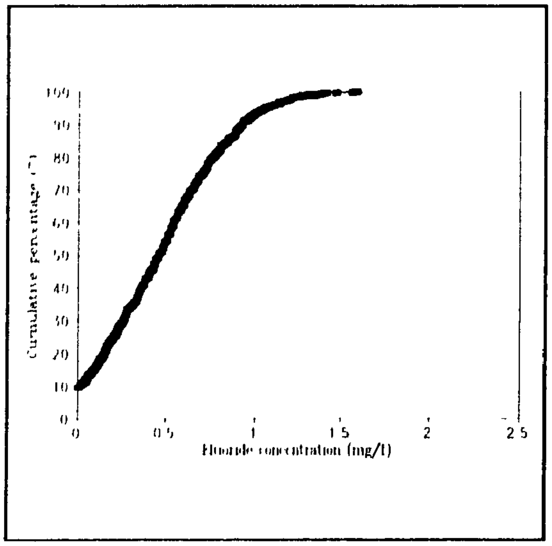

Figure 4.10. Fluoride Frequency Distribution in the MUC Wastewater (Fall 1992).

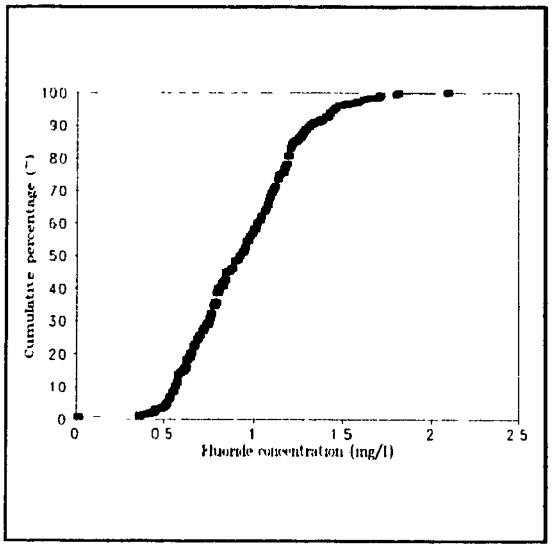

Figure 4.11. Fluoride Frequency Distribution in the MUC Wastewater (Winter 1992-93).

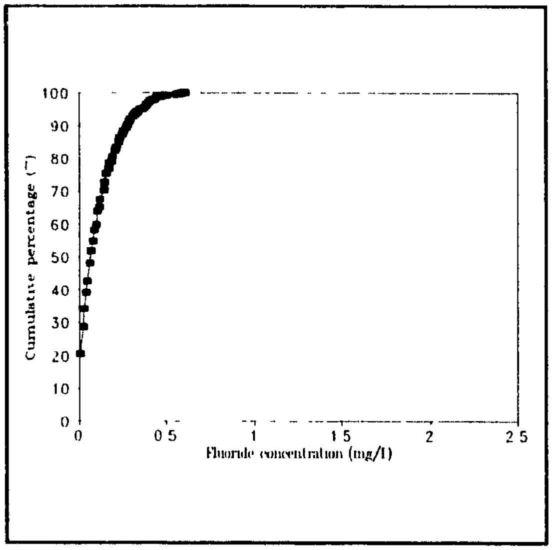

Figure 4.12. Fluoride Frequency Distribution in the MUC Wastewater (Spring 1993).

Figures 4.8 & 4.12 show a sharp slope, indicating that high cumulative percentages correspond to low fluoride concentrations. It can hence be concluded, that, during spring, there is a very high percentage of samples having very low fluoride concentrations.

On the other hand, Figures 4.9, 4.10 & 4.11 show a milder slope, indicating that there is a smaller percentage of samples having higher fluoride concentrations.

It is also interesting to see in Figures 4.8, 4.10 & 4.12 the very high percentage of samples having fluoride concentrations at or below the detection limit (0 01 mg/L)

Based on the frequency distributions shown in Figures 4.8 through 4 12, the percentile distributions of fluoride concentrations were determined. These are presented in Table 4.4. These do not include the effect of outliers that were screened and removed in Section 4.1.2.

Table 4.4. Percentile Distributions of Fluoride Concentrations.

Season	Percentile distribution of fluoride concentration (mg/L)		
	10%	50%	99%
Spring 1992	0.01	0.15	0.58
Summer 1992	0.17	0 57	1 90
Fall 1992	0.02	0.46	1.44
Winter 1992	0.57	0.93	1 76
Spring 1993	0.01	0 07	0.54

Table 4.4 demonstrates the wide range of fluoride variations, with a correspondingly high ratio of maximum to minimum. This confirms the results obtained in the previous

Section, indicating that unexpectedly high fluoride concentrations are occasionally encountered in the raw wastewater. It is suspected, with reasonable likelihood, that these may have resulted from unauthorized industrial discharges. This will be further investigated in the following Section by checking the mode (or most frequent value) and comparing it to the mean.

Comparison Between the Mean and the Most Frequent Fluoride Concentrations

The most frequently occurring fluoride concentrations (modes), for each month, were determined based on the corresponding histograms. Results are shown in Table 4.5.

Table 4.5. Comparison Between the Mode and the Mean Fluoride Concentration in the Raw Wastewater, from June 1992 to May 1993.

Month	Mean (mg/L)	Mode (mg/L)	Difference (mg/L)
June 1992	0.19	0.05	0.14
July 1992	0.72	0.50	0.22
Aug. 1992	0.66	0.65	0.01
Sep. 1992	0.51	0.05	0.46
Oct. 1992	0.50	0.45	0.05
Nov. 1992	0.59	0.60	- 0.01
Dec. 1992	1.08	1.00	0.08
Jan. 1993	1.02	0.75	0.27
Apr. 1993	0.21	0.05	0.16
May 1993	0.08	0.05	0.03

(1) Results for February and March were not included in the present study

The comparison between the mode and the mean shows that, in most cases, the most frequent value is much lower than the mean This can only be explained by the fact that, while most values are generally small, the means tends to be higher because of the presence of extreme points Most of these extreme values can only be due to major discharges in the sewer network. This is especially true if one considers that the fluoride concentrations measured in the raw wastewater are supposed to result from natural sources (except for the portion resulting from the addition of fluoride for the artificial fluoridation of the potable water) and from the domestic habits of the population, and hence are not expected to exhibit such high values nor such wide ranges of fluctuations.

As a conclusion regarding the presence of fluoride in the raw wastewater, it can be noted that a general seasonal trend can be depicted, with fluoride concentrations being lowest during the spring, higher during the summer, lower in the fall, and at their maximum during the winter. These trends can be explained by the combination of several factors, the most important of which are the rate of infiltration and precipitation Nevertheless, a large portion of these variations are accounted for by unidentified sources (estimated in Section 4.5.4). Although a part of these unidentified sources is due to dry fluoride deposits dissolved into the runoff, the largest portion results from industrial discharges. The importance of these "unauthorized" discharges can be evidenced by the wide range of fluctuations of fluoride concentrations, the correspondingly high ratio of maximum to minimum, and the difference between the mean and the most frequent fluoride concentrations.

The wide fluctuations of fluoride concentrations, during selected periods, are graphically illustrated in Appendix A. These graphs are based on unscreened data.

4.2. PRECIPITATION ANALYSIS

4.2.1. General

Precipitation samples were collected daily, from a station located on the roof of the MUC wastewater treatment plant. During winter, the sampling station was equipped with a heating device, making it convenient for snow collection. During dry periods, the dry deposits were also collected and analyzed.

The distinction between the two precipitation components (liquid and dry) is important in several respects, most essentially because only the liquid component will be used to determine the input of fluoride mass by precipitation, when establishing the mass balance It is thus important to point out that "liquid precipitation" corresponds to those days during which actual precipitation was recorded. Consequently, "liquid precipitation" includes, in addition to the actual precipitation, a portion of the dry precipitation that was deposited during that same day, when it was not raining or snowing. "Dry precipitation", on the other hand, refers to the dry deposits that were collected during dry days, when no actual precipitation was recorded.

Based on this distinction, screening of questionable data and estimation of fluoride concentrations in precipitation will be performed for each component separately.

It is now important to note that the fluoride concentrations in the precipitation samples collected at the MUC wastewater treatment plant are assumed to be unaffected by the incineration of the sludge at the treatment plant. This could have been a serious concern especially since no other samples were taken at another location, and it should preferably have been checked by analysing fluoride concentration both in the sludge and the ashes, hoping that no difference would be noted. However, based on the study conducted in 1988 by Gehr *et al* (1989), the comparison between the fluoride concentration in the raw influent and that in the treated effluent at the wastewater treatment plant showed that fluoride is not removed in the physical-chemical treatment process undertaken at the treatment plant. Consequently, fluoride is not expected to be present in the sludge, and it can be reasonably assumed that sludge incineration at the treatment plant does not affect the fluoride concentration in the precipitation samples

4.2.2. Screening Questionable Data Points

Liquid Precipitation

The fluoride concentrations in the liquid precipitation are presented in Table 4 6

Prior to analysing and using the data presented in Table 4 6, these should be investigated for any possible outliers This is an important step to carry out for all experimental data, and more so in this case for precipitation data, since only one sample was collected each day, and no other comparison to existing information can be made Moreover, precipitation, as opposed to wastewater flow, is not a continuous process and drastic changes in atmospheric conditions are quite likely Accordingly, it becomes impossible to determine whether extreme values are "actual" peak fluoride concentrations that have been localized in precipitation, or whether they are simply due to errors which may have arisen during the collection of the samples or at various stages during their measurement.

As discussed in Section 4.1.2 for the wastewater data, the general procedure for eliminating questionable extremes will be based upon the descriptive statistics shown in

Table 4.7. Generally, those values falling beyond ± 3 standard deviations will be considered as outliers (as opposed to ± 2 standard deviations generally considered acceptable in most research) and consequently disregarded from the analysis.

It is very important to stress the fact that, although this procedure is generally used for normally distributed data, it will still be used herein, despite the fact that precipitation data (as expected) are not normally distributed.

Table 4.6. Fluoride Concentrations in Liquid Precipitation between June 1992 and May 1993.

	June	July	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May
1	0.02		0.25				(2)	**1.8**	0.13		(2)	
2	0.01		0.35			(1)	(2)			0.21	(2)	
3		0.01	0.35	0.06		(1)	(2)	0.57			(2)	
4		0.03	0.31	0.08	(2)	(1)	0.29	0.58	(1)		(2)	
5	0.02	0.12	0.34			(1)		(2)	0.20	0.48		(2)
6	0.02	(1)				(1)	0.89	0.27		0.37		0.02
7	0.06	1.32	0.05		(2)		0.93		0.56	0.55		
8		1.25	0.09	(2)	(2)			0.38	0.53	(2)		
9		0.13	1.18		(2)					(2)	(2)	
10		0.16	0.80	0.06	(2)	(1)			(2)	(2)	0.48	
11		(1)	1.35		(2)	(2)				(2)	0.18	
12	(1)	0.21			(2)	(2)			0.66	(2)	0.14	(2)
13	0.03	(1)	0.37			(2)		0.41	0.37	(2)	(1)	0.23
14		0.66				(1)		0.39	0.06	0.12		
15						(1)		0.02				0.18
16		0.16	1.03	0.08	(2)	(2)	0.32	0.17	0.05	0.25	0.17	(2)
17		0.69	(1)	0.42		(2)	(1)	0.22	(2)	0.24	0.20	
18		0.25	(2)	0.36			0.60			1.61		
19	(2)	0.25	0.59		(2)		0.36		(2)	1.34	0.14	(2)
20	(2)				(2)	(1)	0.48	(2)	0.09	(2)	0.12	(2)
21	(2)			0.25	(2)	0.50			(2)	1.20	(2)	(2)
22	(2)			0.14	(2)	0.07	0.26	(2)	(2)	1.23	(2)	
23					(2)	(2)	(1)	0.33	(2)		0.12	
24	(1)	0.33			0.10	(2)	0.60	0.14	0.22		0.11	**2.33**
25	(1)				0.11	0.17	0.38	0.28	0.16		(2)	0.68
26		0.59	(2)	**1.21**	(1)	(2)	0.48		0.23		0.09	0.29
27		0.72	0.34	(2)				0.38				(2)
28	[illegible]		0.11					0.41				(2)
	[illegible]		0.13				(2)	0.28		1.30		0.17
	0.01		0.13				0.59	0.09				
		0.36	0.15				0.67	0.15				0.51

(1) Below detectable limit (0.01 mg/l) considered as 0.005 mg/l

(2) Missing data (i.e. no dry precipitation either, see Table 4.8)

Note: All values are given in mg/l

The highlighted figures are suspected to be outliers

Descriptive statistical results, showing the total number of available data (i.e including those samples that yielded a fluoride concentration below the detection limit of 0.01 mg/L), the minimum, maximum and mean values, the standard deviation and the standard error of the mean, as well as the skewness and the kurtosis, are presented in Table 4.7, for all monthly fluoride concentrations in liquid precipitation, prior to any removal of outliers.

Table 4.7. Descriptive Statistical Results for Monthly Fluoride Concentration in Liquid Precipitation (prior to screening).

Months	Valid cases	Min. (mg/L)	Max. (mg/L)	Mean (mg/L)	St. Error	St.dev. (mg/L)	Skewness	Kurtosis
June 92	13	0.005	0.060	0.030	0.006	0.021	0.327	- 1.462
July 92	20	0.005	1.320	0.363	0.088	0.393	1.170	0.304
Aug. 92	19	0.005	1.350	0.417	0.091	0.395	1.101	0.090
Sep. 92	9	0.060	1.210	0.296	0.123	0.368	1.592	1.284
Oct. 92	3	0.005	0.110	0.072	0.033	0.058	0.372	2.333
Nov. 92	12	0.005	0.500	0.065	0.042	0.145	2.200	3.688
Dec. 92	15	0.005	0.930	0.457	0.070	0.271	0.010	0.830
Jan. 93	18	0.020	1.800	0.382	0.091	0.385	2.674	7.300
Feb. 93	13	0.005	0.660	0.251	0.060	0.213	0.670	1.102
Mar. 93	12	0.120	1.610	0.742	0.158	0.546	0.278	1.807
Apr. 93	12	0.005	0.480	0.147	0.035	0.121	1.461	2.073
May 93	8	0.020	2.330	0.551	0.264	0.748	1.588	1.046

It could be suspected, when examining Table 4.6, that the fluoride concentrations on September 26th, January 1st and May 24th correspond to questionable extremes.

Regarding the maximum fluoride concentration in September (1.21 mg/L), it can be seen from Table 4.7 that it does lie within the +3σ range and it should therefore not be disregarded.

However, concerning the maximum value in January, it can be seen in Table 4.7 that the value of 1.8 mg/L does indeed lie outside its $+3\sigma$ range Hence, based on this criterion along with the combination of quite high skewness and kurtosis factors, the maximum value of 1.80 mg/L will be neglected in further analysis.

As for May, the especially high maximum value of 2.33 mg/L makes it almost obvious that, unless a highly concentrated point discharge had taken place, this extreme point would be due to an analytical error. Indeed, the high value of the standard deviation (0.748 mg/L) and the relatively high value of the standard error support the idea that, although the maximum value falls within the $+3\sigma$ range (which is obvious if one considers the extremely high value of the standard deviation), it should be disregarded in further analysis. Indeed, such a high value, unless justified (which cannot be ascertained in the present study) could seriously affect the mean. Neglecting this value results in a mean and a standard deviation, for May, of 0.297 mg/L and 0.225 mg/L respectively, showing a 46% decrease in the original value of the mean and a decrease in the standard error down to 0.085. These results are now in accordance with the general trend observed for April and extrapolated for June 93 (based on the assumption that it would not differ markedly from June 1992).

At this stage, the high value of the maximum associated with the high standard deviation for March may seem questionable, despite the fact that the maximum value falls within the $+3\sigma$ range Applying the same reasoning and disregarding the maximum value of 1.61 mg/L yields a mean and a standard deviation of 0.663 mg/L and 0.496 mg/L respectively. As opposed to May, disregarding the maximum did not significantly affect the statistical results. Accordingly, the maximum value of 1.61 mg/L will not be neglected in further analyses. It should be pointed out that the noticeable increase in fluoride concentrations during the second half of March may be due either to an analytical error or to a true increase in the fluoride levels in liquid precipitation. Though the latter cannot be firmly dismissed, the former is suspected since all these high values were measured on the same day, on samples that had been stored in the laboratory awaiting analysis.

In conclusion, it can be said that the criteria for screening questionable precipitation data were based on the combination of several important parameters and distributional trends, rather than just one statistic. This is important before taking any conclusive step to eliminate any data. Hence, based on this principle, the maximum values of 1.80 mg/L and 2.33 mg/L for January and May respectively will be neglected in further analysis. The statistical results for January and May were corrected accordingly to exclude these maximum values that were out of range. As for the minimum fluoride concentrations which correspond in most cases to half the detection limit, they were found, for all 12 months, to lie within the boundaries of their respective -3σ. The final descriptive results for fluoride concentrations in liquid precipitation are shown in Table 4.10

Dry Precipitation

In the case of dry precipitation, fluoride results are expressed in terms of mass per area, rather than in terms of concentration. These mass transformations were obtained based on the known concentration of fluoride in the 100 mL volume of deionized water used to rinse the deposits, and on the area of the collector (diameter = 8 in) Sample calculations are shown in Appendix D. The results obtained are shown in Table 4.8

Data presented in Table 4.8 suggest the presence of outliers, especially during September and May. These will be checked and the data screened, based on the same principle as that outlined in the preceding subsection.

Descriptive statistical results of all monthly fluoride concentrations in dry precipitation are presented in Table 4.9, prior to the removal of outliers.

Table 4.8. Specific Fluoride Mass in Dry Precipitation Between June 1992 and May 1993.

	June	July	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May
1		0 493		0 308	(2)	0 062				0 586		0 678
2		(2)		0 247	(2)			1 203	1 264			
3	(1)			(2)				0 894	0 771		0 894	
4	(1)								1 141		0 648	
5				0 401	(2)		1 418				(2)	
6			0 308	(2)	(2)				2 344		(2)	
7				(1)	(2)				0 925	(2)	(2)	
8	(2)					0 123	(2)				(2)	0 956
9	0 123			0 185		(2)	1 264	2 652	1 048			(2)
10	0 185						1 233	3 515				0 894
11	(1)			0 278		1 634	0 956	(2)			0 062	
12			0 648	0 617			1 727	2 528				
13				**2.220**	(2)		1 264					
14	0 154		(2)	1 141	(2)		1 233				1 110	0 462
15	0 123	0 370	1 603	(1)		2 344		1 233	0 678	0 740		
16	0 031											
17	0 062				(2)							(2)
18	0 092				(2)	0 123		0 586	(2)		0 308	(1)
19				(1)	(2)		2 128					
20		(2)	(2)	(1)								
21		(2)	(2)				0 956	(2)				
22		(2)	(2)									**5.396**
23	(2)	(2)	0 740	0 062						3 700		0 123
24			0 432	0 216						3 515		
25		0 894	0 432	0 617						5 211		
26	0 154							0 678		4 317		
27	0 185				(2)	(2)	(2)		1 203	3 762	0 278	
28		0 648		(2)	(2)	(2)	(2)		1 110	3 362	0 802	
29		0 278		(2)	0 247						0 771	
30		0 462		(2)	(2)					3 423	(2)	1 357
31					0 401					2 837		

(1) Below detectable limit
(2) Missing data (i e no wet precipitation either, see Table 4 6)
Note All values are given in kg/km^2
The highlighted figures are suspected to be outliers

Table 4.9 following shows that, except for the maximum in September (as suspected), all the data fall within their respective ±3σ. Hence, the outlier in September will be disregarded from analysis.

However, considering the high value of the skewness and kurtosis factors along with the relatively high value of the standard error, it can be suspected that the maximum in May is also an outlier. Indeed if this value were removed, the mean and standard deviation would become 0.609 kg/km^2 and 0.442 kg/km^2 respectively, a reduction of 42% and 70%. Consequently, the maximum in May will also be disregarded in further analysis, as it introduces large errors in the corresponding statistical results. As for the high values registered in the dry precipitation during the second half of March, the same argument holds as for the liquid precipitation. The final descriptive statistics for dry precipitation are shown in Table 4.11.

Table 4.9. Raw Monthly Results for Fluoride Concentrations in Dry Precipitation (prior to screening).

Months	Valid cases	Min. (kg/km^2)	Max. (kg/km^2)	Mean (kg/km^2)	St. Error	St dev (kg/km^2)	Skewness	Kurtosis
June 92	12	0.015	0.185	0.096	0.019	0.067	0.026	1.760
July 92	6	0.278	0.894	0.524	0.090	0.220	0.528	- 1.338
Aug. 92	6	0.308	1.603	0.694	0.193	0.473	1.040	0.611
Sep. 92	15	0.015	2.220	0.423	0.151	0.584	1.948	3.188
Oct. 92	2	0.247	0.401	0.324	0.077	0.109	0.000	2.750
Nov. 92	3	0.062	0.123	0.103	0.020	0.036	- 0.385	- 2.333
Dec. 92	9	0.956	2.344	1.453	0.135	0.406	0.959	- 0.111
Jan. 93	9	0.586	3.515	1.686	0.349	1.046	0.429	- 1.536
Feb. 93	7	0.894	2.344	1.300	0.180	0.478	1.374	0.353
Mar. 93	12	0.586	5.211	2.775	0.455	1.576	- 0.242	1.533
Apr. 93	6	0.278	1.110	0.668	0.130	0.320	- 0.081	1.745
May 93	11	0.015	5.396	1.044	0.453	1.503	2.124	3.442

4.2.3. Estimation of Fluoride Concentration in Precipitation: Monthly Results and Seasonal Trends

Liquid Precipitation

Final descriptive statistics of monthly fluoride concentrations in liquid precipitation are presented in Table 4.10.

Table 4.10. Final Descriptive Statistics for Fluoride Concentration in Liquid Precipitation

Months	Valid cases	Min. (mg/L)	Max. (mg/L)	Mean (mg/L)	St. Error	St.dev. (mg/L)	Skewness	Kurtosis
June 92	12	0.005	0.060	0.030	0.006	0.021	0.327	- 1.462
July 92	20	0.005	1.320	0.362	0 088	0.394	1.170	0.304
Aug 92	19	0 005	1.350	0.417	0.091	0.395	1.101	- 0.090
Sep 92	9	0.060	1.210	0.296	0.123	0.368	1.592	1.284
Oct. 92	3	0.005	0.110	0.072	0.033	0.058	- 0.372	- 2.333
Nov. 92	12	0.005	0.500	0.065	0.042	0.145	2.200	3.688
Dec. 92	15	0.005	0.930	0.457	0.070	0.271	0.010	- 0.830
Jan. 93	17	0.020	0.580	0.298	0.038	0.157	0.103	- 0.900
Feb. 93	13	0.005	0.660	0.251	0.060	0.213	0.669	- 1.102
Mar. 93	12	0.120	1.610	0.742	0.158	0.546	0.278	- 1.807
Apr. 93	12	0.005	0.480	0.147	0.035	0.121	1.461	2.073
May 93	7	0.020	0.680	0.297	0.085	0.225	0.510	- 1.326

While the mean fluoride concentration generally fluctuates between 0.030 mg/L in June and 0.742 mg/L in March, it can be seen from Table 4.10 that the highest concentrations occur during the winter (December, January, February and March) and to a lesser extent during the summer (July and August), whereas the lowest concentrations take place during the fall (September, October and November) and the spring (April, May and June). The higher concentration encountered during the winter may be justified, in the sense that atmospheric fluoride pollutants, which can reach quite high concentrations, would condense in snow and be gathered in the sample collector. Indeed, particulates are more likely to be entrapped in snow particles, whereas they would simply be washed out with rainfall.

