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Effect of phosphogypsum amendment on fluoride content of soil and plants under rice (*Oryza sativa*)–wheat(*Triticum aestivum*) system in sodic soil of Indo-Gangetic plains

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ABSTRACT

An experiment was conducted during 2006–07 to study the fluoride enrichment in soil as well as crops after phosphogypsum application in the sodic soil and compared with the mineral gypsum treated soils. It was found that the addition of phosphogypsum increased both the total water soluble fluoride (F_{tw}) and total $CaCl_2$ extractable fluoride F_{tCa} in the sodic soil over mineral gypsum treated fields. The F_{tw} in 0–15 cm of the soil layer varied between 3.2 and 3.9 mg/kg, whereas total $CaCl_2$ extractable fluoride varied between 5.6 and 9.0 mg/kg. The total water soluble fluoride were positively correlated with total fluoride concentration (r=0.76, P<0.05) and exchangeable sodium percentage of soil (r=0.75, P<0.05). The fluoride added through phosphogypsum accumulated in the top 30 cm of the soil profile. The yield of rice and wheat indicated that phosphogypsum application resulted higher yield of rice and wheat over the equivalent dose of mineral gypsum. Fluoride concentration in grain, straw of rice and wheat was higher in phosphogypsum treated field. It was 13.5 and 14.3 mg/kg in rice and wheat grain, respectively. Multiple regression analysis showed that F_{tw} together with exchangeable sodium percentage explained fluoride concentration in rice (*oryza sativa* L.)–wheat (*Triticum aestivum* L. emend. Fiori & Paol.) grain better than F_{tw} alone.

Key words: Fluoride, Mineral gypsum, Phosphogypsum, Regression, Rice, Wheat

Phosphogypsum is the principal byproduct in the manufacture of phosphoric acid. Concentrations of fluoride in phosphate rocks are usually high and ranged from 3 to 4% (McLaughlin *et al.* 1996). About 33 to 50% of fluoride present in phosphate rock passes into the resulting fertilizer, while the rest of the F remains in the phosphogypsum wastes. In India, about 11 million tonnes of phosphogypsum is generated every year accumulating huge stock piles at plant sites. Public concerns are being raised about the safety of these disposals and there is a need to restore the environment where these byproducts are accumulated. In India, mineral gypsum had been so far used as an amendment in the amelioration of saline and sodic lands for the agricultural use. Phosphogypsum contains a high proportion of $CaSO_4 \cdot 2H_2O$, is an efficient amendment that has been widely used in the saline-sodic marsh soils from south-western Spain (Domínguez *et al.* 2001). Additionally, using phosphogypsum as an amendment in agricultural soils may dilute its pollutants, such as fluoride, heavy metals and radio-nuclides. India has 6.73 millian ha of salt-affected soils of which 3.77 m ha is sodic soil (Sharma *et al.* 2004). The diminishing stock of mineral gypsum and a vast pillage of phosphogypsum in India, necessitated to explore the possibilities of its use as an amendments of sodic soils.

The use of phosphogypsum as Ca amendment in sodic soil could alter the dynamics of different F species by modifying the alkaline environment of soils and may reduce the solubility of F in soil leading to low activity in soil solution and limiting uptake by crops. High F content in plant can be toxic to plants or toxic to animals consuming it. Fluoride toxicity risk to the grazing animals depend on the total fluoride concentration in the surface soils and the F toxicity risk to plants and the fluoride contamination risk to ground water depends on the soluble soil F concentration (Loganathan *et al.* 2006). It is relevant to devise and monitor the land reclamation practices using phosphogypsum for its fluoride pollution implications in soil, water and crop plant. Hence, a study was conducted to estimate the amount of soluble fluoride (having potential threats to water source) which can be removed by leaching phosphogypsum with water and lime; fluoride uptake in crop plants in the sodic soils amended by phosphogypsum and mineral gypsum

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applied in different combinations and to estimate concentration of different species of fluoride in soil amended by phosphogypsum.

