FLUORIDE ACCUMULATION BY VEGETATION IN THE VICINITY OF A PHOSPHATE FERTILIZER PLANT IN TUNISIA

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SUMMARY: Monthly observations from May through October during the year 2000 on the southwest side of a phosphate fertilizer plant located in the coastal zone of the Sfax region of Tunisia showed that vegetation close to the factory accumulates large quantities of F with variable specific symptoms of toxicity. According to their F content, cultivated species can be classified into five different categories. At the same level of exposure, species with high F content include olive trees (420 µg F/g dry weight), while those with low F content are represented by apricot trees (50 µg F/g dry weight). As expected, F concentrations decreased with increasing distance from the pollution source. Beyond 8 km, they were lower than 30 µg F/ g dry weight. Analysis of atmospheric fluoride revealed a close interrelationship between concentrations of F in the atmosphere and in plant leaves.

Keywords: Airborne fluoride; Almond tree; Apricot tree; Environmental pollution; Fig tree; Olive tree; Phosphate fertilizer plant; Rosebush; Vegetation fluoride.

INTRODUCTION

It is well known that industrial installations producing bricks, phosphate fertilizers, and glass, along with coal-fired power stations and aluminium smelters, are the most important sources of gaseous and particulate fluoride pollution.[1-6] From the 1940s to the 1970s, airborne fluorides, usually in the form of HF or SiF_4, were among the most important air pollutants.[7-10]

Fluorine, unlike sulphur, nitrogen, and even chlorine, is not an essential element for plants. Because the natural occurrence of F in the air is usually close to the detection limit, and plants take up little from the soil, the background concentration in plants is generally quite low (often as low as 1 and usually less than 10 µg F/g dry weight in most species).[7] Since HF and SiF_4 are between 1 and 3 orders of magnitude more toxic than other common pollutants (*e.g.,* O_3, SO_2, PAN, Cl_2, or HCl), relatively small releases of fluorides into the atmosphere can result in extensive damage to plant life.[7,8,11-13]

Gaseous fluorides are absorbed through leaf stomata and move by transpiration into the principal sites of accumulation at the tip and leaf margins,[14,15] where they can cause physiological, biochemical, and structural damage, and even cell death, depending on the concentration in the cell sap.[4,16-19] In addition to direct uptake through their stomata, plants can incorporate fluoride from contaminated soils.[1,20-24] However, in highly polluted areas, direct absorption of airborne fluorides by plant foliage normally masks any soil uptake.[22]

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In Sfax, Tunisia, a phosphate fertilizer factory is the most significant source of F pollution in the atmosphere. Therefore the aim of this work was to evaluate the impact of this air pollutant on plants in the region of the factory. This allowed not only the contamination zones to be delineated, but also the degree of F content in existing cultivated plant species to be determined.

MATERIALS AND METHODS

The study was carried out near Sfax city located 270 km south of Tunis on the northern side of the Golfe de Gabès of the Mediterranean Sea. Sfax accommodates one of the most important industrial complexes in Tunisia. This city is subjected to severe chronic airborne pollutants, among which fluoride compounds emitted by a phosphate fertilizer plant play a major role, where the prevailing winds in this area are mainly from the E and NNE at 2.5 to 5 m/sec.

In order to evaluate the impact of the F pollution source on the environment, we analyzed leaves of plants cultivated in the agricultural region on the SW side of the factory. The five species studied were the olive tree (*Olea europaea*), almond tree (*Amygdalis communis*), fig tree (*Ficus carica*), apricot tree (*Prunus harmonica*), and rosebush (*Rosa agrestis*).

To determine the role of this vegetation in intercepting atmospheric F pollution, leaf samples were gathered from several branches in different parts of the trees and rosebushes. Only leaves in the middle of shoots were taken. Sampling was done during May through October 2000. Samples were taken at distances of 1, 3, 4, 5, 8, 12, and 16 km SW of the factory. Each sampling was repeated 3 times per plant. Control samples were gathered 30 km from the factory. Samples were washed with tap water several times and subsequently dipped into 0.01 M HCl for 5 min followed by thorough washing with deionised water.

Samples were dried in an oven at 80 ºC for 48 hr and ground (<1.0 mm) in a stainless steel mill. For each species a 2-g powdered sample was heating in an oven at 550 ºC until white ashes were formed. After extraction of the ash sample into NaOH solution, F concentrations were determined potentiometrically using a fluoride-specific ion electrode and a reference electrode. For measurement of total F (complexed and free) in solution, the NaOH extract was acidified with acetic acid glacial to pH 5.3 and mixed 1:1 with TISAB buffer. The TISAB buffer contained 57 mL acetic acid, 58 g NaCl and 4 g CDTA per litre, adjusted to pH 5.2 with 6 M NaOH and diluted to 1 L with distilled water.[26]

Atmospheric fluoride concentrations in $\mu g/dm^3$ per day or month were determined from data collected by exposing lime-filter papers to ambient air according to the static method used since 1967 by the INRAT (National Institute of Agronomic Research of Tunisia).

