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FLUORIDE INJURY IN SOME REGIONAL PLANTS GROWN IN THE VICINITY OF BOZÜYÜK CERAMIC FACTORIES AND FUMIGATION CHAMBER STUDIES

BOZÜYÜK SERAMİK ÜRETİM TESİSLERİ CİVARINDA YETİŞTİRİLEN BAZI YÖRE BİTKİLERİNDE FLORÜR HASARI VE FUMİGASYON ODASI ÇALIŞMALARI

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Within the scope of this study, the culture plants barley (TOKAK) and wheat (GEREK 79) species grown in the agricultural fields nearby Akpınar Region in the vicinity of Bozüyük Ceramic factories, were planted in flowerpots. The barley and wheat seedlings of the plants in flowerpots were exposed to various concentrations of hydrofloric acid (HF) vapour in a fumigation chamber for 1, 2, 3 and 5 hours. Control plants and those exposed to HF vapour were let for growth for 20 days after the treatment. Fluoride accumulation and chlorophyll decay in plant leaves were analyzed quantitatively. Experimental data were used to support the field data.

Bu çalışma kapsamında Bozüyük yöresi Akpınar Mevkiinde yerleşik Seramik tesisleri civarındaki tarım arazilerinde kültür bitkisi olarak tarımı yapılan arpa (TOKAK) ve buğday (GEREK 79) türleri saksılarda yetiştirilerek, fumigasyon ortamı haline getirilen seralarda derişimi bilinen hidroflorik asit (HF) buharlarına 1, 2, 3 ve 5 saat sürelerle maruz bırakılmıştır. Yaklaşık 20 gün süreyle büyümesi izlenen bitkilerin yapraklarında biriken florür miktarı ve meydana gelen klorofil kaybı deneysel yolla belirlenmiş ve elde edilen veriler, arazi çalışmalarını desteklemek amacıyla kullanılmıştır.

Keywords: *Fluoride compounds; Barley; Wheat; Fumigation chamber; Industrial air pollution; Ceramic industry*

Anahtar kelimeler: *Florür bileşikleri ; Arpa; Buğday; Fumigasyon odası; Endüstriyel hava kirliliği; Seramik endüstrisi*

Introduction

Airborne inorganic fluoride compounds are originated from mostly aluminium smelters, phosphated fertilizer factories, combustion of poor quality coal and tile/brick, ceramic, glass and steel works. The average levels of inorganic fluoride compounds in clean air range from 0.003 to 0.006 g/m^3 (0.0023-0.0046 ppm). But these concentration values may increase to much higher levels (0.5-270 g/m^3) around industrial emission sources (7,9).

Gaseous fluorides comprise greater than 50% of the total airborne fluoride around industrial regions. Fluoride compounds may be extremely toxic to plants, affecting growth, photosynthesis, respiration and other plant processes. A number of effects of airborne fluoride on plants, growing around major efficient sources. have been reported in the literature (4, 8, 9, 10). More common ones of these effects, reported, have been visible effects such as necrosis and chlorosis. Gaseous forms pass readily through to leaf stomata, while the particulate forms are deposited on the surface of the vegetation, where, if soluble, are readily removed by leaching and consequently cause less damage (10).

Fluoride is the most phytotoxic of the common air pollutants. Gaseous fluoride enters the leaf through the stomata and moves into the transpiration stream to the principle sites of accumulation at the tip and margins of the leaf, where, should the concentration in the cell sap be sufficient, it may impell cell death (10).

Fluoride affects cellular metabolism in much the same general way, although the fundamental mechanisms naturally differ. All plants contain some fluoride, but too much can be toxic. If fluoride accumulates rapidly, toxic amounts may be as little as 10-20 ppm, above the background concentrations of 1-10 ppm in the leaf. This, of course, applies only to the most sensitive plants. Most plants accumulate 100-200 ppm fluoride and normally concentrate several hundred parts per million in their leaves. For most plants however, accumulation of over 50-100 ppm fluoride can exceed a toxic threshold and alter cell metabolism and structure (5, 6, 10). Granulation, plasmolysis, and collapse of the chloroplasts are the earliest microscopic expressions.

Before this happens though, fluoride affects a number of enzymes and metabolic systems. Plants fumigated with hydrofloric acid (HF) can show changes in organic acids, amino acids, free sugars, DNA and RNA phosphorus, and starch and nonstarch polysaccharides' amounts in the plants before any visible symptoms appear.

The inhibition of an enzyme results in the inhibition of the reaction mediated by that enzyme. Although only one step along a pathway of reactions may be affected directly, the entire process is impaired. Such is the case with photosynthesis which has long been known to be inhibited by fluorides. One mechanism of reduction is in the inhibition of chlorophyll. Fluoride may tie up the magnesium ion, central to the molecule. If larger amounts of magnesium are provided, such inhibition, in vitro, can be offset (5). Fluoride may also act on photosynthesis by interfering with the energy processes that involve adenosine phosphates and nucleotides(10).