MATERIALS AND METHODS

The experimental site was located at 26°47'58" N latitude and 80°46'24" E longitude in the salt-affected soils of central Indo-Gangetic plains. The soil in the experimental site was sandy clay loam. The surface soil (0–15 cm) had *p*H 9.8, ECe 1.9 dS/m, organic. C 0.3 g/ kg, CEC 16.7 cmol (+)/ kg. The initial total fluoride content and water-soluble fluoride content in the soil were 283.5 mg/kg and 6.0 mg/kg, respectively. The phosphogypsum sourced from a company located at east coast in the province of Orissa had S 16.4%, Ca 18.8%, Na 0.11%, Al 0.02%, Fe 0.30%, Si 3.35% and P 0.34%, Whereas the mineral gypsum had S 16.1%, Ca 18.3%, Na 0.18%, Al 0.06%, Fe 0.01%, Si 0.82% and P 0.01%.

Field experiments with 6 treatments were laid out in plots of 40 m^2 in a randomized block design having 4 replications. Treatments were T_1, 50 $GR_{M:}$ mineral gypsum applied @ 50% GR (gypsum requirement), ie 10.5 Mg/ ha; T_2, 50 $GR_{PG:}$ phosphogypsum applied @ 10 Mg/ ha (equivalent to 50 GR_M); T_3, 50 GR_{PG}-KFC: phosphogypsum applied @ 10 Mg/ ha, followed by KFC [Karnal grass (*Leptochloa fusca* L. Kunth) as first crop]; T_4, 25 GR_M + 25 $GR_{PG:}$ mineral gypsum applied @ 5.25 Mg/ ha and phosphogypsum applied @ 5 Mg/ ha; T_5, 25 GR_{PG}: phosphogypsum applied @ 5 Mg/ ha, and T_6, 12.5 GR_M+12.5 $GR_{PG:}$ mineral gypsum applied @ 2.62 Mg/ ha and phosphogypsum applied @ 2.5 Mg/ ha. Rice followed by wheat was taken in all the treatments except T_3, where karnal grass was used as first crop to explore the possibility of taking the fodder crop immediately after reclamation, using phosphogypsum.

The plots were ploughed to fine tilth; required phosphogypsum and mineral gypsum were applied, followed by 8 cm irrigations to all plots and allowed for vertical leaching. The irrigation water had *p*H 7.7, EC 0.87 dS/m, RSC 1.0 mmol /litre and SAR 1.16. After 7 days, 'CSR23' rice (*Oryza sativa* L.) was transplanted at row-to-row spacing of 20 cm and hill-to-hill distance of 15 cm. Two suckers of karnal grass were transplanted in the treatment T_3, at row-to-row spacing of 20 cm and hill-to-hill distance of 15 cm. A basal application of half of total N, ie 75 kg N and full dose of P @ 60 kg P_2O_5/ ha was applied at the time of puddling. Rest amount of N was applied in 2 equal splits at tillering and panicle initiation. Irrigation water (8 cm) was applied after 3 days disappearance of ponding water. At maturity the crop was harvested manually, sun-dried for 5 days and threshed to record paddy grain and straw yields. Grain yield of rice was reported on 14% moisture basis in terms of Mg/ ha. The layout of the experimental field was not disturbed for subsequent 'KRL19' wheat crop. Fertilizer (N: $P_2O_{5:}$ K_2O = 60: 60: 40 kg/ ha) was applied as basal dose to all the plots. Half of total N, ie 60 kg N/ ha, was applied in 2 equal splits at first and second irrigations, respectively. The mature wheat crop was harvested from the entire plot and after sun-drying, the harvested material was threshed to record grain yield. The plant and soil samples were taken at harvesting of rice and wheat and processed for analysis.