The general trend is better illustrated in Figure 4.13 displaying the minimum, mean and maximum values for each month.

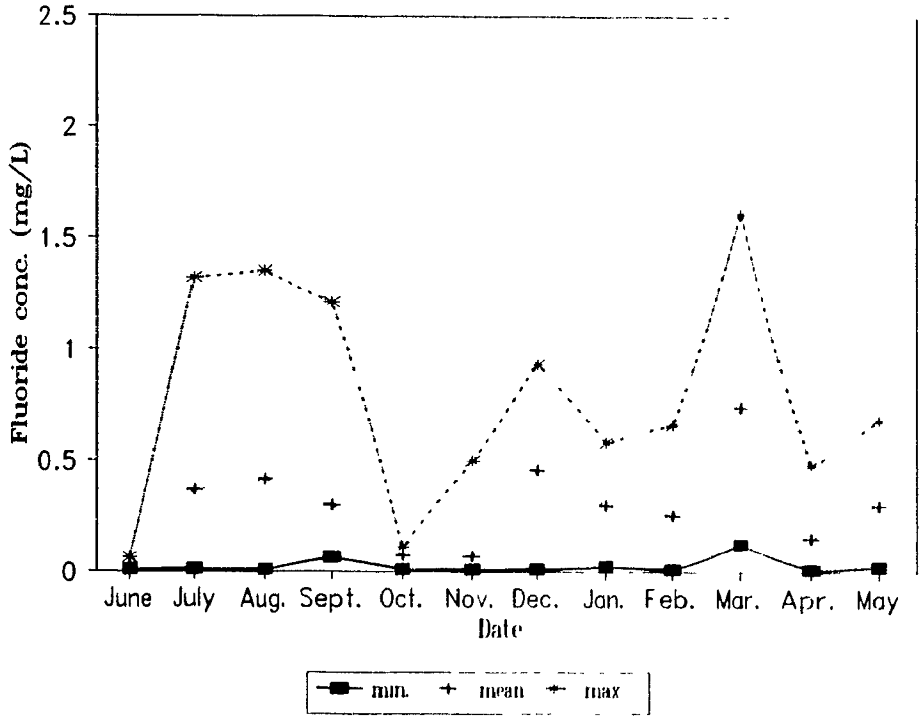

Figure 4.13. Monthly Variation (June 1992 to May 1993) in Liquid Precipitation of the Minimum, Mean and Maximum Fluoride Concentration.

Dry Precipitation

Final descriptive statistics for monthly fluoride concentrations in dry precipitation are presented in Table 4.11.

Table 4.11. Final Descriptive Statistics for Fluoride Concentration in Dry Precipitation.

Months	Valid cases	Min. (kg/km^2)	Max. (kg/km^2)	Mean (kg/km^2)	St. Error	St.dev. (kg/km^2)	Skewness	Kurtosis
June 92	12	0.015	0.185	0.096	0.019	0.067	- 0.026	- 1.760
July 92	6	0.278	0.894	0.524	0.090	0.220	0.528	- 1.338
Aug 92	6	0.308	1.603	0.694	0.193	0.473	1.040	- 0.611
Sep. 92	14	0.015	1.141	0.295	0.085	0.319	1.256	0.874
Oct 92	2	0.247	0.401	0.324	0.077	0.109	0.000	- 2.750
Nov 92	3	0.062	0.123	0.103	0.020	0.036	- 0.385	- 2.333
Dec. 92	9	0.956	2.344	1.453	0.135	0.406	0.959	- 0.111
Jan. 93	9	0.586	3.515	1.686	0.349	1.046	0.429	- 1.536
Feb. 93	7	0.894	2.344	1.300	0.180	0.478	1.374	0.353
Mar. 93	12	0.586	5.211	2.775	0.455	1.576	- 0.242	- 1.533
Apr. 93	6	0.278	1.110	0.668	0.130	0.320	- 0.081	- 1.745
May 93	10	0.015	1.357	0.609	0.140	0.442	0.018	- 1.400

While the mean specific mass generally fluctuates between 0.096 kg/km^2 in June and 2.775 kg/km^2 in March, it can be clearly seen from Table 4.11 that the highest concentrations occur during the winter (December, January, February and March) and to a lesser extent during the summer (July and August) and the spring (April, May), whereas the lowest concentrations take place during the fall (September, October and November). The especially low value in June does not, however, seem to continue the trend for the Spring. The general trend is better illustrated in Figure 4.14, displaying the minimum, mean and maximum values for each month.

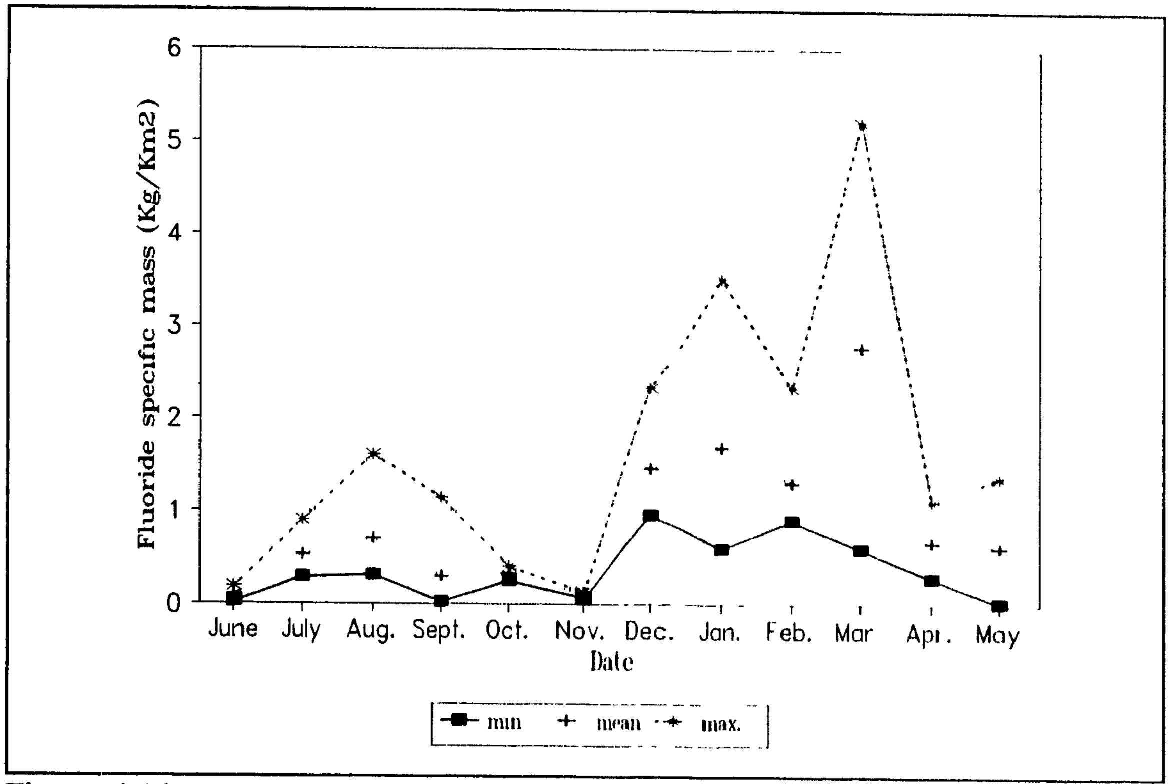

Figure 4.14. Monthly Variation (June 1992 to May 1993) of the Minimum, Mean and Maximum Fluoride Specific Mass in Dry Precipitation.

4.2.4. Parallelism Between Liquid and Dry Precipitation

While the fluoride in both the dry and liquid precipitation generally results from local anthropogenic sources, the fluoride in liquid precipitation may also be due to an enrichment at the air-sea interface. If a parallel variation were to be discerned between the fluoride contents in dry and liquid precipitation, this would suggest that fluoride in precipitation originates only from anthropogenic sources. However, if severe differences in trends were to be witnessed, this could only mean that fluoride also arises by cyclic evaporation of sea salts.

The monthly variations of fluoride levels in liquid and dry precipitation, shown separately in Figures 4.13 and 4.14, are presented, on an average basis, in Figure 4.15.

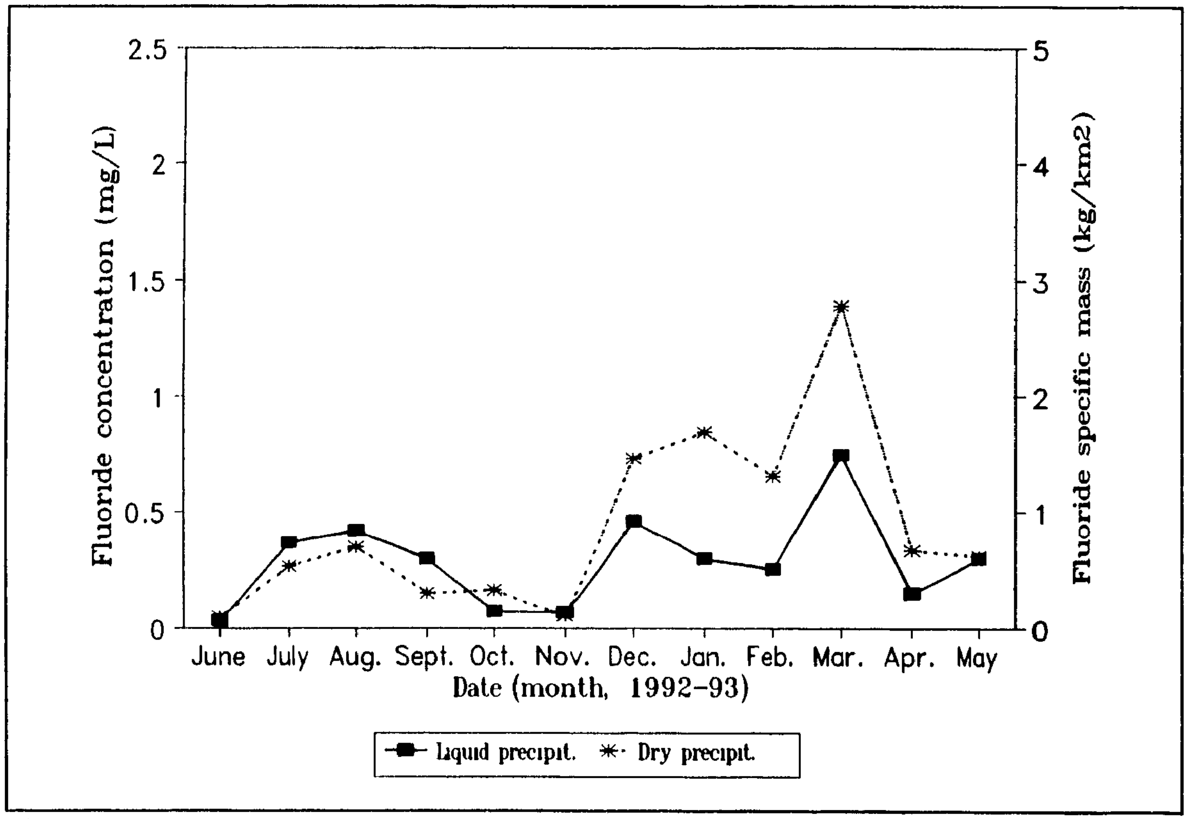

Figure 4.15. A Comparison between the Variations of Average Monthly Fluoride Levels in Liquid and Dry Precipitation.

Figure 4.15 highlights the parallel trends generally witnessed in the variation of the average fluoride contents between the liquid and dry precipitation. Indeed, both series start from a minimum during the spring, increase during the summer, decrease in the fall and reach their maximum during the winter. Although some discrepancies exist (such as in January and May, and to a lesser extent in October), it can generally be concluded, based on the parallelism in variational trends, that fluoride in precipitation results essentially from local anthropogenic sources. This is in accordance with a study conducted by Barnard and Nordstrom (1982b), in which it was established that the majority of fluoride in precipitation samples was derived from anthropogenic sources, suggesting (and confirming by mass balance calculations) that no preferential enrichment at the air-sea interface took place. On the other hand, a study conducted by Carpenter (1969) revealed that a major part of the fluoride in liquid precipitation comes from the air-sea interface. This latter conclusion was confirmed by Mahadevan *et al.* (1986), who showed that, in India, there was definite contribution of natural fluoride through the cycling of sea salt.

Another interesting point emerges from Figure 4.15. Because of the parallelism in the fluoride variation between the liquid and dry precipitation, it can be suspected that the high concentration of fluoride in liquid precipitation may in fact result from the fluoride content in dry fallout rather than from a true fluoride concentration in rainfall. This is suspected to be the case because, as mentioned in Section 4.2.1, "liquid precipitation" corresponds to those days during which actual rainfall or snowfall was recorded, and hence includes, in addition to the actual precipitation, the dry fallout that was deposited, on this rainy or snowy day, during periods when rain or snow where not actually falling. In this context, the studies conducted by Bewers (1972), Barnard and Nordstrom (1982b) and Mahadevan *et al.* (1986) have shown that the background fluoride concentrations in liquid precipitation are generally in the order of 2-20 μg/L, with a mean around 5.8 μg/L. It has also been stated by Barnard and Nordstrom (1982b) that dry precipitation generally has higher fluoride concentrations than wet precipitation, and the inclusion of the dry fallout in liquid precipitation would most probably result in an increase of the fluoride concentration in the liquid component. Based on these studies, it might be suggested that the true fluoride concentrations in liquid precipitation alone are lower than those concentrations reported previously. However, in the absence of other information and more conclusive evidence, the fluoride concentrations in liquid precipitation will not be altered to account for the probable increase resulting from the inclusion of dry fallout

4.2.5. Possibie Correlation Between Chloride and Fluoride in Precipitation

The possible correlation between chloride and fluoride was investigated after careful consideration for outliers, as presented in Section 4.2.2. The correlation coefficient (R^2), based on a linear correlation between the two variables, was 0.30. This shows that no linear association between chloride and fluoride can be established. This result was expected since chloride is very unlikely to be present in precipitation, whereas fluoride peaks have been recorded

4.3. GROUNDWATER CHARACTERISTICS

4.3.1. General

As mentioned previously (Section 3.2.3), groundwater samples were generally collected by means of a bailer, except when the well diameter was too small to fit the bailer, in which case a pump was used. For all the wells, samples were drawn before and after purging. In addition to these, two other samples were taken in the case of the well at Faubourg Quebec. The results of the groundwater analyses are presented in Table 4.12.

Table 4.12 indicates that the initial sample of the stagnant water taken at Faubourg Québec was reddish and very turbid. This was expected, since contamination with iron was suspected (as explained in Section 3.2.3). As for the sample taken from that same well after the storm shower, the water was dark in colour and very turbid, suggesting that a quick recharge of the aquifer had taken place with a corresponding higher content of silty materials.

Table 4.12. Fluoride Concentrations in the Groundwater

Site Specifications		Fluoride conc. (mg/L)		Chloride conc. (mg/L)	Remarks
		w CDTA	w/o CDTA		
Faubourg Quebec	Stagnant water (Mixed sample) (20/7/93)	0.21	0.21	340.0	Reddish sample Very high turbidity
	Stagnant water (Supernatant) (20/7/93)	0.22	0.18	353.18	Yellowish High turbidity
	After a storm (30/7/93)	0.21	0.15	303.84	Dark colour Very high turbidity
	Before purging (31/7/93)	0.24	0.24	317.69	Clear
	After purging (1/8/93)	0.24	0.24	306.33	Clear
Falaises St-Jacques (#6)	Before purging	0.10	0.07	356.22	Yellowish Not clear
	After purging	0.09	0.07	161.79	Dark colour Not clear
Falaises St-Jacques (#6A)	After purging	0.02	0.00	800.00	Yellowish Many air bubbles

Concerning well #6A at Falaises St-Jacques, it is suspected to be unrepresentative of the aquifer characteristics, because (1) it is very shallow, extending only to a depth of 1 m, and (2) results obtained at well #6A were quite different from those of well #6 located at less than 1 m away. Table 4.12 shows that samples drawn from well #6A were characterized by a significant presence of air bubbles, and showed a zero fluoride concentration and a very high chloride concentration. Based on these observations and on the fact that no drastic change of strata was evidenced at that location, the results obtained for well #6A would not be given much importance.

4.3.2. Effect of the Decomplexing Agent

It can be seen, from Table 4.12, that in the case of clear samples, the addition of the decomplexing agent (CDTA) had no effect on the fluoride activity in the waters. However, in the case of high turbidity and coloured samples, the effect of CDTA addition was clear as it lead to a higher concentration of fluoride in solution, resulting from the release of complexed fluoride ions. Fluoride complexes may essentially have been formed in the presence of significant concentrations of aluminum, iron or organic matter. The latter can be associated with higher turbidity, as was the case for the samples herein.

It is interesting to note that the greatest effect was observed for the sample taken after the heavy storm. The corresponding increase in fluoride concentration after the addition of CDTA was 40%, which is highly significant. This may implicate a higher concentration of silty organic material, due to the quick recharge of the aquifer. Another significant increase (22%) was observed for the supernatant from the stagnant water. When comparing it to the mixed sample, where the CDTA had no effect, this suggests that most of the interfering ions are still present in suspension and did not settle out from the supernatant.

It can therefore be concluded that, in the case of the groundwater, the addition of CDTA was essential to ensure the release of free fluoride ions. However, this does not hold for MUC wastewaters, since it was shown by Gehr et al. (1989) that the decomplexing agent had no effect on the fluoride activity in the wastewaters, and that all fluoride was present in the free ionic form. Consequently, analyses performed on MUC wastewaters did not warrant the addition of CDTA.

4.3.3. Effect of Purging

When comparing fluoride concentrations in samples taken before and after purging the wells (Table 4.12), no significant difference could be noted. Since this practice was undertaken to make sure that these samples were truly representative of the groundwater quality, without any stagnant water effects or external interferences, two possible conclusions may be drawn: (1) no external interference occurs, and the waters present in the wells are effectively representative of the groundwater, or (2) any external input to the wells, whether by infiltration, run-off, recharge by precipitation, or simply rusted piping polluting the stagnant water, does not contribute to the presence of fluoride in these waters. This latter conclusion is supported by the following facts: (1) infiltration is assumed not to contribute significantly, essentially because of the absence of nearby agricultural lands where irrigation would be done with fluoridated waters, (2) except for a few highly concentrated precipitation samples, the fluoride concentration in precipitations was generally found to be low; and (3) the piping was plastic coated, and no rusting would have occurred.

4.3.4. Estimation of Fluoride Concentrations in the Groundwater

Taking into consideration the above-mentioned conclusions, and neglecting results obtained for well #6A as discussed earlier, it can be seen from Table 4.12 that fluoride concentrations in the groundwater range between 0.07 and 0.24 mg/L. These results are in accordance with those obtained by Goulet and Frigon (1980), who report an overall average fluoride concentration for the Province of Québec of 0.133 mg/L, with the following geographical distributions: an average fluoride concentration of 0.414 mg/L for the Low-lands, 0.187 mg/L for the Laurentian area, and 0.066 mg/L for the Appalaches region. Similar concentrations were reported by Lalonde (1976) and Simard and Desrosiers (1979).

Consequently, during the course of this study, the average fluoride value of 0.13 mg/L, which is also the average fluoride concentration in the St-Lawrence river, will be adopted as that representative of the groundwater quality.

4.4. MELTING SALTS CHARACTERISTICS

Because they were suspected to contribute to fluoride concentrations in MUC wastewaters (Gehr *et al.*, 1989), the melting salts used by the City of Montréal were analyzed, at various concentrations. Fluoride and chloride concentrations, in addition to the pH, were analyzed in order to determine the fluoride content of these salts, and to try to obtain any possible correlation between the two ions. The results of the analyses for 50, 100, 500 and 1,000 mg/L of salt are shown in Table 4.13.

Contrary to what was suspected, results presented in Table 4.13 show that the fluoride concentration of the melting salts used by the City of Montréal is zero. On the other hand, the chloride concentration increases proportionally to increasing salt concentrations, as expected. The linear relationship (R_2 = 0.998) between chloride concentrations and melting salts concentrations is illustrated in Figure 4.16. The pH, with an average of 6.20, is not affected by increasing salt concentrations.

The absence of correlation between fluoride and chloride concentrations in the melting salts makes it difficult to use the trend in chloride variations in order to estimate the input of fluoride due to precipitation, essentially during the winter season, when these salts are used. If a parallel trend were observed similarly for both fluoride and chloride concentrations, it would have been a determining factor in distinguishing between the fluoride input by precipitation and that by industrial discharges, during the winter season. However, in the absence of such a correlated trend, no definite conclusions can be drawn, and mass balances will be used to assess the various sources of fluoride.

Table 4.13. Results of Analyses Performed on the Melting Salts Used by the City of Montréal.

Salt concentration (mg/L)	Fluoride conc. (mg/L)	Chloride conc. (mg/L)	pH
50	0.00	38.85	6.22
100	0.00	55.16	6.14
500	0.00	288.50	6.16
1000	0.00	614.72	6.36

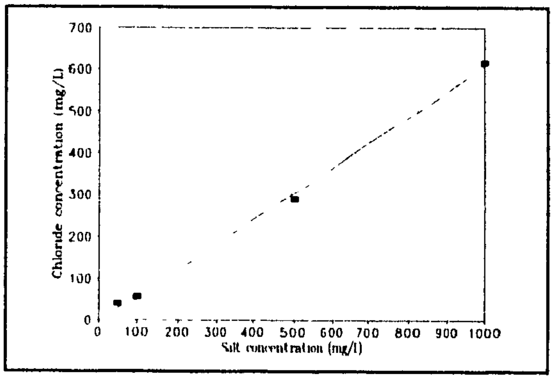

Figure 4.16. Variation of Chloride Concentrations with Melting Salts Concentrations.

4.5. FLUORIDE MASS BALANCE: ESTIMATION OF FLUORIDE RESULTING FROM UNIDENTIFIED SOURCES

4.5.1. General Description of the MUC Wastewater Treatment Plant

Since 1984, when it was first commissioned, the MUC wastewater treatment plant services all the municipalities of the Montréal Urban Community. Wastewater is channelled to the treatment plant by a series of sewers and interceptors. Except for the municipalities of the West Island and possibly certain basins of Rivière des Prairies and Pointe-aux-Trembles which have separate sewers, all other municipalities on the Island of Montréal have a combined sewer system. In addition to channelling municipal wastewaters and precipitation, the combined sewer network is subject to infiltration and stormwater inputs. Infiltration, which is defined as the groundwater that reaches the sewer system through damaged conduits, fissured joints or fractured manholes, causes a dilution of the water in the sewers.

4.5.2. Formulation of the Fluoride Mass Balance at the Inlet to the MUC Wastewater Treatment Plant

When establishing the fluoride mass balance at the inlet to the MUC wastewater treatment plant, the following sources of fluoride input should be considered:

* the fluoride content of precipitation,
* the fluoride content in infiltration,
* the natural fluoride content of the potable water,
* the artificial fluoride content of fluoridated waters incoming from those municipalities which resort to fluoridation,
* the fluoride input resulting from the domestic habits of the population (e.g., food and fluoride-containing dental products)
* the fluoride resulting from unidentified sources. The latter includes the fluoride resulting from "accidental" industrial discharges, as well as, though to a lesser extent, that resulting from the dry fallout dissolved into runoff.

These various sources are graphically illustrated in Figure 4.17.

