RESPONSE OF LOCAL CROPS TO HYDROGEN FLUORIDE POLLUTION EMITTED FROM BRICK KILNS IN THE VICINITY OF PESHAWAR, PAKISTAN

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ABSTRACT: *Aim:* To investigate the impact of fluoride (F) pollution on local varieties of wheat (*Triticum aestivum* L., varieties Pirsabak, Janbaz, and Atta Habib), tomato (*Solanum lycopersicum* L., varieties Sahil, Chinar, and Roma), and clover (*Trifolium repens* L., varieties Shaftal and Barseem, and *Medicago sativa* L. [Alfa alfa]). *Method:* The F levels in the oven-dried leaves of plants grown at F-polluted locations 50–100 m from brick kilns in Urmarh village (UV), Peshawar, Khyber Pukhtunkhwa, Pakistan, and at a control location, distant from any brick kiln industries on a University of Agriculture Peshawar (UAP) research farm, were measured with a fluoride sensitive electrode. *Results:* The three wheat varieties grown at the UV site showed visible foliar injuries and the F levels, on a dry weight basis, were significantly higher ($p<0.05$) in the Pirsabak (9.3 ppm) and Janbaz (9 ppm) varieties compared to the Atta Habib variety (6.66 ppm). The wheat grown at the control UAP site did not show any visible foliar injury, and, compared to the UV site, the F content (2.3–4.0 ppm) was significantly lower ($p<0.05$). The three tomato varieties grown at the UV site showed visible foliar injuries and the F level was significantly higher ($p<0.05$) in the Pahil variety (23.6 ppm) compared to the Chinar (18 ppm) and Roma (11 ppm) varieties. The tomatoes grown at the control UAP site did not show any visible foliar injury, and, compared to the UV site, the F content (2.6–4.6 ppm) was significantly lower ($p<0.05$). The F level in the Shaftal clover variety (50.1 ppm) grown at the UV site was significantly higher ($p<0.05$) F than that in the Barseem variety (44.6 ppm) and Alfa alfa (38 ppm). Compared to the UV site, the F content (14–19 ppm) of the clover grown at the control UAP site was significantly lower ($p<0.05$). *Conclusions:* It was concluded that different cultivars of the same crop can respond differently to fluoride pollution. We found the Pirsabak and Janbaz wheat varieties, the Sahil tomato variety, and the Shaftal clover variety were more sensitive to F pollution than the Atta Habib wheat variety, the Chinar and Roma tomato varieties, and the Barseem and Alfa alfa clover varieties, respectively. We therefore suggest that fluoride-resistant cultivars be cultivated in areas that may be polluted with fluoride.

Key words; Brick kilns; Clover; Hydrogen fluoride; Pakistan; Tomato; Wheat.

INTRODUCTION

The Khyber Pakhtunkhwa province (KPK) is considered to be the leading province in Pakistan for the brick kiln industry. Surveys have shown that Peshawar, Mardan, and Charsadda are famous brick producing cities in KPK. Most of the population in KPK has migrated from remote areas to cities for education and seeking jobs. There is a high demand for bricks in Afghanistan. Brick kiln and vehicular emissions are the major sources of air pollution in the Peshawar region.[1] The brick kiln emissions not only affect human health but also damage vegetation and the ecosystem overall. The local population and livestock living near brick kilns are greatly affected by hydrogen fluoride (HF) emissions that can cause skeletal fluorosis with excess amounts of fluoride in the bones and skeleton, dental fluorosis, and non-skeletal fluorosis. Pregnant women and children are particularly at risk for developing to fluorosis.[1]

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According to Khalid and Mansab,[2] higher concentration of HF are found near coal burning factories such as those in brick kilns areas. Producing bricks in brick kilns involves heating bricks made from fine clay, up to 1,100ºC, and results in the release a high concentration of HF. The majority of the brick kilns in developing countries are situated in the suburban areas adjacent to the cities, and are mostly unauthorized by the government.[3] An ambient air F concentration of 0.1 ppm was recorded in the ambient environment while higher concentrations (9.21–25 mg/kg) were found at brick kilns.[4]