The fluoride content in unwashed, water washed and lime washed phosphogypsum was carried out by the procedure described by Motalane and Strydom (2004).The total fluoride in the soil, mineral gypsum and phosphogypsum was determined by NaOH fusion technique using fluoride ion selective electrode (McQuaker and Gurney 1977), water soluble fluoride was determined by shaking 10 g of soil with 50 ml of distilled water (1: 5 soil: solution ratio) on a rotary shaker for 2 hr and the fluoride was determined by fluoride ion selective electrode (FISE) method. Calcium chloride ($CaCl_2$) extractable fluoride was determined by shaking 16 g of soil with 0.01 M $CaCl_2$ solution for 16 hr (Larsen and Widdowson 1971). The fluoride concentration measured in water and $CaCl_2$ extracts before the addition of TISAB-IV (4g CDTA +58 g NaCl + 57 ml glacial acetic acid in 1 litre distilled water adjusted to *p*H 5.2 by using 6N NaOH) is the free fluoride ion concentration (F_w and F_{Ca}, respectively) and after the addition of TISAB IV is the total soluble fluoride concentration in the water (F_{tw}) and $CaCl_2$ extracts (F_{tCa}) (consisting of both AlF complex and free fluoride). The vegetation samples of rice and wheat were segregated into grain, straw and husk, dried at 70°C and grounded to pass through 0.2 mm sieve. The fluoride determination in these samples was carried out by extracting with 0.1_N $HClO_4$ (Villa 1979).The statistical analysis were done by using the procedure described by Gomez and Gomez (1983).

RESULTS AND DISCUSSION

Fluoride forms in phosphogypsum

The effect of leaching phosphogypsum with lime was also studied as possible method to remove F from phosphogypsum before agricultural use. The results for unwashed, water washed and lime washed PPL phosphogypsums were 0.107 + 0.002 (RSD = 2%), 0.099 + 0.002 (RSD = 2%) and 0.097 + 0.001 (RSD = 4%), respectively.When the phosphogypsum was washed with water, 7.48% of the total fluoride was soluble and removed. The water-soluble fluoride poses a potential threat to the under ground aquifers when it is mobilized due to seepage during the rainy season. The phosphogypsum used in this study contains more than 92.52% water insoluble fluoride having little significance to groundwater pollution. Water-soluble fluoride exists on the surface of the gypsum crystals and in the interstices of agglomerated crystals and water insoluble fluoride is taken up in the structure when gypsum was formed (Motalane and Strydom 2004). The lime washing removed a very small fraction, i e 9.35% F-from phosphogypsum and is a weak F purifying method.

Soluble fluoride in soil

The water soluble fluoride and $CaCl_2$ extractable fluoride concentration are presented in Table 1. The addition of phosphogypsum @10 Mg/ ha increased both the total water soluble (F_{tw}) and total $CaCl_2$ extractable F (F_{tCa}) in the 0–15 cm layer of sodic soil over the mineral gypsum treated (10.5 Mg/ha) field. These treatments resulted a decrease in water soluble as well as $CaCl_2$ extractable fluoride in 0–15 cm soil layer over the initial experimental soil, whereas no such decrease was observed in 15–30 cm soil layer. This indicated that mineral gypsum and/or phosphogypsum when applied to the top 0–15 cm soil layer, the calcium present in these materials reduced the water soluble fluoride in sodic soil, which may be due to formation of insoluble CaF_2 in the gypsum-treated plots. Reduced exchangeable sodium per cent caused lower OH^-concentration due to phosphogypsum application may be ascribed to reduced F concentration in sodic soil over its initial value. The solubility of F in the soil is controlled mainly through adsorption by inorganic constituent of the soil and soil *p*H (Loganathan *et al.* 2003).