Combining these sources results in the following mass balance for fluoride at the inlet to the MUC wastewater treatment plant:

$$QC = Q_pC_p + Q_iC_i + Q_{nf}C_{nf} + Q_fC_f + Q_dC_d + S \qquad (4.1)$$

where the different terms can be identified as follows:

Q is the average flowrate at the inlet to the MUC wastewater treatment plant (m^3/s)

C is the mean fluoride concentration measured at the inlet to the station (mg/L)

Q_f is the flowrate of the fluoridated water which is returned to the sewer network (m^3/s)

C_f is the average fluoride concentration in the fluoridated potable water which is returned to the sewer (mg/L)

Q_{nf} is the flowrate of the non-fluoridated water which is returned to the sewer network (m^3/s)

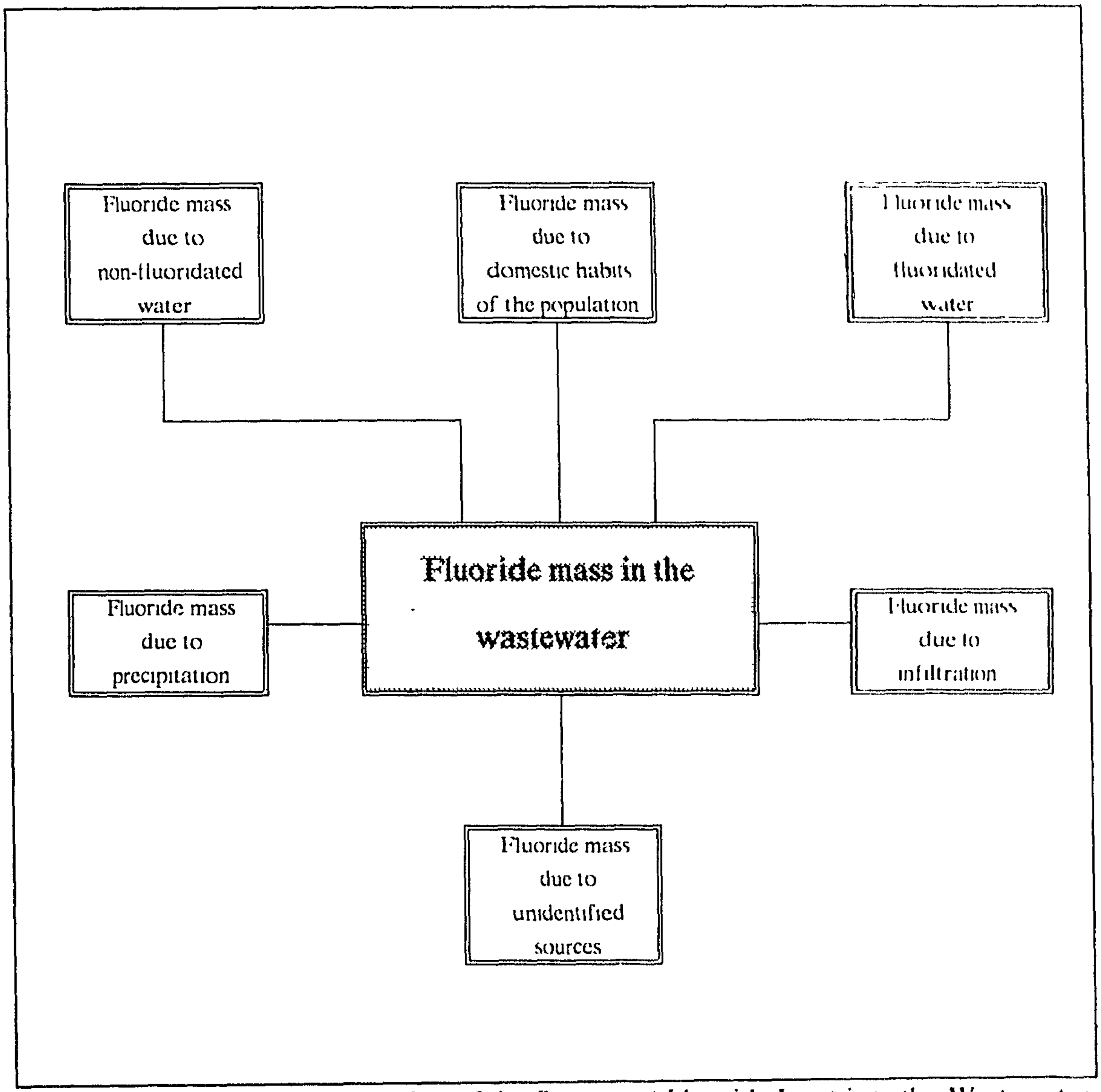

Figure 4.17. Graphical Illustration of the Sources of Fluoride Input into the Wastewater.

C_{nf} is the average fluoride concentration in the non-fluoridated potable water which is returned to the sewer network (mg/L)

Q_p is the average rate of fluoride precipitation (m^3/s)

C_p is the average fluoride concentration in precipitation (mg/L)

Q_i is the average flowrate of infiltration waters (m^3/s)

C_i is the average fluoride concentration in infiltration (mg/L)

Q_d is the average flowrate of the domestic sewage, i.e. $Q_f + Q_{nf}$, (m^3/s)

C_d is the increase in fluoride concentration resulting from the domestic habits of the population (mg/L)

S is the average fluoride flux resulting from unidentified sources.

Rearranging Equation 4.1 allows the determination of the fluoride mass resulting from unidentified sources:

$$S = QC - (Q_pC_p + Q_iC_i + Q_{nf}C_{nf} + Q_fC_f + Q_dC_d) \qquad (4.2)$$

It should be noted that Equations 4.1 and 4.2 are comparable to the mass balance equations established by Gehr and Leduc (1992), except for the components related to the precipitation and the domestic habits of the population. In fact, the precipitation contribution was not accounted for by Gehr and Leduc (1992), since their study was mainly undertaken during dry weather periods. Based on their recommendations however, the present study was intended to cover all the seasons, thus taking into account the contribution of the precipitation. As for the fluoride input from the domestic habits of the population, it was considered, in the study conducted by Gehr and Leduc (1992) as part of the unidentified sources. Considering the contribution of the domestic habits as a separate component, as is done in the present study, yields a better estimation of the truly unidentified sources.

4.5.3. Evaluation of the Mass Balance Components

Fluoride Mass in the Wastewater

(i) Determination of the fluoride concentration in the raw wastewater (C)

As mentioned in Section 3.2.1, the fluoride concentration in wastewater was measured daily for all 24 composite samples corresponding to the 24 hours of sampling in each day.

* Replacing missing hourly data within a day:

Where one or more hourly samples were missing within the course of the day due to the clogging of the automatic sampler or a break in the current at the treatment plant, the missing value was replaced by the average of the two adjacent samples. When several consequent samples were missing, the same principle was followed, and the missing values were replaced by the moving average of the two closest values. This procedure for replacing the missing data by the average of the adjacent fluoride values was considered to give the best picture of the fluoride variation. An alternative method of replacing the missing data by the mean for the day was investigated, but it was considered to dampen the effect of fluoride variation, thus giving an underestimated fluoride concentration, especially in the case of large peaks. Hence, replacing the missing data by the average of the two adjacent points was preferred for the purposes of this research and therefore adopted herein. In total, for the duration of the project from June 1992 to May 1993, during those days where sampling actually took place, only 5% of the hourly data were missing and were replaced according to the method discussed above. These missing hourly data do not include those days during which sampling was interrupted. Such missing daily data will be addressed in the following paragraph.

* Replacing missing daily data within a month:

In addition to few hourly missing data, several daily data are unavailable. As discussed in Section 3.2.1, the continuous sampling and analysis of the 24 daily samples were interrupted for a few days in September and November 1992, and for longer periods in October and December 1992, as well as in January and April 1993. Due to these large gaps (extending for as many as 14 consecutive days), it becomes practically impossible to predict the variation in daily fluoride concentration based on adjacent values. Hence, replacing missing values based on adjacent data points would involve a great many uncertainties and hence induce large errors.

Accordingly, the analysis will be undertaken on an average monthly basis, based on the available number of samples. It is clear that this procedure, which is equivalent to replacing the missing data by the monthly average, will also involve several uncertainties however less acute than those induced when trying to predict missing data based on adjacent values.

It should also be pointed out that, in addition to those daily interruptions, the analysis was discontinued entirely during February and March 1993. Consequently, those two months will be disregarded in the yearly mass balance.

All daily fluoride concentrations obtained from the analysis of wastewater samples are shown in Appendix B.

(ii) Determination of the wastewater flow (Q)

In the absence of hourly flow data, which can only be available from the MUC wastewater treatment plant in the year following actual recording, mean daily flow data were used (Purenne, 1993). These were obtained from the daily operation records of the MUC wastewater treatment plant. The total flow at the station resulting from both the North and South interceptors was used for the fluoride mass balance calculations. These daily values are presented in Table C.1 (Appendix C) and the monthly average shown in Table 4.14.

Table 4.14. Average Monthly Flow of Raw Wastewater from June 1992 to May 1993

Month	Raw wastewater flow (m^3/s)
June 1992	13.6
July 1992	16.5
Aug. 1992	15.3
Sep. 1992	15.7
Oct. 1992	17.1
Nov. 1992	19.4
Dec. 1992	15.2
Jan. 1993	18.6
Feb. 1993	17.1$^{(1)}$
Mar. 1993	19.9$^{(1)}$
Apr. 1993	29.7
May 1993	17.6

(1) Not used in the current study

It can be seen, from Table 4.14, that the flow reaches a very high value during April, 1993 (29.7 m^3/s). Although higher flows are indeed expected during spring because of snow melting, this value seems especially high as compared to the average flow registered at the MUC wastewater treatment plant in April 1992 (19.38 m^3/s). The maximum flow in that year was registered in March 1992 (20.20 m^3/s) due to earlier snow melting (Purenne, 1993). This comparison is intended to highlight the fact that flow trends may vary from one year to another depending primarily on the atmospheric conditions, since the domestic and industrial inputs, though increasing with population and industrial expansion, do not differ markedly. As far as the mass balance analysis is concerned, the high flow in April is expected to cause the corresponding fluoride mass to increase markedly. This effect will be seen in the following subsection.

(iii) Determination of fluoride mass in the wastewater (QC)

The daily fluoride mass was determined based on daily flow data and hourly fluoride concentrations. It is apparent that this combination will have a dampening effect, especially when high flows are associated with high fluoride concentrations. However, in the absence of more accurate flow data, this practice was considered to give a reasonable estimation of the mass of fluoride returned to the sewers. The detailed values of the daily fluoride mass in the wastewater are shown in Table D.1 (Appendix D), and the monthly mean values resulting from the daily analysis are shown in Table 4.15.

It is important to mention that the mass of fluoride in the wastewater was determined as a monthly average, based on the available data. For example, as reported in Table 4.15, 19.9 metric tonnes of fluoride were contained in the raw sewage during the month of October This value is determined as the average of the fluoride masses actually obtained during the 8 days of sampling, scaled up to an equivalent of 30 days.

It can be seen in Table 4.15 following that the fluoride mass in raw wastewater is lowest during May and June and highest during December and January. Thus, in general, the mass of fluoride in the raw wastewater is highest during winter and lowest during spring. This is true even if one considers the relatively high fluoride mass in April which is only due to the exceptionally high flow that occurred during that month.

Table 4.15. Fluoride Mass in the Raw Wastewater from June 1992 to May 1993

Month	Fluoride mass in raw wastewater (metric tonnes)	Days	
		Total	Available
June 1992	6.6	30	25
July 1992	33.7	31	26
Aug. 1992	28.9	31	25
Sep. 1992	20.1	30	24
Oct. 1992	19.9	31	8
Nov. 1992	27.9	30	17
Dec. 1992	43.9	31	4
Jan. 1993	41.6	31	15
Feb. 1993	(1)	28	
Mar. 1993	(1)	31	
Apr. 1993	13.7	30	18
May 1993	3.58	31	24

(1) Not included in the current study

Fluoride Mass Due to Precipitation

(i) Determination of the fluoride concentration in precipitation (C_p)

As mentioned in Section 3.2.2, the fluoride concentration in precipitation was obtained daily from one sample collected at the MUC wastewater treatment plant. Precipitation was separated into dry (dry deposits) and liquid (snow and rain) precipitation. Although dry deposits will be ultimately deposited on the ground and may find their way to the sewers through runoff and infiltration, their contribution will not be addressed within the scope of this research, and they will be considered as part of the non-identified sources. Consequently, only liquid precipitation will be considered to contribute to the fluoride mass that reaches the sewer system as a result of precipitation.

* Replacing missing data points

In the case of precipitation data, there were only a few missing data points, for days during which problems with the collection of the sample were encountered. In addition, sample collection was interrupted during the first two weeks in October and April. In all cases, the missing data were replaced by the average of the corresponding month.

The analysis of the precipitation data were presented and discussed in Section 4.2.3. Based on Table 4.6 (after the removal of outliers), the average monthly fluoride concentrations in precipitation were determined and are shown in Table 4.16.

Table 4.16. Average Monthly Fluoride Concentration in Liquid Precipitation.

Month	Fluoride concentration in precipitation (mg/L)	Days	
		Total	Available
June 1992	0.03	16	12
July 1992	0.36	20	20
Aug. 1992	0.42	21	19
Sep. 1992	0.30	11	9
Oct. 1992	0.07	16	3
Nov. 1992	0.06	20	12
Dec. 1992	0.46	19	15
Jan. 1993	0.30	20	17
Feb. 1993	0.25(1)	19	13
Mar. 1993	0.74(1)	19	12
Apr. 1993	0.15	19	12
May 1993	0.30	16	7

(1) Not used in the current study.

(ii) Determination of the precipitation flow rates (Q_p)

The volumes of precipitation (mm) were obtained from all the sampling stations located in the Montréal Urban Community, namely Dorval, St-Anne de Bellevue, McTavish (McGill), Ste Geneviève, Rivière des Prairies, and Montréal Lafontaine. These are shown in Appendix C.

Generally, determining the total volume and flow of precipitation over a given area involves the separation of that area into various watersheds, with the precipitation contribution being obtained for each of these hydrologic basins based on their respective areas and topography, as well as their coefficients of infiltration and permeability. However, this approach, which constitutes a study by itself, was deemed too involved for the purpose of the current research, and another alternative was investigated. It was then thought that a rough approximation of the whole Island as one hydrologic basin (the total area is given in Table 4.17) would give a reasonable estimate of the average flow of precipitation.

Table 4.17. Total Area Drained by the MUC Sewer Network (Dao Dank, 1993).

North End	245.46 km^2
South-West End	57.17 km^2
South-East End	192.13 km^2

Moreover, it was suggested by Dao Dank (1993) that only 60% of the volume of precipitation is expected to contribute to the sewer system, whereas the remaining part will be lost to evaporation, soil infiltration and direct runoff. It is essential to note that this percentage of interception is an estimate for the whole Island of Montréal and was used in the absence of more precise information. In fact, since the permeability coefficient depends primarily on the soil characteristics, this percentage varies notably from one location to another, increasing in heavily urbanized areas such as downtown Montréal and decreasing in agricultural and less densely populated areas, such as the Northern part of the Island.

Hence, assuming that precipitation is uniformly distributed over the whole area of the Montréal Urban Community (Table 4.17), and considering a 60% percentage of interception, the estimated precipitation flows were calculated accordingly and are presented in Table 4.18.

It is clear, from the highlighted figures in Table 4.18 following that the estimated precipitation flows do not represent the actual situation. The presence of these extremely high precipitation flows (several-fold the wastewater flow) suggests that this approach, based on the assumption that the precipitation is uniformly distributed over the whole area of the MUC should not be undertaken. As a matter of fact, it was observed from the precipitation volume data (shown in Appendix C) that several storms have taken place at localized areas. Consequently, it could no longer be assumed that precipitation would contribute equally to the whole area and the corresponding volume of precipitation could not be simply obtained by multiplying the average volume obtained from all stations by the area of the Island that is drained by the sewer system.

As a conclusion, it can be noted that the determination of the precipitation flow intercepted by the sewer requires very involved considerations, the combination of which cannot be addressed and evaluated in the current study. These include wind speed and direction, intensity and duration of storm, topography of the area and direction of slopes, percentage of interception, importance of direct runoff, etc.

Table 4.18. Estimated Precipitation Flow (m^3/s) (based on the assumption of the uniformity of distribution and 60% interception).

	June	July	Aug.	Sep.	Oct.	Nov.	Dec.	Jan	Feb	Mar	Apr	May
1	4.0		9.3				3.4	4.3	1.7		**89.7**	
2	0.7		1.6			**44.1**	3.1			1.4	13.8	
3		**87.3**	20.0	**140.8**		**43.0**	2.6	5.2			4.0	
4		23.2	**86.2**	1.6	1.0	13.8	0.7	**116.1**	0.7		3.7	
5	**58.4**	14.6	3.1			14.2		62.7	7.4	10.9		16.5
6	14.6	4.0				1.6	3.1	4.8		0.7		**83.1**
7	25.2	9.6	13.8		0.7		3.6		4.8	8.8		
8		**52.1**	24.1	**92.6**	0.7			7.4	4.8	5.8		
9		23.0	**35.1**		**109.7**					9.7	5.5	
10		5.6	4.1	22.3	23.7	23.2			1.4	11.7	**45.0**	
11		1.7	1.4		7.7	17.2				13.8	5.5	
12	21.7	**73.4**			11.1	**35.9**			22.7	2.4	8.6	7.0
13	5.5	12.2	1.0			7.7		**37.6**	**80.3**	**70.6**	4.1	4.0
14		3.9				1.9		3.6	4.1	24.3		
15						7.4		5.5				14.6
16		2.8	3.1	6.2	**53.0**	3.4	2.8	1.4	**32.9**	4.9	29.1	2.6
17		**89.4**	1.4	4.1		2.5	12.6	4.1	10.4	5.0	**36.4**	
18		26.9	4.9	7.2			5.0			7.2		
19	**78.6**	13.8	0.7		10.3		10.8		1.4	5.8	15.8	11.1
20	4.1				5.5	5.5	12.8	4.5	5.5	6.2	**32.1**	11.2
21	1.2			**35.8**	8.0	13.1			16.4	19.5	**51.4**	14.2
22	0.7			**48.0**	3.1	15.0	2.8	**39.1**	17.2	11.3	**71.0**	
23					17.2	**33.4**	5.7	3.9	4.8		**35.8**	
24	9.6	0.7			20.9	9.7	6.9	27.7	2.2		0.7	**63.8**
25	5.5				5.5	9.6	4.7	2.4	3.1		**43.5**	4.4
26		14.4	12.7	13.4	4.1	**33.3**	2.1		4.1		4.1	2.4
27		2.1	18.4	13.3				4.8				1.4
28	1.4		21.3					11.7				0.7
29	29.3		27.5				7.4	17.0		4.5		4.6
30	9.6		16.0				1.7	9.6				
31		**97.6**	5.5				6.7	**38.3**				**60.4**

Hence, as a result of the large number of unknowns that are involved and assumptions that need to be taken into account, as well as the errors induced thereby, it was preferred to consider the flow due to precipitation as the difference between total and dry weather flows. The latter could only be obtained on a monthly basis for the year 1992 (Purenne, 1993). As for the period between January and May 1993, dry weather flows were estimated based on a comparison with the results of the previous year obtained from the

MUC wastewater treatment plant (Purenne, 1993) and on the rainfall and snow data for the current year obtained from Environment Canada and the Ministry of the Environment of Quebec (Gauthier and Mercier, 1993). These dry weather flows are presented in Table 4.19.

Table 4.19. Average Monthly Dry Weather Flow from June 1992 to May 1993.

Month	Dry Weather Flow (m^3/s)
June 1992	12.8
July 1992	14.9
Aug. 1992	14.1
Sep. 1992	14.6
Oct. 1992	16.3
Nov. 1992	17.1
Dec. 1992	15.2
Jan. 1993	16.5
Feb. 1993	17.0(1)
Mar. 1993	19.8(1)
Apr. 1993	23.0(2)
May 1993	15.5(2)

(1) Not used in the current study.
(2) Estimated based on total flow (MUC, 1992) and precipitation data (Gauthier and Mercier, 1993).

Because dry weather flow includes snow melting (Purenne, 1993), the high estimated flow in April seems reasonable and in accordance with the fact that snow melting occurred during that month in 1993. Table C.1 (Appendix C) shows the high total flows corresponding to April 1993.

Since the analysis pertaining to precipitation flow requires dry weather flow data which can only be obtained on a monthly basis, it will be performed as a monthly average. The monthly average precipitation flows are shown in Table 4.20.

Table 4.20. Average Monthly Flow of Liquid Precipitation from June 1992 to May 1993.

Month	Precipitation Flow (m^3/s)
June 1992	0.8
July 1992	1.6
Aug. 1992	1.2
Sep. 1992	1.1
Oct. 1992	0.8
Nov. 1992	1.3
Dec. 1992	0.0
Jan. 1993	2.1
Feb. 1993	0.1(1)
Mar. 1993	0.1(1)
Apr. 1993	6.7(2)
May 1993	2.1(2)

(1) Not used in the current study.
(2) Based on estimated values of dry weather flow

As seen in Table 4.20, the flow of precipitation in December, as obtained from the difference between total and actual dry weather flows is zero. This is in accordance with the precipitation data obtained from Environment Canada and the Ministry of the Environment of Quebec (Gauthier and Mercier, 1993) which show that almost no precipitation took place during that month. As for the greatest precipitation flow, it occurred during April. This value, obtained from the difference between total and estimated dry weather flows, is also in accordance with available precipitation information which shows that April 1993 is the month, between June 1992 and May 1993, during which precipitation (both in the forms of rainfall and snow) was highest.

(iii) Determination of the fluoride mass resulting from liquid precipitation (Q_pC_p)

The fluoride mass flow to the sewer resulting from liquid precipitation was determined based on the fluoride concentration in liquid precipitation and the volume of precipitation obtained in the two previous subsections. The results are presented in Table 4.21.

Table 4.21. Mass of Fluoride Resulting from Liquid Precipitation, between June 1992 and May 1993.

Month	Fluoride mass in precipitation (metric tonnes)	Days	
		Total	Available
June 1992	0.06	16	12
July 1992	1.56	20	20
Aug. 1992	1.34	21	19
Sep. 1992	0.84	11	9
Oct. 1992	0.15	16	3
Nov. 1992	0.22	20	12
Dec. 1992	0.00	19	15
Jan. 1993	1.68	20	17
Feb. 1993	0.06(1)	19	13
Mar. 1993	0.20(1)	19	12
Apr. 1993	2.55(2)	19	12
May 1993	1.67(2)	16	7

(1) Not included in the current study.
(2) Based on estimated values of dry weather flow.

It can be seen from Table 4.21 that the greatest mass of fluoride resulting from precipitation occurs during August 1992 and April 1993, as well as, though to a slightly lesser extent, during July 1992, January and May 1993. In August 1992, as well as in January and May 1993, the high value of the fluoride mass is due to the combination of high precipitation flowrates (Table 4.20) and relatively high fluoride concentration in the precipitation (Table 4.16). In April 1993 however, the increase in the fluoride mass is solely due to the high flowrate (Table 4.20). Indeed, the fluoride concentration in precipitation was found to be low during that month (Table 4 16).

Fluoride Mass Resulting from Infiltration

(i) <u>Determination of the fluoride concentration in infiltration water</u> (C_i)

As discussed in Section 4.5.1, the combined sewer network is subject to infiltration, defined as the groundwater that reaches the sewer through fractured conduits, fissured joints and fractured manholes. Accordingly, the fluoride concentration in infiltration waters is considered to be that of the groundwater. This has been determined, in Section 3.4, to be 0.13 mg/L. It should be pointed that this value is close to, however not the same as, the one used by Gehr and Leduc (1992). Due to the lack of measured data during their study, they estimated the concentration of fluoride in infiltration waters to be 0.16 mg/L, based on the 50th percentile given in Stumm and Morgan (1981).

