HYDROGEN FLUORIDE EFFECTS ON LOCAL MUNG BEAN AND MAIZE CEREAL CROPS FROM PERI-URBAN BRICK KILNS IN SOUTH ASIA

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SUMMARY: Increased urbanisation throughout South Asia has increased the number and output of the brick kilns that typically surround major cities, but the environmental and health impacts of their atmospheric emissions are poorly understood in Pakistan. We report the negative effects of hydrogen fluoride (HF) emissions from brick kilns near Peshawar, Pakistan on mung bean (*Vigna radiata* cv. MN 92) and maize (*Zea mays* cv. Azam). HF air concentrations, and fluoride concentrations of mung bean and maize grains, were greater close to brick kilns than at more distant sites. The 100-grain weight of mung bean and maize close to brick kilns was significantly lower, by about 30% and 45% respectively, than at control sites. These findings, added to evidence of major impacts on local fruit orchards in this area, suggest that fluoride emissions from brick kilns may have a significant impact on peri-urban agriculture in South Asia.

Keywords: 100-grain weight; Air pollution; Brick kiln emissions; Food security; Hydrogen fluoride damage; Maize; Mung bean; Pakistan; Peri-urban agriculture; South Asia.

INTRODUCTION

Hydrogen fluoride (HF) is a major phytotoxic pollutant, which is emitted from industrial sources, including ceramic and, phosphate factories, and brick kilns.[1] The negative effects of HF on crops may be a growing and unrecognised problem in South Asia, due to increases in population and construction increasing the number of brick kilns.[1] Brick kilns in South Asia are often located in and around cities on agricultural land and pollutants emitted from these brick kilns have been shown to directly affect peri-urban arable crops and fruit orchards.[2] These brick kilns emits hydrocarbons (HC's) nitrogen oxides (NOx) and sulphur dioxide (SO_2). However, HF is likely to be the most important contributor to this local crop damage.[3] Accumulation of fluoride in edible parts of plants can also potentially cause problems for human and livestock health, while crops and varieties vary in sensitivity to HF, and the effects are also modified by environmental conditions.

The work reported in this paper extends the study of Ahmad et al.,[1] in which severe foliar injury in local fruit orchards close to the Pakistani city of Peshawar, previously of unknown cause, was shown to be due to elevated HF emissions. There are an estimated 400–450 brick kilns operating throughout the year in agricultural areas around this city. Their design is that of a traditional Bull's

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Trench kiln.[1,2] The brick kilns in the Peshawar region are poorly regulated, with no modern technology to control the emissions, and are fuelled by engine oil, tyres and low quality coal. The aim of this additional study was to assess the impacts of local brick kilns on the grain biomass and fluoride content of local mung bean and maize crops. Mung bean and maize are important crops in South Asia, but the effects of HF on them in this part of the world are currently unknown.

MATERIALS AND METHODS

Peshawar is located 510 m above sea level at 34ºN 71ºE in Pakistan. Three sites were selected in and around Peshawar. One site (BKF) was situated within 500 m of active brick kilns in several different wind directions. The other two locations acted as control sites: the Agricultural Research Institute (ARI), and the Agricultural University (AUP) are located 18 km north-east, and 25 km west, respectively, of the brick kiln area. The selected BKF site was surrounded by 8 brick kilns within one km radius to minimise the effects of wind direction. The nearest brick kiln was at the distance of 50 m. Atmospheric HF and SO_2 concentrations were measured at each site from February to June 2008 using passive samplers, and were analysed by the method of Ferm et al.[4] Further details of the study area and atmospheric measurements are provided by Ahmad et al.[1] as the present work was carried out at the same time.

Mung bean (*Vigna radiata* cv. MN 92) grain samples were collected in May 2008, from six fields in each of the ARI, AUP, and BKF sites. Ten pods were harvested from each of the four corners, and the middle of each field (using a ‘W’ sampling design) in order to get a homogenized sample. Maize (*Zea mays* cv. Azam) cobs were harvested from adjacent fields at the same sites in mid-June 2008, using the same sampling design. Each harvested sample was weighed, and then dried at 70°C for 48 hr.

After drying, the harvested samples were crushed in the palm covered with plastic gloves to separate the grains from the pods and cobs. Six samples of each dried harvest sample were then weighed on a Shimadzu AY 220 electronic balance to determine the biomass per 100 grains. The harvested samples were then divided into two sub-sets. One half was washed with deionised water, dried again, and then ground with a mortar and pestle, while the other half was directly ground with a mortar and pestle, without washing. Mung bean and maize grain fluoride concentrations in both the washed and unwashed samples were then determined by the acid digestion method,[5] using a fluoride-sensitive electrode (ISE F 800 DIN, WTW Weilheim, Germany) coupled to an ion meter (Inolab pH/Ion 735, WTW Weilheim, Germany).

The data for all parameters were explored for skewness, kurtosis and normality, using the Shapiro-Wilk test, and parameters showing major deviations from a normal distribution were normalised using log transformation. One-way ANOVA was then used to determine whether there were significant differences between the sites. Tukey’s post hoc test was used for multiple comparisons at $p<0.05$. A paired sample t-test was used to determine the significance of differences between the washed and unwashed samples within each site. All data were analysed using the statistical programme SPSS version 19.0.

RESULTS AND DISCUSSION

The total fluoride content of mung bean and maize grain in both unwashed and washed samples from the BKF site was significantly higher, by approximately a factor of two, than that at the ARI and AUP sites (Table).

