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A BIOMONITORING STUDY TO DETECT ATMOSPHERIC FLUORIDE IN EGYPT: PASSIVE BIOMONITORING

BY

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ABSTRACT

The Egyptian Copper works at Hagar-El-Noatia east of Alexandria produces High fluoride emissions which have been responsible for damage to vegetation in the area close to the plant.

This study attempted to monitor gaseous and particulate fluoride (F) through the use of indigenous plants as bioindicators and bioaccumulators (monitors).

Foliage samples were collected from dominant tree species located up to 3 km downwind from the smelter and, were analyzed after washing for their fluoride concentrations.

Among the native trees studied casuarina was the most efficient bio-accumulator of gaseous fluoride followed by eucalyptus, willow and ficus. High fluoride levels which exceeded the normal background (10 μg F/g) were confined to an area 0.5 km radius.

Visible injury symptoms occurred on relatively sensitive species, native eucalyptus trees and cultivated grape vines were among the most sensitive species sampled.

Fluoride levels in vegetation and air decreased with increasing

distance from the smelter. Atmospheric fluoride concentrations up to 0.8 μg F/m^3 was recorded occasionally near the smelter but concentration generally ranged from 0.3-0.5 μg F/m^3.

A temporal trend was also observed with both gaseous fluoride accumulation inside and particulate deposition on the surface of the foliage with a significant decrease in the summer (June-July) and marked increase in the fall (October-November). Meteorological factors influencing fluoride transport and dispersion were discussed as possible causes for this pattern.

Fluoride accumulation in soil was also monitored and was found to depend on climatic variations.

It was concluded that casuarina and eucalyptus can be considered as good candidates in future biomonitoring efforts and that grapevines should not be cultivated in the area in view of their high sensitivity to F.

INTRODUCTION

Fluoride is a relatively common and abundant element of the earth's crust. It is present in soils as fluoride, and in minerals, such as fluorspar, biotite, apatite, hornblend, and muscovite (USEPA, 1976).

Injury to vegetation has been one of the earliest manifestations of air pollution. The most significant and sometimes devastating effects were attributed to sulfur dioxide and fluoride gases (Heck & Brandt, 1976). Although Heck *et al.* (1973) ranked fluoride fifth in importance after ozone, sulfur dioxide, oxidants other than ozone (peroxyacyl nitrates, nitrogen oxides) and pesticides with respect to the amount of plant damage produced in the U.S.A, fluoride problems have provided more than their share of controversies and litigation throughout the world. Fluoride is also the most phytotoxic of the common air pollutants and it may cause injury to susceptible species at atmospheric concentrations as low as 1 ppb or ca. 0.8 μgF/m^3 (10 to 1000 times lower than those of the other major pollutants) (Weinstein, 1977 and NAS, 1971). Furthermore, fluoride has one unique and important characteristic, it accumulates in plant tissues and ingestion can cause diseases in herbivores (Weinstein, 1979).

Atmospheric fluoride reaches the plant in the form of a gas, particulate matter or gaseous fluoride adsorbed to particles (Murray, 1982). The most phytotoxic and best studied form of atmospheric fluoride is gaseous hydrogen fluoride (HF). Although silicon tetrafluoride (SiF_4) and fluorosilicic acid (H_2SiF_2) may be evolved, atmospheric reactions probably convert them to HF before they reach the plant (Bowen, 1988). Particulate materials form a large proportion of present-day atmospheric pollutants. F seems to be present in particulate matter as either a water-soluble salt, such as sodium fluoride, or a water insoluble complex, such as sodium aluminum fluorosilicate (cryolite). Insoluble forms of F are characteristically low in phytotoxicity, and soluble particulate fluorides are of infrequent occurrence. Therefore, phytotoxicity of atmospheric fluoride is usually attributable to airborne gaseous HF (Murray, 1982).

Most developed countries in the world have acknowledged the seriousness of the bioenvironmental impact of pollutants such as fluoride and set standards to protect the public and its welfare. The "National Ambient Air Quality Standards" (NAAQS) and the "New Source Performance Standards" (NSPS), established by the United States Environmental Protection Agency (EPA) under the "Clean Air Act" (1971) and their subsequent amendments, are examples of such precautions. However, such guidelines were not set for HF in the Egyptian Law of the Environment (Law 4/1994) and the Prime Ministerial Decree No.: 338/1995. The establishment of air quality standards for protection of vegetation and other living systems depends on the availability of suitable information about the criteria of plant susceptibility to the air pollutant in question. Economical losses in yield and/or quality of our crops due to air pollution go often undetected except in few cases where some monitoring was performed. Also, these losses can be seldom related to one or more specific air pollutants with any degree of accuracy and certainty.

Industrial processes which utilizes fluorine containing material can be potential sources of atmospheric fluoride. In the manufacture of aluminum, alumina is dissolved in molten cryolite and reduced electrolytically. Both cryolite and fluorite, which is also present in the process, contain fluoride and are added to lower the bath melting point. In the electrolyte cell fluorine is evolved in gases such as hydrogen fluoride (HF), or as particulates matter such as fluoride salts (USEPA, 1976 and Pickering *et al*, 1988).

The Egyptian Copper Works is situated at Hagar El-Noatia in the east sector of the city of Alexandria. This industrial plant has long been suspected as a major source of HF pollution in the area. The main industrial activity is the melting of crude aluminum blocks in two large smelters each with a 20-30 tons capacity. The smelters are alternatively operated on a 24hr continuous basis and both cryolite (Na_3AlF_6) and calcium fluoride (CaF_2) are used in the melting process (personal communications). Owing to the fact that no strict environmental control measures are demanded or enforced, as yet by the Egyptian Law for the Environment (1994) each of the two aluminum smelters possess only a 25 m high stack, which means that the gaseous plume from the stack could reach the ground at a distance of about 265 m from the smelter according to calculations using the "Gaussian Plume" equation and the Pasquill categories (Moore, 1977).

The area surrounding the plant supports a variety of both native and cultivated tree and crop species, in addition to halfa which borders the banks of El-Mahmoudia Canal and all the drainage canals in the area.

Field surveys are the most valuable means of periodically assessing the status of vegetation in an area where air pollution is a potential or real matter of concern (Tonneijck, 1989; Mignanego *et al.*, 1992; and Gimeno *et al.*, 1995). The field survey attempts to answer the question: Is air pollution a potential or real matter of concern in the study area? or alternatively - Does this area have a significant air pollution problem?.

Many variables affect the design of a field survey. The type of emission source (point, line, or area source), the nature of the pollutant emitted (gaseous or aerosols etc.), the meteorological and topographic conditions existing in the study area, and the type of vegetation (farmland, forest, annual or perennial crops etc.) (Skelly *et al.*, 1979). The establishment of a monitoring and surveillance program for air pollution can be a difficult and costly operation as it often involves expensive instrumentation for physical or chemical analysis of air (Tonneijck & Posthumus, 1987).

Some pollutants, among which is fluoride, can be monitored by alternate methods, such as the measurement of accumulation in plants or animals or by visual assessment of plants known to be sensitive (biomonitoring). Plants have been universally used in field surveys to determine the existence, the accumulation and the phytotoxicity of fluoride both as indicators and as monitors around industrial sources (Laurence, 1982; O'Connor & Horsman, 1982; Dongu *et al.*, 1985; Bowen, 1988; Innes & Boswell, 1990; Vike & Habjorg, 1995; Klumpp *et al.*, 1996; and Katoh, 1998). An "indicator plant" is one, which exhibits clear-cut injury symptoms when exposed to phytotoxic concentrations of a specific pollutant or pollutant mixture, while a monitor plant (also defined "accumulator plant" in some literature) is a plant used for qualitative and quantitative control of environmental pollutants. Monitor plants could be either "passive monitors" (one that exists in the ecosystem already), or "active monitors" (one that is introduced into the ecosystem) (Arndt, 1982 and Manning, 1993). Those plants are characterized by their ability to accumulate the pollutant compound without changing its chemical nature by metabolism, with the result that the pollutant may be analyzed in the plant material after some time by physical/chemical methods. It is therefore possible with accumulator plants to both identify and quantify a pollution burden (amount accumulated/period of exposure). The use of plants as bioindicators and biomonitors (accumulators) has been thoroughly documented. Several reviews exist on the subject (Mannig & Feder, 1980; Posthumus, 1982, Steubing & Jager 1982; and Tonneijck & Posthumus, 1987).