Statistical analyses were performed with the STATISTICA package (Statistical Analysis System, Version 5) using Anova system with Tukey's test.

RESULTS

As indicated in the Materials and Methods, five plant species belonging to four families were sampled during the survey of the area. The characteristic signs of F phytotoxicity were visible in almost all species but to varying degrees. Leaf blade necroses appeared at different times and varied according to the degree of sensitivity of the species. The almond tree and especially the apricot tree began to show signs intoxication beginning in June with respective F contents of 110 and 65 µg/g dry weight as illustrated in Figure 1 for an apricot leaf. These signs appeared by July for the fig tree and the rosebush with respective F contents of 190 and 70 µg/g dry weight. In contrast, the olive tree did not show any morphological abnormalities such as chlorosis, leaf curling, or necrosis.

Figure 1. Damage to an apricot tree leaf caused by fluoride from the Sfax phosphate fertilizer factory.

Mean leaf F concentrations were significantly higher in the polluted sites than in the control area. These concentrations in washed leaves collected 1 km SW of the fertilizer plant show that the rate of uptake differs greatly among the five species during May through October in the year 2000 (Figure 2). The leaf concentration of F varied from 30 µg/g dry weight in the rosebush to 420 µg/g dry weight in the olive tree ($P<0.05$). On the other hand, large increases in the foliar F concentration during the exposure periods were detected each month in all species, increasing significantly from May through October. However, the plants in the control area 30 km SW of the pollution source did not show significant changes in their levels of foliar F.

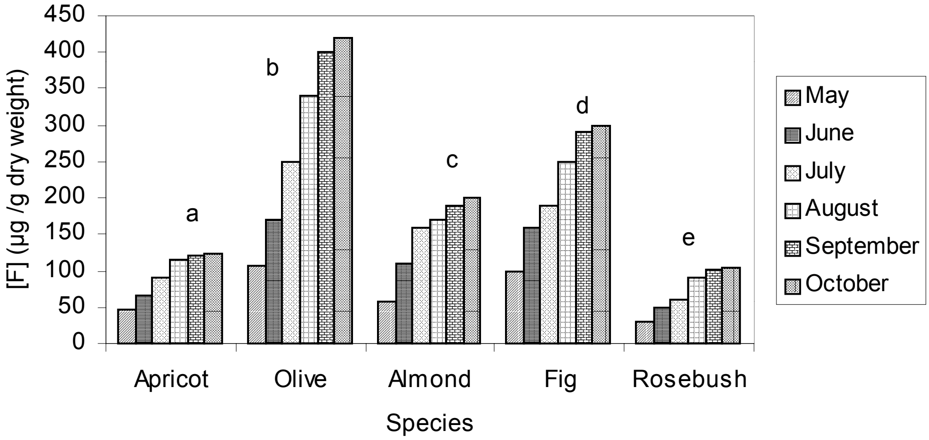
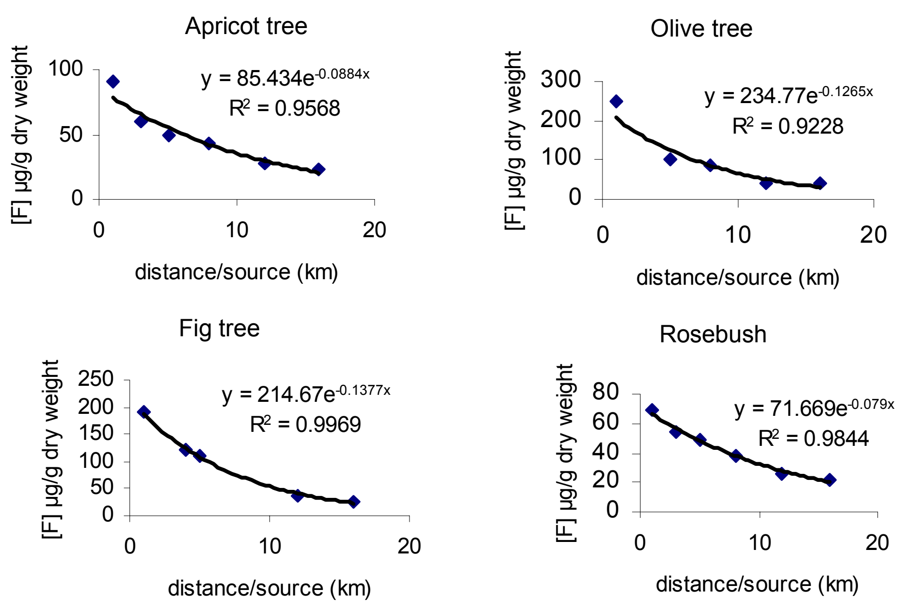