Most of the barley and wheat plants in Bozüyük ceramic region showed tip necrosis of tip burn on leaves and glumes. Meteorological measurements of wind direction showed that winds from the northeast, northwest, southeast and southwest are characteristics of the region. The prevailing winds coming from ceramic factories have caused considerable losses. Nearly 15 ceramic and brick factories are located in this area and about 746 ha of barley and wheat fields were affected. Indeed, ceramic and brick factories are sources of inorganic fluoride pollution (7, 9, 10) and marginal scorch of banana leaves caused by air-pollutant fluoride emitted from brick factories has been found in southern Taiwan. Sun and Su (1985) have reported foliage disease of rice plants which has been noticed in Ying Ko ceramic area in northern Taiwan (9).

This study had been intented to expose the effects of inorganic fluorides on barley and wheat seedlings. Ambient gaseous and particulate fluoride concentrations were measured in Bozüyük ceramic area, by then determining fluoride concentrations in plant tissue and reproducing the effects of HF on barley and wheat plants. Additionally, a fumigation chamber was used to establish the effects of inorganic fluoride compounds on barley and wheat seedlings.

Materials and Methods

Ambient fluoride measurements

ASTM D3267-80 procedure (2) was used to sample and analyze atmospheric gaseous and particulate fluorides.

Fumigation tests

Two acrylic plastic chambers (2000 mm x 1200 mm x 1200mm) were constructed and set up in an open area at the Anadolu University's Yunusemre Campus in Eskişehir, Turkey. HF solutions of known concentrations were fed continuously and slowly into a dissipating bottle from a large feeding bottle located on top of the fumigation chamber (Fig. 1).

The solution in the dissipating bottle was conducted into the disc-shaped volatilizing surface through a capillary plastic tube (0.5 mm diameter). The dissipating speed was more or less constant, because the feeding speed was maintained at a higher level than the dissipating speed and the amount of solution in the dissipating bottle was kept at a constant level by an overflow duct. Two 9 cm Ø filter papers (volatilizing surface) were attached to the fumigator so that the HF solution could flow from the upper paper to the lower one and ultimately to the run off tube. Two ventilators were used to maintain the HF concentrations at constant levels throughout the fumigation chamber.

Barley (TOKAK) and wheat (GEREK 79) seeds, provided from Eskişehir Agricultural Research Center, were planted in flowerpots. Barley and wheat seedlings (10 days old) of the variety of TOKAK and GEREK 79 in plastic flowerpots, were exposed to various concentrations of HF vapour in the chamber for 1, 2, 3 and 5 hours. Control plants and those exposed to HF vapour were let for growth for 20 days after the treatment. Experiments were carried out from April to May 1992, under the experimental (internal) physical conditions of 15-18°C temperature and of 72% relative humidity.

Quantitative determination of fluoride

HF vapour in the fumigation chamber was first absorbed in NaOH solution (0.001N), then isolated by Williard Winter Distillation(WWD)method and analyzed by spectrophotometric SPADNS method (3).

Leaf samples were washed under running tap water for 30s, dried at 70°C for 24 h and then ground. ASTM D3269-79 method was used to determine fluoride concentrations in plant leaves (3).