This study was prompted by the need for more realistic and nationally applicable guidelines for the existing and subsequently the acceptable levels of the air pollutant fluoride in Egypt ones, which would protect our natural resources. It aimed to establish through biological monitoring, the relationship between the distribution and concentrations of fluoride in the air, plants and soil, and fluoride emission from a stationary industrial source (the aluminum smelter). The investigation had the main objective to establish a complete biomonitoring network including monitoring sites positioned in the direction of the prevailing winds and containing both native and cultivated local species to carry out the following tasks:

a. To determine existing levels of fluoride in vegetation and ambient air and soil in the area

b. To identify fluoride levels arising from the existing industrial source of fluoride

To investigate temporal and spatial variations in vegetation fluoride content and possible causal factors.

MATERIAL AND METHODS

1) THE STUDY AREA:

A) The topography:

The study area east of Alexandria is mainly a flat region dominated by the "El-Mahmoudia" canal and consists of both semi-rural housing district on both banks of the canal and cultivated land in "El-Sabahia" region further to the south and to the south east.

B) The vegetation:

The natural vegetation of the region is varied. Apart from the halfa, a coarse grass growing at the water edges, there are eucalyptus, casuarina, ficus and willow trees of which some are spontaneous and some are cultivated dispersively all over the study area. The region located south and south east of the study area has, in addition to the above native species, no other permanent vegetation of economic significance, but consists of a very dynamic agricultural area. Part of this cultivated land is the experimental farm of the Faculty of Agriculture, Alexandria University. Two or three different crops are raised in this region each year according to the tri-cycle rotation system in the area in which field and row crops are rotated with sod crops to maintain productivity.

C) The climate:

The climatic characteristics of the area are low rainfall and considerable seasonal and diurnal temperature changes, with sunshine occurring throughout the year. The climate is basically biseasonal, with winter lasting from November to March and summer from May to September with short transitional periods intervening. The rainfall occurs largely in the winter and consists of 8 - 15 cm annually. The mean monthly temperature in the area vary from 14.1 2 C in January to 29.9 C in July, and the mean monthly relative humidities vary from 60.9 in January to 80.3 % in July (Meteorological Dept., 1991). Wind direction may vary from a northwestern direction to a northeastern one especially during winter months. Nevertheless, the most frequent wind direction recorded over the city of Alexandria throughout the year was the northwestern direction. Prevailing winds have moderate speeds throughout the year.

2) THE ALUMINUM SMELTER:

The "Egyptian Copper Works" in Hagar El-Noatia is presently the chief supplier of aluminum sheets to other companies. Giant aluminum blocks, which were previously produced by electrolytic reduction from Bauxite (Al_2O_3), an aluminum oxide imported from Australia, at the "Aluminum reduction Plant" in Nagaa Hammady/upper Egypt, are melted in smelters for production of aluminum sheets.

The aluminum is dissolved in molten cryolite (Na_3AlF_6) for the electrolytic reduction. In addition to cryolite, the melt usually contains calcium fluoride (CaF_2), which is used to lower the melting point below 1000 C. It is therefore to be expected that the gaseous emissions from the aluminum smelter would include, in addition to carbon monoxide (CO) and carbon dioxide (CO_2), silicon tetrafluoride (SiF_4), hydrogen fluoride (HF) and particulate fluorides (Weinstein *et al*, 1990). Each of the two smelters operating at Hager El-Noatia possesses a stack of 25 m height. According to calculations using the "Gaussian Plume" equation and the Pasquill Stability Categories, the plume emanating from those stacks would reach the ground level at a distance of about 265 m from the smelter (Moore, 1977).

3) THE FLUORIDE MONITORING PROGRAM:

A) Selection and distribution of the study sites:

The design chosen for this study was the radial design previously described by Skelly *et al.* (1979) and Krupa and Kohut (1976) for a continuous point source (Figure 1). The study sites were established always on the southeast radial transect from the source which according to the meteorological data received in 1991, is the direction of the most frequent wind blowing. Three preliminary monitoring sites were selected to start the study in 1991. Sites at distances of 1000, 2000 and 3000 m downwind from the source on the chosen transect were selected in order to offer the same type of permanent vegetation cover (trees mainly) and to be truly representative of the surrounding area.

The three monitoring sites in 1991 were abandoned in the more detailed study conducted in the 1992 season, owing to the fact that fluoride concentrations in vegetation samples recorded during 1991 were considerably lower than the anticipated fluoride levels calculated on the basis of the amount of HF emitted from an aluminum smelter of such capacity. Six new sites were established in 1992 following the results of the Guassian calculation. The exact height of the stacks at the smelter revealed that the maximum anticipated ground level of fluoride from the plume of the smelter occurs at approximately 265 m downwind in the SE direction.

The monitoring sites selected were positioned at distances of 280, 300, 440, 500, 720, 780 m downwind from the source. Care was given to selection of sites containing more than one of the permanent vegetation species (trees mainly) under study whenever possible as well as easy accessibility by major or minor roads. The site 3 km downwind was treated as a control site in 1992 because very low fluoride concentrations comparable to fluoride content of normal foliar tissue were recorded at this site during 1991.

B) Biological monitoring:

1- Sampling of indigenous tree species:

In the 1991 survey, two tree species were used as passive bioaccumulators of fluoride, *Eucalyptus* sp. and *Casuarina* *cunninghamina*. In the case of eucalyptus, *E. rostrata* was sometimes substituted for *E. citriodora* at some of the monitoring sites under study.

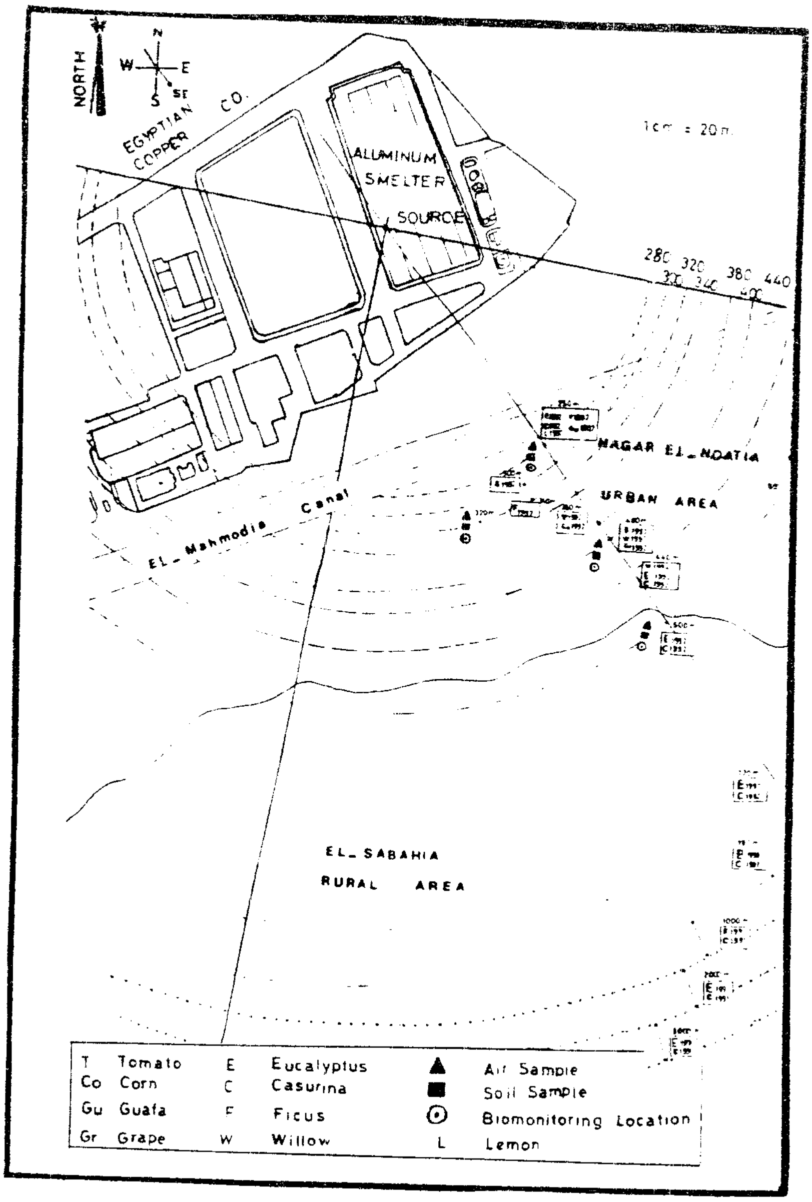

Figure (1): A blow up map of the study area surrounding the aluminum smelter showing the sampling sites during 1991 and 1992 seasons.