Studies have shown that HF has negative impacts on the yield of wheat crops. Visible foliar injuries to the wheat crop were not observed when the level of exposure, at the primary boot stage, was under 0.9 µg HF/m^3 air. It has been reported that when wheat is exposed to HF, the F is accumulated in the plant's vegetative tissues and is not transferred to the mature seed.[5]

Clover (*Trifolium*) is the main fodder crop in the Peshawar region as well as in Pakistan in general. Our previous study[6] revealed a high F content in fruits and leaves near brick kilns at Peshawar compared to fruit leaves collected from control sites (The University of Agriculture Peshawar, Pakistan, and the Agriculture Research Institute). Therefore, the current study was expanded to other crops in the brick kiln area to examine the negative effects of F on different varieties of the same crops grown in the vicinity of the brick kilns, because different varieties show different responses to air pollution. Clover is considered to be F-sensitive and accumulates a high level of F in its leaves. This significantly high F content in clover in the vicinity of brick kilns may cause fluorosis in local cattle. Wheat is important as the main cash crop of Pakistan with a production of 22 million metric tons/year (MMY). Any significant reductions in wheat yield will have drastic effects on the agricultural economy of Pakistan. Tomato is a widely grown fruit in the region, and an important ingredient for local curry dishes. Many varieties fo clover, wheat, and tomato are widely grown around brick kilns in Peshawar. The area of the brick kiln fields of Peshawar is spread over 15 km^2 which includes a large cultivable area. In addition to clover, the leaves of the wheat and tomato are also consumed as fodder by the local livestock, when the clover season ends.

The present study was based on a field survey of F pollution effects on local crops in the vicinity of brick kilns near Peshawar. Clover (*Trifolium repens*), wheat (*Triticum aestivum*), and tomato (*Solanum lycopersicum*) leaves were collected from the vicinity of brick kilns. The aims of the present study were:

(i) to measure the F content in the leaves of various varieties of clover, wheat, and tomato grown in the brick kiln area (in Urmarh village situated on the eastern side of Peshawar city), and in a control area (a research farm of the University of Agriculture, Peshawar located on the western side of Peshawar away from the brick kiln area),

(ii) to assess the degree of damage to local crops from HF,

(iii) and, for the ultimate benefit of farmers and the local economy, to recommend, if possible, plant varieties which are more resistant to HF air pollution-induced reductions in crop yield.

METHODOLOGY

The collection of the plant samples: The brick kiln field is situated on the eastern side of Peshawar city and spreads over 15 km^2. There are approximately 400–450 brick kilns in the area. Some of the brick kilns have been built in clusters in between the cultivated farms. The leaves of different varieties of clover (*Trifolium repens* L., varieties Shaftal and Barseem, and *Medicago sativa* L. [Alfa alfa]), wheat (*Triticum aestivum* L., varieties Pirsabak, Janbaz, and Atta Habib), and tomato (*Solanum lycopersicum* L., varieties Sahil, Chinar, and Roma), were collected at a distance of 50–100 m from brick kilns in Urmarh village (UV) in the brick kiln area on the eastern side of Peshawar city, Peshawar, Khyber Pukhtunkhwa, Pakistan, and in a control area, a research farm of the University of Agriculture, Peshawar (UAP), located on the western side of Peshawar away from the brick kiln area. These crops were selected because of their economic importance to the farmers and the local economy. Leaves of same size and age of the different varieties of clover, wheat and tomato were collected from all the corners of the selected fields to make a composite sample. The sampling was done from in between a cluster of brick kilns in order to take out the effect of wind direction. Leaves of the three varieties of wheat, tomato, and clover were collected from three plots of the same size from both the UV and UAP sites. The samples were put in a marked paper bag and immediately transferred to the Department of Agricultural Chemistry where they were oven dried at 80ºC for 48 hr. The dried samples were then ground and sealed in plastic polyethylene (PE) bottles to avoid any contamination.