(ii) <u>Determination of the flow of infiltration water</u> (Q_i)

It is suggested by Gehr et al. (1989) that the contribution of infiltration varies between 56% and 44% of the dry weather flow, depending respectively on whether the South interceptor is in operation or not. While 44% of the dry weather flow was chosen to represent the contribution of infiltration in the study conducted in 1989, it is now important to realize that the contribution of the South interceptor has to be taken into consideration, hence the use of 56% of the dry weather flow as the infiltration flow. When checking the source of this information, it was pointed out by Dao Dank (1993) that these figures are the result of a study conducted in 1982, when the system was in the early stages of operation. Since no subsequent sampling campaign has been undertaken, these figures had to be used as a reference. It is however clear that they do not accurately represent the present situation and must be altered to account for the probable deterioration of the various installations in the sewer system, essentially the pipes, conduits and manholes. Consequently, taking into account that both the South and North interceptors are in operation, which is most often the case nowadays, it will be considered that, as an annual average, 60% (as opposed to the original 56% considered in 1989) of the dry weather flow will be in the form of infiltration. All monthly values for the flow of infiltration are presented in Table 4.22.

Table 4.22. Average Monthly Flow of Infiltration between June 1992 and May 1993.

Month	Infiltration flow (m^3/s)
June 1992	7.68
July 1992	8.94
Aug. 1992	8.46
Sep. 1992	8.76
Oct. 1992	9.78
Nov. 1992	10.86
Dec. 1992	9.12
Jan. 1993	9.90
Feb. 1993	10.20(1)
Mar. 1993	11.90(1)
Apr. 1993	13.80(2)
May 1993	9.30(2)

(1) Not used in the current study.
(2) Based on estimated values of dry weather flow.

As seen from Table 4.22, the flow of infiltration is rather constant, except for a slight decrease during the summer season. As for the high value in April, it is again explained by the correspondingly high dry weather flow.

(iii) Determination of the fluoride mass resulting from infiltration (Q_iC_i)

The monthly average fluoride mass flow to the sewer as a result of infiltration was calculated, based on the fluoride concentration in infiltration and the flow of infiltration water obtained in the two preceding subsections. These results are shown in Table 4.23.

Table 4.23. Average Monthly Mass of Fluoride Resulting from Infiltration, between June 1992 and May 1993.

Month	Fluoride mass due to infiltration (metric tonnes)
June 1992	2.59
July 1992	3.11
Aug. 1992	2.94
Sep. 1992	2.95
Oct. 1992	3.40
Nov. 1992	3.66
Dec. 1992	3.18
Jan. 1993	3.45
Feb. 1993	3.21(1)
Mar. 1993	4.14(1)
Apr. 1993	4.65(2)
May 1993	3.24(2)

(1) Not used in the current study
(2) Based on estimated values of dry weather flow.

As expected from the relatively constant values of the infiltration flow (Table 4.22) and the constant value of the fluoride concentration in infiltration water, the mass of fluoride resulting from infiltration is generally constant, with a slight increase in April, as anticipated from the previous discussions.

Fluoride Mass Due to Non-Fluoridated Water

(i) Determination of the fluoride concentration in non-fluoridated waters (C_{nf})

Although it is generally estimated that the average fluoride concentration in non-fluoridated water is 0.13 mg/L (Gehr *et al.*, 1989), the exact fluoride concentrations measured at the water treatment plants are presented, on an average monthly basis, in Table 4.24.

Table 4.24. Average Monthly Fluoride Concentrations in Non-Fluoridated Water between June 1992 and May 1993 (Dusault, 1993).

Month	Fluoride concentration in non-fluoridated water (mg/L)
June 1992	0.26
July 1992	0.20
Aug. 1992	0.25
Sep. 1992	0.21
Oct. 1992	0.24
Nov. 1992	0.16
Dec. 1992	0.18
Jan. 1993	0.19
Feb. 1993	0.20(1)
Mar. 1993	0.17(1)
Apr. 1993	0.13
May 1993	0.19

(1) Not included in the current study.

The values shown in Table 4.24 indicate that the average fluoride concentration in non-fluoridated water, which is the same as that in the St-Lawrence river, can no longer be considered to be 0.13 mg/L, as generally used in the literature (Gehr and Leduc, 1992). Indeed, the average fluoride concentration, as obtained herein, is 0.20 mg/L.

(ii) Determination of the flow of non-fluoridated water (Q_{nf})

Table 4.25 shows the domestic water flow rates (both non-fluoridated and fluoridated water flows) at all the water treatment plants operating within the Montréal Urban Community, both in 1988 and 1992.

Table 4.25. Annual Average[1] Flow at the MUC Water Treatment Plants.

Water Treatment Plant	Flow (m^3/s)		Percentage of change between 1988 & 1992 (%)
	1988	1992	
Without Fluoridation			
Montréal [2]	18.40	20.96	+ 13.9
Lachine	0.88	0.69	- 21.6
Pierrefonds	0.72	0.72	0.00
Ste Anne de Bellevue	0.04	0.06	+ 50.0
With Fluoridation			
Dorval	0.44	0.34	- 22.7
Pointe-Claire	0.57	0.79	+ 38.6
Total without fluoridation	20.04	22.43	+ 11.9
Total with fluoridation	1.01	1.13	+ 11.9
Net Total	21.05	23.56	+ 11.9

[1] Represents the global annual average, knowing that the flow is generally reduced during the week-ends and the dead season (Sep. and Oct.), and increased during the summer months.
[2] Includes both treatment plants: Atwater and Charles-J Des Baillet.

It is interesting to see, from Table 4.25, that the total flows of both fluoridated and non-fluoridated water increased in the same proportion (11.9%), resulting in a net increase of 11.9%, between 1988 and 1992. Although greater variations appear from one treatment plant to another, only the total flow for each category is relevant to the present study in as much as it gives an estimate of the distribution of the flow between those with and without fluoridation. These calculations are shown in Table 4.26.

Table 4.26. Contribution of the Various Water Treatment Plants to Total Flow.

Water Treatment Plant	Flow in 1992 (m^3/s)	Percent of total (%)
Without Fluoridation		
Montreal[1]	20.96	89.0
Lachine	0.69	2.9
Pierrefonds	0.72	3.0
Ste Anne de Bellevue	0.06	0.3
With Fluoridation		
Dorval	0.34	1.4
Pointe-Claire	0.79	3.4
Total without fluoridation	22.43	95
Total with fluoridation	1.13	5
Total	23.56	100.0

[1] Includes both water treatment plants: Atwater and Charles-J Des Baillet.

As shown in Table 4.26, the flow of non-fluoridated water represents 95% of the total flow from the water treatment plants on the MUC territory. Based on the assumption that the wastewater flows returned to the sewer are proportional to the flows of water being consumed, and that they are in the same proportion for all water treatment plants, it can be concluded that 95% of the domestic flow results from non-fluoridated waters. Hence, Q_{nf} amounts to 95% of the difference between the total dry weather flow and the flow of infiltration. Average monthly values for Q_{nf} are presented in Table 4.27.

Table 4.27. Average Monthly Flow Resulting from Non-Fluoridated Water between June 1992 and May 1993.

Month	Flow of non-fluoridated water (m^3/s)
June 1992	4.86
July 1992	5.66
Aug. 1992	5.36
Sep. 1992	5.55
Oct. 1992	6.19
Nov. 1992	6.88
Dec. 1992	5.78
Jan. 1993	6.27
Feb. 1993	6.46(1)
Mar. 1993	7.50(1)
Apr. 1993	8.74(2)
May 1993	5.89(2)

(1) Not used in the current study.
(2) Based on estimated values of dry weather flow

It should be noted that this practice is used in the present study in the absence of more detailed information on the actual percentage of water that ultimately reaches the sewer system after consumption. This would effectively depend on several parameters, namely the population density, the variation in water demand within a single day, month, season or year, and the surface area and quality of gardens and agricultural lands

(iii) Determination of the fluoride mass resulting from non-fluoridated water ($Q_{nf}C_{nf}$)

The fluoride mass flow to the sewer as a result of the consumption of non-fluoridated water was calculated based on the fluoride concentration in non-fluoridated water and the flow of non-fluoridated water obtained in the previous two subsections, respectively.

These results, shown in Table 4.28, indicate that the mass of fluoride resulting from non-fluoridated water is relatively constant. This is true since both the flow of fluoridated water and the fluoride concentration in non-fluoridated water do not vary much from one season to another, as seen in the two previous subsections.

Table 4.28. Mass of Fluoride Resulting from the Consumption of Non-Fluoridated Water, between June 1992 and May 1993.

Month	Fluoride mass due to non-fluoridated water (metric tonnes)
June 1992	3.28
July 1992	3.03
Aug. 1992	3.59
Sep. 1992	3.02
Oct. 1992	3.98
Nov. 1992	2.85
Dec. 1992	2.78
Jan. 1993	3.19
Feb. 1993	3.12(1)
Mar. 1993	3.41(1)
Apr. 1993	2.94(2)
May 1993	3.00(2)

(1) Not used in the current study.
(2) Based on estimated values of dry weather flow.

Fluoride Mass Due to Fluoridated Water

(i) Determination of the fluoride concentration in fluoridated water (C_f)

Data obtained from the water treatment plants that resort to fluoridation in their treatment process indicate a mean concentration of 0.96 mg/L, rather than the theoretical value of 1.2 mg/L. Average monthly fluoride concentrations in fluoridated water are presented in Table 4.29.

Table 4.29. Average Monthly Fluoride Concentrations in Fluoridated Water between June 1992 and May 1993 (Dusault, 1993).

Month	Fluoride concentration in fluoridated water (mg/L)
June 1992	0.98
July 1992	0.92
Aug. 1992	1.04
Sep. 1992	1.01
Oct. 1992	0.94
Nov. 1992	0.96
Dec. 1992	0.97
Jan. 1993	0.95
Feb. 1993	0.92(1)
Mar. 1993	0.92(1)
Apr. 1993	0.93
May 1993	0.99

(1) Not used in the current study.

Based on Table 2.5 (Section 2.3), it can be noted that this range of fluoride concentrations corresponds to the optimum during summer and the minimum during winter.

(ii) Determination of the flow of fluoridated water (Q_f)

Following the same principle as for the flow of non-fluoridated water, and based on the results shown in Table 4.26, it can be concluded that the flow resulting from the consumption of fluoridated water represents 5% of the total domestic flow, the latter being equal to the difference between the dry weather flow and the infiltration flow. All average monthly values for Q_f are presented in Table 4.30.

Table 4.30. Estimated Flow Resulting from Fluoridated Water between June 1992 and May 1993.

Month	Flow of fluoridated water (m^3/s)
June 1992	0.26
July 1992	0.30
Aug. 1992	0.28
Sep. 1992	0.29
Oct. 1992	0.33
Nov. 1992	0.36
Dec. 1992	0.30
Jan. 1993	0.33
Feb. 1993	0.34(1)
Mar. 1993	0.40(1)
Apr. 1993	0.46(2)
May 1993	0.31(2)

(1) Not used in the current study.
(2) Based on estimated values of dry weather flow.

(iii) Determination of the fluoride mass resulting from fluoridated water (Q_fC_f)

The fluoride mass flow to the sewer resulting from the consumption of fluoridated water was calculated based on the fluoride concentration in fluoridated water and the flow of non-fluoridated water obtained in the two preceding subsections. The results are shown in Table 4.31.

Table 4.31. Mass of Fluoride Resulting from the Consumption of Fluoridated Water, between June 1992 and May 1993.

Month	Fluoride mass due to fluoridated water (metric tonnes)
June 1992	0.65
July 1992	0.73
Aug. 1992	0.78
Sep. 1992	0.76
Oct. 1992	0.82
Nov. 1992	0.90
Dec. 1992	0.79
Jan. 1993	0.84
Feb. 1993	0.76(1)
Mar. 1993	0.98(1)
Apr. 1993	1.11(2)
May 1993	0.82(2)

(1) Not included in the current study.
(2) Based on estimated values of dry weather flow

Table 4.31 shows that the mass of fluoride resulting from artificially fluoridated water is relatively constant, with the highest value being witnessed in April 1993 and the lowest in June 1992. This variation can be explained by the slight fluctuations of the flow of fluoridated water which is highest in April and lowest in June (Table 4.30).

Fluoride Mass Resulting from the Domestic Habits of the Population

(i) Determination of the fluoride concentration in the domestic sewage (C_d)

The typical mineral increase in fluoride concentration resulting from domestic water use is estimated to vary between 0.2 and 0.4 mg/L (Metcalf and Eddy, 1991). Two scenarios will thus be considered, based on these two concentrations.

(ii) Determination of the domestic sewage flow (Q_d)

The domestic sewage flow can be obtained as the difference between the dry weather flow and the infiltration flow. It is also the total of the fluoridated and non-fluoridated flows. The domestic sewage flow is hence determined based on Tables 4.27 and 4.30. Monthly average values are shown in Table 4.32.

Table 4.32. Average Monthly Domestic Sewage Flow.

Month	Domestic sewage flow (m^3/s)
June 1992	5.12
July 1992	5.96
Aug. 1992	5.64
Sep. 1992	5.84
Oct. 1992	6.52
Nov. 1992	7.24
Dec. 1992	6.08
Jan. 1993	6.60
Feb. 1993	6.80(1)
Mar. 1993	7.90(1)
Apr. 1993	9.20
May 1993	6.20

(1) Not used in the current study.

(iii) Determination of fluoride mass resulting from the domestic habits of the population (Q_dC_d)

The mass of fluoride resulting from the domestic habits of the population is determined based on the fluoride concentrations and the domestic sewage flow obtained in the previous subsections. These results are presented in Table 4.33.

Table 4.33. Mass of Fluoride Resulting from the Domestic Habits of the Population, between June 1992 and May 1993.

Month	Fluoride mass (metric tonnes)	
	Minimum (2)	Maximum (3)
June 1992	2.65	5.30
July 1992	3.19	6.38
Aug. 1992	3.02	6.04
Sep. 1992	3.03	6.05
Oct. 1992	3.49	6.98
Nov. 1992	3.75	7.50
Dec. 1992	3.26	6.51
Jan. 1993	3.54	7.07
Feb. 1993	3.29(1)	6.58(1)
Mar. 1993	4.23(1)	8.46(1)
Apr. 1993	4.77	9.54
May 1993	3.32	6.64

(1) Not included in the current study.
(2) Based on a fluoride concentration of 0.2 mg/L.
(3) Based on a fluoride concentration of 0.4 mg/L.

As expected, Table 4.33 shows that the mass of fluoride resulting from the domestic habits of the population is relatively constant. Only the minimum fluoride input will henceforth be considered from this source, in order to determine the worst-case scenario as far as the contribution of unidentified sources are concerned (Eq. 4.2). These results will be presented in the following section.

4.5.4. Fluoride Mass Resulting from Non-Identified Sources

The fluoride mass resulting from non-identified sources was calculated based on Equation 4.2 and the information presented in Tables 4.15, 4.21, 4.23, 4.28 and 4.31.

Due to the assumptions taken when performing the mass balance, and the uncertainties involved, along with the unavailability of necessary information and the relatively large number of missing daily data, a daily analysis of the fluoride mass resulting from non-identified sources was impossible. As in the previous sections, the analysis was performed on an average monthly basis. Both a seasonal and annual estimation will also be performed (excluding the two months of February and March). A seasonal variation occurs because the mass of fluoride varies with both the water consumption and the fluoride concentration, which are known to vary from one season to another. The annual average mass sheds light on the importance of the fluoride mass that finds its way to the sewer, from unidentified sources. Note that the total annual average does not account for the two winter months of February and March. This is important to point out since the mass of fluoride during those two months is expected to be much higher than the rest, due to the combination of higher fluoride concentrations (Gehr *et al.*, 1989) and higher flows. Indeed, higher flow rates were registered at the wastewater treatment plant during the winter (Table C.1, Appendix C), and fluoride concentrations in the raw wastewater during January also increased significantly (Table 4.2). In general, the mass balance, which is subject to several uncertainties (as already discussed), is only intended to give an estimate of the contribution of the various components involved and should not be viewed as a means to reach an accurate numerical value.

Final results for the mass of fluoride resulting from all sources are presented in Table 4.34.

Table 4.34. Estimation of the Mass of Fluoride Resulting from All Sources, between June 1992 and May 1993(1).

Source Contribution	June	July	Aug.	Sept	Oct	Nov	Dec	Jan	Apr	May
Precipitation	0.06	1.56	1.34	0.84	0.15	0.22	0.00	1.68	2.55	1.68
Infiltration	2.59	3.11	2.94	2.95	3.40	3.66	3.18	3.45	4.65	3.24
Non-fluoridated	3.28	3.03	3.59	3.02	3.98	2.85	2.78	3.19	2.94	3.00
Fluoridated	0.65	0.73	0.78	0.76	0.82	0.90	0.79	0.84	1.11	0.82
Domestic habits	2.65	3.19	3.02	3.03	3.49	3.75	3.26	3.54	4.77	3.32
Unidentified	(2)	22.06	17.18	9.53	8.09	16.51	33.92	28.92	(2)	(2)
Total in Wastewater	6.60	33.68	28.86	20.14	19.94	27.90	43.92	41.61	13.66	3.58

(1) Values for February and March are not included in the present study.
(2) Calculations yielded a negative value
Note: All mass values are given in metric tonnes.

It can be noticed, from Table 4.34, that the mass of fluoride resulting from infiltration and that resulting from non-fluoridated water constitute, among the identified sources of fluoride, the major input of fluoride into the wastewater. However, the largest portion is still accounted for by the unidentified fluoride sources. The importance of unidentified sources, in terms of percentage of the total fluoride content in the wastewater, is shown in Table 4.35.

Indeed, Table 4.35 shows that the unidentified sources of fluoride may reach as high as 77.22% of the total mass fluoride input to the wastewater treatment plant. In general however, the average annual percentage will vary around 50%, which is higher than the 40% figure obtained by Gehr *et al.* (1989).

Table 4.35. Importance of Unidentified Sources of Fluoride.

Month	Percentage of unidentified sources
June 1992	(2)
July 1992	65.5
Aug. 1992	59.5
Sep. 1992	47.3
Oct. 1992	40.6
Nov. 1992	59.2
Dec. 1992	77.2
Jan. 1993	69.5
Feb. 1993	(1)
Mar. 1993	(1)
Apr. 1993	(2)
May 1993	(2)

(1) Not included in the current study.
(2) Calculations yielded negative mass.

Despite the fact that the approximations and uncertainties used when performing the mass balance calculations may have lead to a slight overestimation of the unidentified fluoride sources, the high percentages shown in Table 4.34 are alarming and should not be ignored. It is important to note that, though the unidentified sources of fluoride can result from the dry precipitation that returns to the sewer system through runoff, they consist mainly of industrial discharges.

An interesting trend is depicted during the spring, when the percentage of unidentified sources of fluoride undergoes a net decrease, as shown by the negative values obtained for June 1992, as well as for April and May 1993. At this point, it should be mentioned that these negative results should not be viewed as a mathematical error but rather as an overestimation of certain parameters that led to the overestimation of one or various fluoride sources. Indeed, the probable overestimation of the precipitation and infiltration contributions, along with the very small fluoride mass in the raw wastewater due to the dilution of the water following snow melting, result in a rather negligible fluoride mass resulting from other sources.

In general, it can be said that, although an exact comparison cannot be made, due to the unavailability of data for the same time of year, the results obtained herein for the contribution of the unidentified sources are notably higher than those obtained by Gehr *et al.* (1989). This is the case, even if the domestic habits of the population were considered by Gehr *et al.* (1989) as part of the unidentified sources, while the present study addresses the input by the domestic habits as a separate component, hence decreasing the absolute value of the unidentified sources. The study conducted by Gehr *et al.* (1989), between February and May 1989, showed that 132 kg/day are due to unidentified sources (including the domestic habits of the population). In the present study, however, it was determined that an average of 375 kg/day of fluoride are discharged into the sewer network, as a result of unidentified sources (excluding the domestic habits of the population). This difference may arise from the fact that the present study includes the whole year (except for February and March) and is thus more representative of the actual situation.

As a conclusion regarding the importance of the levels of unidentified sources of fluoride that enter the sewer system, it can be noted that the mass of fluoride resulting from unidentified sources is minimal during the spring. On the other hand, during the summer, the fall and the winter, the mass of fluoride resulting from unidentified sources accounts for quite a high percentage of the total fluoride mass in the wastewater. The average annual percentage can range around 50% (Figure 4.18), with a maximum at 77.22% (Table 4.35). The contributions of all fluoride sources are shown, on an annual average basis, in Figure 4.18.

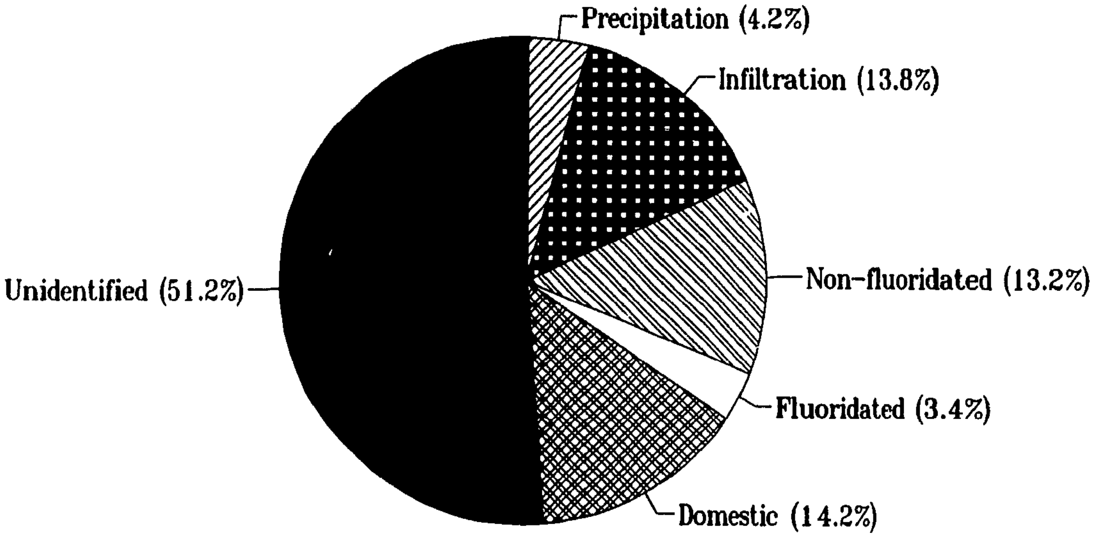

Figure 4.18. Percent Contribution of Fluoride Sources to the MUC Raw Wastewater (June 1992 to May 1993).

5. CONCLUSIONS AND RECOMMENDATIONS

Fluoride in the Wastewater

Continuous hourly monitoring of fluoride concentrations in the raw wastewater flowing to the Montréal Urban Community Wastewater Treatment Plant, between June 1992 and May 1993, showed a wide range of fluoride levels, with the maximum values possibly reaching as high as 4-fold the mean, and well over two orders higher than the minimum values. This suggests that unexpectedly high fluoride concentrations are occasionally encountered in the raw wastewater. It is suspected, with reasonable likelihood, that these may have resulted from unauthorized industrial discharges.