Table. ANOVA results showing the comparison between the fluoride (F) content, sulphur (S) content, and the 100-grain weight of mung bean and maize grain collected from three sites in Peshawar, Pakistan: the Agricultural Research Institute (ARI), the Agricultural University, Peshawar (AUP), and a brick kiln fluoride-emitting site (BKF)

Parameter	df	F	Significance	Post hoc
Mung bean F grain content (unwashed)	2,15	68.5	0.000	BKF>ARI,AUP
Mung bean F grain content (washed)	2,15	125.7	0.000	BKF>ARI,AUP
Mung bean grain biomass/100grains	2,15	22.5	0.000	ARI,AUP>BKF
Mung bean S grain content (unwashed)	2,15	2.50	0.120	Not significant
Maize F grain content (unwashed)	2,15	154.6	0.000	BKF>ARI,AUP
Maize F grain content (washed)	2,15	70.44	0.000	BKF>ARI,AUP
Maize grain biomass/100grains	2,15	31.47	0.000	ARI>AUP>BKF

Post-hoc differences were tested for significance at p=0.05.

There was no significant difference between the fluoride content of the unwashed and washed mung bean and maize grain samples at all three sites (Table). There was also no detectable fluoride residue found in the deionised water used for washing the cereal grain samples. The mean sulphur content of unwashed mung bean samples at BKF, AUP, and ARI also did not differ significantly between sites (Table), with values of 5.0, 6.2, and 6.2 mg/kg (dw), respectively.

The 100-grain weight of unwashed mung bean grain at BKF was decreased significantly, by 35%, and 26%, compared to AUP and ARI, respectively (Table). However, there was no significant difference in the values between AUP and ARI sites. Similarly, the 100-grain weight of unwashed maize grain at BKF was significantly decreased, being 55% and 33% lower than at AUP and ARI respectively. However, unlike mung bean, the 100-grain weight of maize at AUP was significantly higher than that of ARI (Table).

The HF air concentration at the BKF site, as reported by Ahmad et al.,[1] was 0.2 μg/m^3 in February to April, increasing to 0.3 μg/m^3 in May; in contrast, the HF concentration was below detection limit (<0.1μg/m^3) over the whole period at ARI and AUP. [6] Concentrations of HF above 0.2 μg/m^3 for an extended period have been identified as phytotoxic to sensitive crop species, while exposure to a concentration of 0.3 μg/m^3 for 3 consecutive months is sufficient to cause visible foliar injuries to sensitive crops. The findings of this study are also consistent with those of Franzaring et al.,[7] Pandey,[8] and Murray,[9] who all concluded that HF concentrations of 0.2 μg/m^3 can affect sensitive plant species.[10] In contrast, SO_2 concentrations were lower at BKF (8.0 μg/m^3) than at ARI (16.2 μg/m^3) or AUP (12.3 μg/m^3), and all the measured concentrations were below the critical level for SO_2 for adverse effects on crops of 30 μg/m^3 as an annual mean concentration. Hence, HF is much more likely than SO_2 to be the cause of the observed effects.

The fluoride content of both washed and unwashed samples at BKF were significantly higher than that of AUP and ARI, most probably due to the HF emissions from brick kilns. The washed samples did not varied significantly from unwashed samples, suggesting that the additional fluoride accumulated in the grains was mainly due to the uptake of gaseous fluoride through the stomata rather than direct deposition of fluoride on the grains from the atmosphere. Furthermore, our measurements may also underestimate the actual level of contamination of the grain after harvest. Local practice is that grains are separated directly in threshing machines in open fields and during this process a lot of dust settles on the grains. After threshing, the grains, with the additional dust, are then directly crushed in the mills. The sulphur content of mung bean grains was not significantly different between the sites, suggesting that SO_2 is not significant factor damaging the local crops.

In the current study maize accumulated higher fluoride contents than mung bean, while the effect of proximity to brick kilns on 100-grain weight was also greater in maize than mung bean. Ahmad et al.[1] also reported significant visible foliar injury to maize in the same area. To our knowledge, there are no experimental comparisons of the sensitivity of the two species to HF, although Leone et al.[11] reported that maize plants were more sensitive than tomato to atmospheric fluoride. Our data only include 100 grain- weight, and not total yield per hectare, but if fluoride is responsible for the reductions in mung bean and maize yields around brick kilns throughout peri-urban areas of the sub-continent, this should be considered as a major environmental problem, given the importance of mung bean and maize as protein source and cash crops in South Asia, respectively. This threat extends to vegetable crops, as shown by Jha et al.[12,13] who found that elevated fluoride levels near brick kilns in India reduced the growth of onions, spinach, and okra.

South Asia is home to more than a billion people and hundreds of brick kilns surround almost every large city. The significance of particulate emissions from the traditional Bull Trench kilns in the region is increasingly recognised; for example, Guttikunda and Goel[14] recently estimated that 4–17% of the 7,300–16,200 premature deaths caused annually by particulate air pollution in Delhi were due to emissions from the estimated 1000 brick kilns around the city. Our study adds further significant evidence to that reported by Ahmad et al.[1] that HF emissions from these brick kilns also have adverse effects on local agriculture. Hence the cumulative effects of brick kiln emissions on crop production and nutritional quality, in addition to those on human health, in peri-urban areas of the sub-continent may be very significant, and further studies of the size and extent of these effects, their economic significance, and the benefits of emission control are urgently needed.

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