F chemical analysis: The measurement of the total F content of the plant leaves were carried out by the method explained previously.[6-7] One gram of the dried material (80ºC) was ignited overnight at 500ºC in nickel crucibles in a furnace. The ash was fused with 1 g sodium hydroxide using a Bunsen burner. After cooling, the fusion product was dissolved with a few milliliters of distilled water and was transferred into a 50 mL PE flask. 12.5 mL aqueous citric acid solution (340g L^{-1}) and 5 mL hydrochloric acid (conc. hydrochloric acid:distilled water, 1:1, v/v) were added and then the solution was adjusted to pH 6.2 using sodium hydroxide, making up a final volume of 50 mL. Twenty-five mL of this solution was mixed with 25mL of a total ionic strength adjustment buffer (TISAB for the F determination, WTW Wilhelm, Germany). The F content of the samples was measured using a F-sensitive electrode (ISE F 800 DIN, WTW Wilhelm, Germany) coupled to an ion meter (Inolab pH/Ion 735 WTW Wilhelm, Germany). The calibration was made using five NaF standard solutions according to the following equation:

$$C_F = 10^{(E-K)}S$$

Where

C_F	=	the F concentration
E	=	the electrode potential
K	=	the intercept
S	=	the slope of the function

Statistical analysis: The data set was analysed to find the means and standard error using MS Excel (2010) and SPSS 19.0. The data set for all the parameters were explored for skewness and kurtosis, and the Shapiro-Wilk test was used to test for the presence of a normal distribution. The parameters showing a major deviation from a normal distribution were normalized by using a log 10 transformation. One-way ANOVA was used for each of the F parameters to determine the level of significance between the sites. Tukey's HSD post hoc test was used for multiple comparisons of the F samples at $p<0.05$.

RESULTS

F content of the three wheat varieties: The three wheat varieties grown at the UV site showed visible foliar injuries and the leaf F levels, on a dry weight basis, were significantly higher ($p<0.05$) in the Pirsabak (9.3 ppm) and Janbaz (9 ppm) varieties compared to the Atta Habib variety (6.66 ppm). The wheat grown at the control UAP site did not show any visible foliar injury, and, compared to the UV site, the leaf F content (2.3–4.0 ppm) was significantly lower ($p<0.05$) (Figure 1).