The monthly mean fluoride concentrations varied between 0.072 mg/L and 1.984 mg/L, with an average over the year of 0.45 mg/L. As opposed to the lower average (0.34 mg/L) obtained by Gehr *et al.* (1989), the increase in the mean value here may be due to the fact that the present study involved a continuous hourly monitoring over a longer period, hence increasing the representativeness of the data and the chances of depicting fluoride peaks. On the other hand, this increase may also have been due to an actual increase in fluoride levels.

A general seasonal trend has been depicted for the variation of fluoride levels in the MUC wastewaters: fluoride concentrations are lowest during the spring, higher during the summer, lower in the fall, and at their maximum during the winter. These trends can be explained by a combination of several factors, the most important of which are the rates of infiltration and precipitation. Nevertheless, the largest portion of these variations are accounted for by unidentified sources. Although part of these unidentified sources are due to dry fluoride deposits dissolved into the runoff, a large portion results from industrial discharges. The importance of these "unauthorized" discharges can be evidenced by the wide range of fluctuations of fluoride concentrations, the correspondingly high ratio of maximum to minimum, and the difference between the mean and the mode.

Fluoride in the Precipitation

Collection of precipitation samples was performed at a station located on the roof of the MUC Wastewater Treatment Plant. Sludge incineration at the plant incinerator is not expected to affect the fluoride concentrations in the precipitation samples.

Daily sampling of the precipitation from a station located at the roof of the MUC Wastewater Treatment Plant showed that the mean fluoride concentration in liquid precipitation generally fluctuates between 0.030 mg/L and 0.741 mg/L, whereas the average fluoride specific mass in dry precipitation ranges between 0.096 kg/km^2 and 2.775 kg/km^2. For both liquid and dry precipitation, the highest levels occur during the winter and to a lesser extent during the summer, whereas the lowest concentrations take place during the fall and the spring.

Because of the parallelism in fluoride variations between the liquid and dry precipitation, it can be suspected that the high concentration of fluoride in liquid precipitation may result actually from the fluoride content in dry fallout rather than a true fluoride concentration in rainfall. Accordingly, it might be suspected that the true fluoride concentrations in liquid precipitation are lower than those determined in the present study. Also, based on the parallelism in variational trends, it can be concluded that fluoride in precipitation results essentially from local anthropogenic sources. The latter two conclusions, however, remain to be confirmed.

Investigation of the possible correlation between chloride and fluoride in precipitation showed that no linear association between chloride and fluoride could be established This result was expected since chloride is very unlikely to be present in precipitation, whereas fluoride peaks have been recorded.

Fluoride in the Groundwater

Groundwater sampling showed that, as opposed to MUC wastewater, the addition of CDTA was essential to ensure the release of free fluoride ions. Purging of the wells had no effect on the fluoride levels in the groundwater. Generally, fluoride concentrations in the groundwater were estimated to range between 0.07 and 0 24 mg/L, with an average value of 0.13 mg/L.

Fluoride in the Melting Salts

Contrary to what was suspected, an analysis of the melting salts used by the City of Montréal showed that these do not contain any fluoride .

Mass Balance Analysis

Important observations pertain to the mass balance calculations, regarding the contribution of precipitation and the fluoride concentration in non-fluoridated water. Only liquid precipitation was considered to contribute to the fluoride mass that reaches the sewer system as a result of precipitation. Although dry deposits will be ultimately deposited on the ground and may also find their way to the sewers through runoff and infiltration, their contribution was not addressed within the scope of this research, and they were considered as part of the non-identified sources. As for the determination of the precipitation flow, this requires very involved considerations, the combination of which was not dealt with in the current study. It was, however, noted that the precipitation was not uniformly distributed over the Island of Montréal. Consequently, the latter cannot be considered as one watershed with uniform characteristics.

It is very important to point out that, although it is generally estimated that the average fluoride concentration in non-fluoridated water, which should be the same as that in the St-Lawrence River, is 0.13 mg/L, it was shown that this can no longer be considered to be so. The average fluoride concentration in the raw water intake at the City's water treatment plants has been measured to be 0.20 mg/L. Thus the estimate used by Gehr *et al.* (1989) is incorrect.

Based on mass balance calculations, it was determined that the mass of fluoride due to infiltration, fluoridated and non-fluoridated waters, as well as that resulting from the domestic habits of the population were relatively constant, whereas the mass of fluoride due to precipitation was highly variable. In general, the mass of fluoride resulting from infiltration and non-fluoridated waters, as well as that due to the domestic habits of the population constitute, among the identified sources of fluoride, the major input of fluoride mass into the wastewater. Nevertheless, the largest portion is still accounted for by the unidentified fluoride sources. These may reach as high as 77.22% of the total mass fluoride input. In general however, the average annual percentage will vary around 50%. The mass balance analysis also showed that, as an annual average, 375 kg/day of fluoride are discharged into the wastewater. Despite the fact that unidentified sources of fluoride cannot be solely seen as resulting from industrial discharges, these high percentages are alarming and should not be ignored.

Recommendations for Further Research

Because of the availability of the large set of data involved herein, which covers a period of one year, it would be interesting to perform a time series analysis in order to study, in depth, the seasonality of fluoride levels variations.

Also, models could be established to predict future fluoride levels and variations.

A refined analysis of the precipitation contribution to the total mass fluoride input should be undertaken. Fluoride concentrations in liquid precipitation should be checked to confirm that high levels are not actually induced by high fluoride levels in the dry fallout. Also, the flow of precipitation needs to be determined more precisely, based on hydrological information for the various watersheds on the Island of Montréal.

Moreover, it is essential to confirm that sludge incineration at the MUC Wastewater Treatment Plant did not affect the fluoride concentrations in the precipitation samples collected from the station located at the roof of the plant. This could be achieved by comparing fluoride concentrations in samples taken from the sludge before incineration to those in samples taken from the ash residues.

When analysing fluoride concentrations in the groundwater, samples were drawn during the summer. The effect, if any, of snow deposition (during the winter) and snow melting (during the spring) should also be determined.

In the process of reviewing the literature concerning fluoride, many references pointed to the correlational effect between fluoride and aluminum. Kraus *et al.* (1992) discussed the evidence that aluminum and fluoride are mutually antagonistic in competing for absorption in the gut. While aluminum (in the form of alum) is known to remove fluoride in water treatment processes, there is no evidence that fluoride has the same effect on aluminum. It would be very interesting to study this aspect of the fluoride-aluminum relationship. The demonstration of such an antagonistic trend, if confirmed, could have a major impact in the medical field.

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APPENDIX A

Graphical Illustrations of Fluoride Concentration Variations in the MUC Wastewater (Prior to Data Screening)

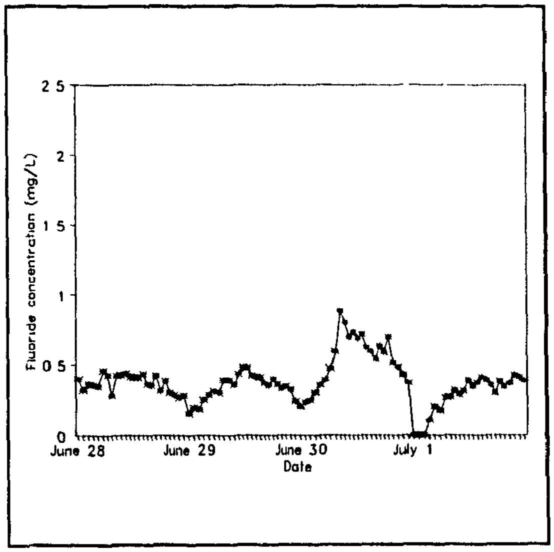

Figure A.1. Hourly Variations of Fluoride Concentrations in the MUC Wastewater (June 28 - July 1, 1992).

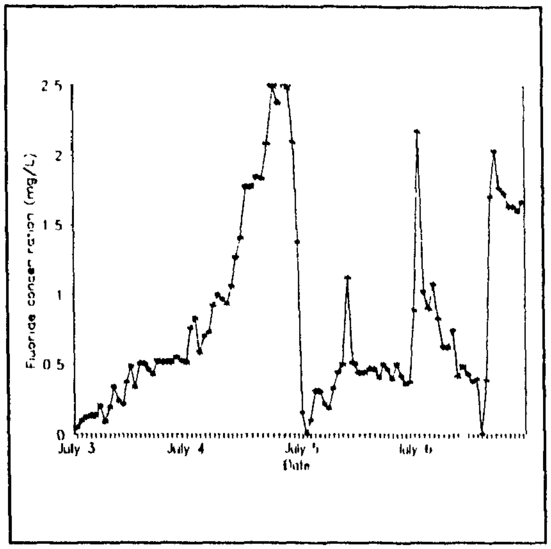

Figure A.2. Hourly Variations of Fluoride Concentrations in the MUC Wastewater (July 3 - 6, 1992).

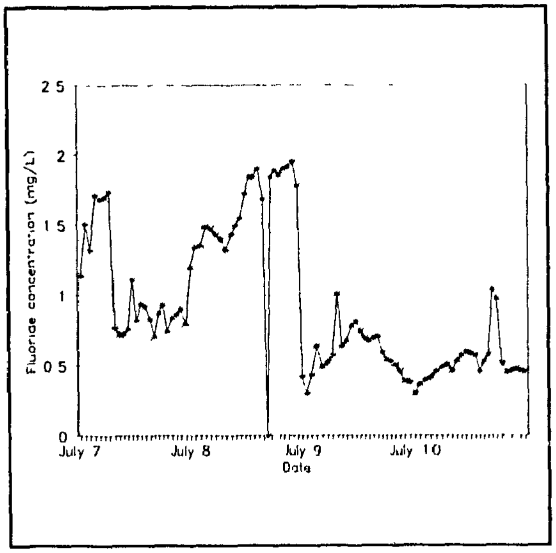

Figure A.3. Hourly Variations Fluoride Concentrations in the MUC Wastewater (July 7 - 10, 1992).

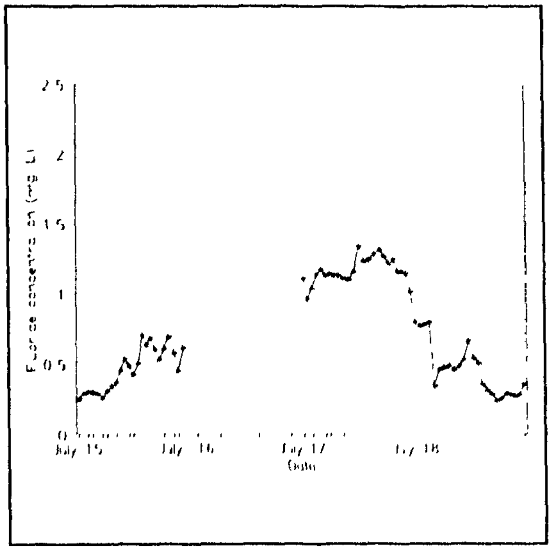

Figure A.4. Hourly Variations of Fluoride Concentrations in the MUC Wastewater (July 15 - 18, 1992).

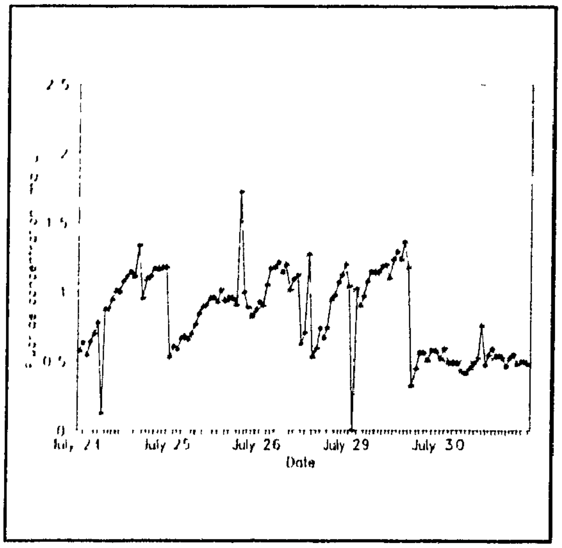

Figure A.5. Hourly Variations of Fluoride Concentrations in the MUC Wastewater (July 24 - 30, 1992).

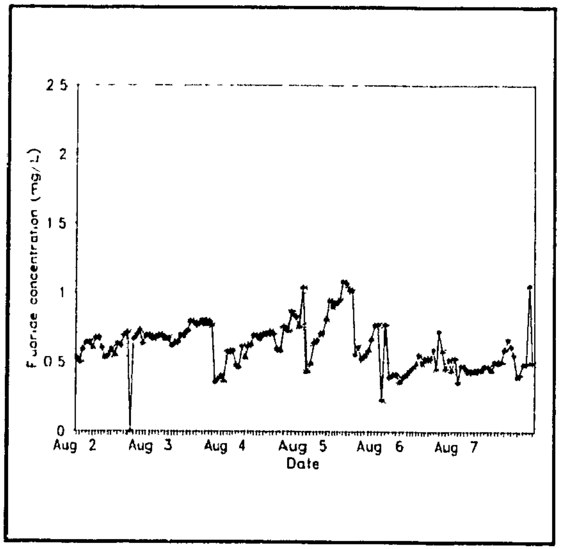

Figure A.6. Hourly Variations of Fluoride Concentrations in the MUC Wastewater (August 2 - 7, 1992).

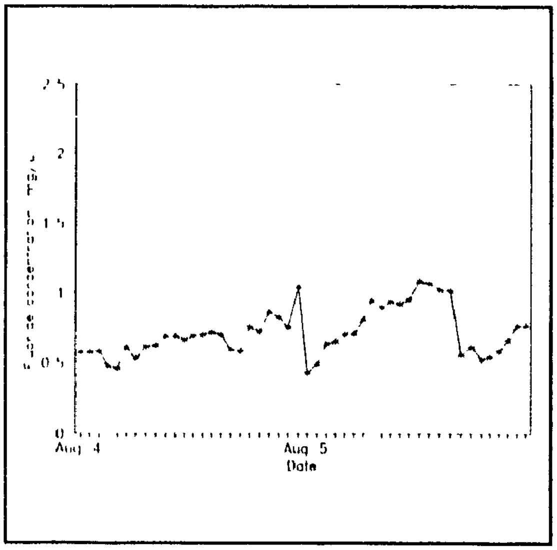

Figure A.7. Hourly Variations of Fluoride Concentrations in the MUC Wastewater (August 4 & 5, 1992).

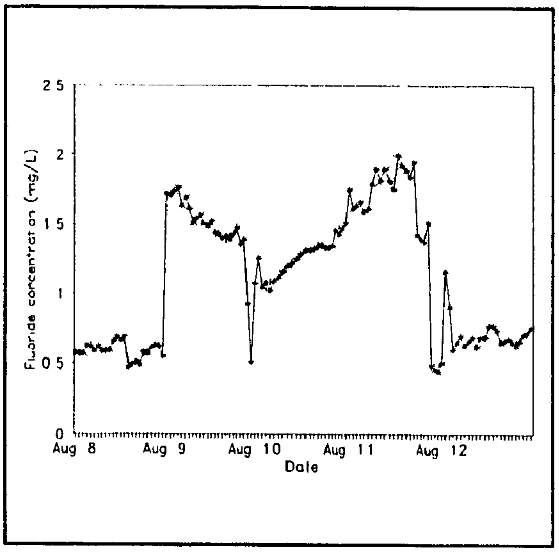

Figure A.8. Hourly Variations of Fluoride Concentrations in the MUC Wastewater (August 8 - 12, 1992).

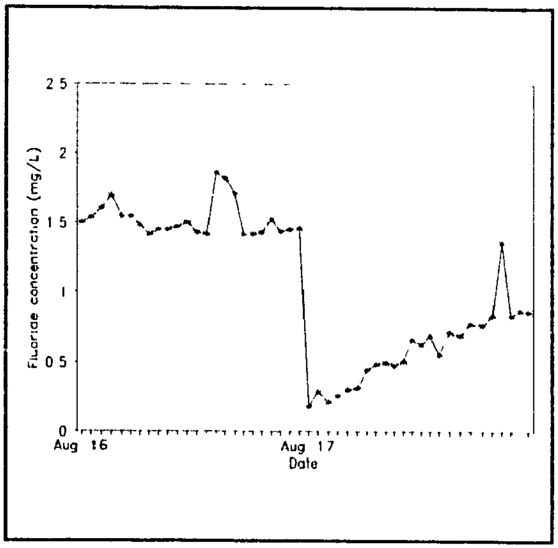

Figure A.9. Hourly Variations of Fluoride Concentrations in the MUC Wastewater (August 16 & 17, 1992).

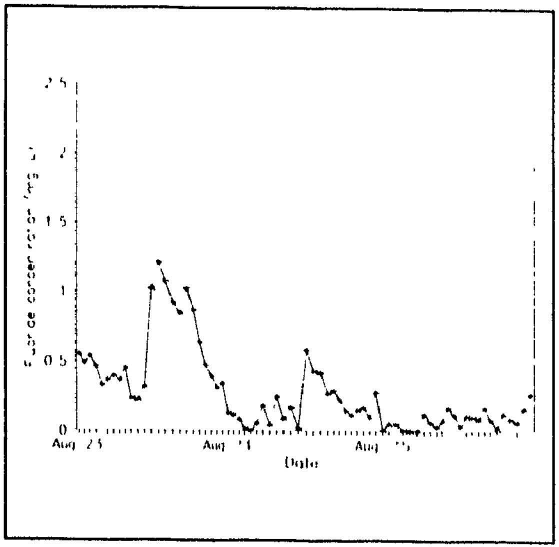

Figure A.10. Hourly Variations of Fluoride Concentrations in the MUC Wastewater (August 23 - 25, 1992).

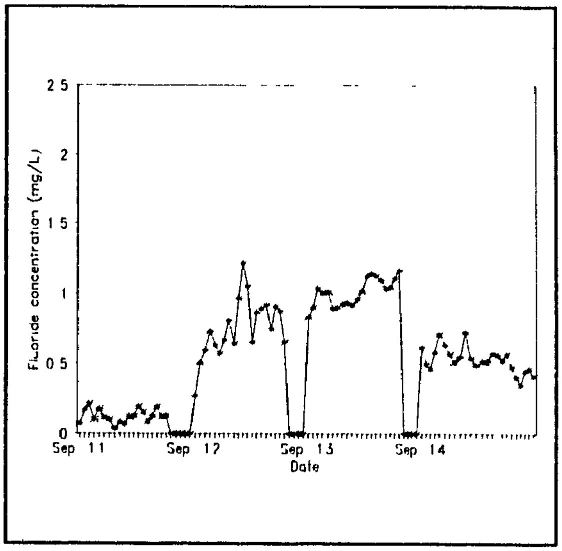

Figure A.11. Hourly Variations of Fluoride Concentrations in the MUC Wastewater (September 11 - 14, 1992).

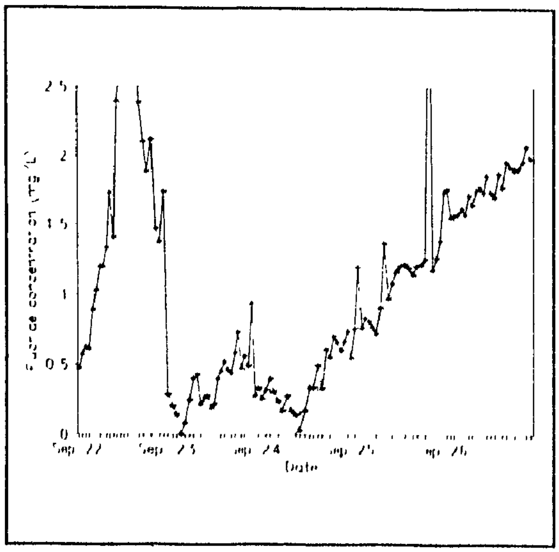

Figure A.12. Hourly Variations of Fluoride Concentrations in the MUC Wastewater (September 22 - 26, 1992).

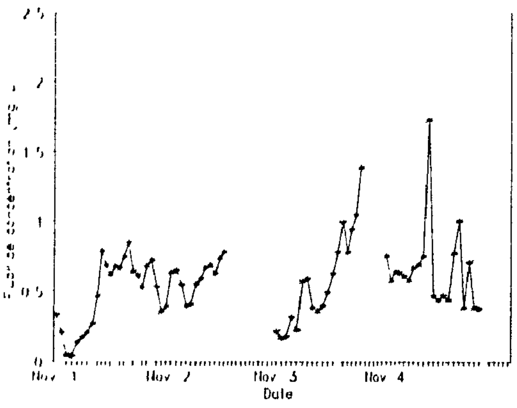

Figure A.13. Hourly Variations of Fluoride Concentrations in the MUC Wastewater (November 1 - 4, 1992).

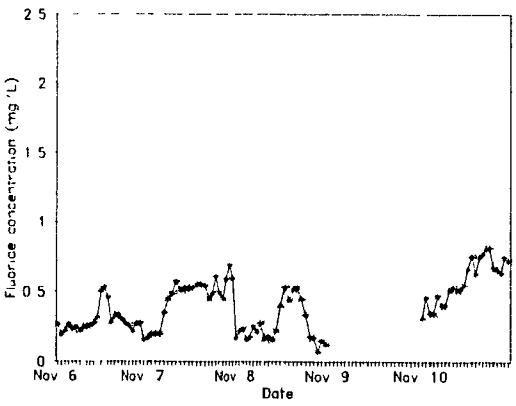

Figure A.14. Hourly Variations of Fluoride Concentrations in the MUC Wastewater (November 6 - 10, 1992).

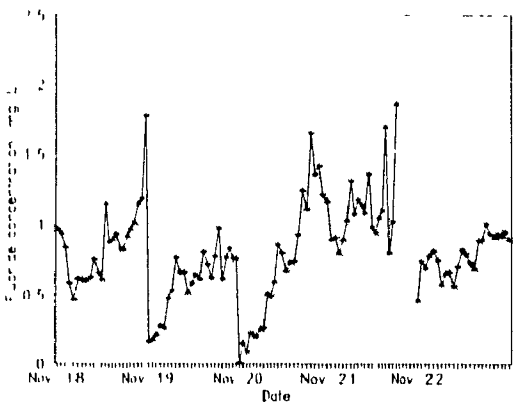

Figure A.15. Hourly Variations of Fluoride Concentrations in the MUC Wastewater (November 18 - 22, 1992).

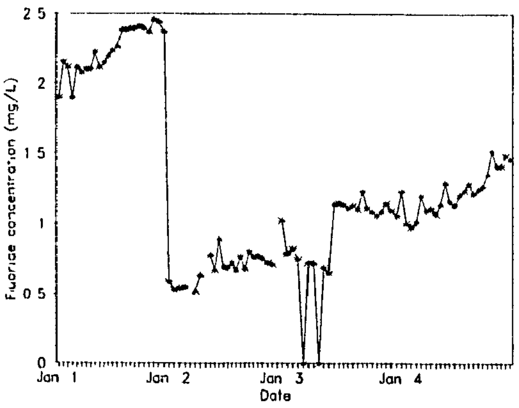

Figure A.16. Hourly Variations of Fluoride Concentrations in the MUC Wastewater (January 1 - 4, 1993).