The 1992 experiment included more plant species; *Ficus nitida* and *Salix babylonica*(Weeping Willow) were used for sampling purposes on the sites where they could be found.

Vegetation sampling was conducted on a weekly schedule during the period from June to December in 1991 and from March to December in 1992.

At each sampling period, freestanding trees of the above species were selected for sampling at each site so that there is unobstructed exposure to the prevailing wind. Leaves were collected from each tree by removing eight small branches representing the four quadrants above and below a horizontal medial line and on both sides of a vertical medial line. Leaves (branchlets in the case of casuarina) taken from the eight branches (at least 3 from each) were combined to make one single sample. Each leaf sample from a tree consisted of no fewer than 24 leaves and was considered to be representative of leaves of different ages and from both sides of the tree, the side facing the prevailing wind from the smelter and the side away from it as recommended by Weinstein *et al.* (1990).

2- Analysis of vegetation samples:

It was previously reported that fluoride could exist in the plume from an aluminum smelter in a gaseous form as hydrogen fluoride (HF) and silicon tetrafluoride (SiF_4) or in a particulate form. Only the gaseous form could be absorbed by the leaf tissue of a plant through the stomata. Consequently, particulate fluoride may accumulate on the leaf surface by dry deposition. Therefore plant samples were washed in a very mild (5% v/v) solution of triton X-100 in deionized water prior to the leaf analysis in order to ensure a meaningful estimate of fluoride accumulation by leaf tissue. On the other hand, the fluoride concentration in the washing solution was analyzed and recorded as an estimate of the amount of particulate fluoride deposited on leaves.

Plant leaves were washed briefly (30 sec) in the detergent solution then rinsed in 3 changes of deionized water. The rinsing solution was changed three times and then pooled together, agitated thoroughly, and a sample was measured for its fluoride content. The washed leaves were air dried for 2-3 hr then oven-dried in a forced air oven for 24-48 hr at 80°C before they were ground in a stainless steel mill to pass through a 40-mesh sieve. Fluoride in leaf tissues was determined by the potentiometric method described by Lodge (1989), using an ion selective electrode (ISE model Orion 9409 connected to a digital pH meter. 0.5 gm of leaf samples were mixed with 10 ml TISAB (Total Ionic Strength Adjustment Buffer), reading were recorded several times and averaged over a 5 minutes period. F was calculated using a sodium fluoride standard curve.

C) Air quality monitoring:

Air samples were collected using a volume air sampler of 45 l/min capacity adjusted to draw one l/min air through a fluoride-absorbing filter.

The filters were prepared by impregnating Whatman filter paper No.4 in a solution of 5% (w/v) of sodium bicarbonate. The filter papers were then oven dried for 24-48 hrs at 80°C and kept in dry polyethylene bags until used (AOAC, 1980).

Air sampling followed the same schedule of plant sampling on a weekly basis. At each sampling occasion the air was drawn through the filter for 5 hrs; then the filter was dismounted and taken back to the lab for analysis.

Analysis of air samples:

Filter papers were soaked in 5 ml of 1/2-strength Total Ionic strength Adjustment Buffer (TISAB) for 1 hr before total fluoride was determined using the potentiometric method (Lodge, 1989).

D) Soil sampling and analysis:

Soil samples were collected during the 1992 experiment at all sites on a monthly basis. Several subsamples were collected randomly over a large area using a soil corer of 2 cm diameter. Subsamples contained surface soil and soil up to a depth of 5 cm. The subsamples were pooled together for each specific site to make a composite sample of about 1/2 kg. The composite samples were then dried in a forced air oven for 24-48 hrs at 80 C and pulverized in a mill. Aliquots (3-4) were taken from each sample and analyzed for extractable fluoride by the potentiometric method using an Orion fluoride specific ion electrode as recommended by Pickering *et al.*, 1988.

RESULTS AND DISCUSSION

1. Monitoring Fluoride in Indigenous Plants:
The 1991 monitoring program.

Three preliminary monitoring sites were selected at this stage of the survey. The sites were all situated on the SE downwind direction from the smelter at distances of 1000, 2000 and 3000 m. It was evident from the 7 months monitoring effort (Figures 2 & 3), that fluoride accumulation in both species of plants used as biomonitors (casuarina and eucalyptus) was lower than the levels anticipated on the basis of fluoride emissions from an aluminum smelter of such capacity. Nevertheless casuarina showed a higher mean of fluoride accumulation (40.9±14.1 μgF/g) than Eucalyptus (26.4±7.8 μgF/g) at site 1000 m.

At the two other sites, 2000 and 3000 m, F content of the foliage was much lower with means of 16.3±7.8 and 6.9±1.3 μgF/g respectively for casuarina and 15.1±4.3 and 6.7±1.1 μgF/g for Eucalyptus. The normal F concentration, which occurs in foliar tissues, was estimated to be 10 μgF/g (ppm) or less (Vike & Habjorg, 1995). Accordingly, site 3000 m was considered at the end of the 1991-monitoring season to be a control site for background levels of fluoride.

The conclusion drawn from this preliminary survey was that high levels of fluoride accumulation in vegetation are confined to an area within approximately 1 Km from the aluminum smelter. On the basis of this deduction new study sites were selected for the 1992-monitoring program.

The 1992 monitoring program

In this phase of the study, 6 new sites were selected on the SE transect (280, 300, 440, 500, 720 and 780 m) the position of which in

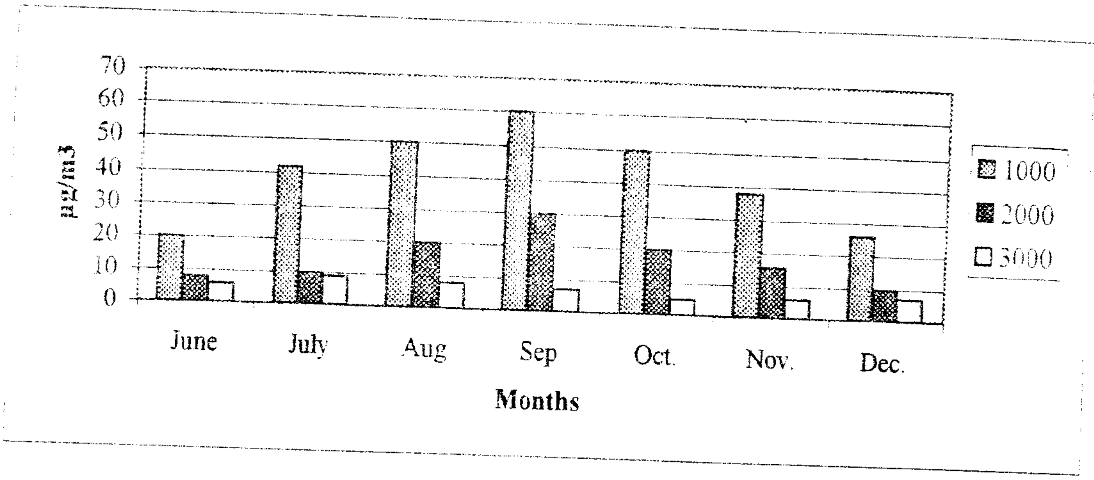

Figure (2): Fluoride content of casuarina branchlets (µg F/g) from June to December 1991