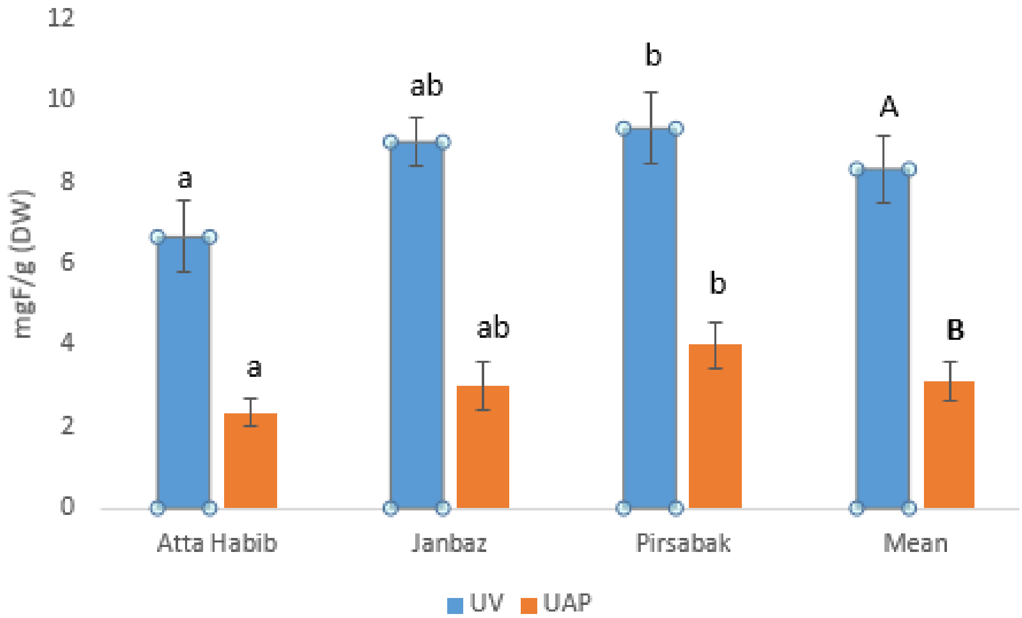

Figure 1. The total fluoride content of the samples of wheat leaves collected from the UV and UAP sites during early summer season. The values are the mean of 4 replicates. The error bars indicate the standard errors of the means. Bars sharing different letters differ significantly from each other at $p<0.05$. For each variety and the mean: columns for UV on left, UAP on right.

Fluoride content the tomato varieties: The three tomato varieties grown at the UV site showed visible foliar injuries and the leaf F level, on a dry weight basis, was significantly higher ($p<0.05$) in the Pahil variety (23.6 ppm) compared to the Chinar (18 ppm) and Roma (11 ppm) varieties. The tomatoes grown at the control UAP site did not show any visible foliar injury, and, compared to the UV site, the leaf F content (range: 2.6–4.6 ppm; Sahil variety= 4.6 ppm, Chinar variety = 2.6 ppm, and Roma variety = 3.3 ppm) was significantly lower ($p<0.05$). The Sahil variety was more sensitive to fluoride at the UV site compared to the Chinar and Roma varieties. The mean leaf F content of the tomato varieties at the UV site (17.6 ppm) was significantly higher ($p<0.05$) than the mean leaf F content of the tomatoes (3.5 ppm) grown at the UAP (Figure 2).

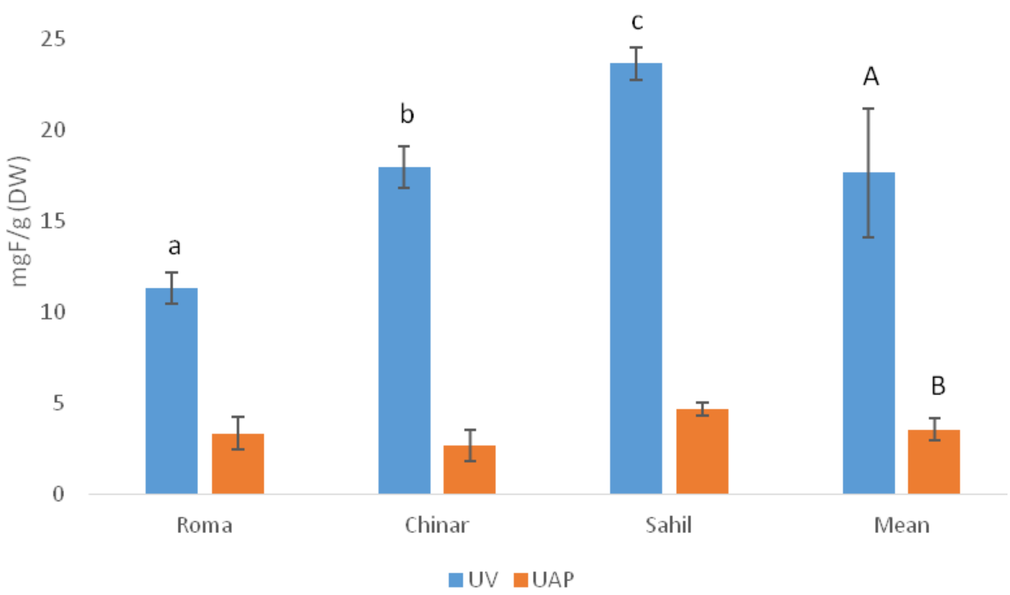

Figure 2. The total fluoride content of the samples of the tomato leaves collected from the UV and UAP sites during the early summer season. The values are the mean of 4 replicates. The error bars indicate the standard errors of the means. Bars sharing different letters differ significantly from each other at p<0.05. For each variety and the mean: columns for UV on left, UAP on right.