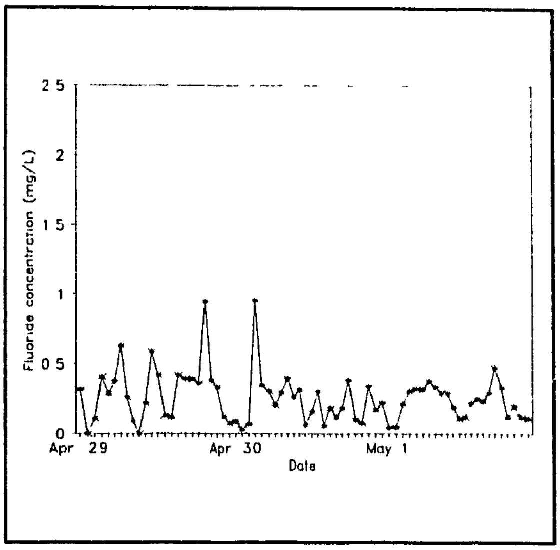

Figure A.17. Hourly Variations of Fluoride Concentrations in the MUC Wastewater (April 29 - May 1, 1993).

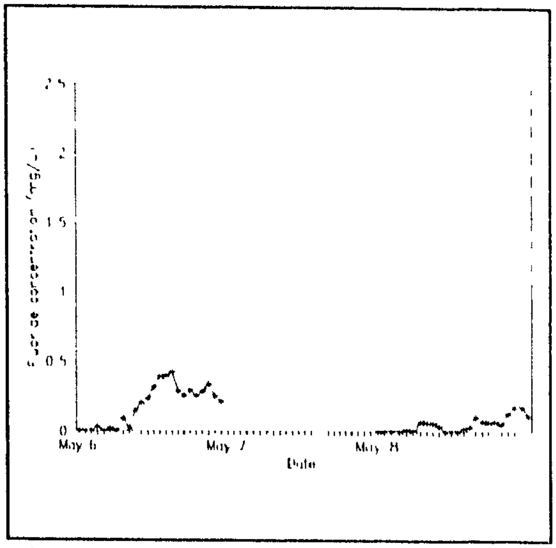

Figure A.18. Hourly Variations of Fluoride Concentrations in the MUC Wastewater (May 6 - 8, 1993).

APPENDIX B

Hourly Fluoride Concentrations in the MUC Raw Wastewater (June 1992 to May 1993)

Table B.1: Hourly Fluoride Concentrations in the MUC Raw Wastewater (June 1992).

Day Time	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
9:00	0.12	0.13	0.14	0.07	0.06	0.13	0.03		0.06	0.07	0.00	0.00	0.04	0.28	0.00		0.23	0.00						0.06	0.00	0.27	0.25	0.40	0.15	0.20	
10:00	0.07	0.08	0.16	0.13	0.06	0.12	0.08		0.04	0.07	0.00	0.00	0.06	0.25	0.00		0.27	0.00						0.21	0.00	0.25	0.24	0.31	0.20	0.23	
11:00	0.11	0.10	0.14	0.06	0.00	0.07	0.09		0.03	0.05	0.00	0.05	0.00	0.21	0.00		0.30	0.00						0.09	0.00	0.31	0.30	0.36	0.18	0.24	
12:00	0.08	0.12	0.09	0.09	0.00	0.13	0.01		0.00	0.07	0.00	0.08	0.00	0.26	0.00		0.31	0.00						0.06	0.00	0.37	0.34	0.35	0.25	0.30	
13:00	0.10	0.08	0.14	0.26	0.00	0.31	0.04		0.20	0.21	0.20	0.12	0.06	0.14	0.00		0.37	0.00					0.00	0.05	0.00	0.48	0.33	0.34	0.28	0.35	
14:00	0.10	0.06	0.16	0.14	0.00	0.23	0.09		0.16	0.18	0.20	0.16	0.09	0.21	0.00		0.27	0.17					0.00	0.03	0.00	0.35	0.37	0.46	0.31	0.39	
15:00	0.07	0.10	0.16	0.12	0.04	0.30	0.17		0.15	0.23	0.22	0.15	0.05	0.23	0.00		0.27	0.11					0.03	0.08	0.00	0.37	0.44	0.43	0.30	0.47	
16:00	0.08	0.12	0.08	0.24	0.07	0.21	0.17		0.14	0.30	0.13	0.15	0.13	0.26	0.00		0.26						0.16	0.14	0.01	0.42	0.43	0.27	0.39	0.59	
17:00	0.10	0.18	0.17	0.15	0.14	0.26	0.12		0.14	0.31	0.11	0.06	0.11	0.22	0.00		0.33						0.14	0.23	0.00	0.45	0.49	0.42	0.39	0.88	
18:00	0.10	0.14	0.18	0.17	0.17	0.27	0.11		0.14	0.25	0.15	0.12	0.16	0.27	0.06		0.35						0.14	0.29	0.04	0.47	0.47	0.43	0.35	0.80	
19:00	0.11	0.15	0.20	0.17	0.14	0.26	0.05		0.16	0.23	0.06	0.06	0.10	0.28	0.04		0.33						0.18	0.29	0.00	0.37	0.64	0.44	0.13	0.69	
20:00	0.12	0.07	0.12	0.17	0.15	0.23	0.05		0.27	0.24	0.31	0.11	0.13	0.27	0.05		0.29						0.23	0.41	0.00	0.33	0.60	0.41	0.48	0.73	
21:00	0.16	0.00	0.00	0.17	0.20	0.24	0.09		0.27	0.14	0.27	0.10	0.02	0.27	0.00		0.30						0.30	0.37	0.00	0.32	0.55	0.41	0.48	0.69	
22:00	0.18	0.00	0.00	0.18	0.23	0.26	0.14		0.22	0.10	0.21	0.13	0.06	0.20	0.00		0.35						0.22	0.26	0.04	0.36	0.62	0.41	0.42	0.72	
23:00	0.14	0.00	0.00	0.16	0.19	0.20	0.12		0.24	0.24	0.09	0.13	0.11	0.31	0.00		0.19						0.20	0.28	0.08	0.42	0.50	0.43	0.41	0.62	
24:00	0.14	0.44	0.00	0.17	0.17	0.17	0.12		0.20	0.15	0.16	0.00	0.15	0.40	0.00		0.17						0.27	0.16	0.12	0.37	0.45	0.36	0.41	0.59	
1:00	0.14	0.00	0.00	0.14	0.16	0.19	0.14		0.10	0.12	0.16	0.02	0.11	0.36	0.00		0.07						0.27	0.20	0.03	0.45	0.52	0.35	0.37	0.54	
2:00	0.1[illegible]	0.00	0.00	0.23	0.14	0.14	0.14		0.11	0.09	0.11	0.00	0.17	0.29	0.00		0.07						0.33	0.13	0.26	0.47	0.46	0.42	0.35	0.63	
3:00	0.16	0.00	0.00	0.10	0.13	0.14	0.14		0.06	0.00	0.10	0.00	0.06	0.30	0.00		0.10						0.35	0.17	0.28	0.4[illegible]	0.50	0.31	0.40	0.59	
4:00	0.1[illegible]	0.00	0.00	0.13	0.14	0.00	0.1[illegible]		0.07	0.02	0.05	0.05	0.1[illegible]	0.21	0.00		0 0						0.35	0.24	0.19	0.40	0.4[illegible]	0.3[illegible]	0.36	0.69	
5:00	0.09	0.00	0.00	0.08	0.2[illegible]	0.02	0.16		0.06	0.00	0.00	0.09	0.21	0.22	0.00		0.02						0.24	0.1[illegible]	0.30	0.6[illegible]	0.4	0.30	0.[illegible]3	[illegible]	
6:00	0.23	0.0[illegible]	0.00	0.01	0	0.02	0.1[illegible]		0.0	0.[illegible]0	0.00	0.00	0.24	0.00	0.00		0.01						0.2[illegible]	0.22	0.34	[illegible]	[illegible]	0.2[illegible]	[illegible]	[illegible]	
7:00	0.0[illegible]	0.04	0.05	0.12	0.06	0.14	0.14		0.08	0.08	0.00	0.02	0.30	0.00	0.00		0.0[illegible]						0.16	[illegible]	0.32	0.63	0.[illegible]	0.26	0.32	0.[illegible]3	
8:00	0.02	0.00	0.04	0.00	0.00	0.09	0.1[illegible]		0.05	0.06	0.00	0.0[illegible]	0.23	0.00	0.00		0.0[illegible]						0.1[illegible]	0	0.24	0.39	[illegible]	0.2	0.24	0	

Notes (1) values are given in mg/L. (2) zero values correspond to those below detection limits (i.e. <0.01 mg/L.)

Table B.2: Hourly Fluoride Concentrations in the MUC Raw Wastewater (July 1992).

Day / Time	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
9:00	0.00		0.04	0.51	0.15	0.88	1.14	1.19	0.42	0.30	0.46	0.44	0.47	0.50	0.24	0.23	1.11	0.79	0.40					0.57	0.53	0.92	1.04	0.38	0.43	0.51	0.45
10:00	0.00		0.09	0.75	0.00	2.17	1.50	1.34	0.30	0.37	0.45	0.31	0.29	0.52	0.29	0.23	0.96	0.77	0.36					0.64	0.61	0.89		0.48	0.46	0.59	0.51
11:00	0.00		0.12	0.82	0.10	1.02	1.32	1.35	0.43	0.40	0.46	0.33	0.30	0.54	0.30	0.54	1.04	0.78	0.39					0.54	0.58	1.05	1.02	0.53	0.55	0.44	0.59
12:00	0.11		0.13	0.58	0.30	0.89	1.71	1.48	0.64	0.41	0.46	0.37	0.34	0.55	0.30	0.37	1.14	0.79	0.43					0.64	0.66	1.16	0.89	0.49	0.59	0.48	0.59
13:00	0.20		0.13	0.69	0.30	1.07	1.68	1.47	0.49	0.46	0.45	0.47	0.47	0.58	0.29	0.45	1.17	0.34	0.38					0.69	0.68	1.17	0.9	0.49	0.48	0.49	0.58
14:00	0.16		0.20	0.72	0.21	0.82	1.69	1.43	0.52	0.49	0.54	0.44	0.46	0.62	0.26		1.13	0.46	0.39					0.78	0.65	1.21	1.07	0.43	0.55	0.42	0.59
15:00	0.26		0.08	0.91	0.18	0.62	1.73	1.40	0.57	0.50	0.54	0.41	0.44	0.66	0.31	1.57	1.14	0.48	0.41					0.12	0.69	1.14	1.14	0.46	0.52	0.40	0.57
16:00	0.26		0.18	1.00	0.32	0.61	0.76	1.32	1.00	0.46	0.53	0.32	0.67	0.70	0.34	1.32	1.13	0.48	0.55					0.87	0.76	1.19	1.14	0.49	0.53	0.44	0.59
17:00	0.31		0.33	0.96	0.44	0.74	0.72	1.43	0.63	0.53		0.29	0.53	0.29	0.37	1.31	1.13	0.46	0.53					0.88	0.94	1.01	1.14	0.50	0.43	0.48	0.52
18:00	0.28		0.23	0.93	0.49	0.41	0.72	1.49	0.67	0.57		0.25	0.32	0.38	0.45	1.22	1.11	0.48	0.52					0.94	0.89	1.09	1.18	0.48	0.35	0.52	0.56
19:00	0.31		0.21	1.06	1.12	0.48	0.75	1.55	0.78	0.59		0.25	0.00	0.20	0.53	1.24	1.10	0.53	0.51					1.01	0.90	1.12	1.19	0.44	0.37	0.75	0.53
20:00	0.39		0.37	1.26	0.51	0.43	1.11	1.72	0.81	0.58		0.21	0.36	0.22	0.48	1.30	1.15	0.66	0.51					0.99	0.95	0.62	1.10	0.54	0.41	0.47	0.64
21:00	0.34		0.48	1.40	0.43	0.37	0.81	1.84	0.74	0.57		0.25	0.43	0.34	0.42	1.34	1.34	0.54	0.51					1.07	0.96	0.70	1.23	0.62	0.49	0.54	0.65
22.00	0.37		0.33	1.77	0.44	0.39	0.93	1.84	0.69	0.46		0.28	0.55	0.51	0.50	1.38	1.23	0.51	0.42					1.11	0.93	1.27	1.29	0.68	0.52	0.59	0.67
23:00	0.41		0.50	1.77	0.46		0.92	1.90	0.67	0.53		0.32	0.55	0.35	0.70	1.43	1.24	0.35	0.48					1.14	1.01	0.53	1.23	0.64	0.57	0.53	0.69
24:00	0.39		0.50	1.84	0.46	0.38	0.82	1.68	0.69	0.57		0.34	0.56	0.46	0.63	1.44	1.28	0.31	0.54					1.11	0.93	0.59	1.36	0.58	0.51	0.54	0.73
1:00	0.35		0.46	1.83	0.40	1.69	0.70		0.70	1.04		0.40	0.91	0.46	0.68	1.38	1.31	0.28	0.49					1.33	0.96	0.74	1.17	0.57	1.01	0.52	0.72
2:00	0.29		0.43	2.08	0.49	2.03	0.87	1.84	0.59	0.97		0.41	0.85	0.46	0.60	1.31	1.26	0.24	0.51					0.95	0.95	0.66	0.31	0.49	0.43	0.46	0.74
3:00	0.38		0.52	2.49	0.46	1.75	0.93	1.89	0.54	0.51		0.39	0.89	0.40	0.53	1.39	1.21	0.25	0.52					1.09	0.90	0.74	0.44	0.46	0.59	0.57	0.72
4:00	0.34		0.51	2.37	0.39	1.72	0.74	1.85	0.53	0.45		0.37	0.94	0.31	0.60	1.32	1.24	0.29	0.39					1.11	1.72	0.94	0.56	0.49	0.57	0.55	0.77
5:00	0.37		0.51	2.52	0.49	1.62	0.83	1.90	0.50	0.46		0.37	0.88	0.33	0.69	1.30	1.15	0.28	0.52					1.16	0.99	0.98	0.56	0.52	0.64	0.48	0.74
6:00	0.43		0.51	2.47	0.41	1.62	0.86	1.91	0.46	0.48		0.36	0.89	0.28	0.57	1.29	1.15	0.27	0.52					1.15	0.89	1.06	0.50	0.55	0.69	0.49	0.80
7:00	0.41		0.55	2.09	0.35	1.59	0.90	1.95	0.39	0.46		0.29	0.88	0.35	0.45	1.13	1.14	0.28	0.53					1.17	0.81	1.12	0.58	0.55	0.66	0.49	0.83
8:00	0.38		0.52	1.37	0.37	1.66	0.79	1.78	0.38	0.46		0.27	0.70	0.58	0.61	1.09	1.01	0.35	0.50					1.17	0.86	1.19	0.57	0.48	0.65	0.48	0.76

Notes: (1) values are given in mg/L; (2) zero values correspond to those below detection limits (i e., < 0.01 mg/L)

Table B.3: Hourly Fluoride Concentrations in the MUC Raw Wastewater (August, 1992).

Day / Time	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
9:00	0.66	0.53	0.66	0.57	0.43	0.22	0.35	0.57	1.72	1.07	1.75	0.51	1.40		0.70	1.50	0.18	0.00	0.85				0.55	0.13	0.00		0.08	0.25	0.16	0.20	0.27
10:00	0.67	0.49	0.67	0.57	0.49	0.77	0.47	0.57	1.71	1.26	1.61	1.16	1.38		0.55	1.54	0.29	0.00	0.84				0.49	0.11	0.05		0.30	0.21	0.15	0.23	0.27
11:00	0.76	0.59	0.69	0.58	0.64	0.38	0.46	0.57	1.74	1.05	1.64	0.91	1.32		0.41	1.60	0.21	0.00	0.81				0.54	0.08	0.05		0.24	0.32	0.24	0.26	0.27
12:00	0.71	0.64	0.69	0.46	0.65	0.40	0.42	0.63	1.76	1.08	1.66	0.60	1.26		0.60	1.69	0.26	0.00	0.89				0.46	0.02	0.00		0.14	0.31	0.25	0.32	0.23
13:00	0.75	0.64	0.66	0.46	0.70	0.41	0.44	0.62	1.64	1.02	1.59	0.65	1.19		0.63	1.55	0.30	0.00	0.99				0.33	0.00	0.00		0.17	0.21	0.21	0.20	0.15
14:00	0.87	0.60	0.67	0.61	0.71	0.35	0.43	0.59	1.69	1.09	1.61	0.70	1.28		0.37	1.55	0.31	0.00	0.98				0.37	0.05	0.00		0.30	0.21	0.18	0.20	0.17
15:00	0.61	0.67	0.62	0.53	0.81	0.38	0.45	0.62	1.61	1.12	1.79	0.63	1.24		0.22	1.48	0.44	0.00	0.87				0.40	0.18	0.12		0.37	0.31	0.23	0.21	0.14
16:00	0.74	0.67	0.64	0.61	0.94	0.41	0.43	0.59	1.51	1.15	1.90	0.66	1.16		0.25	1.42	0.48	0.00	0.88				0.37	0.04	0.06		0.50	0.34	0.17	0.13	0.18
17:00	0.78	0.60	0.64	0.62	0.89	0.44	0.47	0.59	1.55	1.20	1.81	0.69	1.34		0.18	1.45	0.49	0.00	0.99				0.45	0.24	0.03		0.53	0.30	0.22	0.16	0.14
18:00	0.97	0.53	0.69	0.69	0.93	0.46	0.46	0.59	1.57	1.22	1.90	0.62	2.00		0.19	1.45	0.48	0.00	0.93				0.23	0.08	0.07		0.60	0.32	0.17	0.10	0.20
19:00	0.67	0.55	0.69	0.69	0.92	0.49	0.43	0.66	1.50	1.25	1.81	0.69	1.05		0.15	1.47	0.51	0.00	0.99				0.22	0.16	0.16		0.49	0.40	0.10	0.00	0.11
20:00	0.59	0.59	0.72	0.66	0.95	0.55	0.50	0.69	1.48	1.29	1.75	0.69	1.90		0.14	1.50	0.66	0.00	0.98				0.32	0.02	0.11		0.34	0.31	0.13	0.12	0.10
21:00	0.[illegible]3	0.55	0.79	0.69	1.08	0.49	0.49	0.66	1.53	1.32	2.00	0.78	1.10		0.14	1.43	0.62	0.00	0.99				1.02	0.58	0.03		0.42	0.23	0.13	0.08	0.1[illegible]
22:00	0.74	0.63	0.78	0.70	1.06	0.53	0.50	0.69	1.44	1.32	1.92	0.78	1.13		0.15	1.42	0.69	0.00	1.01				1.21	0.43	0.11		0.42	0.17	0.10	0.14	0.0[illegible]
23:00	0.70	0.61	0.76	0.72	1.02	0.52	0.59	0.47	1.43	1.33	1.89	0.74	1.19		0.37	1.86	0.55	0.00	0.92				1.07	0.42	0.10		0.38	0.24	0.14	0.21	0.18
24:00	0.70	0.69	0.78	0.70	1.0[illegible]	0.53	0.66	0.49	1.40	1.35	1.84	0.65	1.26		0.30	1.82	0.72	0.00	0.96				0.92	0.27	0.08		0.31	0.33	0.11	0.17	0.1[illegible]
1:00	0.72	0.71	0.80	0.59	0.55	0.59	0.61	0.51	1.42	1.36	1.95	0.66	1.24		0.14	1.71	0.69	0.00	1.14				0.65	0.29	0.16		0.31	0.14	0.10	0.19	0.11
2:00	0.66	0.00	0.77	0.58	0.61	0.45	0.55	0.49	1.39	1.34	1.43	0.68	1.15			1.42	0.78	0.00	1.01				1.02	0.23	0.08		0.44	0.02	0.06	0.14	0.18
3:00	0.77	0.66	0.79	0.78	0.52	0.72	0.39	0.58	1.43	1.34	1.40	0.65	1.17		0.15	1.42	0.77	0.00	1.05				0.8[illegible]	0.14	0.02		0.33	0.18	0.10	0.14	0.11
4:00	0.77	0.69	0.76	0.72	0.54	0.58	0.40	0.57	1.47	1.35	1.38	0.63	1.16		0.06	1.43	0.53	0.00	1.02				0.64	0	0.[illegible]2		0.42	0.30	0.00	0.15	0.14
5:00	0.93	0.73	0.3[illegible]	0.56	0.55	0.45	0.48	0.61	1.36	1.46	1.[illegible]1	0.66	1.14		0.04	1.53	1.36	0.00	0.91				0.45	0.14	0.05		0.34	0.32	0.00	0.[illegible]5	0.[illegible]4
6:00	0.59	0.63	0.3[illegible]	0.52	0.66	0.52	0.49	0.64	1.39	1.43	0.49	0	1.1		0.06	1.44	0.63	0.00	0.89				0.40	0.[illegible]6	0.06		0.[illegible]	0.3	0.00	0.[illegible]6	0.03
7:00	0.55	0.69	0.40	0.75	0.76	0.43	[illegible].05	0.62	0.93	1.4[illegible]	0.46	0.72	[illegible].13		0.[illegible]	[illegible]	0.[illegible]	0.00	[illegible].03				0.3[illegible]	0.[illegible]0	0.[illegible]		0.[illegible]2	0.40	0.06	0.[illegible]5	0.06
8:00	0.5[illegible]	0.69	0.3[illegible]	0.[illegible]	0.7[illegible]	0.52	0.49	0.5[illegible]	0.[illegible]	[illegible].51	0.4[illegible]	0.[illegible]6	1.14		0.24	[illegible].46	0.56	0.00	0.[illegible]9				0.34	0.2	0.26		0.[illegible]	0.[illegible]	0.06	0.[illegible]2	0.13

Notes (1) values are given in mg l . (2) zero values correspond to those below detection limits (i.e. < 0.01 mg l)

Table B.4: Hourly Fluoride Concentrations in the MUC Raw Wastewater (September 1992).