The data on ionic species of fluoride (Table 1) indicated that there was negligible amount of AlF complexes in all the treatments; this may be due to limited AlF formation in the alkaline *p*H range in the treated sodic soil. A greater reduction in exchangeable sodium percentage in soil was recorded in the phosphogypsum treated field as compared to mineral gypsum. The water-soluble fluoride of surface soil (0–15 cm) under 12.5 GR_M + 12.5 GR_{PG} and 25 GR_{PG} treatments was statistically (P=0.05) at par with water-soluble fluoride under 50 GR_{PG}, despite comparative lesser fluoride addition by the former treatments than the later. This may be due to comparatively higher soil exchangeable per cent under 25 GR_{PG} and 12.5 GR_M–12.5 GR_{PG}, which have resulted higher solubility of fluoride. With the application of amendments, total soluble F in 0–15 cm of the soil layer varied from 3.2 to 3.9 mg/kg (F_{tw}) and 5.6 to 9.0 mg/kg (F_{tCa}). There was a significant difference in the total water-soluble fluoride and total $CaCl_2$ extractable F in 0–15 cm soil, however at 0–30 cm soil depth both the extractant resulted similar fluoride concentration. The Ca saturation of 0–15 cm soil depth may have resulted reduced water-soluble F. With respect to ground water pollution, water-soluble F may serve as good indicator as compared to $CaCl_2$ extractable F. Calcium chloride extractable fluoride is more sensitive measure of recent fluoride contamination (Mc Laughlin *et al.* 2001). Increased concentration of $CaCl_2$ extractable fluoride in the top soil of phosphogypsum treated field over the mineral gypsum applied plots suggested the increased fluoride enrichment in sodic soil due to phosphogypsum application. However, the risk of ground water contamination and phyto-toxicity is reduced, as the reduced exchangeable percentage in the phosphogypsum treated plots decreases the soluble fluoride. The water-soluble F ranged from 0.25 to 19.13 mg/ kg with a mean of 4.19 mg/ kg in the productive upper Indo-Gangetic plains of Haryana (Grewal *et al.* 1996). The study indicated that soluble F concentration in sodic soil of Indo-Gangetic plains due to one time amendment with phosphogypsum @ 10 Mg /ha is unlikely to be phyto-toxic.

Total fluoride

Application of 10 Mg/ha phosphogypsum as amendment, adds 10.7 kg F/ ha to the soil. The total fluoride concentration on the surface soil (0–15 cm) varied from 272.9 mg/ kg to 277.5 mg/ kg in the treatment 50–GR_M and 50 GR_{PG}, respectively (Fig 1) resulting an increase of 4.6 mg/kg total fluoride in the latter treatment over the former. Total fluoride concentrations in the top soils of phosphogypsum-treated plots are below the reported range of fluoride concentration in most countries (Loganatahan 2006). Therefore, the risk of fluoride toxicity to livestock grazing on phosphogypsum reclaimed soil due to soil ingestion is very low. The data on the mobility of the fluoride after one year of rice wheat rotations, recorded in terms of total fluoride up to the depth of 120 cm, revealed that the added fluoride from phosphogypsum accumulated in the top 30 cm of the soil profile. The reduce exchangeable sodium percentage due to applied phosphogypsum may have hastened the formation of CaF_2 in the top soil. The retention of fluoride in the Ca-

Table 1 Total soluble fluoride in soil (mg/kg)

Treatment	Water soluble F (1: 5)				$CaCl_2$ extractable F (mg/kg)					
	F_w		F_{tw}		F_{Ca}		F_{tCa}		ESP	
	0–15	15–30	0–15	15–30	0–15	15–30	0–15	15–30	0–15	15–30
50–GR_M	2.9	5.6	3.2	5.9	5.3	6	5.6	6.3	20.4	27.3
50 GR_{PG}	3.6	5.8	3.9	6.1	8.5	5.7	8.9	5.9	18.3	25.2
50 GR_{PG}-KFC	3.5	5.2	3.7	5.5	7.7	5.3	8.1	5.7	17.8	23.5
25GR_M+25 GR_{PG}	3.2	6.4	3.4	6.3	8.3	7.4	9.0	7.7	19.4	25.6
25 GR_{PG}	3.3	7.2	3.7	7.5	8.4	7.9	8.7	8.2	25.2	30.8
12.5GR_M+12.5 GR_{PG}	3.2	6.9	3.6	7.2	8.1	7.5	8.3	7.8	26.5	31.6
LSD (P=0.05)	0.5	1.2	0.5	1.1	2.3	0.8	2.5	0.7	1.5	2.0

GR_M, Gypsum requirement as mineral gypsum; GR_{PG}, phosphogypsum requirement equivalent to mineral gypsum