Fluoride content of the clover varieties: The F level in the leaves, on a dry weight basis, of the Shaftal clover variety (50.1 ppm) grown at the UV site was significantly higher (p<0.05) F than that in the Barseem variety (44.6 ppm) and Alfa alfa (38 ppm) (Figure 3).

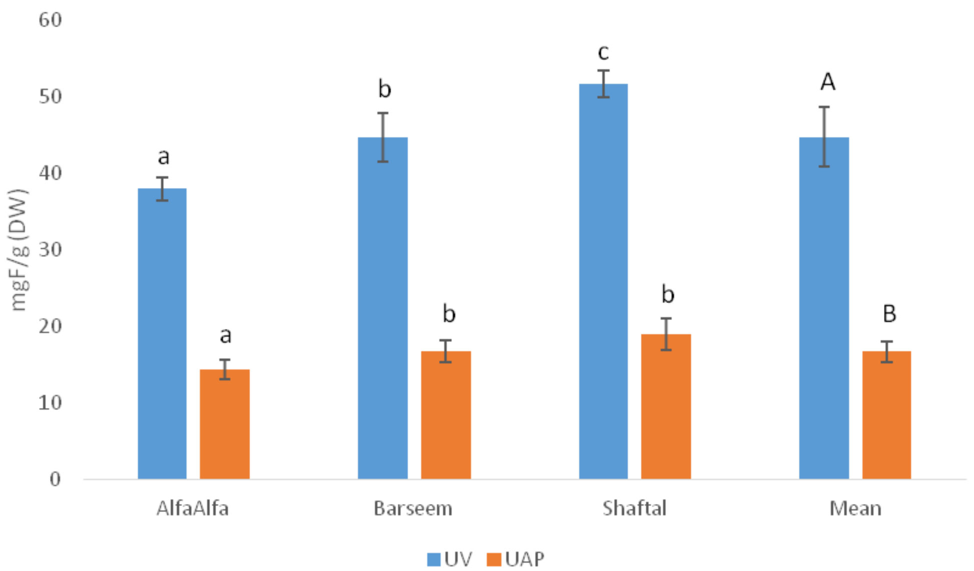

Figure 3. The total fluoride content of the samples of the clover leaves collected from the UV and UAP sites during the early summer season. The values are the mean of 4 replicates. The error bars indicate the standard errors of the means. Bars sharing different letters differ significantly from each other at p<0.05. For each variety and the mean: columns for UV on left, UAP on right.

Compared to the UV site, the leaf F content (range; 14–19 ppm, Shaftal variety= 19 ppm, Barseem variety= 16 ppm, and Alfa alfa= 14 ppm)) of the clover grown at the control UAP site was significantly lower ($p<0.05$). The mean F content of the clover leaves at the UV site (44.6 ppm) was significantly higher ($p<0.05$, 174%) than the mean clover leaf content (16.3 ppm) at the UAP control site. The sensitivity of clover varieties to F at the UAP was Shaftal>Barseem>AlfaAlfa (Figure 3).

The highest mean leaf F level in the three crops which were analysed was in the varieties of clover grown at the UV site (>40 ppm) followed by the UV tomato plants (18 ppm), and the UV wheat plants (<10 ppm). The crops grown at the UAP site did not have a high leaf F content or visible signs of F toxicity. The results show that, in a F-polluted area, compared to the varieties of tomato and wheat, the fodder crop of clover has a significantly greater tendency to accumulate F in its leaves (Figure 4).