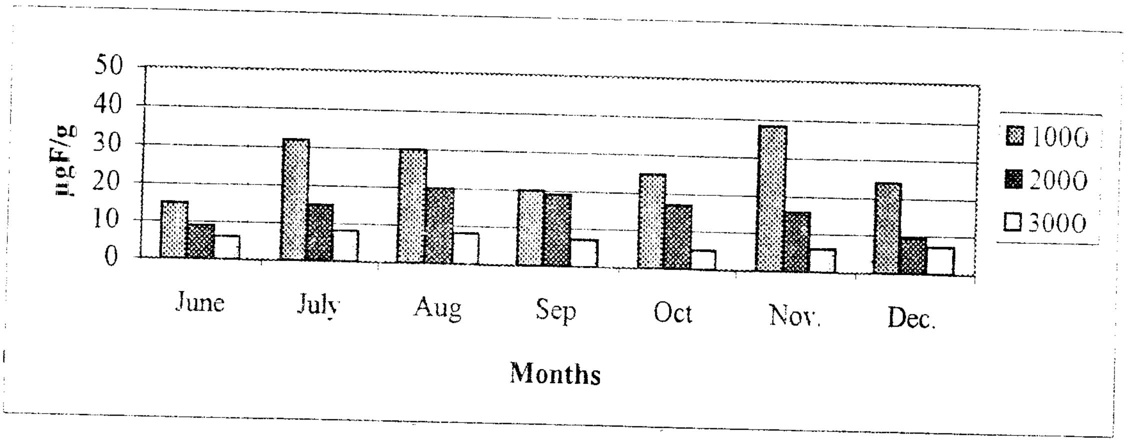

Figure (3): Fluoride content of eucalyptus leaves (µg F/g) form June to December 1991.

accumulator of all species sampled. Average F levels in branchlet tissues from casuarina trees over a 10 months period was 352.8 ±136.3 μgF/g dry weight. Eucalyptus and ficus accumulated less F than casuarina (288.3 ±85.2 and 70.3 ±12.1 μgF/g, respectively) as shown in Figures (4, 5, and 6). Comparable data were reported by Harrison (1983) with poplar leaves at a 250 m distance from a phosphate-fertilizer plant. However only eucalyptus trees showed marked signs of fluoride injury in the form of tip and margins chlorosis and necrosis. This indicates that eucalyptus was more sensitive to F than casuarina. This was in agreement with the work of O'connor and Horsman (1992), and Bowen (1988). The sensitivity of eucalyptus to F also explains the lower levels of F accumulated by the leaves (Peterson, 1993). The most tolerant species are often the most efficient accumulators of fluoride. The likely explanation for this is that when the sensitive species are injured (metabolically or physiologically) by a given dose of F, continued absorption and accumulation are reduced. Moreover, the threshold for injury and the amount of accumulated F would be vastly different in different species (Peterson, 1993).

The data of the particulate fluoride presented in figures (7, 8, and 9) as μgF/l of washing solution allows an approximate estimation of the amount of dry deposition of fluoride forms such as cryolite (Na_3AlF_6), aluminum fluoride (AlF_3), calcium fluoride (CaF_2) and chiolite ($Na_5Al_3F_{14}$) (Murray, 1982). The deposition of particulate fluoride at this station showed the same trend, as the accumulation of gaseous fluoride in the foliar tissues of casuarina branchlets. More F was accumulated on the surface of the green branchlets than any of the other species under study.

The superiority of casuarina as a bio-accumulator may be in part due to its morphology. *Casuarina* spp. possess a very abundant number of needle-like branchlets, which allow for a greater surface area for deposition as well as for gas exchange with the surrounding air.

Dry F accumulation on the surface of casuarina branchlets averaged 3615 ±1317.8 μgF/l of washing solution over the 10 months monitoring period. Eucalyptus followed with an average of 2,291±375.4 μgF/l. Ficus showed the least ability for surface accumulation of F 1,359 ±219.8 μgF/l. Willow trees could not be found for sampling at this site.

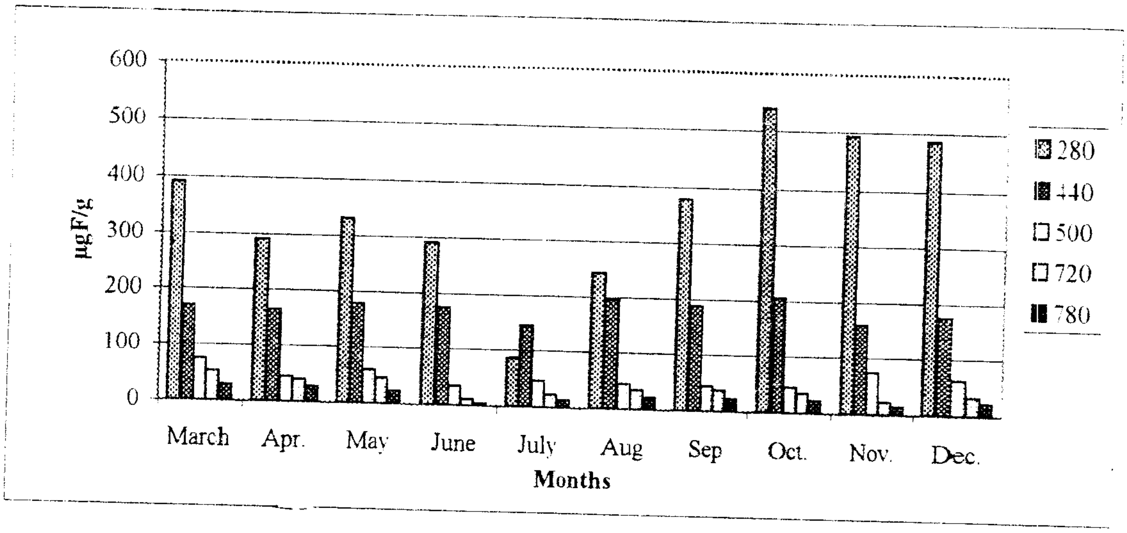

Figure (4): Fluoride content of casuarina branchlets (µg F/g) collected at different study sites in the vicinity of the aluminum smelter from March to December 1992.

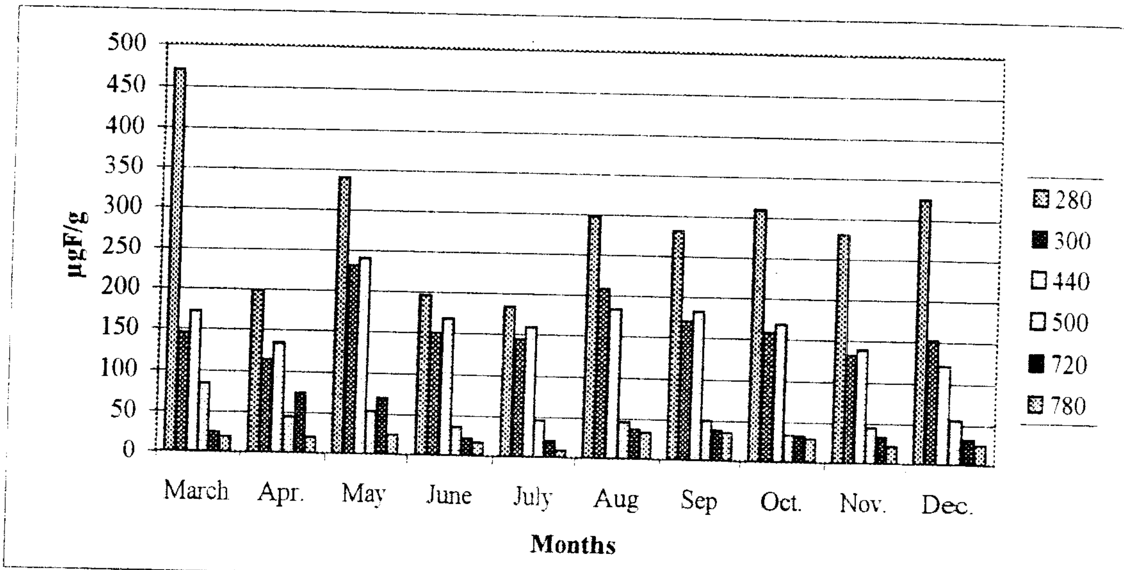

Figure (5): Fluoride content of eucalyptus leaves (µg F/g) collected at different study sites in the vicinity of the aluminum smelter from March to December 1992.