Day Time	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
9:00	0.00	0.11	0.00	0.00		0.07	0.11		0.00	0.12	0.07	0.27	0.83	0.61	0.05	0.22	0.81	0.61	0.26	0.21	0.49	0.48	0.28	0.27	0.55	1.74					
10:00	0.09	0.09	0.00	0.00		0.12	0.06		0.00	0.12	0.16	0.50	0.90	0.49	0.00	0.18	0.80	0.69	0.36	0.20	0.55	0.57	0.20	0.33	0.75	1.76					
11:00	0.10	0.10	0.00	0.03		0.13	0.10		0.00	0.02	0.21	0.59	1.04	0.46	0.17	0.34	0.85	0.72	0.38	0.26	0.62	0.62	0.14	0.25	1.20	1.56					
12:00	0.08	0.11	0.00	0.00		0.06	0.00		0.00	0.25	0.10	0.73	1.00	0.58	0.27	0.42	0.85	0.83	0.38	0.22	0.69	0.61	0.00	0.31	0.76	1.57					
13:00	0.13	0.08	0.00	0.01		0.06	0.02		0.08	0.23	0.17	0.63	1.01	0.71	0.36	0.51	0.93	0.84	0.29	0.15	0.64	0.89	0.08	0.40	0.83	1.58					
14:00	0.15	0.00	0.00	0.00		0.00	0.05		0.07	0.16	0.12	0.57	0.89	0.64	0.13	0.37	0.97	0.89	0.36	0.14	0.76	1.03	0.24	0.30	0.81	1.62					
15:00	0.16	0.05	0.00	0.06		0.01	0.10		0.06	0.11	0.10	0.66	0.90	0.57	0.44	0.50	0.75	0.87	0.38	0.20	0.78	1.20	0.40	0.24	0.77	1.58					
16:00	0.25	0.05	0.00	0.11		0.02	0.00		0.00	0.22	0.03	0.81	0.93	0.51	0.57	0.54	0.86	0.89	0.46	0.11	0.81	1.20	0.43	0.16	0.72	1.72					
17:00	0.20	0.03	0.00	0.09		0.00	0.00		0.08	0.21	0.08	0.64	0.93	0.55	0.55	0.46	0.90	1.10	0.41	0.18	0.81	1.34	0.22	0.27	0.91	1.65					
18:00	0.10	0.00	0.00	0.02		0.00	0.02		0.11	0.33	0.07	0.97	0.92	0.72	0.63	0.35	0.90	0.96	0.40	0.22	0.48	1.73	0.26	0.17	1.37	1.75					
19:00	0.00	0.00	0.00	0.00		0.94	0.00		0.18	0.38	0.12	1.22	0.96	0.54	0.68	0.43	0.89	0.95	0.44	0.15	0.46	1.41	0.27	0.14	0.98	1.78					
20:00	0.00	0.00	0.00	0.02		0.14	0.06		0.15	0.29	0.12	1.05	1.02	0.49	0.80	0.36	0.94	0.96	0.46	0.14	0.58	2.40	0.19	0.03	1.08	1.74					
21:00	0.00	0.00	0.00	0.06		0.07	0.00		0.09	0.24	0.19	0.65	1.13	0.51		0.43	0.89	1.00	0.41	0.14	0.61	3.09	0.22	0.17	1.16	1.86					
22:00	0.00	0.00	0.00	0.01		0.06	0.00		0.19	0.29	0.15	0.87	1.14	0.51	0.73	0.33	0.94	1.01	0.49	0.15	0.46	3.14	0.40	0.31	1.21	1.74					
23:00	0.00	0.00	0.00	0.04		0.02	0.00		0.13	0.10	0.08	0.89	1.13	0.57	0.81	0.31	0.85	1.02	0.48	0.15	0.48	2.75	0.45	0.34	1.22	1.71					
24:00	0.08	0.00	0.00	0.03		0.06	0.00		0.15	0.00	0.13	0.92	1.10	0.56	0.81	0.43	0.81	1.01	0.56	0.16	0.53	2.90	0.52	0.49	1.19	1.87					
1:00	0.12	0.00	0.00	0.15		0.00	0.00		0.01	0.05	0.19	0.74	1.04	0.52	0.85	0.43	0.85	0.98	0.54	0.14	0.55	3.19	0.46	0.33	1.14	1.78					
2:00	0.01	0.00	0.00	0.15		0.12	0.00		0.21	0.02	0.12	0.91	1.05	0.57	0.85	0.51	0.81	0.97	0.59	0.20	0.73	2.38	0.43	0.61	1.21	1.96					
3:00	0.10	0.00	0.00	0.14		0.00	0.00		0.19	0.00	0.13	0.88	1.11	0.48	0.91	0.37	0.77	0.89	0.72	0.18	0.55	2.10	0.58	0.55	1.22	1.92					
4:00	0.04	0.00	0.00	0.18		0.01	0.00		0.11	0.00	0.00	0.65	1.16	0.40	0.89	0.31	0.93	1.02	0.71	0.15	0.47	1.89	0.73	0.70	1.26	1.90					
5:00	0.00	0.00	0.00	0.16		0.08	0.00		0.10	0.00				0.34	0.86	0.22	0.85	0.96	0.72	0.16	0.59	2.12	0.48	0.66	4.31	1.91					
6:00	0.03	0.00	0.00	0.19		0.05	0.00		0.09	0.00				0.44	1.04	0.11	0.75	1.05	0.78	0.16	0.69	1.47	0.56	0.60	1.18	1.96					
7:00	0.09	0.00	0.00	0.15		0.06	0.00		0.10	0.02				0.46	0.99	0.28	0.67	1.06	0.76	0.12	0.64	1.38	0.49	0.66	1.27	2.08					
8:00	0.06	0.00	0.00	0.00		0.01	0.00		0.00	0.00				0.41	1.21	0.27	0.62	1.14	0.71	0.05	0.51	1.74	0.93	0.74	1.39	1.99					

Notes: (1) values are given in mg/L; (2) zero values correspond to those below detection limit (i.e., <0.01 mg/L).

Table B.5: Hourly Fluoride Concentrations in the MUC Raw Wastewater (October 1992).

Day / Time	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
9:00																							0.54	0.37	0.00	0.69		0.34	0.35	0.41	0.26
10:00																							0.44	0.46	0.23	0.53		0.33	0.38	0.51	0.51
11:00																							0.53	0.38	0.24	0.59		0.23	0.43	0.68	0.40
12:00																							0.41		0.28	0.67		0.23	0.36	0.63	0.42
13:00																							0.44		0.35	0.43		0.12	0.27	0.57	0.49
14:00																							0.43		0.31	0.57		0.05	0.34	0.66	0.41
15:00																							0.55		0.33	0.55		0.26	0.39	0.57	0.51
16:00																							0.43		0.35	0.59		0.29	0.49	0.71	0.56
17:00																							0.38		0.40	0.72		0.36	0.64	0.80	0.42
18:00																							0.31		0.26	0.64		0.37	0.63	0.61	0.53
19:00																							0.27		0.19	0.59		0.33	0.49	0.67	0.59
20:00																							0.34		0.33	0.93		0.38	0.49	0.61	0.57
21:00																							0.29		0.23	0.85		0.36	0.46	0.71	0.81
22:00																							0.29		0.21	0.74		0.26		0.66	0.69
23:00																							0.25		0.26	0.74		0.31		0.74	0.77
24:00																							0.28		0.55	0.64		0.43		0.48	0.57
1:00																							0.66		0.51	0.84		0.53		0.36	0.80
2:00																									0.43	0.66		0.49		0.44	0.74
3:00																									0.46	0.57		0.45		0.56	0.65
4:00																									0.52	0.82		0.42		0.59	0.72
5:00																									0.40	0.75		0.62		0.56	0.84
6:00																									0.35	0.76		0.59		0.69	0.69
7:00																										[illegible]		0.57		0.74	0.61
8:00																										0.92		[illegible]		[illegible]	0.66

Notes (1) values are given in mg/L, (2) zero values correspond to those below detection limits (i.e. <0.01 mg/L)

Table B.6: Hourly Fluoride concentrations in the MUC Raw Wastewater (November 1992).

Day / Time	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
9.00	0.34	0.64	0.22	0.75	0.25	0.26	0.16	0.17		0.31					0.88	0.51		0.97	0.16	0.01	0.89	0.46			0.27						
10.00	0.21	0.65	0.16	0.58	0.41	0.19	0.16	0.22		0.46					0.89	0.51		0.93	0.17	0.15	0.91	0.74			0.28						
11.00	0.04	0.55	0.18	0.64	0.33	0.22	0.20	0.23		0.35					0.69	0.31		0.84	0.21	0.09	0.80	0.69			0.38						
12.00	0.04	0.40	0.32	0.64	0.31	0.26	0.20	0.16		0.35					0.70	0.27		0.58	0.27	0.22	0.89	0.78			0.44						
13.00	0.14	0.41	0.23	0.61	0.25	0.23	0.20	0.17		0.47					0.55	0.31		0.46	0.26	0.21	1.03	0.81			0.48						
14.00	0.17	0.55	0.57	0.58	0.22	0.24	0.35	0.25		0.40					0.57	0.51		0.61	0.47	0.20	1.31	0.74			0.53						
15.00	0.21	0.59	0.59	0.67	0.24	0.22	0.44	0.21		0.40					0.85	0.43		0.60	0.53	0.25	1.07	0.57			0.43						
16.00	0.27	0.67	0.38	0.69	0.25	0.24	0.48	0.27		0.51					0.81	0.37		0.60	0.76	0.26	1.17	0.65			0.53						
17.00	0.47	0.69	0.36	0.75	0.27	0.25	0.57	0.16		0.53					0.69	0.43		0.62	0.66	0.51	1.14	0.66			0.96						
18.00	0.79	0.63	0.40	1.73	0.26	0.26	0.51	0.18		0.51					0.36	0.34		0.75	0.66	0.49	1.08	0.56			0.53						
19.00	0.69	0.74	0.49	0.47	0.35	0.27	0.53	0.15		0.52					0.53	0.50		0.66	0.51	0.59	1.36	0.70			0.47						
20.00	0.62	0.78	0.63	0.44	0.33	0.32	0.52	0.22		0.55					0.57	0.41		0.61	0.58	0.85	0.98	0.82			0.67						
21.00	0.68	0.43	0.78	0.47	0.23	0.50	0.53	0.40		0.66					0.74	0.40		1.14	0.64	0.80	0.94	0.79			0.74						
22.00	0.67	0.76	0.99	0.44	0.34	0.53	0.55	0.53		0.75					0.78	0.40		0.88	0.61	0.67	1.05	0.73			0.74						
23.00	0.74	0.55	0.78	0.78	0.34	0.46	0.55	0.44		0.63					0.86	0.35		0.89	0.81	0.73	1.10	0.69			0.93						
24.00	0.85	0.50	0.94	1.00	0.36	0.28	0.54	0.51		0.74					0.92	0.39		0.93	0.72	0.74	1.69	0.89			0.93						
1.00	0.64	0.62	1.05	0.38	0.38	0.33	0.44	0.53		0.77					0.79	0.25		0.83	0.62	0.93	0.80	0.89			1.11						
2.00	0.61	0.45	1.39	0.71	0.34	0.34	0.48	0.44		0.81					0.88	0.31		0.82	0.78	1.24	1.02	1.00			1.38						
3.00	0.53	0.99	0.48	0.38	0.33	0.30	0.61	0.33		0.81					0.77	0.34		0.92	0.98	1.11	1.86	0.93			1.29						
4.00	0.68	0.53	0.53	0.38	0.35	0.27	0.49	0.17		0.67					0.64	0.33		0.97	0.61	1.65		0.91			0.87						
5.00	0.72	0.55	0.48		0.34	0.26	0.45	0.17		0.66					0.61	0.40		1.01	0.77	1.36		0.93			1.50						
6.00	0.53	0.39	0.55		0.40	0.22	0.59	0.06		0.64					0.64	0.38		1.14	0.83	1.42		0.92			1.54						
7.00	0.35	0.44	0.45		0.34	0.27	0.69	0.15		0.74					0.70	0.60		1.18	0.76	1.21		0.95			1.55						
8.00	0.39	0.48	0.57			0.27	0.59	0.12		0.72					0.74	0.61		1.78	0.75	1.16		0.89			1.94						

Notes: (1) values are given in mg/L, (2) zero values correspond to those below detection limits (i.e., < 0.01 mg/L).

Table B.7: Hourly Fluoride Concentrations in the MUC Raw Wastewater (December 1992).

Day Time	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
9:00				1.06														0.00										1.29			0.91
10:00				0.93														0.99										0.80			0.88
11:00				0.97														2.09										1.06			0.98
12:00				1.00														0.50										1.19			1.13
13:00				1.02														0.58										0.92			1.30
14:00				1.02														0.61										0.85			1.21
15:00				0.93														0.72										0.89			1.19
16:00																		0.65										1.06			1.20
17:00																		0.96										1.05			1.21
18:00																		1.02										0.94			1.18
19:00																		1.07										0.93			1.21
20:00																		1.09										0.91			1.23
21:00																		1.26										1.11			1.71
22:00																		1.21										1.05			1.57
23:00																		1.33										1.15			0.95
24:00																		1.32													1.08
1:00																		0.00													
2:00				0.59														1.45													1.19
3:00				0.60														1.45													1.15
4:00				0.55														1.42													1.32
5:00				0.68														1.43													1.45
6:00				0.77														1.65													1.53
7:00				0.84														1.51													[illegible]
8:00				0.92														1.50													1.61

Notes. (1) values are given in mg/L; (2) zero values correspond to those below detection limits (i.e. <0.01 mg/L)

Table B.8: Hourly Fluoride Concentrations in the MUC Raw Wastewater (January 1993).

Day Time	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
9:00	1.90	0.59	1.02	1.22		1.20	0.44	1.07	0.81	0.80	0.58	1.27	1.20	0.81	0.36				0.69												
10:00	2.16	0.53	0.78	1.00		0.54	0.53	1.21	0.96	0.77	1.10	1.34	1.18	0.96	0.59				0.81												
11:00	2.12	0.54	0.82	0.98		0.40	0.55	1.20	1.17	0.74	0.89	1.37	1.22	0.88	0.55				0.86												
12:00	1.90	0.55	0.74	1.01		0.55	0.57	1.20	0.96	0.77	0.85	1.39	1.21	0.85	0.51																
13:00	2.12			1.19		0.46	0.57		0.7[illegible]	0.74	0.76	1.43	1.46	0.89	0.45																
14:00	2.08	0.52	0.72	1.09		0.64	0.65		0.83	1.17	0.80		1.48	1.00	0.66																
15:00	2.10	0.64	0.72	1.11		0.42	0.64		0.81	0.72	0.92			1.04	0.71																
16:00	2.10			1.06		0.53	0.69		0.99	0.78	0.84			1.10	0.71																
17:00	2.23	0.78	0.69	1.14		0.60	0.52		1.08	0.80	0.80			0.89	0.59																
18:00	2.12	0.67	0.65	1.29		0.57	0.57		1.06	1.22	0.74			1.04	0.92																
19:00	2.14	0.89	0.60	1.15		0.78	0.59		0.98	0.96	0.82			1.09	0.95																
20:00	2.20	0.69	0.61	1.13		0.79	0.64		0.62	0.78	0.83			1.00	0.86																
21:00	2.24	0.69	0.60	1.20		0.66	0.67		0.53	0.66	0.85			1.14	1.15																
22:00	2.27	0.72	0.58	1.23		0.64	0.66		0.51	0.96	0.85			0.99	0.78																
23:00	2.38	0.67	0.59	1.28		0.59	0.67		0.82	0.83	0.85			0.98	0.80																
24:00	2.38	0.76	0.57	1.21		0.62	0.64		0.55	0.78	0.84			1.32	0.82																
1:00	2.40	0.68	0.66	1.24		0.73	0.64		0.56	0.80	1.12			1.28	1.12																
2:00	2.40	0.80	0.58	1.26		0.71	0.67		0.46	0.80	1.61			1.18	0.69																
3:00	2.41	0.76	0.56	1.35		0.61	0.59			0.78	1.15			1.10	0.67																
4:00	2.40	0.77	0.54	1.51		0.76	0.58			0.73	0.88			1.14	0.93																
5:00	2.37	0.75	0.56	1.41		0.69	0.65				0.89			1.18	0.85																
6:00	2.46	0.72	0.61	1.41		0.78	0.57				1.04			1.20	0.79																
7:00	2.44	0.71	0.57	1.48		0.80	0.79				0.89			1.12	0.95																
8:00	2.37		0.54	1.46		0.49	1.71			0.75	0.63			1.02	0.73																

Notes: (1) values are given in mg/L; (2) zero values correspond to those below detection limits (i.e., <0.01 mg/L)

Table B.9: Hourly Fluoride Concentrations in the MUC Raw Wastewater (April 1993).

Day Time	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
9:00											0.09	0.23	0.07	0.43	0.31	0.24	0.06	0.05	0.44	0.14				0.09	0.08	0.06	0.00	0.00	0.00	0.07	
10:00											0.04	0.25	0.10	0.40	0.09	0.11	0.11	0.20	0.30	0.00				0.21	0.14	0.00	0.17	0.05	0.31	0.08	
11:00											0.14	0.24	0.11	0.35	0.35	0.20	0.13	0.16	0.35	0.09				0.00	0.02	1.86	0.16	0.00	0.00	0.03	
12:00											0.20	0.20	0.09	0.40	0.32	0.26	0.00	0.16	0.58	0.29				0.02	0.06	0.09	0.00	0.00	0.11	0.07	
13:00											0.04	0.23	0.11	0.38	0.23	0.23	0.20	0.25	0.43	0.00				0.08	0.02	0.14	0.23	0.00	0.40	0.95	
14:00											0.07	0.17	0.08	0.41	0.47	0.17	0.16	0.17	0.30	0.00				0.20	0.00	0.21	0.16	0.00	0.28	0.34	
15:00											0.10	0.15	0.02	0.35	0.32	0.17	0.09	0.18	0.42	0.00				0.12	0.00	0.23	0.10	0.00	0.37	0.30	
16:00											0.18	0.17	0.06	0.31	0.31	0.16	0.06	0.40	0.40	0.00				0.04	0.11	0.20	0.16	0.00	0.62	0.20	
17:00											0.25	0.18	0.08	0.31	0.00	0.08	0.17	0.38	0.37	0.00				0.00	0.05	0.14	0.15	0.00	0.26	0.29	
18:00											0.04	0.21	0.00	0.32	0.33	0.23	0.00	0.14	0.43	0.00				0.03	0.00	0.09	0.13	0.00	0.09	0.39	
19:00											0.09	0.18	0.04	0.39	0.18	0.28	0.07	0.17	0.32	0.00				0.09	0.00	0.16	0.00	0.00	0.00	0.26	
20:00											0.14	0.20	0.1[illegible]	0.41	0.12	0.16	0.06	0.17	0.30	0.00				0.18	0.00	0.14	0.13	0.00	0.22	0.31	
21:00											0.17	0.15	0.04	0.29	0.16	0.23	0.16	0.13	0.44	0.00				0.13	0.00	0.14	0.22	0.00	0.58	0.06	
22:00											0.03	0.15	0.13	0.38	0.02	0.26	0.00	0.12	0.44	0.00				0.16	0.06	0.13	0.00	0.00	0.41	0.15	
23:00											0.02	0.16	0.00	0.46	0.30	0.16	0.03	0.20	0.55	0.00				0.00	0.02	0.14	0.00	0.00	0.13	0.30	
24:00											0.06	0.20	0.06	0.27	0.32	0.16	0.11	0.07	0.50	0.00				0.18	0.04	0.11	0.00	0.00	0.11	0.06	
1:00											0.04	0.15	0.04	0.34	0.31	0.19	0.06	0.16	0.27	0.00				0.15	0.00	0.00	0.00	0.00	0.41	0.18	
2:00											0.07	0.16	0.08	0.35	0.00	0.22	0.00	0.15	0.35	0.00				0.14	0.14	0.08	0.00	0.00	0.39	0.11	
3:00											0.08	0.16	0.02	0.40	0.21	0.24	0.01	0.26	0.28	0.00				0.05	0.00	0.15	0.00	0.00	0.38	0.38	
4:00											0.12	0.18	0.05	0.35	0.23	0.25	0.06	0.27	0.25	0.00				0.07	0.03	0.13	0.00	0.00	0.35	0.35	
5:00											0.03	0.15	0.06	0.35	0.26	0.13	0.03	0.15	0.36	0.00				0.11	0.02	0.05	0.00	0.00	0.94	0.10	
6:00											0.06	0.21	0.11	0.30	0.00	0.07	0.00	0.08	0.27	0.00				0.12	0.25	0.06	0.00	0.00	0.38	0.07	
7:00											0.07	0.21	0.04	0.40	0.21	0.27	0.00	0.14	0.12	0.00				0.05	0.03	0.06	0.00	0.00	0.33	0.34	
8:00											0.07	0.00	0.02	0.00	0.33	0.21	0.00	0.05	0.20	0.00				0.07	0.00	0.09	0.00	0.00	0.12	0.16	

Notes. (1) values are given in mg/L; (2) zero values are those below detection limits (i.e., <0.01 mg/L.)

Table B.10: Hourly Fluoride Concentrations in the MUC Raw Wastewater (May 1993).

Day / Time	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
9:00	0.22	0.24	0.21	0.03		0.00		0.00		0.06	0.02	0.11	0.04	0.01	0.11		0.02	0.04				0.09	0.02	0.00	0.04	0.00	0.09	0.18	0.08	0.16	0.04
10:00	0.04	0.24	0.08	0.00		0.00		0.00		0.05	0.09	0.32	0.00	0.00	0.09		0.05	0.10				0.05	0.02	0.00	0.03	0.00	0.23	0.11	0.06	0.28	0.02
11:00	0.04	0.24	0.11	0.13		0.00		0.00		0.02	0.02	0.05	0.03	0.00	0.08		0.03	0.07				0.06	0.00	0.00	0.03	0.00	0.16	0.07	0.07	0.33	0.11
12.00	0.21	0.20	0.01	0.11		0.03		0.00		0.01	0.09	0.11	0.03	0.00	0.01		0.02	0.04				0.10	0.02	0.00	0.03	0.00	0.11	0.06	0.04	0.16	0.01
13:00	0.30	0.15	0.10	0.07		0.00		0.02		0.00	0.09	0.10	0.02	0.00	0.12		0.02	0.00				0.11	0.02	0.00	0.02	0.00	0.07	0.14	0.13	0.13	0.06
14:00	0.32	0.26	0.07	0.20		0.02		0.00		0.02	0.03	0.05	0.04	0.00	0.00		0.05	0.04				0.04	0.00	0.00	0.05	0.00	0.06	0.11	0.09	0.05	0.11
15:00	0.31	0.14	0.13	0.13		0.00		0.07		0.02	0.08	0.11	0.06	0.00	0.06		0.04	0.04				0.04	0.02	0.00	0.02	0.00	0.16	0.06	0.11	0.03	0.24
16:00	0.37	0.11	0.05	0.24		0.09		0.06		0.00	0.13	0.06	0.02	0.01	0.01		0.04	0.03				0.03	0.00	0.00	0.03	0.00	0.10	0.06	0.06	0.04	0.18
17:00	0.33	0.24	0.19	0.19		0.02		0.06		0.03	0.03	0.10	0.02	0.00	0.14		0.05	0.03				0.02	0.02	0.00	0.00	0.00	0.09	0.05	0.06	0.40	0.03
18:00	0.29	0.10	0.00	0.26		0.14		0.04		0.02	0.02	0.00	0.02	0.00	0.07		0.02	0.02				0.02	0.01	0.00	0.00	0.00	0.09	0.06	0.14	0.26	0.04
19:00	0.29	0.14	0.02	0.27		0.20		0.00		0.00	0.04	0.03	0.02	0.00	0.11		0.02	0.02				0.03	0.02	0.00	0.03	0.00	0.10	0.08	0.10	0.18	0.10
20:00	0.18	0.13	0.14	0.27		0.23		0.00		0.02	0.04	0.08	0.04	0.01	0.09		0.02	0.04				0.04	0.03	0.00	0.00	0.00	0.17	0.09	0.08	0.12	0.11
21:00	0.11	0.02	0.01	0.23		0.31		0.00		0.04	0.14	0.06	0.03	0.05	0.13		0.05	0.04				0.02	0.02	0.00	0.00	0.00	0.09	0.13	0.07	0.08	0.11
22.00	0.11	0.07	0.00	0.28		0.39		0.02		0.00	0.07	0.06	0.03	0.00	0.22		0.03	0.06				0.00	0.00	0.00	0.02	0.00	0.21	0.11	0.06	0.03	0.06
23:00	0.22	0.14	0.06	0.38		0.40		0.03		0.03	0.03	0.02	0.04	0.00	0.24		0.05	0.04				0.03	0.00	0.00	0.03	0.00	0.14	0.05	0.06	0.12	0.15
24:00	0.24	0.09	0.00	0.27		0.42		0.11		0.00	0.04	0.00	0.02	0.00	0.18		0.02	0.04				0.06	0.02	0.00	0.02	0.00	0.15	0.06	0.05	0.25	0.18
1:00	0.23	0.14	0.00	0.33		0.29		0.07		0.04	0.07	0.04	0.02	0.00	0.15		0.00	0.02				0.06	0.03	0.00	0.00	0.00	0.12	0.06	0.07	0.27	0.16
2.00	0.29	0.15	0.03	0.39		0.25		0.07		0.02	0.07	0.05	0.01	0.00	0.00		0.00	0.00				0.00	0.03	0.00	0.01	0.00	0.21	0.15	0.06	0.23	0.22
3:00	0.47	0.14	0.00	0.21		0.29		0.07		0.00	0.03	0.05	0.02	0.00	0.08		0.00	0.00				0.00	0.02	0.00	0.00	0.00	0.12	0.04	0.09	0.16	0.01
4:00	0.33	0.18	0.03	0.27		0.25		0.06		0.00	0.02	0.02	0.05	0.00	0.22		0.02	0.00				0.02	0.03	0.00	0.00	0.00	0.09	0.07	0.08	0.17	0.03
5:00	0.11	0.23	0.00	0.21		0.28		0.13		0.04	0.08	0.07	0.01	0.00	0.08		0.00	0.00				0.04	0.02	0.00	0.03	0.00	0.08	0.10	0.07	0.14	0.04
6:00	0.20	0.25	0.01	0.18		0.34		0.17		0.00	0.08	0.00	0.02	0.00	0.01		0.00	0.00				0.03	0.03	0.00	0.02	0.00	0.06	0.08	0.06	0.08	0.06
7:00	0.11	0.14	0.00	0.15		0.25		0.17		0.00	0.06	0.00	0.05	0.00	0.01		0.02	0.00				0.03	0.02	0.00	0.00	0.00	0.06	0.06	0.05	0.02	0.10
8:00	0.11	0.21	0.00	0.23		0.21		0.11		0.04	0.09	0.00	0.21	0.02	0.00		0.00	0.00				0.02	0.00	0.00	0.00	0.00	0.09	0.05	0.05	0.03	0.09

Notes: (1) values are given in mg/L; (2) zero values are those below detection limits (i.e., <0.01 mg/L).