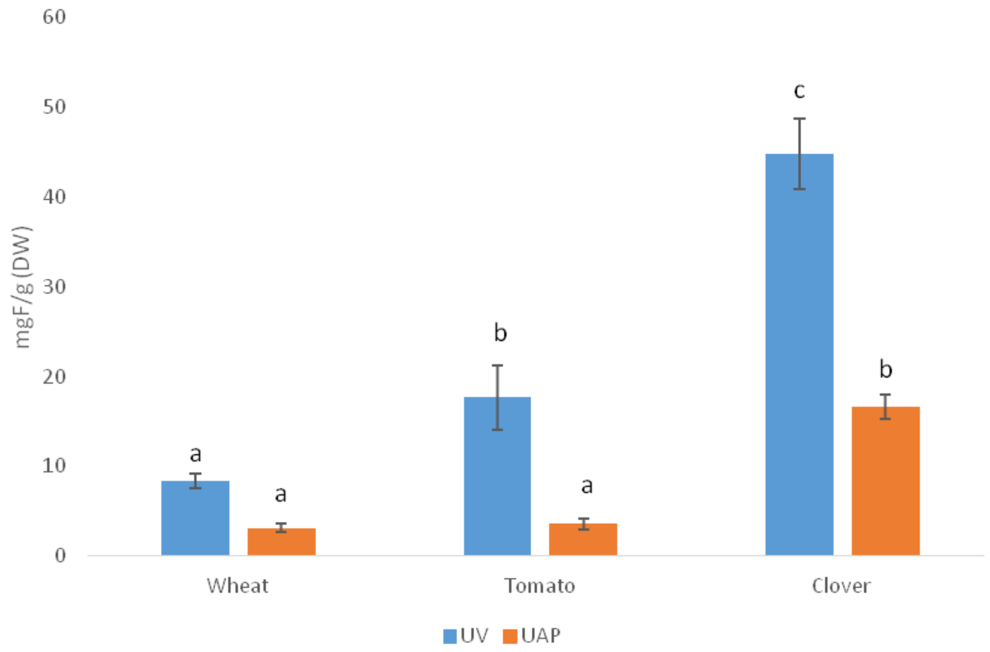

Figure 4. The total fluoride content of the samples of the wheat, tomato, and clover leaves collected from the UV and UAP sites during the early summer season. The values are the mean of 4 replicates. The error bars indicate the standard errors of the means. Bars sharing different letters differ significantly from each other at $p<0.05$. For each plant, the columns for UV are in blue on the left and for UAP in orange on the right.

DISCUSSION

One of the main aims of the current study was to assess the F content in different varieties of wheat, tomato, and clover crops grown locally in Peshawar, Pakistan, to see if it was possible to determine which varieties were more resistant to F. This information would be relevant to farmers. The wheat and tomato varieties grown at the UV showed visible HF foliar injury while the clover varieties grown in the brick kiln UV site showed no visible foliar injuries. However, this does not mean that the clover varieties are not sensitive to F in terms of growth and yield. F can accumulate in the leaves of the plant after being be taken up from the soil or can directly enter via stomata and be deposited in the transpiration stream, which can then affect the photosynthetic activity of the plant. Ahmad et al.[6] observed no foliar injuries to wheat and clover in the same area. Davison et al.,[8] found that wheat subjected to 0.3 µg F/m^3 in an open top chamber (OTC) did not have any fluoride-induced injuries. Maclean et a.,[9] fumigated wheat at the rate of 0.6 µg F/m^3 for 72 hr and similarly did not find any foliar injuries. In the same manner, tomato has also been reported to be a crop which is resistant to developing F-induced foliar injuries[10-11] and tomato plants are not sensitive to HF fumigation. However, the atmospheric HF pollution can reduce the dry matter content in some plants including tomato and oats.

In the current study, it was important to identify the resistant crop varieties that accumulate less fluoride from the soil (calcium and water soluble fluoride) and the atmosphere (HF) as different varieties may show different responses to fluoride pollution due to their different genetic make ups and the environmental conditions.[12] It is clear from the current study that the leaf F content of the Pirsabak and Janbaz wheat varieties tend to accumulate more fluoride than to Atta Habib variety when grown at the UV site. The resistance of Atta Habib to fluoride might be due to its different genetic make up or it might be due to the variety having a high content of Ca and Mg that could help detoxify the fluoride entering via the transpiration stream. The fluoride content of the same varieties at the UAP site was significantly lower, suggesting that the high fluoride content was due to the HF emitted from brick kilns at the UV site.