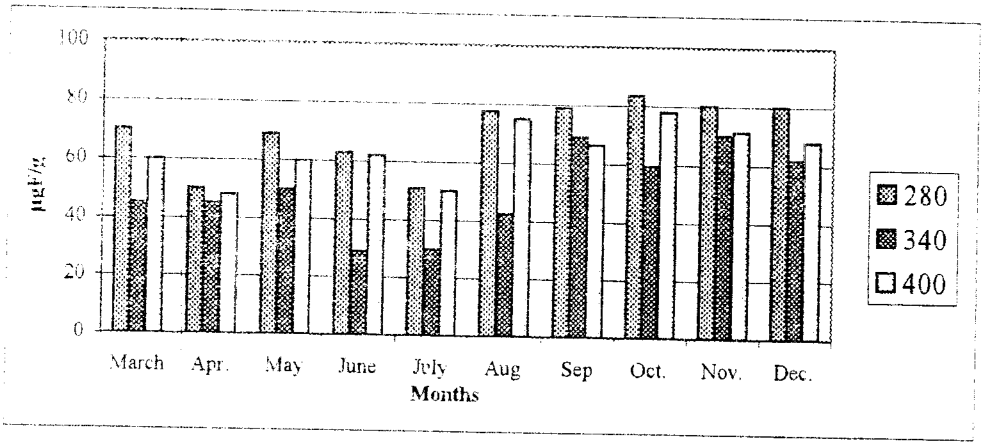

Figure (6): Fluoride content of ficus leaves (μg F/g) collected at different study sites in the vicinity of the aluminum smelter from March to December 1992.

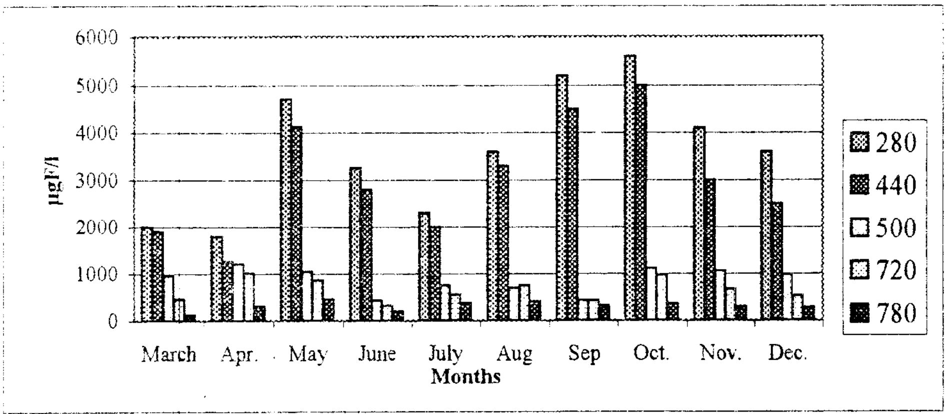

Figure (7): Fluoride concentration in the washing solutions of casuarina branchlets (μg F/litre) collected at different study sites in the vicinity of the aluminum smelter from March to December 1992.

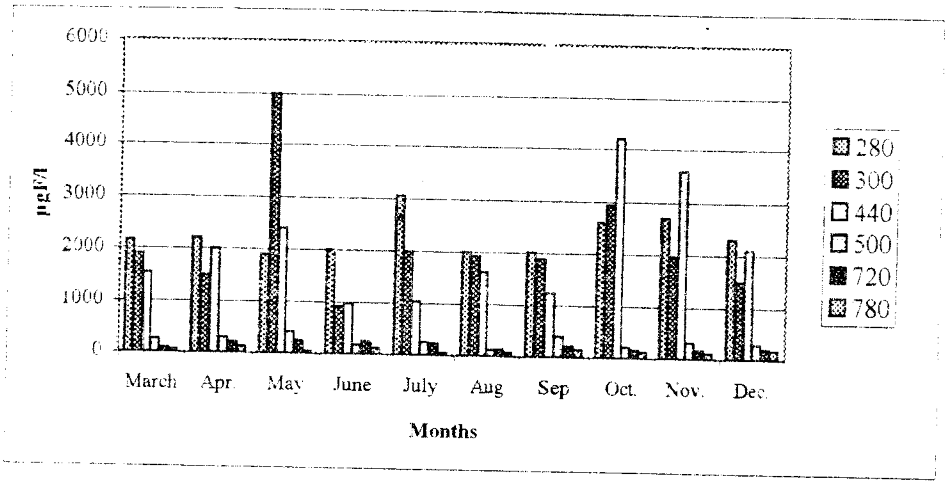

Figure (8): Fluoride concentration in the washing solutions of eucalyptus leaves (μg F/litre) collected at different study sites in the vicinity of the aluminum smelter from March to December 1992.

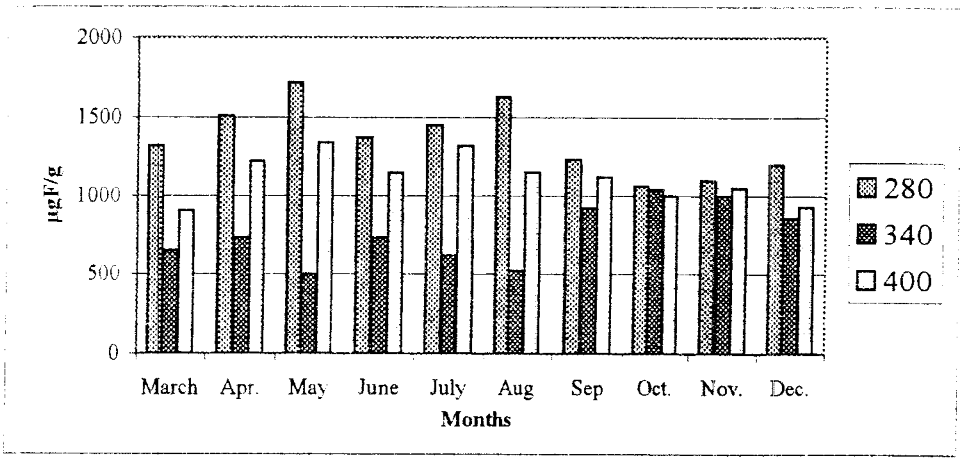

Figure (9): Fluoride concentration in the washing solutions of ficus leaves (μg F/litre) collected at different study sites in the vicinity of the aluminum smelter from March to December 1992.

<u>Site 300 :</u>

This site was only partially in the downwind direction. At this distance from the smelter, the only freestanding trees were eucalyptus at 300 m and ficus at 340 m. The trees were positioned more towards the south than the southeast transect. Consequently the content of the leaves of both species studied were considerably lower than those recorded at site 280 and to some extent even lower than those recorded farther away from the smelter at sites 400 m and 440 m (Figures 5 and 6). F content of the leaves ranged from 230 µgF/g (Eucalyptus-May) to 29 µgF/g (Ficus-June) with an average of 160.5 ±34.4 and 50.2 ±14.6 µgF/g for both species respectively. It is evident that eucalyptus was a significantly superior accumulator of gaseous fluoride than ficus.

Dry fluoride deposition at this site was also higher on eucalyptus leaves than on ficus leaves (Figures 8 & 9). The amounts of fluoride particulates on ficus leaves (757.1 ±191.7 µgF/l) were considerably lower than those observed at site 280 (1379 ±224.9 µgF/l) as well as at site 400 (1118.8 ±149.3 µgF/l) which is a more distant site from the smelter. This decrease in dry deposition may be due to the fact that ficus trees at this site were away from the general prevailing wind direction (SE). However, eucalyptus trees at 300 m did not show a similar decrease in particulate fluoride levels (2152 ±1121.9 µgF/l) when compared to the 280 and 400 sites (2646 ±1135.8 and 2068 ±1079.3 µgF/l respectively). The only effect was that due to the distance from the smelter.

<u>Site 440</u> :

All the species under study were sampled at this station. Ficus leaves collected from trees at 400m distance in the SE direction were considered a part of this site. Willow on the other hand could only be sampled at this site and was absent at all other sites of the monitoring program, therefore samples were collected from willow found at 400m distance in addition to those samples taken from the actual monitoring station at 440m.

Casuarina accumulated the largest amount of gaseous F in the range of 206.7 µgF/g (October) to 146 µgF/g (July). At this site, the species arranged in descending order in term of efficiency as gaseous F station at 440m.

Casuarina accumulated the largest amount of gaseous F in the range of 206.7 µgF/g (October) to 146 µgF/g (July). At this site, the species arranged in descending order in term of efficiency as gaseous F accumulators were as follows: casuarina, eucalyptus, willow then ficus with averages of 177.1 ±17.8, 166.1 ±32.9, 99.4 ±22.4, 63.9 ±9.9 µgF/g respectively (Figures 4, 5, 6 and 10). Willow leaves sampled at 400m accumulated higher gaseous F than those sampled at 440m (Fig. 10). This decrease in F content of the plant tissues was a function of the increased distance from the source.