APPENDIX C

Wastewater Flow and Precipitation Volume Data

Table C.1 Average Daily Wastewater Flows at the MUC Wastewater Treatment Plant, between June 1992 and May 1993 (Purenne, 1993)

Date	June	July	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May
1	14.2	12.5	25.7	15.8	16.4	14.3	18.2	13.5	16.3	16.7	20.4	19.5
2	12.9	12.9	13.6	16.6	16	15.8	16.1	13.7	18.7	17.4	20.7	19
3	15.1	13.2	12.2	24	16.3	32.1	17.8	13.9	16.8	18.7	20.7	20.6
4	12.1	27.9	29.8	17.2	14.3	21.9	17	28.1	17.9	17	21.1	17.8
5	13	14.7	21.1	13.7	16.5	20.6	16	37.2	16.1	14.6	28.5	17.8
6	25.1	15.4	15.4	12.4	15.3	20.9	15.2	19.3	16.8	16	31.8	32.5
7	15.4	17.4	13.5	13.8	17.8	16.8	15.6	19.3	16.3	16.4	31.7	18.7
8	14.3	17.8	13.8	17.9	14.3	16	16	18.1	18.6	17.3	31.3	15.7
9	12.8	26.7	16.2	19.7	24.3	17.3	16.3	17	18.7	18.9	33.3	14.7
10	11.8	18.5	14.4	19.5	25.8	18.5	15.2	16.7	15	18.7	42	16.6
11	14.3	15.4	18.3	16.1	13.5	26.3	14.9	16.9	14.2	17.3	42.9	18.3
12	13	16.6	16.4	14.1	14.6	20.8	16.8	16.1	14.6	18.4	35.9	17.3
13	13.8	27.3	14.7	12.4	16.1	28.2	14.9	17.1	14.5	16.7	31.1	17.8
14	12.4	14.6	17.9	14.7	16.4	18	15.1	16.1	15.7	13.3	30.4	16.4
15	11.3	14.6	15.1	12.7	16.1	18.6	15.3	17	16.9	18.3	27.7	17.7
16	13.5	14.6	14.8	15.7	21.8	17.2	15.2	15.7	15.6	10.8	27.4	15.5
17	12.1	19.7	14.2	13.9	18	18.6	17.3	15.6	17	19.1	39	15.6
18	14	23.9	12.1	14.2	13.9	17.1	16.9	16	16.5	16.2	24.6	15
19	19.3	18.4	13.1	13.7	16.5	15.7	13.9	16.1	18.8	17.7	22.8	18.2
20	15.3	13.6	12	11.7	17.9	17.5	18.4	16.1	18.9	16.2	25.5	17.3
21	12	13.8	13.4	15.8	18.1	20	16.2	14.6	16	14.9	36.8	18.1
22	13.4	13.9	14.7	25.6	17.4	17.4	15.8	30	17.6	19.7	38.3	16.1
23	13.3	16	14.4	14.8	17.5	27.8	15.2	24.2	17.7	17.2	45	14.6
24	12.7	16.8	14	16.3	25.9	20.3	14.8	25.4	18.5	18	30.2	26.3
25	13.1	15.3	14.1	17.4	17.1	20.1	13.2	23.5	21.4	22	33.9	17
26	12.3	16.5	12.6	17.1	17.4	22.3	12.4	18.3	21.3	26.2	27.6	14.8
27	11.8	13	14.5	15.7	17.4	23.5	14	16.8	16.3	31.4	24.8	14.4
28	11.5	11.5	14.8	16.4	16.3	18.7	13.4	18	16	33	22.8	12.7
29	12.8	15.7	18.9	12.4	16.6	16.6	14.5	15.9		36	22.2	12.6
30	21	15.5	12	15.3	16.1	17.8	14.7	16.4		34.3	21.3	12.9
31		19.9	14.3		14.4		14.7	14.8		28.1		24

Note: All values are in m3/s

Table C.2. Available Daily Precipitation Volumes (Gauthier and Mercier, 1993).

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
JUNE 92																															
Riviere des prairies	1.2				17.9	1.2	1.3					11.6							14.5					2.2					17		
Montreal Lafontaine	1.2																														
Ste Anne De Bellevue	0.8				25	1	5.8					5.6	0.2						27.6		0.4	0.2		2.4	2.4				7.8	1.2	
Ste Genevieve	1.2				22.6	0.6	8					4.8	0.6						24					3.2	2				9.8	1.8	
McGill	0.4	0.2			18.7	0.4	8					6.4							26		0.2	0.2		3.6				0.4	7.8	0.6	
Dorval	2.2				0.8	18	13.6					3.2	4						22.2	1.2	0.4			2.6	0.4				0.2	7.6	
JULY 92																															
Riviere des prairies			20.7	2	1.9		4.4	24.1	3.8	3.4		32.4					28.1	11.2	1.6							2.7					39.3
Ste Anne De Bellevue			29.6	1.4	9	0.2		13.6		0.5		22.4	0.2	0.6			26.6	6						0.2		6.2	0.6				25.8
Ste Genevieve			35.8	1.8	3	0.3		13.6		1		23	0.6			0.8	22.8	13.6								2.2					23.4
McGill			37.3	2.1	5.1	1.4	1.2	19.1			0.6	19.2		2.2			22.7	5.7								5.4					30
Dorval			3.6	26.4	2.2	2.8		5.4	9.6		0.4	9.8	9.8	0.6			29.8	2.6	6.4							4.4					23.4
AUGUST 92																															
Riviere des prairies	2.6		4.4	30.5			4			1								2.5								7	5.4	4			
Ste Genevieve	2	0.6	8.4	10				7.4		1.6			0.4			1.4		1.6								0.4	2.6	7.6		1.2	
McGill	2.4	0.4	4.7	27.6	0.6			6.6		1.2	0.2					0.4	0.4	1.4									4.8	12.6	0.8	0.6	3
Dorval	3.8	0.4		26.2	1.2				10.2	1	0.6		0.2				0.4	0.2	0.2								8.6	0.4	15.2	12	0.2
SEPTEMBER 92																															
Riviere des prairies			3.1					10.7		2.8						3.2	1.2	3.8			15.1	7.6				4.1	2.9				
Ste Genevieve			35					35		6.5						0.4	2.4	[illegible]			17	6.2				6	3.6				
McTavish			[illegible]	[illegible]				33.4		8.2								1			6	[illegible]				[illegible]	5.2				
Dorval			[illegible]	0.2				25.6		5.2							[illegible]	1.8			6.5	7.2				3.5	3.5				

Note: All values are in mm

Table C.2. (cont'd) Available Daily Precipitation Volumes (Gauthier and Mercier, 1993).

OCTOBER 92	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
Riviere des prairies				0 3			0 2	0 2	25 6	0 2	3	5 8				13 7					3 6	1 2	1	0	8						
Ste Anne De Bellevue									16 7	13 6	2 4	4 7																			
Ste Genevieve									38 8		1 2	1 6				1 0			3 2	3 8	0 6	0 6	2	3 4		1 2					
McTavish									40		2 2	2				8 6			6	0 6	2 1		3 6	6 3							
Dorval									36 4		2 4	2				19 4			4 2	0 4	3		4 2	4 6							
NOVEMBER																															
Riviere des prairies		24 1	0 2	5	2 9					7	4 5	15									4	9	9 4	3 9		10					
														11																	
Ste Anne De Bellevue		9	33 2	4 4	4 2	0 7				4 8	6 3	10	2 5				0 7				4 3		12 6		2 6	10 6					
Ste Genevieve		23 2	0 4	6 8	4 8					9 6	3 6	9 6									5	8 6	5 6	4 2		9 8					
																1	8 6														
McTavish		2 2	3 8												4 3		1 6			1 6	2 8	1 1	10 4		2 2	8 7					
Dorval		5 6	25	5 1	4 6	0 2				5 6	5 6	7 2	2								3	2	10 6	0 4	3 6	9 4					
														0 6	11		2 2														
DECEMBER 92																															
Riviere des prairies		1															4 2		5												1
	1					1 6																	1 4								1 5
Ste Anne De Bellevue	0 7		1 1														1 6	2		4 5				2 2	1 1				0 8		1 1
Ste Genevieve	0 6	0 8														1	5 4		4										4		4
	2					0 2														1 6			1 6		2	0 6					0 6
McTavish	1						1 1										2 7	0 9		7 1				3 2	1				2 6		
Dorval	1		0 4													0 6	4 4		0 4	4 4									2 2	0 5	5 1
	0 6			0 2			1													1		0 8	2	0 6					1 2		0 6
JANUARY 93																															
Riviere des prairies				30 1																		7 3		12 9							
					4 8										1 8												1 8	6 6		2 8	12 8
Ste Anne De Bellevue																															
				40	26 5																										
McTavish																															
	1 5		1 1	39 2	31 5			2 5					11 5	1 3						1 3		3 8	2	10 1	0 8		1	1 2	5 5		8 8
Dorval			2 4	25 8	25 4																	13	1	9							
	1		1		2 4	1 4		1 8					10 4	0 6	1 4	0 4	1 2						0 4	0 2	0 6		1 4	2 4	4 4		1 8

Note: All values are in mm.

Table C.2. (cont'd) Available Daily Precipitation Volumes (Gauthier and Mercier, 1993).

FEBRUARY 93	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
Riviere des prairies					1 2		2.6					15 4	10			9 4					13	1 4									
Ste Anne De Bellevue												1 4	21 6	1 1		10 2	3 1			1 6	2	4	0 9	0 9							
McTavish	0 8				2.1								29 6	1 5		8 1	4 2				0 9	8	1 5		0 9	1 2					
Dorval	0 2			0 2	3 2		0 2	1 4		0 4		3	32.2	1		10 6	1 8		0 4		3 2	6 6	1 8	0 4							
MARCH 93																															
Ste Anne De Bellevue					2			1 6	3 3	3	4 1		12.1	4 6		0 6	1				7 1										
McTavish					2 1		4 9	1 1	2 6	3 2	5 1	0 7	18.3	6 6		2.7	2 6	2 1	1 7		3 5	3 3							1 3		
Dorval		0 4			5 4	0 2	0.2	2 4	2 6	4	2.8		31 2	10		1	1 4 0 8			1 8	6 4										
APRIL 93																															
Ste Anne De Bellevue	18.4	5 3		0.7						18	2 1	0 9	1 2			5 8	7 8			3 3	14 5	33 8	12.4		11 3						
McTavish	28.7	4 1	1 3	2.3					1 6	5 5	1 5	5 4				10 6	14 2		3 6	12.9	16	26 4	16 8		13 3	1 2					
Dorval										15 8	1 2	1 2				9	9 8		5 6	11 8	14 4	21 6	6 6	0 2	13 4						
	31 2	2 6	1	0 2																		0 8	5 8								
MAY 93																															
Ste Anne De Bellevue					3 5	24 3						2 9	1 6		5 7	0 7			4	1 6	4 9			15 1	1 7		0 6				13 4
McTavish					3 5	25 4						0 8	1 3		3 4	0 8			0 6	4 2	4 1			21 9	2 1	0 8			1 7		22 5
Dorval					7 4	22 8						2 4	0 6		3 6				4 4	4	3 4			18 7	0 4	0 6	0 2	0 2	[illegible]		[illegible]

Note All values are in mm

APPENDIX D

Sample Calculations

Table D.1 Average Daily Mass of Fluoride in the MUC Raw Wastewater between June 1992 and May 1993

Date	June	July	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May
1	0.14	0.30	1.67	0.10		0.59		0.75				0.33
2	0.09		0.70	0.04		0.80		0.83				0.27
3	0.10	0.38	0.69			1.56		1.45				0.09
4	0.14	2.90	1.72	0.10		1.03	1.11	2.97				0.30
5	0.12	0.49	1.38			0.56						
6	0.37	1.32	0.64	0.09		0.53		1.08				0.16
7	0.14	1.56	0.58	0.03		0.66		1.10				
8		2.48	0.70			0.36		1.32				0.09
9	0.14	1.36	2.05	0.15				1.15				
10	0.14	0.84	1.57	0.22		0.93		1.18			1.89	0.03
11	0.16	0.64	2.47	0.18				1.31			0.31	0.10
12	0.08	0.49	1.60	0.91				3.06			0.58	0.08
13	0.14	1.34	1.61	1.05				1.36			0.17	0.05
14	0.24	0.56		0.67				1.46			0.96	0.01
15	0.01	0.59	0.34	0.72		1.15		1.11			0.51	0.11
16	0.27	1.40	1.95	0.49		0.60					0.47	
17	0.22	1.98	0.73	1.01							0.22	0.03
18	0.02	0.94		1.15		1.21	1.78				0.37	0.04
19		0.75	1.08	0.60		0.80					0.71	
20				0.17		1.03					0.25	
21				0.82		1.59						
22				2.67		1.17						0.05
23	0.19		0.72	0.48	0.68							0.02
24	0.20	1.35	0.21	0.53	0.15						0.25	
25	0.11	1.14	0.10	1.59	0.54	1.26					0.13	0.03
26	0.43	1.37		2.35	1.04						0.26	
27	0.46	1.06	0.43								0.16	0.15
28	0.36	0.51	0.35		0.52		1.19				0.03	0.09
29	0.37	0.73	0.21		0.62						0.50	0.08
30	0.87	0.68	0.17		0.86						0.36	0.16
31		1.11	0.18		0.74		1.59					0.19

Note All values are in metric tonnes

Table D.2 Fluoride Concentrations in Dry Precipitation as Measured from the Calibration Curve Based on Electrode Readings (between June 1992 and May 1993)

Date	June	July	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May
1		0.160		0.100		0.020				0.190		0.220
2				0.080				0.390	0.410			
3	0.005								0.290	0.250		0.290
4	0.005									0.370		0.210
5				0.130			0.460					
6			0.100						0.760			
7				0.005				0.300				
8						0.040						0.310
9	0.040			0.060			0.410	0.860	0.340			
10	0.060						0.400	1.140				0.290
11	0.005			0.090			0.530	0.310				0.020
12			0.210	0.200			0.560	0.820				
13				0.720			0.410					
14	0.050			0.370			0.400				0.360	0.150
15	0.040	0.120	0.520	0.005			0.760		0.400	0.220	0.240	
16	0.010											
17	0.020											
18	0.030					0.040		0.190			0.100	0.005
19				0.005				0.690				
20				0.005								
21							0.310					
22												1.750
23			0.240	0.020						1.200		0.040
24			0.140	0.070						1.140		
25		0.290	0.140	0.200						1.690		
26	0.050							0.220		1.400		
27	0.060								0.390	1.220	0.090	
28		0.210							0.360	1.090	0.260	
29		0.090									0.250	
30		0.150								1.110		0.440
31					0.130					0.920		

Note: All values are in mg/l

Converting the fluoride concentrations (mg/L) shown in Table D.2 to specific fluoride mass (kg/km^2) requires information data related to:

(1) the volume of deionized water used to rinse the collector, in order to collect the dry fallout, and
(2) the surface area of the collector.

The concentration transformations are best illustrated by a sample calculation. Taking, for instance, the value on July 1st, 1992:

<u>Fluoride concentration</u> = 0.16 mg/L (as shown in Table D.2. This was determined from the calibration curve, based on the electrode reading)

<u>Volume of deionized water</u> = 0.1 L (as used daily by the technicians to rinse the collector in order to collect the dry fallout)

Then,

<u>Mass of fluoride in the collector</u> = 0.016 mg or $0.016*10^{-3}$ g

<u>Diameter of collector</u> = 8 in = 20.32 cm or 0.2032 m

<u>Area of collector</u> = $\pi d^2/4 = 0.03243$ m^2

Hence,

<u>Specific mass of fluoride</u> = $0.016*10^{-3}$ g per 0.03243 m^2
or, 493.38 g per 1 km^2
or, 0.493kg/km^2.

This value is shown in Table 4.8, for July 1st, 1992.

APPENDIX E

Site Specifications of Groundwater Wells

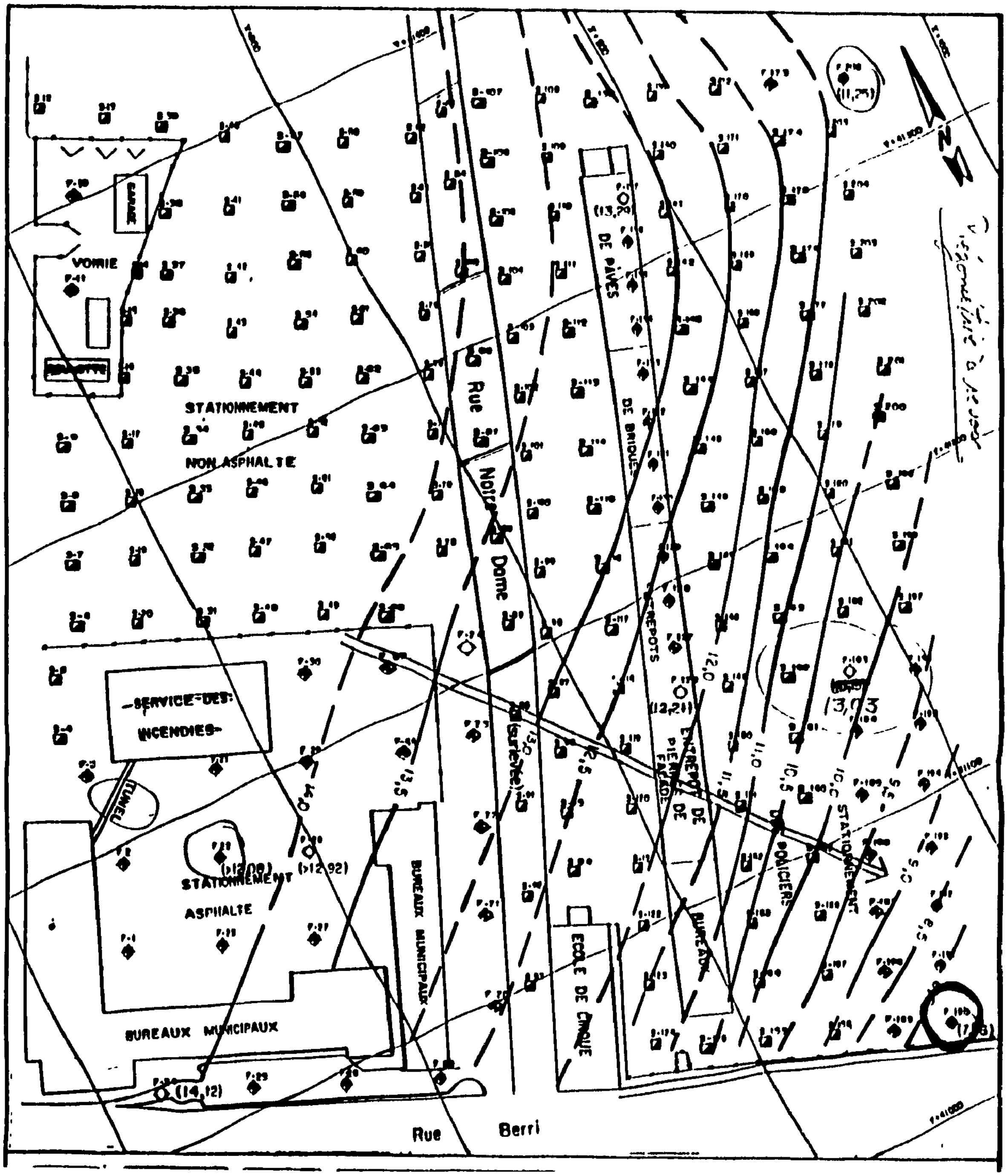

Figure E.1. Site Location of Groundwater Wells at Faubourg Québec.

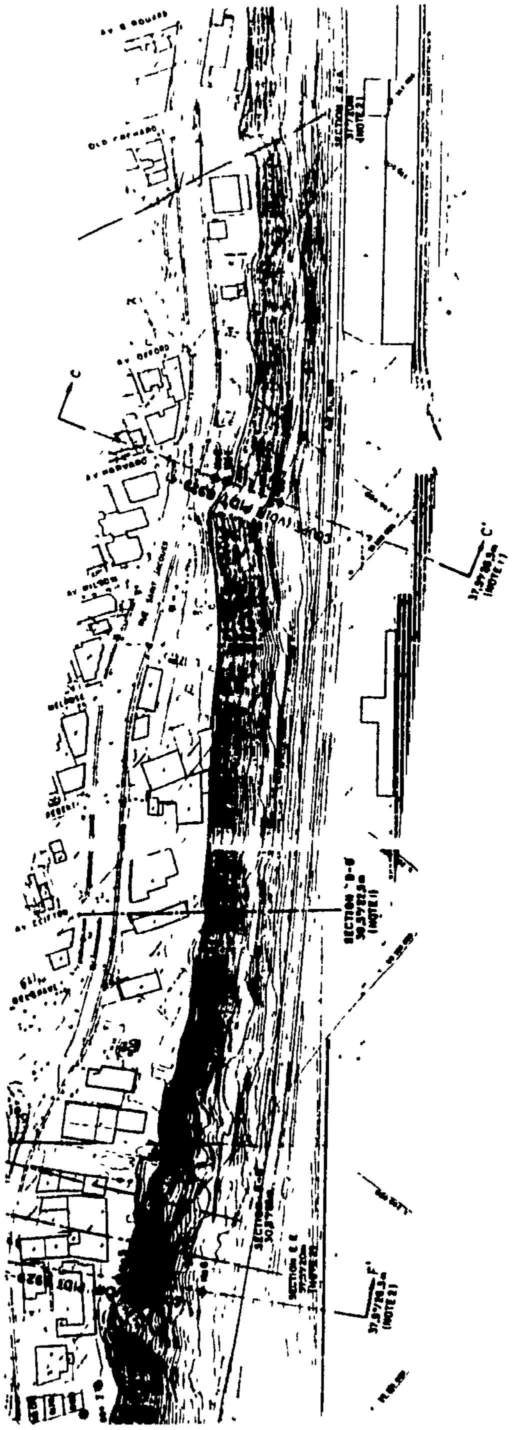

Figure E.2. Site Location of Groudwater Wells at Falaises St-Jacques.