Figure 2. Foliar F content of cultivated species growing 1 km SW of the fertilizer plant during the year 2000. Means with different letters reflect significant differences (P=0.05) using the Tukey test.

The average foliar content of the F in leaves collected at different distances from the phosphate fertilizers is presented in Figure 3.



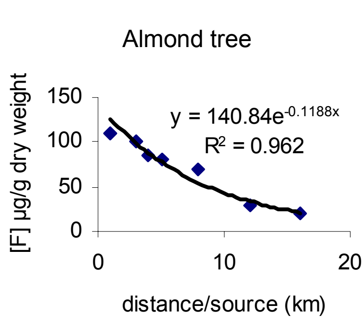


Figure 3. Mean fluoride accumulation in leaves on July 2000 as a function of the distance from the phosphate fertilizer factory.

As expected, the F content in the leaves of the different species decreased exponentially with increasing distance from the factory with a negative linear correlation between distance from the factory and leaf F concentration for each species. The highest accumulation was found, as expected, closest to the fertilizer plant (1 km), where the F accumulation was two or more times higher than at the site 8 km distance. Farther out, F concentrations decreased progressively and reached the values of the control species at a distance of 16 km from the source.

As expected, an inverse exponential relationship was found between atmospheric fluoride concentrations expressed in µg/dm^3 per day and distance from the factory (Figure 4).

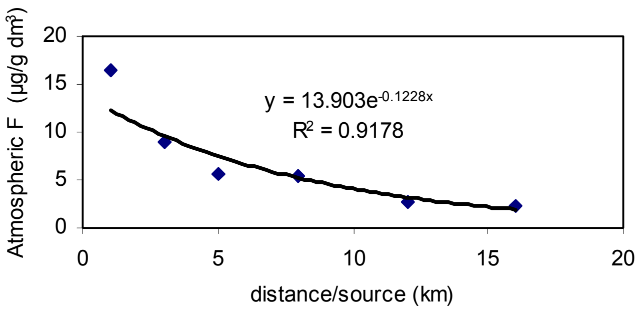


Figure 4. Mean atmospheric fluoride as a function of the distance from the fertilizer factory in the year 2000.

DISCUSSION

Large differences in foliar F concentration were observed among the different plant species. However, critical concentrations for toxicity depend on the kind of species. Leaves of the apricot tree, one of the most sensitive to F toxicity, may become necrotic with 65 µg F/g dry weight. Others plants *e.g.*, the olive tree, can accumulate up to 300 µg F/g dry weight in their leaves without exhibiting any symptoms of F toxicity. Accordingly, we divide the plant species we studied into four classes: apricot tree—highly sensitive, almond tree—sensitive, fig tree and rosebush—slightly sensitive, and olive tree—tolerant. Weinstein and Davison[8,9] report that highly sensitive categories include plants that show visible injury at the farthest distance from the source, while nonsensitive (tolerant) plants show little or no injury even when they are adjacent to the source. Fluoride-induced symptoms have often been described.[8,26-28]

Our results show that F accumulation in leaves differs substantially among the five species studied, with high F content characterizing olive trees. Preferential accumulation of F by olive trees seems to be related to the tendency of this plant to accumulate F. In fact, the height of a plant, interception surface characteristics, roughness, age, and leaf configuration play an important role in the retention of pollutants. Since large differences in fluoride concentrations among different plant species are observed,[4] large variations in the degree of tolerance to F pollution should also be expected.[29]

Some of this variability is due to differences in length of accumulation periods, as well as different mechanisms through which accumulation takes place. Absorption and the accumulation of F are more important in trees with evergreen foliage (olive tree) than in those with deciduous leaves. It was also observed in our work that there was a highly significant correlation between foliar F concentration and atmospheric F concentration up to a distance of 16 km from the pollution source. Similar correlations between atmospheric F concentration and F concentrations in trees leaves and leaf damage have been reported by others.[30-32]

ACKNOWLEDGEMENTS

We would like to thank Mr. Kamel Gargouri for the statistical analysis of the results.

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