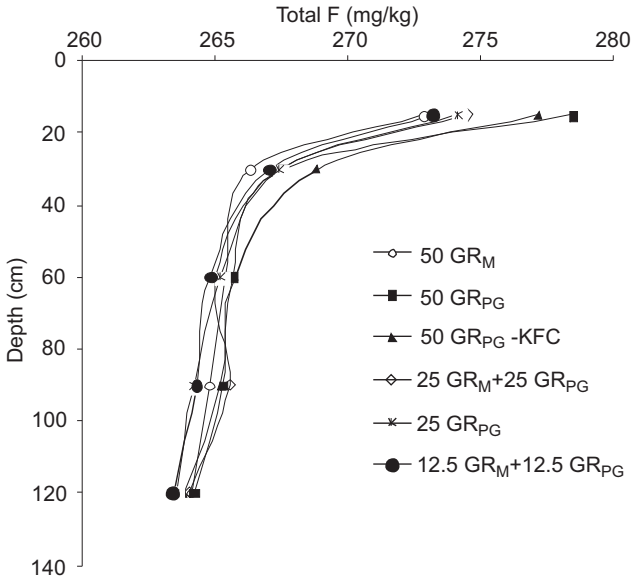

Fig 1 Effect of phosphogypsum on the total F (mg/kg) content in soil profile after rice and wheat
GR_M, Gypsum requirement as mineral gypsum, GR_{PG}, phosphogypsum requirement equivalent to mineral gypsum, KFC, karnal grass taken as first crop

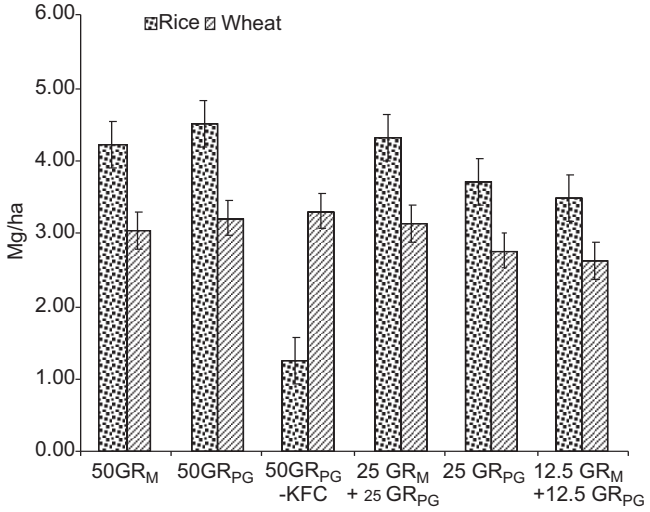

Fig 2 Effect of phosphogypsum on the grain yield of rice and wheat (Bar represent the LSD value significant at probability level of P=0.05)
GR_M, Gypsum requirement as mineral gypsum; GR_{PG}, phosphogypsum requirement equivalent to mineral gypsum; KFC, karnal grass taken as first crop

amended top soil is possibly due to precipitation of fluoride as CaF_2. Diffusive mobility of F is reduced in a Ca-amended soil (Rai *et al*. 2007). Monitoring of fluoride movement over the periods is advisable if phosphogypsum are to be used as amendments in sodic soil.

Rice and wheat yield

The yield data on rice, wheat and karnal grass expressed as equivalent yield of rice, influenced by the application of phosphogypsum in the sodic soil presented in Fig 2. Application of phosphogypsum @ 10 Mg/ ha resulted slightly higher yield of 4.5 Mg/ ha over the treatment 50 GR_M (4.22 Mg/ha) and 25GR_M+25 GR_{PG} (4.32 Mg/ha). Similarly, application of phosphogypsum @ 5 Mg/ha resulted comparatively higher yield over 12.5GR_M +12.5 GR_{PG}. The treatment with karnal grass yielded lowest equivalent yield of rice because of its low market price. Though 10.7 kg of fluoride was added through the addition of 10 tonnes/ha phosphogypsum, it did not have a negative effect on the rice yield. Similarly, the yield of follow up wheat resulted similar increase in the yield in the phosphogypsum-treated field as recorded in rice. The wheat crop grown in the field preceded by the karnal grass yielded statistically at par yield with that of 50 GR_{PG}.