Similar data were observed with particulate fluoride. Casuarina had also the highest surface F deposition of all the species studied at this site (1168.1 ±152.9µgF/L) (Figure 7).

It was evident from this study that ficus (Figures 6 and 9) was the least successful of the tree species selected as bio-accumulators for either gaseous or particulate fluoride. This could be due to the waxy surface of the leaves, which in the case of particulate fluoride would, to some extent, decrease the chances of particulate adsorbance onto the leaf surface and also makes gas exchange more difficult. In addition, it could increase desorbance and wash out of the accumulated particles from the leaf surface and thus allow for loss of accumulated fluoride.

Willow on the other hand accumulated a fair amount of particulate F externally (Figure 11). The average of dry deposition was 1469 ±196.2 and 1207 ±121.1 µgF/g for willow sampled at 400 and 440m distances in the SE transect respectively.

<u>Sites 500, 720 and 780:</u>

Only casuarina and eucalyptus were existent at these sites. Data presented in Figures 4 & 5 show that F content of the tissues in both species followed the same trend of accumulation observed at the sites nearer the smelter, with casuarina being the superior accumulator of gaseous fluoride. Concentrations of fluoride decreased with increasing distance from the smelter. At site 780 the levels of F in the foliar tissues did not exceed, but were actually lower than those recorded in the previous season (1991) at 1 Km distance from the smelter and averaged

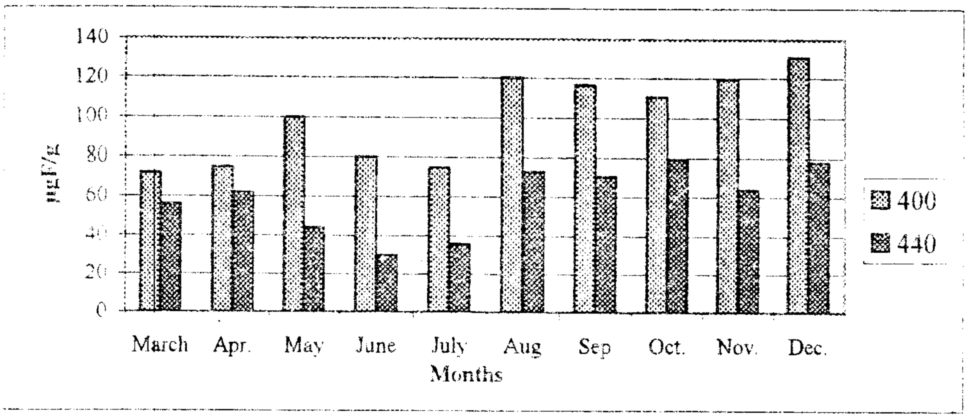

Figure (10): Fluoride content of willow leaves (μg F/g) collected at different study sites in the vicinity of the aluminum smelter from March to December 1992.

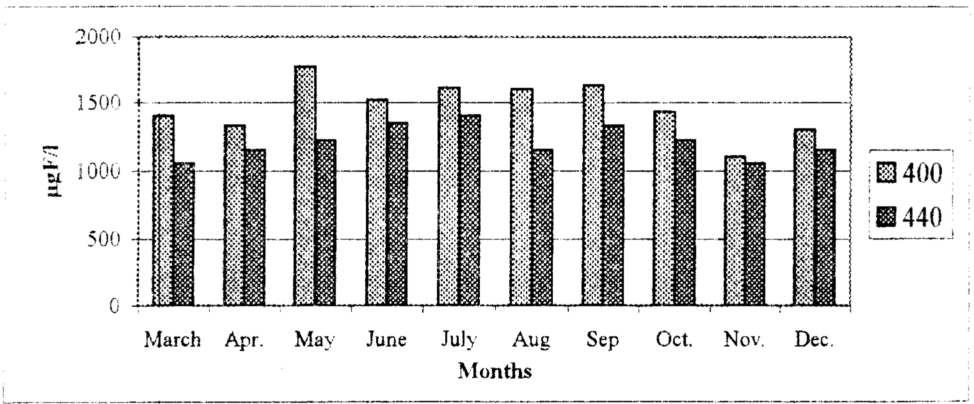

Figure (11): Fluoride concentration in the washing solutions of willow leaves (μg F/litre) collected at different study sites in the vicinity of the aluminum smelter from March to December 1992.

distance. Casuarina branchlets accumulated significantly higher F on their surfaces than eucalyptus leaves.

B. Spatial distribution of fluoride in tree species

The general spatial trend of the survey was a decrease in vegetation-fluoride levels with increasing distance from the aluminum smelter. Gaseous fluoride accumulation was highest at site 280 m followed, in descending order, by the levels at sites 440, 300, 500, 720, 780, and 1000. Levels at more distant sites were at or below the threshold for accumulation and were considered normal background levels (O'connor & Horsman, 1982 and Vike & Habjorg, 1995). Vegetation at the sites situated to the south of the smelter showed lower F accumulation than sites positioned in the SE direction (downwind direction) since the NW was established as the direction of the most frequent wind prevailing into the area according to the meteorological data obtained from the Egyptian Meteorological Dept. (1991). This data supports the belief that the most frequent dispersion of F in the plume emitted from the aluminum smelter occurs towards the southeast direction throughout the year. The highest fluoride levels in the form of particulate fluoride were also recorded at the site (280 m) downwind from the smelter where the maximum ground level from the plume was expected by calculations from the "Gaussian Plume".

C. Temporal variation of fluoride in tree species:

Gaseous as well as particulate fluoride accumulated by all the tree species under study at all sites followed a temporal trend of decreased levels during the summer (June and July) and increased levels in the fall (September, October and November). A correlation between this annual trend of fluoride accumulation by vegetation and the annual fluctuation in wind speed and direction and other environmental factors could be established.

Wind velocity is a major factor influencing the horizontal over the vegetation in the downwind direction (US-EPA, 1976). The reduction in wind speed during the month of June (4.1 m/sec) and July (3.6 m/sec) coincided with a noticeable decline in vegetation-fluoride levels both within and on the external surfaces of the leaves. Conversely the increase in wind velocity during the fall months (5-6 m/sec) was concomitant with higher levels of both gaseous and particulate fluoride. Similar results were reported by O'connor and Horsman (1982), Bowen (1988) and Vike & Habjorg (1995). As wind grow stronger, fluoride emissions are transported faster and to greater distances downwind. In addition, higher wind speeds allow a greater ability to carry particulates (El-Shazley, 1989 and El-Shazley *et al.* (1990). Summer decline in foliar fluoride concentrations could also be attributed to restricted fluoride uptake caused by stomatal closure due to the increased rates of transpiration. A similar phenomenon was reported where summer water deficits caused the stomata to close and subsequently related to a restricted fluoride uptake (Bowen, 1988).

Another seasonal trend was observed with most tree species at most monitoring sites but was more evident and consistent with data concerning particulate fluoride than with gaseous fluoride levels. Levels of external fluoride deposition recorded in the early spring, mainly March, and during December were usually below the annual average at any site and with most species studied. It is a fact that monthly means rainfall increases markedly and gradually from December to February. The decrease in external fluoride levels may have been caused by rain washing of particulates fluoride from the leaf surfaces. The low levels of particulates recorded in March are easily explained as a result of the continuous wash out of surface fluoride by heavy rains, which the area receives during winter months. Values of particulates fluoride accumulation recorded during December were only slightly below average probably because rainfall is at a minimum during November and December which causes only a partial wash down of dry deposition.

The above discussed temporal trends were true for casuarina (Figure 7), eucalyptus (Figure 8) and willow (Figure 11). On the other hand, ficus did not closely follows the same pattern.

Gaseous fluoride, was not consistently lower in March and

December, but decline in F content of the leaves at the end of the rainy winter season could be linked to the leaching out of absorbed fluoride from foliar tissues (Bowen, 1988).