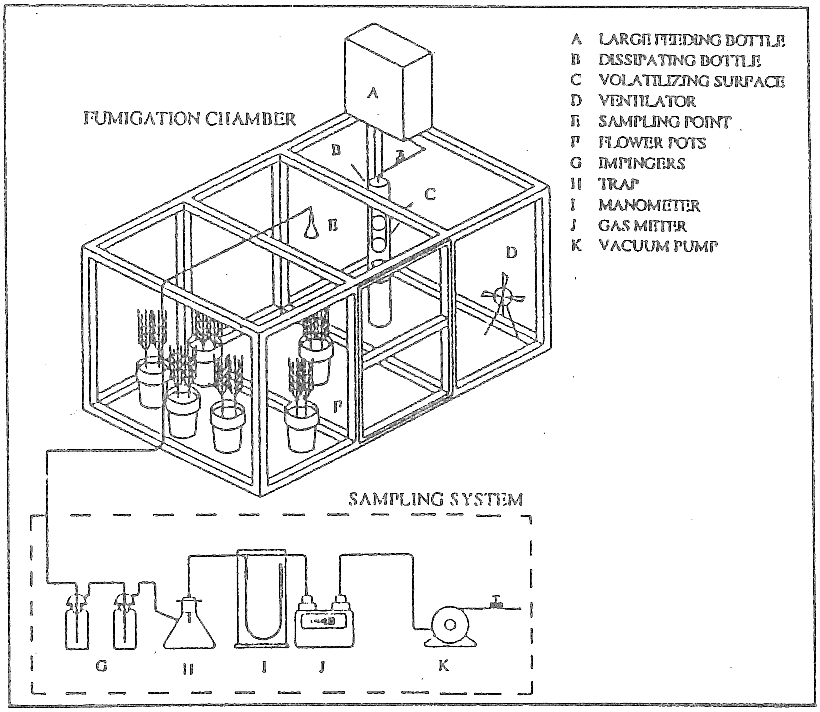

Fig.1. Fumigation chamber and HF sampling system

Table 1.Average ambient inorganic fluoride compounds' concentrations in Bozüyük, Turkey, in 1992

Fluoride compounds	Mean concentrations ($\mu g/m^3$) (*)	Maximum concentrations ($\mu g/m^3$)
Gaseous fluoride compounds	73	270
Particulate fluoride compounds	75	403
Total fluoride compounds	149	149

(*) Arithmetic mean for 4 months

Quantitative determination of chlorophyll

Total chlorophyll, chlorophyll-a and chlorophyll-b components were analyzed by spectrophotometric method (1).

Results and Discussion

Field studies

Monthly average values of the inorganic fluoride concentrations in the vicinity of Bozüyük ceramic region measured during the period of from July to November 1992 are listed in Table 1. The inorganic gaseous fluorides concentrations ranged from 6 to 270 $\mu g/m^3$, with an average of 73 $\mu g/m^3$.

Fumigation studies

Ten - days - old barley and wheat seedlings exposed to atmospheric HF of 238-384 $\mu g/m^3$ (mean 300 $\mu g/m^3$) for 1, 2, 3 and 5 hours in the fumigation chamber developed acute symptomps of tip necrosis-and chronic symptoms of yellowing and mottling 20 days later. These symptoms were similar to those occuring in nature. Control seedlings remained healthy throughout the experiments. Fumigated leaves contained much higher concentrations of fluoride than non-treated leaves (Table 3). Fumigated leaves contained much lower concentrations of chlorophyll than non-treated leaves (Table 4).

Table 2. Fluoride concentrations in barley and wheat tissues collected from Bozüyük

Plant tissue sample	Fluoride concentration ($\mu g/g$)
Barley leaves	273
Barley roots	271
Wheat leaves	284
Wheat roots	285

Fluoride concentration in control barley leaves unexposed to atmospheric HF was 60 μg/gram
Fluoride concentration in control wheat leaves unexposed to atmospheric HF was 85 μg/gram

Table.3. Fluoride concentrations in plant leaves exposed and unexposed to atmospheric HF

Plant leaf	Exposure to HF	Fluoride concentration (μg/g)
Barley	Unexposed 1 hour 2 hours 3 hours 5 hours	63.3 173.5 105.3 111.6 115.2
Wheat	Unexposed 1 hour 2 hours 3 hours 5 hours	87.2 141.5 67 78.1 180.2

Table.4. Chlorophyll concentration in plant leaves with and wihout exposure to atmospheric HF

Plant leaf	Exposure to HF	Chlorophyll concentration (mg/g)		
		a	b	Total
Barley	Unexposed 1 hour 2 hours 3 hours 5 hours	1.150 0.849 1.141 1.004 0.679	0.400 0.217 0.265 0.263 0.205	1.500 1.067 1.405 1.266 0.984
Wheat	Unexposed 1 hour 2 hours 3 hours 5 hours	1.138 0.513 0.826 0.344 0.825	0.324 0.141 0.202 0.093 0.251	1.461 0.653 1.028 0.437 1.075

(a) Fluoride exposed wheat and barley leaves were found to contain more fluoride than the unexposed, both in the field and infumigation chambers.

(b) The symptoms are similar to those caused by fluoride toxicity on other monocothyledonous plants.

(c) Fluoride concentration in barley and wheat leaves increased with increasingseverity of theinjury. There was a 2-3 fold difference in fluoride concentration between healthy and severely injured leaves exposed to HF vapours in fumigation chamber (Table 3). The difference was 4-5 fold in fluoride concentration between healthy and severely injured leaves collected contain much higher fluoride concentrations than non-treated leaves, as expected.

(d) Chlorophyll concentration in barley and wheat leaves decreased with increasing fumigation duration (Table 4).

(e) Fumigation of barley and wheat seedlings with HF induced leaf yellowing, mottling and tip necrosis, similar to those observed in the nature.

(f) Disease-induced leaves were found to contain much higher fluoride concentrations than non-treated leaves, as expected.

(g) Because of the high fluoride content found in the tissues, barley and wheat straws collected from areas nearby ceramic and brick factories are not recommended to be used as animal food (9).

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