The wheat variety of Atta Habib was more resistant to HF at the brick kiln site than the Pirsabak and Janbaz varieties. Similarly, at the UV site, the Roma tomato variety was more resistant to F-pollution than the Chinar and Sahil varieties which had a higher fluoride content in their leaves. Stevens et al.[13] investigated the toxicity of HF on tomato and oats and concluded that it significantly reduced the dry matter in both plants. The tomato was more sensitive to HF compared to the oats. In the current study, the dry matter was assessed for the wheat, tomato, and clover varieties as it was difficult to measure in the field conditions. However, it is imperative to carry out pot experiments in order to evaluate the effect of HF on the biomass of the local crops. The Shaftal and Barseem varieties of clover, *Trifolium repens L.,*were found to have a significantly higher fluoride content compared to Alfa alfa (clover) at the UV brick kiln site.

These findings are very important as these crops are important economically for the region and as wheat and tomatoes are commonly used by the lower and middle classes of the population. Wheat is the main staple crop while tomato is the main ingredient of recipes that are used daily. An increased fluoride uptake by wheat and tomato crops could put the population at risk for developing fluoride toxicity. Clover is the main fodder crop for livestock and is known to be able to have a high fluoride content, mainly in the leaves. Arnesen[15] conducted pot experiments on the fluoride content in clover and grasses grown in soil. He concluded that there was high correlation between the F content of clover leaves and the amounts of water- and calcium- extractable fluoride in the soil when increasing amounts of NaF were added to two uncontaminated soils. Stevens et al.[15] assessed the risk of F concentrations reaching phytotoxic or zootoxic concentrations in the pasture plants (trifoliums) commonly found in Australia. Their modelling data suggested that the pasture plants will not get phytotoxic levels of fluoride if the pH levels in the soil are neutral However, these plants will be at risk to F toxicity when grown in F-polluted areas with high levels of phosphate fertilizer application and with a soil pH which is either very high (alkaline) or very low (acidic) resulting in the risk of zootoxic concentrations of F in the shoots of the plants. These findings suggest that the local fodder crops are at risk to having a high fluoride content because of the highly alkaline soil and the high atmospheric HF concentration in the air around the brick kilns. The local soil is also deficient in organic matter, nitrogen, and phosphorus resulting in a high rate of application of nitrogen and phosphate fertilizers, which means that the local fodder may get a zootoxic level of F with fluorosis resulting in the local grazing animals.

The study is the second of its kind in Peshawar with an earlier study by Ahmad et al. reporting on sensitive fruit orchards and crops in the same area and suggesting that a further study be carried out to identify the resistant crop species. The resistance of some crop varieties to HF might be due to the presence of a higher content of Ca and Mg. When fluoride enters a plant via the transpiration stream it can disrupt certain metabolic process and can damage the strength of the cell wall. However, if the fluoride comes into direct contact with Ca it may convert to the less soluble and biologically active CaF which would limit the F-induced damage.[13] Mg is the central ion of chlorophyll and functions as a bridge between phosphoryl groups.[16] Fluoride may enter a plant via the stomata and go to a mesophyll cell, where it may connect with the Mg present in the chloroplast and cause a disruption of the photosynthetic activity. Plants that maintain a high amount of Ca in the cell wall and Mg in the chloroplast inside the leaf are likely to be more resistant to fluoride-induced injuries.[1]

Our suggestion is that the resistant varieties of wheat, tomato, and clover crops might have maintained higher amounts of Ca and Mg in their leaves to negate the effects of the fluoride emitted from the brick kilns. However, a future study of the effects of high atmospheric HF levels on plants should be done which includes an analysis of Ca, Mg, and other macro and micro nutrients.