2. Monitoring Fluoride in Cultivated Species:

Data presented in Figure (12) show the F content of some plant species, which were cultivated in the area of the aluminum smelter at the time of the survey at different sites. Among the plant species sampled grapes accumulated the greatest amount of gaseous F despite the fact that they were located at site 400 m. The mean F content of grape leaves (271 µgF/g) was higher than the amount accumulated by casuarina and eucalyptus at this site (177.1 and 166.9 µgF/g) respectively.

Guava and lemon sampled at site 280 accumulated 175.7 and 165.6 µgF/g respectively, thus they were less efficient than casuarina or eucalyptus but superior to willow and ficus. No comparison could be drawn for tomato and corn, which were both sampled at site 380 because they existed for a short period of time only and could not be compared with tree species with permanent leaf cover which could absorb F throughout the year.

Grape (at site 400) and guava (at site 280) leaves showed similar rates of external deposition of particulate F (3343.3 and 3875 µgF/l respectively) to casuarina. Lemon (at site 280) on the other hand showed lower dry F deposition (2941.7 µgF/l) as was recorded with eucalyptus. The same temporal trends observed with the native tree species discussed above were followed by the cultivated species. Gaseous as well as particulate fluoride accumulation in and on the leaves showed a marked declined in July (Summer) and a significant increase in September, October and November (Figures 12 and 13). In addition, dry fluoride deposition decreased considerably in December as a consequence of rainfall.

3- Monitoring Fluoride in the Air

The results of the air sampling are summarized in Figure (14). From these data a temporal variation in gaseous fluoride in the air can be established showing increased levels in the fall months (October, November and December) and decreased levels in the summer months mainly in June and July. This annual fluctuation in F concentration in the air was in agreement with the temporal trends observed with fluoride

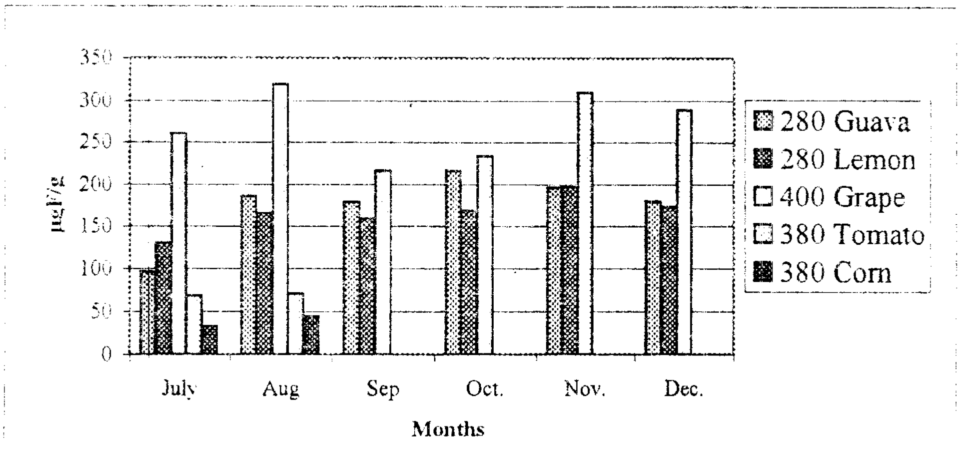

Figure (12): Fluoride contents of leaf samples from different plants (μg F/g) collected at different study sites in the vicinity of the aluminum smelter from March to December 1992.

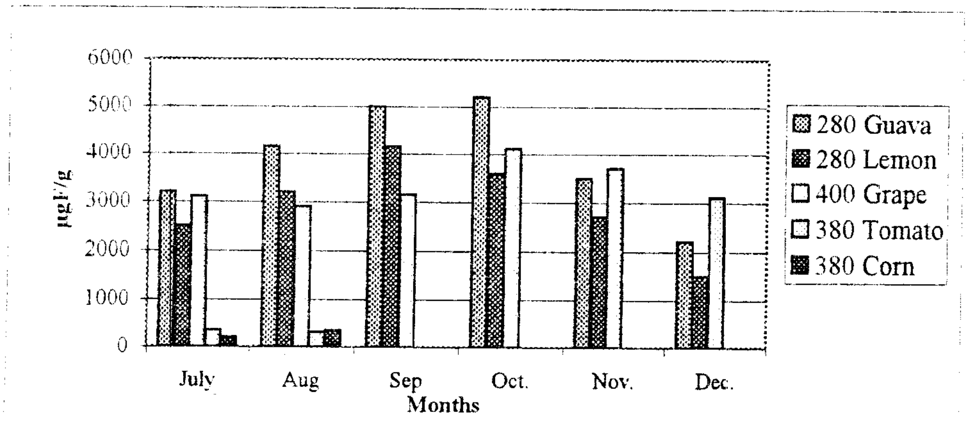

Figure (13): Fluoride concentration in the washing solutions of different plants (μg F/litre) collected at different study sites in the vicinity of the aluminum smelter from March to December 1992.

contents of the leaf tissues of biomonitoring tree species, previously reported. It can also be ascribed to annual variations in meteorological factors such as wind speed and atmospheric stability and temperature.

Wind speed is concerned mainly with the horizontal movement of the air containing the pollutant, and thus affects the horizontal dispersion of the pollutant. Lower values in wind speed are normally recorded in the summer. From table 1 wind velocity values were 4.1m/sec. for June and 3.6 m/sec for July. Conversely, higher wind speeds are observed in fall months (5-6 m/sec.). The reduction in wind

velocity in the summer coincided with deceased levels of F in the air. This could be simply explained as a result of decreased horizontal dispersion and transport of gaseous fluoride from the source over the study area. In the fall, stronger horizontal movement of the air results in higher levels of gaseous fluoride (Harrison, 1983). Atmospheric stability is also a very important factor affecting vertical mixing and vertical pollution dispersion. A good deal of the atmospheric turbulence is associated with thermal turbulence, in which mixing is enhanced due to temperature variations between different altitudes (US-EPA, 1976).

The seasonal change in temperature affects the rate of vertical mixing and dispersion of a pollutant. In summer months when the sun is shining, the surface of the earth is warmed effectively. This heat is then transferred by conduction to the atmosphere near the ground, increasing the air temperature as a result. This warmer, less dense air then rises and the cooler, denser air of the upper atmosphere descends. Any pollutant emitted into the air under these conditions is caught in this vertical mixing and dispersed rather rapidly. The result of the convectively unstable air in summer months (June, July) was in fact concomitant with low levels of gaseous F in the air (Figure 14). On the other hand, the stability of the air prevailing in fall months due to the cooled weather resulted in more convectively stable air conditions causing less vertical mixing and less dispersion, and thus higher levels of gaseous fluoride in the air (De Temmerman *et al.*, 1986).

4-Monitoring Fluoride in the Soil:

The background values for F in the soil (14-45 µgF/g) within the region where the smelter is located were comparable to normal levels found by other investigators (Polomaski *et al.*, 1982 and Fuhler, *et al.*, 1982).

The levels of fluoride in soil samples collected at 4 of the survey sites (Figure 15) showed an inverse relationship with distance from the aluminum smelter in the direction of the prevailing winds. Fluoride concentrations in the soil collected at site 320 (123.1 μgF/g) were lower than those collected at a further site from the industrial plant (185μgF/g at site 400). As previously mentioned, site 300 was partially shifted from the SE direction and positioned more towards the S direction, in that case less atmospheric deposition of particulate fluoride would be expected at this site.A temporal trend could be observed from these data. Fluoride levels in soil samples collected during the fall and early winter (September-December) were the highest recorded data throughout the study period, whereas values for June were lower than average. This pattern was similar to the temporal pattern of fluoride levels in vegetation previously discussed. The amount of total fluoride in soil is mainly a function of dry deposition of F particulates carried by the air from the smelter (Murray, 1982). The high wind velocities which can be associated with the fall season cause higher amount of suspended F particulates to be transported downwind over the area (El-Shazely, 1989 and El-Shazley *et al.*, 1990), allowing for more dry deposition on the soil surface. The inverse is true for the summer season when the lowest wind speed values are usually recorded. Another significant source of soil fluoride is the wet deposition of particulates as well as gaseous fluoride which can be ascribed to the rainfall washing both forms of F from the air (Murray, 1982) and also the accumulated particulate fluoride from plant leaf surface. Increases in soil fluoride due to wet deposition were noticed in the present survey especially during December when the rainy season begins and the month of March which marks the end of the rainy season in Egypt. The fact that those two temporal increases in fluoride concentration in soil coincided with a drop in the accumulation of particulate fluoride on the leaf surfaces of all the plant species under study, further supports the idea that wet deposition is an important factor in increasing soil F levels.