Fluoride content in rice and wheat

The result obtained in this investigation showed an increase in the fluoride concentration in the rice grain, straw and husk in the phosphogysum treated over mineral gypsum-treated plots. The fluoride content in the different part of rice varied from 7.5 to 13.5 mg/ kg in grain, 16.6 to 28.8 mg/ kg in straw and 13.0 to 28.3 mg/kg in the husk (Table 2). The fluoride content in rice increased with increase in application of fluoride as a result of added phosphogypsum and decreased with decrease in ESP of the soil. The karnal grass known for its salt tolerance and higher ions uptake, however showed less F concentration in tissues as compared to the rice straw.

The fluoride content in wheat ranged from 8.0 to 13.5 mg/kg (grain) and 14.3 to 21.2 mg/kg (straw).The highest fluoride content in grain and straw was recorded in the treatment 50 GR_{PG}, Karnal grass. The karnal grass grown as first crop, hypothesized to reduce the fluoride load in soil and subsequently in plant, could not yield any expected result. The F content in the wheat straw is having dietary significance as it is used as cattle fodder in north India. The maximum fluoride concentration observed

Table 2 Fluoride content (mg/kg) in rice and wheat

Treatment	Rice			Wheat	
	Grain	Straw	Husk	Grain	Straw
50 GR_M	7.5	16.5	13.0	8.0	14.3
50 GR_{PG}	13.5	28.8	28.3	12.5	20.2
50 GR_{PG}-KFC		14.7		13.5	21.2
25GR_M+25 GR_{PG}	8.8	17.5	15.5	9.0	16.0
25 GR_{PG}	9.8	19.7	18.5	9.4	16.8
12.5GR_M+12.5 GR_{PG}	9.2	18.8	18.3	9.2	16.2
LSD (*P*=0.05)	2.2	3.3	4.2	1.5	2.9

Table 3 Multiple regression models for concentration of fluoride in rice and wheat

mg F/ kg rice grain =0.927F_{tw}–0.41 ESP of soil	R^2 =0.935, P<0.001
mg F/kg rice grain =0.629 F_{tCa}–0.35 ESP of soil	R^2 =0.481, P<0.01
mg F/ kg rice straw =0.493F_{tw}–0.01 ESP of soil	R^2 =0.242, P<0.10
mg F/ kg rice straw =0.389F_{tCa}–0.03 ESP of soil	R^2 =0.150, P<0.10
mg F/ kg wheat grain =0.695F_{tw}–0.56 ESP of soil	R^2 =0.768, P<0.001
mg F/ kg wheat grain =0.449 F_{tCa}–0.57 ESP of soil	R^2 =0.489, P<0.05
mg F/ kg wheat straw =0.726F_{tw} –0.51 ESP of soil	R^2 =0.766, P<0.001
mg F/ kg wheat straw =0.522F_{tCa}–0.53 ESP of soil	R^2 =0.511, P<0.005

ESP, Exchangeable sodium percentage

in wheat straw in the phosphogypsum-treated plots was 21.2 mg/ kg, which is much less than the zootoxic threshold in herbage of 30 mg/kg (Davis 1980).The results of field experiment thus suggest that one time application of phosphogypsum @ 10.0 Mg/ ha with the F levels in this range would pose no problem of zoo-toxicity when used as amendment in sodic soil.

Multiple regression analysis showed that F_{tw} together with ESP explained fluoride concentration in rice and wheat grain better than F_{tw} alone. Water-soluble fluoride concentration and soil exchangeable percentage together explained 93.5% and 76.8% of variation in the fluoride concentration in rice and wheat grain, respectively (Table 3).While the F_{tw} alone explained 77.44% and 46.24% variation in the fluoride concentration in the rice and wheat grain, respectively. The F_{tCa} and exchangeable percentage of soil explained only 48.1 and 48.9% variation in fluoride concentration in rice and wheat grain, respectively. Therefore, F_{tw} is better predictor of fluoride in rice and wheat grain

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