In the present study, the relative degrees of fluoride sensitivity in the selected crop varieties, as measured by the leaf concentrations of F (ppm) with those with higher F levels being more sensitive, were:

(i) Wheat: Pirsabak (9.3 ppm) > Janbaz (9 ppm) > Atta Habib (6.66 ppm),

(ii) Tomato: Sahil (23.6 ppm) > Chinar (18 ppm) > Roma (11 ppm),

and (iii) Clover: Shaftal (50.1 ppm) > Barseem (44.6 ppm) > Alfa alfa (38 ppm).

The soil fluoride content was not measured as Ahmad et a.,[6] concluded that the Peshawar soil was calcareous with a high Ca and pH. The fluoride content would be irrelevant to the local crops as fluoride is bound to the Al and Fe in the soil when the pH is high.[14,17] Therefore, bioavailability of fluoride from the soil to the crop is highly unlikely. The atmospheric HF from the brick kilns is the main source of fluoride for the population in Peshawar.

Brick kilns are on the rise in South Asia and hundreds of brick kilns can be found around every major city. Large quantities of bricks are produced in a traditional Bulls Trench way in many places of Asia. China and India are the two largest producers of bricks with their combined production being more than 50% of the total world production.[18] Although, brick kilns are regarded as being small scale industries they contribute a huge amount of air pollution which causes deterioration of the environment. The problem is on the rise globally as the number of brick kilns in Asia, including in Pakistan, is tied to the economic growth and urbanization of the region. In addition, the industry uses fine clay for brick making that has more suspended particulates and a higher sulphur and fluoride content.[1] These brick kilns also use poor quality coal and other toxic materials as fuel, such as used rubber tires. This pollution produced by brick kilns is thus produced by toxic emissions from both the product (bricks) and the fuel used. In India, fire clay bricks are produced in approximately 42,000 small and medium scale brick kilns which normally operate by using 4–5 million metric tonnes of coal each year.[19] There are around 7,000 registered brick kilns in Pakistan and they are poorly regulated. They are mostly built on agricultural land and therefore the nearby crops are vulnerable to being adversely affected by them. The bricks are made in brick kilns via an old method (Bull's trench) that produces too much air pollution because of uncontrolled emissions from the fire.

The present study found that the HF pollution from brick kilns can cause foliar injury as well as having negative effects on its growth and quality. However, there were some limitations to the current study. Due to a low budget and the crops affected by the brick kilns growing on a vast area, it was difficult to conduct a detailed survey of every crop species. The security situation was also not very good as the area is adjacent to a tribal area (lawless region) near Afghanistan. From an agricultural point of view, it is imperative to conduct a detailed HF foliar injury survey along with controlled experiments in the field and in the laboratory.

CONCLUSIONS

After measuring the F content of the leaves of wheat varieties grown in the HF-contaminated site near the UV brick kilns, we concluded that the Atta Habib variety was significantly more resistant to fluoride compared to the Janbaz and Pirsabak varieties which accumulated higher fluoride concentrations in their leaves. The Roma variety of tomato was less sensitive to fluoride toxicity compared to the Chinar and Sahil varieties, and hence Roma is considered to be the best variety for growing in areas near brick kilns. All three varieties of clover examined accumulated a high amount of fluoride in their leaves, with the Shaftal variety having approximately 50 ppm (DW), the Barseem variety 45 ppm (DW) and Alfalfa 38 ppm (DW). We concluded that trifolium fodder crops can be responsible for fluorosis in livestock animals feeding in brick kiln areas as a result of the high accumulation of fluoride in clover leaves. Therefore, we recommend that a detailed and thorough survey be carried out on the levels of pollution by fluoride and other toxic pollutants around the brick kilns in Peshawar and other major cities of Pakistan. The authorities concerned with pollution should establish a threshold level for fluoride pollution in the atmosphere and in the soil used for growing crops in Pakistan as the current study relied on previous studies carried out in other regions of the world. As clover accumulates a high amount of fluoride in its leaves, more research is needed on the fluoride concentrations in the blood of livestock living in brick kilns areas and the levels of fluoride in their products, such as milk and meat.

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