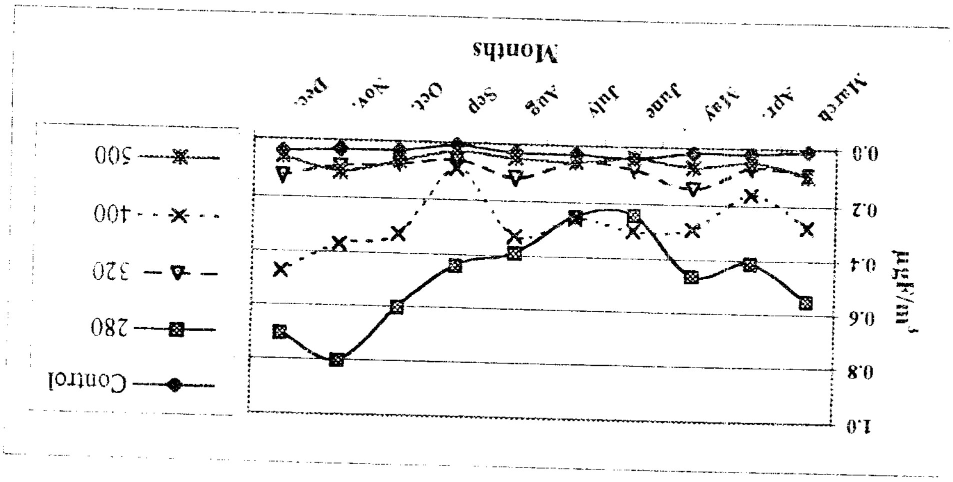

Figure (14): Monthly average of fluoride concentration (μg F/m³) in air samples collected at the study sites in the vicinity of the aluminum smelter during1992

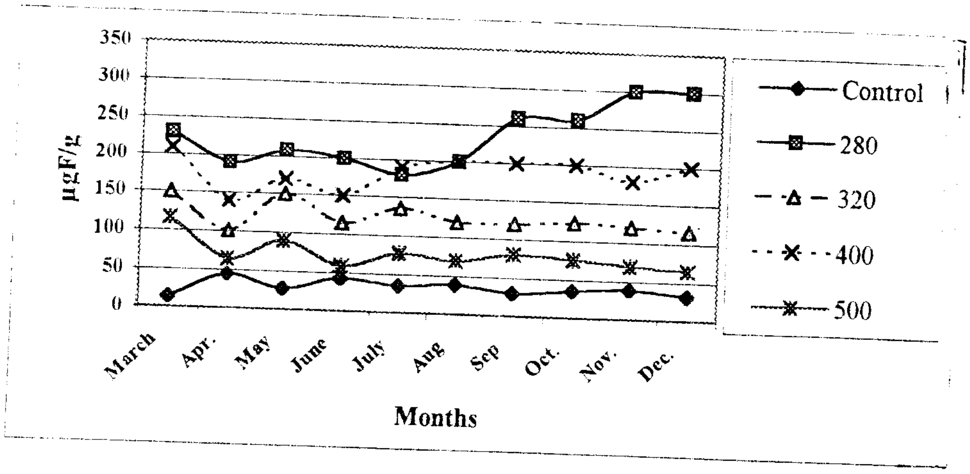

Figure (15): Monthly average of fluoride concentration (μg F/g) in soil samples collected at the study sites in the vicinity of the aluminum smelter during1992.

A major input of F into the soil may result from decaying plant tissues (mainly leaves) which contained elevated fluoride concentrations as a result of uptake from the atmosphere. Fluoride may pass into the soil following leaf abscission fallout decay and incorporation into the soil. However, this source of soil F was not very likely in our survey. Tree species found in the study area were mostly evergreens which lose their leaves very gradually and at a very slow rate throughout the year, unlike the deciduous trees which shed all of their leaves at the end of the fall season and which are native in colder and temperate climates.

CONCLUSION

The fluoride concentration reported in this study were generally in agreement with earlier reports in other studies of fluoride in vegetation, air and soil in similarly polluted area in various parts of the world.

This study shows that the present survey design, involving sampling of vegetation within a 1 Km radius around the smelter is adequate in view of the dispersion of the plume from the smelter's stacks. However, a few more sites are needed in the upwind direction from the smelter to allow the measurement of fluoride in the air monitoring into the study area and in vegetation not subjected to plume exposure for reasons of comparisons. Also this could rule out or confirm the existence of another source of fluoride pollution to the area.

Casuarina and eucalyptus are highly recommended candidates for additional biomonitoring efforts in the area. Ficus and willow on the other hand, could be sampled in only a few sites and are less successful biomonitors than casuarina or eucalyptus. Therefore, they could be eliminated from any future-surveying program without reducing its effectiveness.

Grape in the area was damaged badly and suffered losses in yield and growth. It is our recommendation that grape should not be cultivated in the area in the vicinity of the smelter and that other crops showing high tolerance to fluoride injury should be considered.

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الملخص العربي

دراسة لرصد ملوث الهواء فلوريد فى مصر باستخدام النباتات كوسائل رصد بيولوجية

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** قسم الدراسات البيئية – معهد الدراسات العليا و البحوث – جامعة الإسكندرية

ينبعث من مداخن مصانع شركة النحاس المصرية التى تنتج الألومنيوم كميات عالية من ملوث الهواء الفلوريد يعتقد أنها تسببت فى الإضرار بالنباتات المنزرعة فى المنطقة حول المصنع.

هدفت هذه الدراسة التى تمت خلال عامى ١٩٩١ و ١٩٩٢ إلى تقدير مستويات الفلوريد الغازى و الصلب من خلال برنامج رصد للملوث باستخدام النباتات الحولية و الأشجار المستديمة كوسائل رصد حيوى.

تم جمع عينات ورقية من أغلب أنواع الأشجار السائدة و الموجودة فى حيز يبلغ ٣ كيلومتر من المصنع فى اتجاه هبوب الرياح الحاملة لعوادم المداخن ، ثم غسيلها لفصل الجزيئات الصلبة العالقة على أسطحها و تقدير الفلوريد المتراكم بداخل و خارج الأوراق.

وجد أن أشجار الكازورينا الموجودة بمنطقة الدراسة كانت تحتوى على أعلى نسب من الفلوريد يليها أشجار الكافور و الصفصاف و الفيكس على الترتيب. كما أن أعلى تركيزات للفلوريد تم رصدها فى نقط الرصد التى تقع فى حدود نصف كيلومتر من المصنع، و فاقت هذه التركيزات المستوى العادى للفلوريد فى الأوراق و الذى يقدر بـ ١٠ ميكروجرام فلوريد/ جرام.

سجلت أعراض الإصابة بالفلوريد على بعض النباتات الحساسة مثل أشجار الكافور و العنب.كما وجد أن مستوى الفلوريد فى النبات و الهواء يقل مع زيادة المسافة من المصدر. و قد سجلت مستويات فلوريد فى الهواء تصل إلى ٨, ميكروجرام/متر مكعب فى بعض نقاط المراقبة و لكن المستويات تراوحت

غالبا بين ٣, – ٥, ميكروجرام / متر مكعب. كذلك تم تسجيل تراكم الفلوريد فى التربة و علاقة ذلك بالتغيرات الجوية.

لوحظ أن تراكم كل من غاز الفلوريد و الدقائق الصلبة يتغير زمنيا تبعـــا للتأثيرات الجوية و المناخية فى المنطقة ، حيث يقل التركيز فى فصل الصيـــف خلال شهرى يونيو و يوليو و يزداد خلال شهرى أكتوبر و نوفمبر مما يدل على أهمية الأحوال الجوية كعنصر هام فى انتقال و تشتت الفلوريد فى الجو.

أوصى البحث باستخدام كل من أشجار الكازورينا و الكافور كمؤشـــرات للرصد البيئى الحيوى للفلوريد نظرا لكفاءتهما فى امتصاص و تخزين الملـــوث ، كما أوصى بمنع زراعة العنب فى المنطقة القريبة من المصنع بسبب حساســـيته الشديدة للفلوريد.